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XXVI

TITOLO TESI

Theoretical Investigations of New Materials Properties for the Storage and Release of Hydrogen and Proton Transfer in PEMFCs

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Abstract

A future *hydrogen based society*, i.e. a society in which hydrogen is the primary energy carrier, is widely viewed as a solution to many of the energy related problems of the world. However, for the *hydrogen based society* to become realizable, several technical difficulties must be dealt with: an efficient production and distribution of hydrogen, fuel cells of sufficient durability to allow for long-term use, fuel cell catalysts that minimize precious-metal content, high-temperature/low-humidity proton exchange membranes.

Furthermore, widespread adoption of hydrogen as a vehicular fuel depends critically upon the ability to store hydrogen on-board at high volumetric and gravimetric densities, as well as on the ability to extract/insert it at sufficiently rapid rates. As current storage methods based on physical means (high-pressure gas or cryogenic liquefaction) are unlikely to satisfy targets for performance and cost, a global research effort focusing on the development of chemical means for storing hydrogen has recently emerged. The most relevant categories of storage materials, which have received the most attention from the research community are: (1) conventional metal hydrides, (2) complex hydrides, (3) sorbents, and (4) chemical hydrides. Each of these categories possesses interesting properties, but none of them fulfils all the requirements established by the U.S. Department of Energy (DOE) for on-board hydrogen storage systems.

Among the known materials that would enable high-volume automotive applications, ammonia–borane is a leading candidate as a potential hydrogen source and storage material owing to its high hydrogen storage capacity. Homogeneous transition-metal-catalyzed dehydrogenation of ammonia–borane and its derivatives amine-boranes is attracting considerable attention. Nevertheless, despite the number of organometallic complexes able to induce the dehydrogenation and although the process is well established, mechanistic insight is still lacking for many systems.

Amide the several transition metal catalysts proposed to assist the process, the latent twelve-electron complex $[Rh\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}\text{-}(Me_2HNBH_3)_2]BAr^F{}_4$ is the first example of a significantly more open transition-metal fragment, which contain a bis(σ-amine–borane) binding motif. It should be, therefore, worth investigating whether amine-boranes dehydrocoupling reactions can be influenced by bis(σ-amine–borane) binding motifs. For this reason, DFT calculations have been carried out to explore mechanistic alternatives that ultimately lead to the formation of the amine-borane cyclic dimer $[BH_2NMe_2]_2$ by

hydrogen elimination. All the details concerning our investigation are presented in **Chapter 3**. Since it was been demonstrated that Rh chelating bis-phosphine complexes are extremely efficient catalysts for the dehydrogenation, unlike the monodentate phosphine complexes, other Rh-based catalysts object of our interest are $[Rh(Ph_2P(CH_2)n\text{-}PPh_2)(C_6H_5F)]^+$ (n=3–5) complexes containing chelating bis-phosphine ligands. Experimental findings have underlined a dependency of the rate of dehydrocoupling reactions of H_3BNMe_2H on the P–Rh–P bite angle, β -angle. Therefore, a Density Functional Theory (DFT) investigation of the possible mechanistic routes of dehydrocoupling of the prototypical secondary dimethylamine-borane, BH_3NHMe_2, assisted by Rh-chelating bis-phosphine complexes has been carried out in order to confirm the experimental evidences by which the catalytic efficiency of such systems is due to formation of Rh(III) dihydride complexes, which rapidly lose H_2 and reform Rh(I) species and to evaluate the influence that the structure of the ligand, namely the chelating phosphine P-Rh-P bite angle, has on the rate of the reaction. Useful and imteresting results are reported in a work presented in **Chapter 3**. Given that it was discovered that also the more abundant alkali metal are active for the catalytic dehydrocoupling of Me_2NHBH_3, a quantum-mechanical investigations of the β-diketiminato Mg and Ca complexes, $[HC\{(Me)CN(2,6\text{-}^iPr_2C_6H_3)\}_2M(THF)_n\{N(SiMe_3)_2\}]$ (M=Mg, Ca), was performed in order to prove the viability of the pathways of the mechanistic scheme proposed on the basis of the experimental findings and to compare the behaviors of Mg and Ca complexes to assess whether differences in radius and charge density can be considered responsible of the observed differences in reactivity. This study was extended to several more or less bulky amine–boranes in order to examine the influence that the steric demand can have on the course of the reaction. In **Chapter 3** the mechanistic investigation will be illustrated in more detail.

As mentioned above, in the perspective of an *hydrogen based society* an intense research has to be devoted to the development of powerful and efficient Fuel Cells. These systems, in fact, are regarded as key components for exploitation of the energy stored in hydrogen molecules. Among the various types of proton conducting electrolytes, that are the most essential parts of a fuel cell unit, polymer electrolyte membranes (PEMs) are regarded as viable candidates since they enable operation of the cells at desirably low temperatures. DFT investigation has been performed with the aim to explore the proton conductivity mechanism in P4VI membranes, both neutral and doped with phosphoric acid. Although further detailed investigations dealing with a more realistic model are necessary, our study, presented in **Chapter 4**, can be considered as the starting point in order to shed light on all the mechanistic aspects involved in the proton conductivity mechanism of pure and acid-based P4VI.

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Chapter 1

Hydrogen: the energy of the future

Energy is essential for human existence and development. One of the main strategic objectives is to develop a world sustainable energy economy for the future. At present, the only renewable energy carrier that could be synthesized efficiently without material limitations and in real-time is hydrogen. Hydrogen is versatile, clean, safe, and cheap. The widespread use of hydrogen and fuel cell vehicles would enable a profitable transition from an economy based on the use of fossil fuels.

Nowadays, at least 80 % of the energy that people use to drive, heat their homes, and power gadgets comes from fossil fuels such as coal, oil, and natural gas. Traditional biomass, nuclear energy, and large-scale hydropower account largely for the remainder. Modern forms of renewable energy play only a relatively small role at present (on the order of a few percent of the world's current supply mix). Although energy consumption from sustainable energy sources is rapidly increasing, the overall contribution is still too little (see figure 1.1).

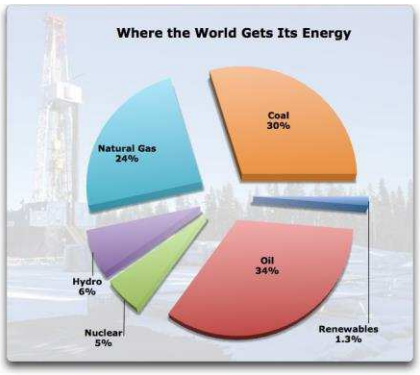


Figure 1.1. Global energy consumption by source 2011.

However, fossil fuels are not renewable and currently known reserves would not last for longer than a few decades. This is so much the case when considering that the rate of energy consumption is expected to increase because of both, the rapidly growing world population and the (reasonable) assumption that inhabitants of less developed countries would wish to increase energy demand, a desire which should not be refused[1].

In addition to that, production of energy by burning carbon based fuels inevitably leads to an increasing level of carbon dioxide[2] in the atmosphere, thus aggravating greenhouse effect and its global adverse consequences: rising sea levels and increasingly harsh weather conditions are just two of the main problems that we have to take into account.

Not less important are geopolitical tensions arising from the non-uniform distribution of fossil resources throughout the world.

Because of these problems, the challenge is to find highly efficient ways to produce, deliver, and use energy that enhance quality of life but do not threaten the environment and climate or strain geopolitical relations.

In this context, *hydrogen*[3-6] is a promising alternative to fossil fuels. The potential of hydrogen to play an important role as alternative sustainable source was coming into serious consideration along the last 30 years, and a name for this paradigm was coined: "*Hydrogen Economy*"[7-9].

Hydrogen is abundant and generously distributed throughout the world without regard for national boundaries. Hydrogen is the lightest most abundant element in the Universe and is highly present on the surface of the earth as part of a number of compounds including water, hydrocarbons

and biomass. H_2 is colourless, odourless, tasteless and nontoxic under normal conditions. However, since hydrogen (as such) is not freely available on earth, it cannot be used as a *primary energy source*. Referring to hydrogen as a fuel in the same sense as we refer to petrol or natural gas is misleading. Energy is needed in the first place to produce hydrogen (e.g., from water) that can then act as an energy vector[10] (or carrier). Therefore, when we consider hydrogen in this sense we have to think to a network composed of three functional steps: **production, storage** and **use**[7] (figure 1.2).

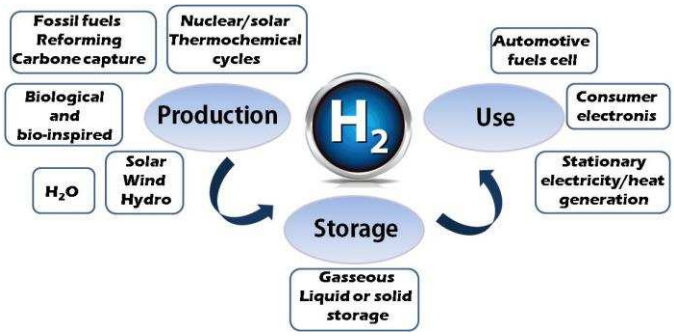


Figure 1.2. Hydrogen life cycle as a network composed of three functional steps: *production, storage* and *use*.

1.1. Production of Hydrogen

As mentioned above, hydrogen is not naturally present as H_2 and it must be produced. It occurs in chemical compounds such as water and the organic compounds of biomass, that have to be chemically transformed to yield H_2.

Today most hydrogen is produced from steam reforming[11] of natural gas or higher hydrocarbons. However, this way of production hydrogen does not reduce the use of fossil fuels but rather shifts them from end use to an earlier production step; and it still releases CO_2 to the environment. Thus, to achieve the benefits of the so-called "*hydrogen economy*" it could be produced from alternative methods[12] to the conventional steam reforming that include water electrolysis with electricity produced from sustainable energy sources, e.g. solar, wind, hydro power or directly from photolysis, or various biogas production options using gasification or pyrolysis processes or biomass fermentation with microorganisms. Newly developed photo-electrochemical and thermo-chemical processes including using microbial electrolysis cells as well as tailored molecules that can facilitate the splitting of water molecules into hydrogen and oxygen with lower energy requirements than conventional electrolysis should be advantageously exploited.

1.2. The Hydrogen Storage Problem

The problem of storing hydrogen[13,14] safely and effectively is one of the major technological barriers currently preventing the widespread adoption of hydrogen as an energy carrier and the subsequent transition to the *hydrogen economy*.

The fundamental difficulty of storing hydrogen as a liquid or compressed gas is evident in the hydrogen p-T phase diagram shown in Fig. 1.3.

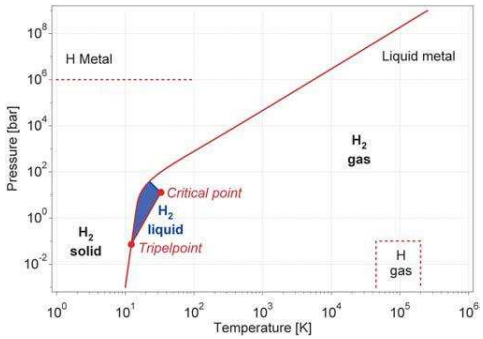


Figure 1.3. Primitive phase diagram for hydrogen.

At low temperatures hydrogen is a solid with a density of 70.6 kg·m^{-3} at -262°C and it is a gas at higher temperatures with a density of 0.089886 kg·m^{-3} at 0°C and a pressure of 1 bar. A small zone starting at the triple point and ending at the critical point exhibits the liquid hydrogen with a density of 70.8 kg·m^{-3} at -253°C. At ambient temperature (25°C) hydrogen is a gas. The strong repulsion interaction between hydrogen molecules is responsible for the low critical temperature (T_c=240°C) of hydrogen gas. Hydrogen storage basically implies the reduction of the enormous volume of the hydrogen gas: 1 kg of hydrogen at ambient temperature and atmospheric pressure takes a volume of 11 m^3. In order to increase the hydrogen density in a storage system, work must either be applied to compress hydrogen, or the temperature has to be decreased below the critical temperature, or finally, the repulsion has to be reduced by the interaction of hydrogen with another material. The second important criterion for a hydrogen storage system is the reversibility of the hydrogen uptake and release. Considering these observations, several different methods of storing hydrogen are available.

The traditional storage methods based on *physical means* allow to store hydrogen in both the gaseous state, using high pressure storage tanks, and the liquid form, using cryogenic temperatures (−253 °C). Even if liquid phase gives much lower pressures for storage, as well as a higher energy density, it imposes severe energy costs because up to 40% of its energy content can be lost to liquefaction. Industrial facilities and laboratories are already accustomed to handle both ways but these options are viable just for the stationary consumption of hydrogen in large plants that can accommodate large weights and volumes. In table 1.1. is reported a comparison between the three main physical hydrogen storage methods.

Table 1.1. Comparison of hydrogen storage methods.

Method	ρ_m (wt%)[a]	ρ_m (kgm^{-3})[b]	T (K)[c]	p (bar)[d]	Description
Compressed gas	13	<40	273	800	Compressed hydrogen gas; lightweight, high-pressure cylinder
Liquid	Varies	70.8	21.5	1	Liquid hydrogen, continuous loss of a few % per day at RT
Physisorpition	≈2	20	77	100	Physical adsorption by porous materials, fully reversible

For transportation use, the on-board storage of hydrogen is a far more difficult challenge. The Department of Energy (DOE)[15] originally setup a series of metrics, shown in table 1.2., that hydrogen would have to meet or exceed for it to become economically viable as a gasoline equivalent.

Table 1.2. Summary of DOE hydrogen storage targets.

		TARGETS		
Storage Parameter	Units	2010	2015	Ultimate
System gravimetric capacity	kWh/kg	1.5	1.8	2.5
	wt% H2	4.5	5.5	7.5
System volumetric capacity	kWh/L	0.9	1.3	2.3
	g H2/L	28	40	70
H_2 delivery temp. (to FC)	°C	-40/85	-40/85	-40/95-105
Operating pressure (min./max.)	MPa	0.5/1.2	0.5/1.2	0.3/1.2
Kinetics	(g H2/s)/kW	0.2	0.2	0.2
Cost	$/kWh net	To be determined		

The need for a hydrogen storage material that meets DOE requirements, has prompted research to explore chemical means[14] for storing hydrogen. In particular, the search for materials capable of safe and cost effective storage and on-board transport of hydrogen constitutes a major issue in the energy sector and a large effort is being made worldwide in the attempt to develop functional hydrogen storage materials.

In many hydride-type materials, hydrogen density is up to 170 g H_2 /L[17] that is a factor of more than two order of magnitude greater with respect to liquid hydrogen. The high hydrogen densities achievable using these materials makes this approach the most attractive mean for achieving the Ultimate DOE storage targets.

Among storage materials the most relevant compounds are: (1) conventional metal hydrides, (2) complex hydrides, (3) sorbents, and (4) chemical hydrides (see table 1.3.).

Table 1.3. Overview of the properties of the major hydrogen storage materials classes. Trends for technical challenges for each class are delineated by acronym: I (insuffient) indicates significant challenges remain towards achieving DOE targets; S (satisfactory) signifies satisfactory performance; G (good) indicatessome improvement is required

	$LaNiH_6$	**$NaAlH_4$**	**MOF-5**	**NH_3-BH_3**
	Hydrogen form a metallic bond with the host metal atoms	*Hydrogen covalently bonded as stable "complex" anions*	*Physisorption of molecular hydrogen to high surface area sorbent*	*Hydrogen covalently bonded in material & utilized as single use "fuel"*
Volumetric Capacity	*G*	*G*	*S*	*G*
Gravimetric Capacity	*I*	*G*	*G*	*G*
Reversibility	*G*	*G*	*G*	*I*
Thermodynamics	*G*	*G*	*I*	*S*
Kinetics	*G*	*I*	*G*	*S*
Efficiency	*G*	*G*	*G*	*R*

Automotive applications of conventional metal hydrides are not generally very convenient because of too low gravimetric density. In addition, thermodynamics of H bonding is either too strong or too weak in order to obtain an easy hydrogen insertion/removal. For these reasons, the focus is addressed to the development of conventional metal hydrides alloying with other elements with the aim to improve hydrogen capacity and reaction enthalpy.

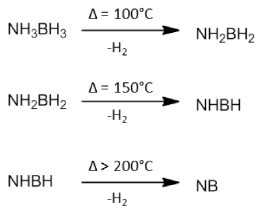
"Complex hydrides" are a class of ionic hydrogen-containing compounds which consist of metal cations, such as Li, Na, Mg, or Ca, and hydrogen-containing "complex" anions as, for example, borohydrides (BH_4^-),[18] alanates (AlH_4^-)[22], and amides (NH_2^-)[23], in which hydrogen atoms are covalently bonded to central atoms. As a consequence, complex hydrides are grouped under the chemisorptive hydrogen storage mechanism. Initially, complex hydrides were not considered for reversible hydrogen storage because of their ostensible disability to both release and take-up hydrogen over many cycles due to unfavorable hydrogen reaction thermodynamics and/or their slow kinetics. However, in 1996 was demonstrated the reversibility of hydrogen storage in $NaAlH_4$ at moderate conditions upon the addition of a titanium-based catalyst[21] with the consequent re-ignited interest in complex hydrides and the development of several novel approaches for improving the thermodynamic and/or kinetic properties of several complex hydrides.

Sorbent materials represent another potential strategy to storage hydrogen. In this case, molecular hydrogen interacts with sorbents through weak physisorptive attraction. Therefore, the amount of hydrogen adsorbed proportionally depends on the sorbent's surface. Among the different types of sorbents material carbon-based materials[23-27] and metal–organic frameworks (MOFs)[28,29] have quickly emerged as promising candidate for hydrogen storage. However, the general limitation of these compounds is the weak van der Waals Interaction between molecular hydrogen and the sorbent. To solve this problem a noteworthy approach achieving improved hydrogen binding in sorbents involves the addition of a small amount of hydrogen dissociation catalyst (such as Pd or Pt) along with a carbon-based bridging substance[30].

Similar to complex hydrides, "chemical hydrides" can contain large quantities of hydrogen by mass and volume. A few prominent examples of chemical hydride reactions include hydrolysis of sodium borohydride ($NaBH_4$)[31,32] and thermal decomposition of ammonia-borane (NH_3BH_3)[33]. In particular, these latter compounds have attracted increasing attention as very promising chemical hydrogen storage materials thanks to both their commercial availability and physical and chemical properties.

1.2.1. Ammonia-borane and its derivatives amine-boranes

Ammonia–borane (H_3NBH_3, AB) and its derivatives amine-boranes are excellent hydrogen storage materials candidates. As the NB unit is isoelectronic with CC, these materials are viewed as inorganic analogues of hydrocarbons. However, NH_xBH_x compounds are solids rather than gases at room temperature due to their greater polarity and stronger intermolecular interactions relative to organic analogues. The inherent polarity results from the different electronegativities of the B and N atoms that are 2.0 and 3.0 respectively. This allows it to eliminate hydrogen by combining protic and hydridic hydrogen atoms. As solids, they provide far more favorable volumetric densities than do the corresponding gaseous hydrocarbons. The two hydrogen-rich materials ammonium borohydride (NH_4BH_4) and ammonia-borane (NH_3BH_3) were first prepared in the mid-1950s as part of the US government's program to develop boron-based jet fuels[34]. NH_4BH_4 releases hydrogen slowly at temperatures above 40°C and thus is too unstable for applications at room temperature. On the other hand, ammonia-borane NH_3BH_3 (AB) is a stable solid at room temperature and, finally culminating in formation of ceramic boron nitride (BN). The simplest hydrogen release method is to just heat it up[35]. The dehydrogenation of AB during heating is known to be a stepwise process (Scheme 1.1.):

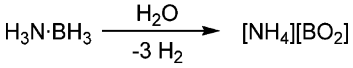


Schema 1.1. Thermal decomposition of AB.

This process, which is only partially understood, is the subject of extensive theoretical as well as thermodynamic considerations.

The hydrogen release in the first step begins concurrently with the melting of the hydride and the breaking of the intermolecular hydrogen bonds. The decomposition of $(NH_2BH_2)_x$ in the second step is typically hindered by the formation of gaseous products other than hydrogen, such as borazine. This last compound is an inorganic analogue of benzene that is highly undesirable in the H_2 feed.

The other main method used to release hydrogen from ammonia-borane is hydrolysis[36] (see Scheme1.2.).



Scheme 1.2. Hydrolysis of AB.

Ammonia-borane undergoes hydrolysis only very slowly at room temperature in basic water, but the rate is accelerated by lowering the pH or increasing the temperature. Most of the research in this area has focused on the search for transition-metal catalysts to increase the rate of AB hydrolysis. Nonetheless, the use of hydrolysis as a method for hydrogen delivery in a fuel cell powered car is impractical for several reasons. AB is only moderately soluble in water and the regeneration of the spent fuel is impracticable due to the difficulty of reducing B-O bonds formed[37]. Hence, while this technology has great promise in certain areas such as emergency power backup, it is too inefficient to work in the transportation sector.

Even if AB is a strong candidate for on-board hydrogen storage three additional physical obstacles must be overcome: 1) the rates of H_2 release at temperatures below 85°C must be increased, 2) borazine formation must be prevented, and 3) reversibility must be demonstrated.

Furthermore, in order to use AB to release hydrogen for utilization in vehicles powered by fuel cells it is necessary to develop fast, controlled, and complete release systems. The hydrogen release needs to be fast enough to power fuel cells in times of acceleration when more energy is needed. It needs also to be controllable, so that it can be turned off, and have a consistent release rate in order to avoid spikes of hydrogen when it is not needed. Lastly, in order to achieve a high materials weight percent, most of the hydrogen needs to be released or the hydrogen yield will be very low.

In this context, considerable interest has recently been addressed to develop catalytic systems that can dehydrogenate ammonia-borane and its derivatives amine–boranes. Whereas thermal dehydrogenation typically produces a myriad of intermediates, transition-metal-catalyzed reactions tend to be more selective thanks to the role metal center plays in controlling kinetics and product distributions for dehydrocoupling reactions that form linear or cyclic oligomers and polymers alongside the concomitant release of H_2. Transition-metal catalysts are also used to activate alkylated amine-boranes. Researches have shown that both heterogeneous[38,39] (e.g. Rh(0)) and homogeneous[40-45] (e.g. Ti) catalysts effectively promote amine-borane dehydrocoupling with useful scope and activity.

However, although the majority of the research has focused the attention on mid or later transition metal catalysis, recently, big interest has been also addressed to cheaper and more abundant metals of Groups 1 and 2[46,47] which are competent for the dehydrogenation of amine-boranes

In both cases, dehydrocoupling is a rather complex process that is the subject of extensive theoretical as well as thermodynamic considerations.

1.3. Use of Hydrogen

Once produced, Hydrogen can be burned directly as a fuel in an appropriately adapted internal combustion engine; this is considered a transition strategy toward widespread use of hydrogen for transportation. The US and Russia have testflown commercial airliners with jet engines

modified to burn hydrogen. Similarly, BMW, Ford and Mazda have produced road testing cars powered by hydrogen internal combustion engines.

Alternatively, hydrogen can also be used in fuel cells for transportation or power generation[48]. According to the U.S. Department of Energy (DOE), hydrogen fuel cells have a wide variety of potential applications in several major areas, such as *portable* applications that include consumer electronics and *transportation*, where hydrogen fuel cells can be used for basic propulsion.

Fuel cell technologies offer great promise for energy conversion because they deliver energy densities that are orders of magnitude greater than conventional batteries and capacitors and comparable to the power and energy densities of internal combustion engines. They have the potential to replace internal combustion engine vehicles and provide power in stationary and portable power applications because they are energy-efficient, clean, and fuel-flexible.

1.3.1. What is a fuel cell?

Fuel cells is an electrochemical device that generate electricity by a chemical reaction. Every fuel cell has two electrodes, one positive and one negative, called, respectively, anode and cathode. The reactions that produce electricity take place at the electrodes. Every fuel cell has also an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which speeds the reactions at the electrodes. In particular, at the anode electrons and ions from the fuel are obtained, while at the cathode the ions are converted into waste chemicals like water[49,50].

Fuel cells are classified primarily by the type of electrolyte they employ which determine the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel which is used, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. Some types of fuel cells work well for small portable applications or for powering cars. Others may be useful for use in stationary power generation plants. There are several types of fuel cells currently under development[51], each with its own advantages, limitations, and potential applications. A few of the most promising types of fuel cells include: phosphoric acid fuel cells (PAFC), proton exchange membrane fuel cells (PEMFC), moltencarbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), alkaline fuel cells (AFC). More details of these important fuel cells are shown in Table 1.4. Among these, proton exchange membrane fuel cells are the most promising device type for application in vehicular systems[52].

Table 1.4. Fuel cells comparison chart.

Fuel Cell Type	Common Electrolyte	Operating Temp.	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly-perfluorosulfonic acid	50 – 100°C 122– 212°F	• Solid electrolyte reduces corrosion and electrolyte management problems • Low temperature • Quick start-up	• Requires expensive catalysts • High sensitivity to fuel impurities • Low temperature waste heat • Waste heat temperature not suitable for combined heat and power (CHP)
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 – 100°C 194 – 212°F	• Cathode reaction faster in alkaline electrolyte, higher performance	• Expensive removal of CO from fuel and air streams required (CO degrades the electrolyte)
Phospohoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 – 200°C 302 – 392 °F	• Higher overall efficiency with CHP • Increased tolerance to impurities in hydrogen	• Requires expensive platinum catalysts • Low current and power • Large size/weight
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 – 700°C 1112– 1292 °F	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature speeds corrosion and breakdown of cell components • Complex electrolyte management • Slow start-up
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	650 – 1000°C 1202 – 1832 °F	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte reduces electrolyte management problems • Suitable for CHP • Hybrid/GT cycle	• High temperature enhances corrosion and breakdown of cell components • Slow start-up • Brittleness of ceramic electrolyte with thermal cycling

1.3.1.1. PEMFC

PEMFC is the most likely candidate for transportation applications[53]. The PEMFC has a high power density and a relatively low operating temperature (ranging from 20 to 100 °C). The low operating temperature means that the PEMFC is self-starting without the need of external warm up and readily generating electricity which makes it particularly promising.

A hydrogen-powered PEMFC consists of two electrodes and a separator polymer membrane as shown in Fig 1.4.

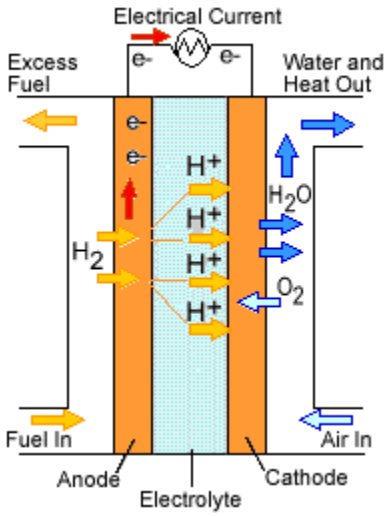


Figure 1.4. Polymer Electrolyte Membrane Fuel Cell (PEMFC).

Hydrogen is supplied to the anode and air is channeled to the cathode. The electrochemical reactions taking place at the electrodes are:

Anode: $H_2 \rightarrow 2H^+ + 2e^-$
Cathode: $1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall reaction: $H_2 + 1/2\ O_2 \rightarrow H_2O$ + Electrical energy + Heat

At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons. The polymer electrolyte membrane (PEM) allows only the protons to pass through it to the cathode. The electrons travel along an external circuit to the cathode, creating an electrical current.

At the cathode, the electrons and protons combine with oxygen to form water which is the only waste product of hydrogen fueled PEMFCs.

The most commonly known and studied PEMs are based on Perfluorosulfonic acid membranes such as Nafion®[54]. The conductivity of these perfluorosulfonic acid polymers membranes is stongly dependent on the presence of water to solvate the protons dissociated from the sulfonic acid groups. Consequently, the operating temperature is limited to below the boiling point of water (100 °C), typically 60-90 °C, at atmospheric pressure. This is a severe drawback because the use of a polymer membrane electrolyte at temperatures above 100 °C is desirable[55,56] for several reasons. Firstly, the reaction kinetics is enhanced and the catalytic activity increased at higher temperatures for both electrodes. Secondly, there is reduced poisoning of catalysts by fuel impurities such as carbon monoxide (CO). This poisoning effect has been shown to be very temperature-dependent; that is, CO adsorption is less pronounced with increasing temperature.

The need for a PEM that retains a high level of proton conductivity at elevated temperatures (100–200 °C) and relatively low humidity (RH ~ 25–30%) has become known as the “high

temperature membrane problem". A molecule that can be used as a proton solvent alternative to water should present several specific characteristics[57-63]:

- it should have a higher boiling point than water;
- it should be amphoteric in the sense that it can behave both as a protogenic and proton acceptor group;
- it must form a dynamic hydrogen bond network which is important for fast proton transport.

Typical amphoteric molecules are heterocycles such as imidazole, pyrazole, benzimidazole and triazole, that all have quite high proton conductivity in the liquid state.

Similarly to water, such systems show a proton conductivity mechanism known as Grotthuss mechanism[64-66] in which the transport of an excess proton is described by the diffusion of a structural defect in a hydrogen bond network, see figure 1.5.

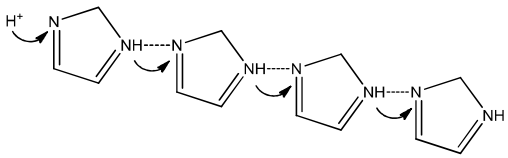


Figure 1.5. Grotthuss-type proton conductivity mechanism in Imidazole systems.

However, the potential use of liquid imidazole in fuel cells has a big limitation due to its leakage into the electrode areas, which leads to a permanent damage to the membrane and an increase of poisoning risk of the Pt-electrode.[67] This leakage problem can be avoided by the immobilization of the imidazole groups to the membrane materials[68-73]. In fact, unlike water, they can be incorporated into the polymer structure to further reduce their volatility during operation. Following this strategy, several N-heterocyclic polymers have been produced and, among these, poly(4-vinyl-imidazole), P4VI, is one of the first anhydrous proton conductors studied.[74,75] As in liquid imidazole, it is expected that also in this system proton conductivity involves Grotthuss mechanism.[76-79] Furthermore, some experimental evidences have shown that the adding of a strong acid, generally phosphoric or sulfuric acid,[80] leads to a proton conductivity that is several orders of magnitude higher than pure systems[81,82] (maximum values in the range 10-5 to 10-4 S/cm) but, at the same time, it is still order of magnitudes lower than that provided by fluorosulfonic acid membranes (10-1 S/cm). However, a detailed understanding of the involved mechanistic aspects could be essential in order to design new materials with better performance.

Referents

(1) M.I. Hoffert, *Nature*, **1998**, 395, 891; Energy Information Administration, *International Energy Outlook 2004*, **2004**, rep. no. DOE/EIA-0484, available at http://www.eia.doe.gov/oiaf/ieo.

(2) R. S. Eckaus, Comparing the Effects of Greenhouse Gas Emissions on Global Warming. *The Energy Journal* **1992**, *13*, 25.

(3) J. A. Turner, *Science*, **1999**, 285, 687.

(4) M. Schrope, *Nature*, **2000**, 414, 682.

(5) J. A. Turner, *Science*, **2004**, 305, 972.

(6) R. F. Service, *Science*, **2004**, 305, 958.

(7) G.W. Crabtree, M. S. Dresselhaus, M. V. Buchanan, *Physics Today*, **2004**, 39.

(8) F. Schüth, B. Bogdanovic, M. Felderhoff, *Chem. Commun.*, **2004**, 2249.

(9) *The Hydrogen Energy Transition*, ed. D. Sperling and J. S. Cannon, Elsevier, Amsterdam, **2004**.

(10) *Hydrogen as an Energy Vector*, ed. A. A. Strub and G. Imarisio, Comission of the European Communities, D. Reidel Publishing Co., Dordrecht, **1980**.

(11) *Natural Gas Reforming*.
http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html.

(12) *The Hydrogen Economy*: Opportunities, Costs, Barriers and R&D Needs, Committee on Alternatives and Strategies for Future Hydrogen Production and Use, The National Academies Press, Washington, D.C., **2004**.

(13) Note that the volumetric energy density of 70 MPa hydrogen, 1.3 kWh/L, which is the density of the gas alone, is unable to satisfy the 2015 DOE system-level targets due to the additional volume required for system components such as the containment vessel.

(14) J. Y, A. Sudik, C. Wolvertonb, D. J. Siegelwa, *Chem. Soc. Rev.*, **2010**, 39, 656

(15) S. Dillich, *2009 DOE Hydrogen Program & Vehicle Technologies Program* http://www.hydrogen.energy.gov/pdfs/review09/st_0_dillich.pdf. DOE has recently lowered the 2015 gravimetric total system target to only 5.5 total system weight %.

(16) A. C. Switendick, *Phys. Chem. N. F.*, **1979**, 117, 89.

(17) Based on the crystal structure of VH2 and assuming a materials density equal to the single-crystal density.

(18) A. Züttel, S. Rentsch, P. Fisher, P. Wenger, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Alloys Compd.*, **2003**, 356, 515.

(19) A. Züttel, P. Wenger, S. Rentsch and P. Sudan, *J. Power Sources*, **2003**, 118, 1.

(20) Y. Nakamori, H. Li, K. Miwa, S. Towata and S. Orimo, *Mater. Trans.*, **2006**, 47, 1898.

(21) B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.*, **1997**, 253, 1.

(22) P. Chen, Z. T. Xiong, J. Z. Luo, J. Y. Lin, K. L. Tan, *Nature*, **2002**, 420, 302.

(23) E. Poirier, R. Chahine, P. Benard, G. Dorval-Douville, L. Lafi, P. A. Chandonia, *Langmuir*, **2006**, 22, 8784.

(24) R. Ströbel, J. Garche, P. T. Moseley, L. Jörissen, G. Wolf, *J. Power Sources*, **2006**, 159, 781.

(25) Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, S. B. Zhang, *Phys. Rev. Lett.*, **2005**, 94, 155504.

(26) A. C. Dillon, M. J. Heben, *Appl. Phys. A: Mater. Sci. Process.*, **2001**, 72, 133.

(27) R. Chahine, T. K. Bose, *Int. J. Hydrogen Energy*, **1994**, 19, 161.

(28) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, **1999**, 402, 276.

(29) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.*, **2001**, 34, 319

(30) Y. Li, R. T. Yang, *J. Am. Chem. Soc.*, **2006**, 128, 8136.

(31) S. C. Amendola, M. Binder, S. L. Sharp-Goldman, M. T. Kelly, P. J. Petillo, US Pat., 6,534,033 B1, 2003.

(32) Q. Zhang, G. M. Smith, Y. Wu, Int. J. *Hydrogen Energy*, **2007**, 32, 4731.

(33) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.*, **2007**, 2613.

(34) D. M. Schubert, *Borax Pioneer*, **2001**, *20*.

(35) M. G.Hu, R. A. Geanangel, W. W. Wendlandt, *Thermochim. Acta*. **1978**, *23*, 249255.

(36) M. Chandra, Q. Xu, *Journal of Power Sources*, **2006**,156,190.

(37) C. N. Smythe, C. J. Gordon, *Eur. J. Inorg. Chem.* **2010**, 509.

(38) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424.

(39) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Comm.* **2001**, 962.

(40) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048.
(41) V. Pons, R. T. Baker, N. K.Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. D. A. Grant, Dixon, *Chem. Comm.* **2008**, 6597.
(42) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844.
(43) P. M. Zimmerman, A. Paul, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 5418.
(44) X. Yang, M. B. Hall, *J. Organomet. Chem.* **2009**, *694*, 2831.
(45) D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Comm.* **2007**, 3297.
(46) M. S. Hill, G. Kociok-Köhn, T. P. Robinson, *Chem. Commun.,* 8**2010**, 46, 757
(47) M. S. Hill, M. Hodgson, D. J. Liptrot, Mary F. Mahon *Dalton Trans.*, **2011**, 40, 7783.
(48) a) A. Schäfer, J. B. Heywood, M. A. Weiss, *Energy* **2006**, *31*, 2064; b) Prospects for a hydrogen economy, *Parliamentary Office of Science and Technology,* **2002**, number 186.
(49) X. Li, *Principles of Fuel Cells*; Taylor & Francis: New York, **2006**.
(50) W. Vielstich, *Fuel Cells: Modern Processes for the Electrochemical Production of Energy*.
(51) John Wiley & Sons Ltd.: London, **1970**; *Shah RK. Fuel cell science and technology, chapter introduction. New Delhi: Springer, New York and Anamaya Publishers;* ***2007***.
(52) A. C. Dupuis, *Progress in Materials Science*, **2011**, 56, 289.
(53) X. Ye, H. Bai, Ho WSW. *Journal of Membrane Science*, **2006**, 279, 570.
(54) (a) V. D. Noto, E. Negro, J.-Y. Sanchez, C. Iojoiu, *J. Am. Chem. Soc.*, **2010**, 132, 2183; (b) C. Iojoiu, M. Hana, Y. Molmeret, M. Martinez, L. Cointeaux, N. El Kissi, J. Teles, J.-C. Leprêtre, P. Judeinstein, J.-Y. Sanchez, *Fuel Cells*, **2010**, 10, 778; (c) C. Iojoiu, M. Martinez, M. Hanna, Y. Molmeret, L. Cointeaux, J.-C. Leprêtre, N. E. Kissi, J. Guindet, P. Judeinstein and J.-Y. Sanchez, *Polym. Adv. Technol.*, **2008**, 19, 1406; d) WG. Grot, *Macromol. Symposia*,**1994**, 82, 161.
(55) RW. Kopitzke, CA. Linkous, HR. Anderson, GL. Nelson, *J. Electrochem. Soc.* **2000**,147,1677.
(56) Y. Gao, GP. Robertson, MD. Guiver, X .Jian, *J. Polym. Sci. Part A Polym. Chem.*, **2003**, 41, 497.
(57) O. Savadogo, *Journal of Power Sources*, **2004**, 127,135.
(58) BCH. Steele, A. Heinzel *Nature*, **200**, 414, 345.
(59) C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, AB. Bocarsly, *Journal of Power Sources*, **2001**,103,1.
(60) Q. Li, R. He, JO. Jensen, NJ. Bjerrum, *Chemistry of Materials*, **2003**, 15(26), 4896.
(61) B. Smitha, S. Sridhar, AA. Khan, *Journal of Membrane Science*, **2005**, 259,10.
(62) WHJ. Hogarth, JCDd Costa, GQ. Lu, *Journal of Power Sources*, **2005**,142, 223.
(63) MA. Hickner, H. Ghassemi, YS. Kim, BR. Einsla, JE. McGrath, *Chemical Reviews,* **2004**,104, 4587.
(64) a) W. Münch, K. D. Kreuer, W. Silvestri, J. Maier, G. Seifert, *Solid State Ion,* **2001**, 145, 437; b) K. D. Kreuer, S. J. Paddison, E. Spohr, M.Schuster, *Chem. Rev.*, **2004**, 104, 4637
(65) J.T. Daycock, G.P. Jones, J.R.N. Evans, J.M. Thomas, *Nature,* **1968**, 218, 673.
(66) A. Kawada, A.R. McGhie, M.M. Labes, *J. Chem. Phys.* **1970**, 52, 3121.
(67) F. Jiang, H. Pu, W. H. Meyer, Y. Guan, D. Wan, *Electrochimica Acta.* **2008**, 53, 4495.
(68) M. Schuster, T. Rager, A. Noda, K. D. Kreuer, J. Maier, *Fuel Cells*, **2005**,5, 355.
(69) K. D. Kreuer,; *J. Membr. Sci.*, **2001**, 185, 29.
(70) M. Schuster, W. H. Meyer, G. Wegner, H. G. Herz, M. Ise, K. D. Kreuer, J. Maier, *Solid State Ionics*, **2001**, 145, 85.
(71) M. F. H. Schuster, W. H. Meyer, M. Schuster, K. D. Kreuer, *Chem. Mater.*, **2004**, 16, 329.
(72) M. F. H. Schuster, W. H. Meyer, *Annu. Rev. Mater. Res.*, **2003**, 33, 233.
(73) J. C. Perrson, P. Jannasch, *Chem. Mater.*, **2003**, 15, 3044.
(74) A.Bozkurt, W. H. Meyer, *Solid State Ionics.,* **2001**, 138, 259.
(75) A. Bozkurt, W.H. Meyer, J. Gutmann, G. Wegner, *Solid State Ionics,* **2003**,164,169.
(76) K. D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier, *Electrochim. Acta,* **1998**, 43, 1281.
(77) A. Bozkurt, W.H. Meyer, *Solid State Ionics,* **2001,** 138, 259.
(78) N. Agmon, *Chem. Phys. Lett,*, **1995**, 244, 456.
(79) I. Alkorta, J. Elguero, *Org. Biomol. Chem.*, **2006**, 4, 3096.
(80) H. Pu, W. H. Meyer, G. Wegner, *Macromolecular Chemistry and Physics,* **2001,** 202, 1478.
(81) A. Bozkurt, W.H. Meyer, *Journal of Polymer Science: Part B: Polymer Physics*, **2001**, 39, 1987.

(82) H. Steininger, M. Schuster, K.D. Kreuer, J. Maier, *Solid State Ionics*, **2006,** 177, 2457.

Chapter 2

Theoretical background

The development of Density Functional Theory has been decisive for the theoretical investigation of many-electron systems. Unlike traditional methods, such as Hartree–Fock theory and its descendants based on the complex many-electron wavefunction, it is based on electron density that is a function of only three spatial coordinates. The relatively low computational costs together with the growing number of applications make DFT an unparalleled approach in theoretical chemistry.

All the properties of a system can be, in principle, described through the solutions Schrödinger's equation. In most cases, however, time-independent form **(2.1)** is sufficient to describe the chemistry of the ground state

$$\hat{\mathrm{H}}|\Phi\rangle = E|\Phi\rangle \qquad \textbf{(2.1)}$$

where E is the energy, H is a hermitian Hamiltonian operator and $|\Phi\rangle$ is the wavefunction.

For a general N electrons and M nuclei system, the Hamiltonian operator is:

$$\hat{\mathrm{H}} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1,j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1,B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad \textbf{(2.2)}$$

where i and j are indexes referring to the electrons whereas A and B refer to the nuclei, r represent the distances between particles, M the masses of the atoms and Z their charges. ∇^2 represents the Laplacian operator for the kinetic energy of electrons in the first term in eq. **(2.2)** and of the nuclei in the second one, respectively; the third term represent the coulomb attraction between electrons and nuclei; the last two terms represent the electron-electron repulsion and nuclei-nuclei. [1,2]

The exact solution of the Schrödinger's equation is only possible for systems that contain just one electron (hydrogen atom). When many-electron systems are considered, such an equation become too complex to be solved and the adoption of approximations is absolutely necessary. The main one is the Born-Oppenheimer approximation[3] that neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron. Because of this difference, the nuclei move much more slowly than the electrons and, therefore, they may be considered as moving under the field of fixed nuclei. The mathematical consequence is that the total molecular wavefunction can be separated into a product of an electronic wave function and a nuclear one. In this context, the kinetic energy of nuclei in eq. **(2.2)** can thus be ignored and the nucleus-nucleus repulsion considered a constant for certain geometry. In conclusion, the description of the motion of N electrons in a fixed potential due to the nuclei is described by the so-called electronic Hamiltonian:

$$\hat{\mathrm{H}}_{\mathrm{elec}} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1,j>i}^{N}\frac{1}{r_{ij}} \qquad \textbf{(2.3)}$$

that in a synthetic form becomes:

$$\hat{\mathrm{H}}_{\mathrm{elec}} = \hat{T} + \hat{U}_{ext} + \hat{U}_{ee} \qquad \textbf{(2.4)}$$

while, the Schrödinger equation involving the electronic Hamiltonian is given by:

$$\mathrm{H}_{elec}\Phi_{elec} = E_{elec}\Phi_{elec} \qquad \textbf{(2.5)}$$

where Φ_{elec} is the electronic wavefunction, which describes the motion of the electrons depending *explicitly* on the electronic coordinates but *parametrically* on the nuclear coordinates, i.e. for different arrangements of the nuclei, Φ_{elec} is a different function of the electronic coordinates.

The total energy for fixed nuclei must also include the constant nuclear repulsion. Therefore its expression is given by:

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad \textbf{(2.6)}$$

Since the electronic problem has been solved, it is possible to solve the motion of the nuclei considering the same assumptions. The electronic coordinates can be reasonable replaced by their average values, averaged over the electronic wavefunction, as the electrons move much faster than the nuclei. This then generates a nuclear Hamiltonian for the motion of the nuclei in the average field of the electrons:

$$\hat{H}_{nucl} = -\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 + E_{elec}(\{R_A\}) + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad \textbf{(2.7)}$$

The solution of the corresponding nuclear Schrödinger equation:

$$\mathrm{H}_{nucl}\Phi_{nucl} = E\Phi_{nucl} \qquad \textbf{(2.8)}$$

It describes the vibration, rotation and translation of a molecule.

It is worth noting that $E_{tot}(\{R_A\})$ provides a potential for nuclear motion. This means that the nuclei move on a potential energy surface [2] (PES) which are solutions to the *electronic* Schrödinger equation. Under the Born-Oppenheimer approximation, the PES is independent of the nuclear masses and is the same for isotopic molecules.

2.1. Density functional theory

Another completely different approach to solve the many electron problem is given by the use of Density functional theory (DFT). It allows us to compute all the properties of systems consisting of nuclei and electrons by the electron density $\rho(r)$ which is function of three variables $\rho(r) = f(x,y,z)$. The square of the wavefunction, in fact, is a direct measure of electron density. Total electron density

due to N electrons can be defined as N-times the integral of square of wavefunction over the spin coordinates of all electrons and over all but one of the spatial variables:

$$\rho(r) = N\int ...\int |\Psi(x_1, x_2, ..., x_N|^2 d\sigma_1 dx_2 ...dx_N \qquad \textbf{(2.9)}$$

Therefore, ρ(r) is the probability of finding any of N-electrons within a volume element *dr* with arbitrary spin and integrating (2.10) over all space the number of electrons N can be determined:

$$\int \rho(r) dr = N \qquad \textbf{(2.10)}$$

Unlike the wavefunction, the electron density is observable and can be measured experimentally, e.g by X-ray diffraction.

The basic framework for the modern Density functional methods, introduced by Hohenberg and Kohn[4], is the fact the ground state properties are functional of the electron density. They proposed two theorems. The first states that "every observable of a stationary quantum mechanical system (including energy) can be calculated, in principle exactly, from the ground-state density alone, i.e., every observable can be written as a functional of the ground- state density. The external potential $\hat{U}_{ext}$ is determined by the electron density (within an additive constant). Since ρ determines the number of electrons, it follows that ρ(r) also determines the ground state wavefunction Φ and all other electronic properties of the system, including the kinetic energy of electron T_e and the repulsion energy among electrons U_{ee}. In other words, the total ground state energy is a functional of the density with the following components:

$$E_{tot}[\rho(r)] = T_e[\rho(r)] + U_{ee}[\rho(r)] + U_{ext}[\rho(r)] = F[\rho(r)] + U_{ext}[\rho(r)] \qquad \textbf{(2.11)}$$

where $F[\rho(r)]$ is universal, i.e. its form does not depend on the particular system under consideration.

The second HK theorem provides the energy variational principle, analogous to the variational principle for the wave function. In particular, for a trial density $\int \tilde{\rho}(r)$ such that $\int \tilde{\rho}(r) \geq 0$ and for which $\int \tilde{\rho}(r) dr = N$

$$E_0 \leq E[\tilde{\rho}] \qquad \textbf{(2.12)}$$

This implies that any calculated energy is always higher than or equal to the true ground state energy.

Although the Hohenberg-Kohn theorems lay the foundation for the modern DFT, a mean to compute the E_{tot} from $\rho(r)$ is not given since the exact form of the functional F[ρ(r)] is not known. This represents the major part of complexities of the many-electron problems

An interesting approach to approximate the universal functional $F[\rho(r)]$, containing the kinetic and electron-electron functionals, was proposed by Kohn and Sham[5]. They introduced a fictitious system of N non-interacting electrons subject to an "external" potential $U_{ext}[\rho]$. Such a potential has to be chosen so that the ground state density of the non-interacting system is the same as that of the interacting one. In the non-interacting system the kinetic energy $T_s[\rho]$ and electron density are known exactly. Considering that a significant component of the electron-electron interaction will be the classical Coulomb interaction $J[\rho]$, the energy functional can be rearranged as:

$$E[\rho] = T_s[\rho] + U_{ext}[\rho] + J[\rho] + E_{XC}[\rho] \qquad \textbf{(2.13)}$$

where *exchange-correlation functional*[6-8] has been introduced:

$$E_{XC}[\rho] = (T[\rho] - T_s[\rho]) + (U_{ee}[\rho] - J[\rho]) \qquad \textbf{(2.14)}$$

in which the residual part of the true kinetic energy, T, which is not covered by T_S, is simply added to the non-classical electrostatic contributions. In other words, the exchange-correlation energy E_{XC} is the functional which contains everything that is unknown.

The generation of approximations for E_{xc} has led to a large and still rapidly expanding field of research[9]. An approach to compute the E_{xc} is based on the assumption that the electrons are subject to a constant external potential and thus the charge density is constant and can be treated as an homogeneous electron gas. The E_{xc} of a such system can be calculated exactly. On these considerations is based the Local Spin Density Approximation, LSDA[10]. Although LSDA can be considered as a remarkably fruitful approximation to describe reliably properties such as structure, vibrational frequencies, elastic moduli and phase stability (of similar structures) for many systems, it gives, however, significant errors in computing energy differences between systems in which energy distribution is not uniform.

A natural progression beyond the LSDA is thus the generalized gradient approximation (GGA) in which a generalized gradient terms is included. A huge number of functionals within the GGA family[11-22] have been developed. The first exchange functional was developed by Becke and was named B88[11]. It contains an empirical parameter that was determined fitting the exactly known exchange energies of the rare gas atoms He through Rn. A most popular correlation functional is due

to Lee, Yang and Parr[16] from whose abbreviations is derived the name LYP. In principle, each exchange functional could be combined with any of the correlation functionals, but only a few combinations are currently used. Among theme, a combination of the two functionals presented above give the BLYP[23] that is widely exploited.

2.2. Hybrid functional

The development of Hybrid functionals has given a significant contribution to the density functional theory. The basic idea behind the hybrid functionals is to mix the exact exchange Hartree-Fock energies with those obtained from DFT methods in order to improve performance. The parameters determining the weight of each individual functional are typically derived from experimental evidences. [24]

The most used functional in computational chemistry is the **B3LYP** that has the following form:

$$E_{XC}^{B3LYP} = (1-a)E_X^{LSDA} + aE_X^{HF} + bE_X^{B88} + cE_C^{LYP} + (1-c)E_C^{VWN} \qquad \textbf{(2.15)}$$

in which Becke exchange functional (B88)[11] is added to the Lee, Yang and Parr (LYP)[16] and Vosko, Wilk and Nusair VWN[8] correlation functionals alongside a 20% of exact HF exchange.

Several benchmark studies have tested the ability of B3LYP functional to reproduce many chemical properties.[25] Therefore, considering its good accuracy, this functional has been used in order to compute the structure optimizations that will be discussed in in chapter IV.

However, in the works concerning the dehydrocoupling reactions of amine-boranes catalyzed by transition and alkali metals reported in Chapter III, a different exchange correlation functional, named B3PW91[26,23], was used in order to estimate the energies of the stationary points on the reaction paths.

2.3. Basis sets.

A basis set is a mathematical description of the orbitals of a system, which is used for approximate theoretical calculation or modeling. It was J. Slater who first turned to orbital computation using basis sets, known as Slater Type Orbitals (STOs) that are hydrogen-like exponentials[10] of the form $e^{-\xi r}$. Although these functions reproduce very closely the molecular orbitals, they are very difficult to compute.

For this reason, F. Boys suggested a modification to the wavefunction by introducing Gaussian type functions[27,28] which contain the exponential $e^{-\alpha r^2}$. The main difference between the STOs and Gaussian type functions is the squared variable **r** in the exponential function in the latter. This feature makes these functions very easy to evaluate but, at the same time, the shape of the radial portion of the orbital is not good, leading to a loss of accuracy. The strategy that is widely used for polyatomic systems is to combine the faster calculation speed of GTOs with the better STOs representation of the molecular orbital[29]. As a consequence, a set of basis functions developed as a

linear combination of GTOs are properly combined to approximate the radial shape of the STOs functions.

The basis set can be divided into:

- Minimal basis sets: that are very faster but give inaccurate results (i.e. STO-3G);
- Split valence basis sets: they are typically X-YZG (double zeta basis). In this case, X refers to the number of primitive Gaussians comprising each core atomic orbital. The Y and Z indicate that each valence orbital is composed of the two sets of basis functions, the first one composed of Y primitive Gaussian functions whereas the second composed of Z primitive Gaussian functions. The split valence triple zeta X-YZWG is also used.

Another mean that can be used in order to improve a basis set is adding a polarization functions, i.e. d-type functions to the first row atoms Li-F and p-type functions to H. In addition, when an atom is in an anion or in an excited state, the loosely bond electrons, which are responsible for the energy in the tail of the wave function, become much more important. To compensate for this area, computational scientists use **diffuse** functions.

When the system under investigation contains transition metals a more elaborated approach is used. In this case, in fact, relativistic effects are important and they need to be taken into account. Because of the velocities sufficiently near the speed of light that core electrons reach, they manifest relativistic effects. A non-relativistic Hamiltonian operator is incapable of accounting for such effects, which can be significantly for many chemical properties. As a consequence, the use of relativistic pseudopotentials[30] or effective core potential (ECPs) that replace the complicated effects of the motion of the core electrons of an atom and its nucleus with an effective potential can overcome this difficulty without significant computational efforts. Among available ECP basis sets, the commonly used ones were formulated as LanL,[31] CEP,[32] and SDD.[33,34] Advantages in using SDD ECP for the description of the core electron of Rh metal are widely available in literature. For this reason, we also decide to use this pseudopotential in our work.

References

(1) I. R. Levine, Quantum Chemistry, 5th ed.; Prentice Hall: New Jersey, **2000.**

(2) A.Szabo, N. S. Ostlund, Modern Quantum Chemistry: Introduction To Advanced Electronic Structure Theory, McGraw-Hill,Inc. **1989**.

(3) M. Born, J. R Oppenheimer., *Ann. Phys.* **1927**, 84, 457.

(4) P.Hohenberg, W. Kohn, *Phys. Rev.* **1964**, 136, B864.

(5) W. Kohn, L. Sham, *J. Phys. Rev.* **1965**, 140, A1133.

(6) J. P. Perdew, A. Zunger, *Phys. Rev. B* ,**1981**, 23, 5048.

(7) J. P. Perdew and Y. Wang, *Phys. Rev. B*, **1992**, 45, 13244.

(8) S.H.Vosko, L.Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200.

(9) R. G. Parr, W.Yang, Density Functional Theory of the Electronic Structure of Molecules; Oxford University Press: New York, **1989**.

(10) Cramer, C.J. Essential of Computational Chemistry Theories and Models; Wiley, John & Sons, Incorporated: England, **2002**.

(11) A. D. Becke, *Phys. Rev. A* **1988** 38 3098.

(12) J. P. Perdew, *Phys. Rev. Lett.* **1985** 55, 1665.

(13) J. P. Perdew, *Phys. Rev B.* **1986** 33, 8822.

(14) A. D. Becke, *J. Chem. Phys.* **1986** 84, 4524.

(15) A. D. Becke, *Phys. Rev. A* **1988** 38, 3098.

(16) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988** 37 785.

(17) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **1992** 46, 6671.

(18) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996 77**, 3865.

(19) J. P. Perdew, M. Ernzerhof, A. Zupan, K. Burke, *J. Chem. Phys.* **1998** 108, 1522.

(20) D. C. Langreth, M. J. Mehl, *Phys. Rev. B*, **1983** 28, 1809.

(21) J. P. Perdew and Y. Wang, *Phys. Rev. B* **1986** 33, 8800.

(22) J. P. Perdew, in *Electronic Structure of Solids 91*, Ed. P. Ziesche and H. Eschrig; Akademie Verlay, Berlin, 1991.

(23) W.Koch, M.C Holthausen,. *A Chemist's Guide to Density Functional Theory,* Wiley-VCH: Weinheim, 2001.

(24) A. D Becke,. *J. Chem. Phys.* **1993**, 98, 1372.

(25) S. F. Sousa, P.A Fernandes, M. J.Ramos; *J. Phys. Chem. A*, **2007**, 111, 10439.

(26) A. D Becke,. *J. Chem. Phys.,* **1993**, *98*, 5648.

(27) T. H. Dunning, *J. Chem. Phys.* **1970** 53 2823.

(28) S. Huzinaga, *J. Chem. Phys.* **1965** 42,1293.

(29) R. F. Stewart, *J. Chem. Phys.* **1970** 52 431.

(30) J. Hafner, From Hamiltonians to Phase Diagrams, Dover, New York, 1988.

(31) P. J.Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, 82, 299.

(32) W. Stevens, M. Krauss, H.Basch, P. G. Jasien, *Can. J. Chem.* **1992**, 70, 612.

(33) T. Leininger, A.Nicklass, H.Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys.* **1996**, 105, 1052 and previous papers by the same group.

(34) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preu *Teor. Chim. Acta* **1990**, *77*, 123.

Chapter 3

Hydrogen Storage Problem:

AB and derivatives as potential candidates

Storage and transport of hydrogen constitute a key enabling technology for the advent of a hydrogen-based energy transition. In this context several efforts have been made by scientific researchers in order to develop safe and practical method for storing hydrogen on board a vehicle. A promising strategy implies the use of ammonia-borane and its derivatives amine-boranes due to the high percentage by weight of available hydrogen and the potential reversibility of hydrogen-release reactions. However, catalysts are needed to assist the release of hydrogen from amine-borane compounds at efficient rates. Several transition and alkali metal catalysts have been reported to effect amine-borane dehydrocoupling reactions.

On-board hydrogen storage remains a grand scientific and technical challenge in commercialization of the hydrogen fuel-cell-powered vehicles. Decades of extensive efforts on various reversible hydrogen storage materials have been largely frustrated by the low hydrogen capacity at the temperatures for the practical operation of proton exchange membrane fuel cell (PEMFC)[1]. Recently, on-demand hydrogen generation from the hydrogen-rich chemical hydrides[2-4] has emerged as an important alternative for on-board hydrogen storage.

Owing to its high hydrogen content, ammonia-borane (NH_3BH_3, AB)[5,6] attracts the most extensive and ever increasing attention as a potential hydrogen storage medium. A number of approaches have now been shown to induce AB H2-release by a range of mechanistic pathways, including activation by transition metal catalysts[7] and alkali metal catalysts[8]. These two different approaches will be described in detail in the 3.1. and 3.2. paragraphs, respectively.

3.1. Transition metal for the dehydrocoupling of amine-boranes

The interest in transition metal catalysis arises from the role the metal center plays in controlling kinetics and product distributions for dehydrocoupling reactions that lead to the formation of linear or cyclic oligomers and polymers alongside the concomitant release of H_2. Both heterogeneous[9,10] and homogeneous catalysis[11-13] have been investigated. Although several investigations on the involved dehydrogenation and dehydrocoupling reactions have been performed, a unified model in which mechanistic clues can be placed in context is still lacking. Experimental and computational findings show that dehydrocoupling of amine-boranes is a rather complex process and both the nature of the catalyst in terms of identity of the metal center, ligands and binding modes and the identity of the amine–borane are important in determining the outcome of the final products. In the subsequent paragraphs all of these aspects will be examined in detail.

3.1.1. Metal centers

There is a growing number of transition metal systems that have been reported to assist the dehydrocoupling of amine–boranes. Goldberg *et al.*,[7a] for example, have shown that room temperature dehydrogenation of AB can be achieved at an appreciable rate using the catalytic iridium pincer complex, [(POCOP^{tBu})Ir(H)$_2$] where POCOP^{tBu}=η^3-1,3-(OP*t*Bu$_2$)$_2$C$_6$H$_3$. Weller[14-16] reported that precious metal such as Rh, Ir, and Ru catalysts are active for ammonia-borane and its derivative mono- and di-alkylamine-boranes dehydrocoupling at room temperature. The reactivity of much more cost-effective Fe-based catalysts has been recently investigated by Baker and co-workers. [11b]

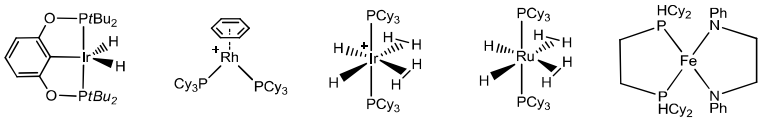


Figura 3.1. Some transition metal catalysts used for the dehydrocoupling of amine-boranes.

Although a clear knowledge of the role of the metal in each step of the dehydrocoupling and of the way in which amine-boranes approach, bind and dehydrocouple at the metal center is crucial

for the control of the kinetics of hydrogen release and products distribution, the information on these fondamental aspects is still today scarce.

3.1.2. Binding modes

The coordination of substrates to transition metal centers occurs *via* σ-bonding interactions. This is thought to be the first step in the catalytic cycle of many reactions prior to formal oxidative addition[17].

It is proved that tertiary amine-boranes coordinate to the metal center in the same mode as their more reactive primary and secondary counterparts but they do not undergo dehydrocoupling because of the lack of an N-H bond.

In 1999 Shimoi[18] and co-workers have characterized the $[M(CO)_5(\eta^1\text{-}H_3BNMe_3)]$ (M = Cr or W) complexes obtained from the reaction between $[M(CO)_6]$ and a tertiary amine–borane substrate H_3BNMe_3, where the coordinated H_3BNMe_3 ligand binds to the metal through one of the B-H bonds in a three-center two-electron bond, 3c-2e, with a relatively weak interaction suggested by the long M-B bond length. The metal–borane bond arises from B–H → M σ donation resulting in a M–H–B hydro-bridged structure for the resulting species. Due to an energy mismatch between the relatively high lying B–H σ* and metal centered orbitals, π backbonding is considered to be minimal in these molecules. The same authors evaluated later the catalytic activity of $[M(CO)_6]$ (M = Cr, W, Mo) towards the more reactive primary and secondary amine-boranes H_3BNHMe_2 and H_3BNH_2Me. Also in this case the catalytic cycle startes with the formation of a complex $[M(CO)_5(\eta^1\text{-}H_3BNH_{3-n}\ Me_n)]$ (M = Cr, W,Mo) (n=1-2).

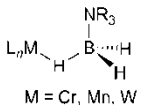


Figure 3.2. Tertiary amine-borane coordinated to metal center through a η^1 B-H bond.

Amine-borane substrates can also coordinate to the metal centers by a η^2 binding motif. In fact, the reaction of H_3BNMe_3 with $[Rh(P^iPr_3)_2(\eta^6\text{-}C_6H_5F)]\text{-}[BArF_4]$ in 1,2-$F_2C_6H_4$ solution leads to the immediate formation of the complex $[Rh(P^iPr_3)_2(\eta^2\text{–}H_3BNMe_3)][BArF_4]$ and elimination of C_6H_5F[19].

Weller and coworkers have developed systems that contain a bis(σ-amine-borane) binding mode. In particular, the $[Rh(\eta^6\text{-}C_6H_5F)\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}]BAr^F{}_4$ complex[15] can coordinate two amine-borane molecules by the desplacement of the labile fluorarene ligand in 1,2-difluorobenzene. The resultant formed complex has a pseudo-octahedral geometry at the rhodium center thanks to the η^1 and η^2 coordinations of the amine-boranes molecules in the apical and equatorial position, respectively.

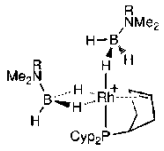


Figure 3.3. Bis(σ-amine-borane) complex containing a η^1 coordinated molecule and a η^2 coordinate in the apical and equatorial position, respectively.

3.1.3. Ligands

Among the several ligands that are widely used in organometallic chemistry, great interest has been focused on phosphines (PR_3) because their ability to stabilize complexes can be easily tuned by careful variation of the electronic and steric properties of the R groups[20]. Phosphines can act as both σ-donor and π-acceptor ligands. Several studies were addressed to probe if the change of the steric and electronic profile of the phosphine could have any consequence on the rate of catalysis for the dehydrocoupling of amine-boranes and observed ground state structures. The available lone pair on the phosphorus atom donates into an empty metal *d* orbital forming a σ-bond, whilst π-backdonation from the metal occurs into the σ* orbital of the P-R bond and the phosphorus dπ component. More electronegative R groups result in a lowering in energy of the P-R σ* orbital making it more accessible to backbonding from the metal. PF_3 has similar π-acceptor character to CO, whilst at the other end of the spectrum, PMe_3 is a relatively weak π-acceptor.

Bi-dentate phosphine ligands also contribute to improve the stability of the complexes, thanks to the well known chelate effect[21]. Particular bond angles or stereochemistries around a metal atom can be imposed by an adequate choice of a chelating ligand; it has been shown also that the catalytic activity is influenced by the bidentate ligands bite angle, β[22,23], that is the P-M-P angle made upon coordination of chelating diphosphine ligands (see figure 3.4.). An important parameter of a bidentate ligand is also the value of its *bite*, given as the distance between the two donor atoms.

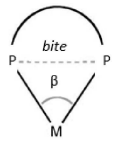


Figure 3.4. β- angle calculated as the P-M-P angle made upon coordination of chelating diphosphine ligands and its associated bite-distance between the Phosphorus atoms.

Studies of the effects of the change of the bite angle of chelating diphosphines in catalysis are abundant in the literature, *e.g.* in hydroformylation[24-26], hydrocyanation[27,28] and cross-coupling reactions[29-31], but not in amine-borane dehydrogenation and dehydrocoupling catalysis.

Recently, Weller and co–workers have underscored the dependency of the rate of dehydrocoupling of H_3BNMe_2H on the P–Rh–P bite angle in di-phosphines complexes. The authors have observed that larger bite angles result in tighter Rh---B interactions in solution and the solid-state and, therefore, in a slower catalysis. On the basis of these important observations, these studies have been extended to more stable chelating phosphines, noting that when systems such as [Rh-

$(Ph_2PCH_2CH_2CH_2PPh_2)]^+$ are used to assist the dehydrocoupling process, turnover rates are two orders of magnitude faster than reported for monodentate phosphine catalysts[32].

3.1.4. Nature of amine-boranes

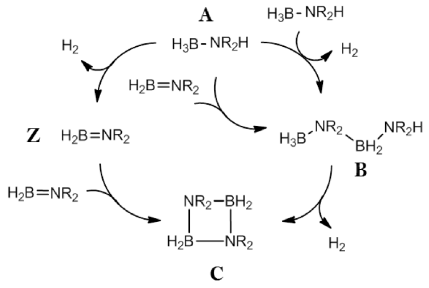
The nature of the amine-borane alkyl groups also influences the course of the process. Several experimental and computational studies have been performed using dimethylamine-borane, DMAB. In fact, mechanistic investigations are more undemanding when secondary amine-boranes are used because of the limited number of possible products that can be formed on dehydrogenation[33]. However different steric demands on the amine-borane imply different behavior during the catalytic dehydrocoupling reactions. For these reasons, Hill and co-workers[8b], for example, have initiated an intense study on the influence that different substrates can have on the mechanism of dehydrocoupling. All the details about these observations will be illustrated later.

Even if tertiary amine-boranes, H_3BNR_3, cannot undergo dehydrocoupling because of the lack of a N-H group, they are ideal ligands just to mimic the proposed interaction of H_3BNR_2H to the metal center[18].

3.1.5. General aspects of dehydrocoupling reactions by Transition metal catalysts

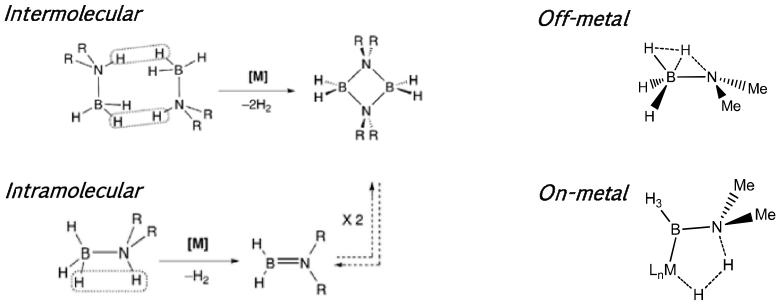
As mentioned above, a great number of transition metal catalysts[35-44] have been proved to be able to assist the dehydrocoupling of the amine-boranes. Computational[43,45-49] and empirical[7b,50,51] studies indicate that transition metal dehydroucoupling is a complex process that generally first involves the coordination of the amine-boranes at the metal center to form the σ-amine-borane complex. Such a complex, in the case of secondary and primary amine-boranes, undergoes a dehydrogenation at the metal center in order to form the amino-borane BH_2NRR' (R=H, R'=alkyl-group or R=R'=alkyl-group).

In scheme 3.1. is shown a general mechanistic scheme for the dehydrocoupling of amine-boranes, A, using transition metal catalysts. According to this simplified and broadly applicable scheme, the dehydrogenation of A leads to the formation of the aminoborane Z. The coupling of the formed Z with A or of two A, by elimination of H_2, forms the linear intermediate diborazane B. Ultimately, the final dimeric product C could be obtained through the dimerization of Z or the dehydrocyclization of B. The latter can be consumed also by B-N bond cleavage.



Scheme 3.1. Hypothesized intermediates and products of the dehydrocoupling reaction of amine-boranes assisted by metal catalysts.

Nevertheless, this schematic representation does not give any information about the role that metal complex plays in such transformations. In this context, two mechanistic alternatives are possible. The so-called *on-metal* mechanism, in which amine-boranes coordinate to the metal center and undergo H transfer with or without the direct involvement of the metal by a variety of mechanistic steps. B-H and N-H hydrogen atoms can be eliminated from the same molecule when the mechanism is *intramolecular*, whereas the process could be *intermolecular* when the two hydrogen atoms belong to different amine-borane molecules. The mechanistic steps are defined *off-metal* if the metal center does not participate in the reaction (see Scheme 3.2.).



Scheme 3.2. Schematic rapresentation of *intermolecular*- (top left side) and *intramolecular*- (down left side) *off-metal*- (top right side) and *on-metal*- (down right side) mechanisms.

Understanding the role that metal center plays in each involved step, and comprising all these mechanistic possibilities in an unified model that is valid for many transition metal catalysts, should be advisable. Recently, Weller *et al.*, on the basis of combined stoichiometric, qualitative catalytic, and kinetic simulation studies using a Rh catalyst complex, have proposed a generic mechanistic scheme that can be useful in explaining and elucidating the behavior of many transition-metal and main-group systems that can be used for the dehydrocoupling of amine-boranes.

Although experimental studies have given significant information about the possible intermediate specie that are formed during the dehydrocoupling reactions, they do not furnish any detailed insights of the mechanistic process. In this context, computational explorations can be very helpful to shed light on the involved complex mechanisms. Actually, only a few number of theoretical investigations are present in literature. What is emerged from these studies is that H transfer could

occur by a variety of mechanistic steps, depending on the metal/ligand combination. In particular, tree different mechanisms have been identified:

- NH proton transfer to a coordinated ligand followed by transfer to the metal (Ni-N-heterocyclic carbene)[45,53];
- intramolecular stepwise transfer of NH and then BH to the metal center (C_{p2}Ti-derivatives)[49];
- concerted NH/BH activation at the metal center (Ir-pincer complexes)[48].

As it will be described in more detail in the subsequent paragraphs, all the routes introduced above are *intramolecular* mechanisms that lead, ultimately, to the formation of the cyclic dimer by an off-metal mechanism. Although, none of the theoretical studies that are now present in literature have underlined the possibilities that an intermolecular process occurs, experimental studies performed by Weller and Baker proposed this kind of mechanism for the Rh-based bis(σ-amine-borane) complex and a Fe-based complex, respectively.

A DFT analysis has been performed by us to prove whether an intermolecular dehydrogenation mechanism for the Rh-based bis(σ-amine-borane) complex leading to the formation of a diborazane, according to Weller and co-workers observations, is available and to verify if the main cyclic dimer final product could be formed through an on metal dehydrocyclization of the diborazane.

Theoretical investigation of Fe-based complex is a work in progress. However, our first investigations have given relevant information showing that the involved mechanism proceeds through the formation of a diborazane species coordinated to the metal center. Nevertheless, the calculated selected viable pathways are hampered by hogh activation energy barriers.

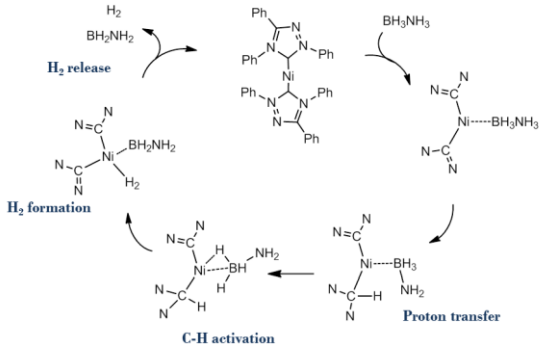
3.1.6. Homogeneous transition metals catalysts at work

The development of new homogeneous transition metal catalysts is an area of growing interest. First, second, and third row transition metals can be used for the dydrocoupling of amine-boranes following different mechanisms and, in many cases, not well understood. Three different examples of homogeneous transition metal catalysts are discussed below.

3.1.6.1. Dehydrogenation of ammonia-borane by $Ni(NHC)_2$

A series of new catalysts based on N-heterocyclic carbine (NHC) nickel complexes[44] were reported by Baker and co-workers. On the basis of experimental findings, Hall *et al.* have perfomed a computational study proposing a mechanism for the release of two equiv. of hydrogen from AB[53]. The first H_2 equiv. release occurs through four main steps: (1) transfer of a proton from N to the unsaturated C in carbene, (2) transfer of H from this C to Ni, (3) transfer of H from B to Ni, and (4) release of H_2 and the unsatured BH_2NH_2 to regenerate the catalyst $Ni(NHC)_2$ (Scheme 3.5.). This DFT investigation underlines the importance of the unsaturated NHC ligands in this catalytic reaction. In fact, instead of B–H or N–H bond activation otherwise hypothesized a proton transfer from nitrogen to the bound carbene carbon occurs. This new C–H bond is activated by the metal and,

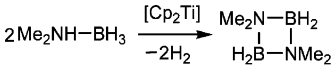
therefore, the subsequent step is the H transfer to the Ni center. Once that another H atom is transferred from B to Ni, a molecule of hydrogen is formed. The energy barriers computed are lower than that of mechanisms that begin with N–H or B–H activations catalyzed by the metal atoms. For this reason, finding new catalysts with higher efficiency featured by unexpected ligand participation may be essential for low energy H atom transfers.



Scheme 3.5. Predicted reaction mechanism and gas-phase relative enthalpies of the first H2 release from ammonia–borane catalyzed by Ni(NHC)2 showing four main steps: (1) transfer of a proton from N to the unsaturated C in carbene, (2) transfer of H from this C to Ni, (3) transfer of H from B to Ni, and (4) release of H2 and H2B–NH2 to regenerate the catalyst Ni(NHC)2.

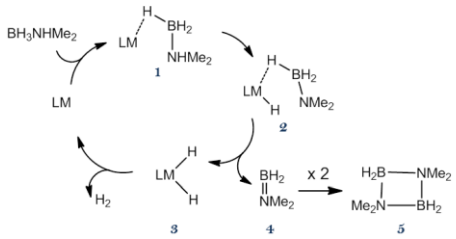
3.1.6.2. Titanocene-Catalyzed Dehydrocoupling of the Adduct Me_2NHBH_3

A recent report[7d] demonstrated that a Ti(II) catalyst, [Cp_2Ti], which is generated in situ by the combination of [Cp_2TiCl_2] and 2 equiv of ^{n}BuLi in toluene, homogeneously catalyzes the reaction shown in Scheme 3.6.



Scheme 3.6.

A computational investigation has been performed by Ohno *et al.*[49] who have investigated both intra and intermolecular dehydrogenation pathways. Their results suggest that the titanocene-catalyzed dehydrocoupling of the adduct Me_2NHBH_3 proceeds through intramolecular, stepwise dehydrogenation followed by dimerization of the resulting monomeric aminoborane species as shown in Scheme 3.7.



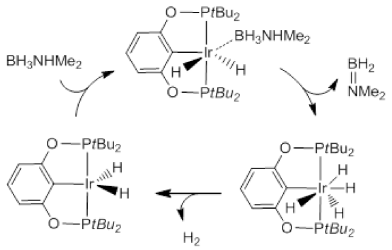
Scheme 3.7. Intramolecular dehydrocoupling pathway of the adduct Me_2NHBH_3 catalyzed by [Cp2Ti].

The dehydrocoupling starts with the coordination of one Me_2NHBH_3 to the Ti center via a hydrogen atom of the BH_3 moiety forming the specie 1 and then proceeds through the intermediate 2 in which newly Ti-H_1 bond and Ti...N interaction are formed. This last minimum undergoes further dehydrogenation with the consequent formation of 3 and the aminoborane 4. The intermediate **3** could easily release H_2, possibly by access of an incoming Me_2NHBH_3 adduct. However, the unsaturated species **4** may undergo dimerization leading to cyclic **5.**

3.1.6.3. Catalyzed Dehydrogenation of Ammonia–Borane by Iridium Dihydrogen Pincer Complex

Goldberg et al.[7a] have shown that room temperature dehydrogenation of AB can be achieved at an appreciable rate using the catalytic iridium pincer complex, [(POCOP^{tBu})Ir(H_2)] where POCOP^{tBu}= η^3-1.3-(OP*t*Bu_2)$_2C_6H_6$. The iridium pincer catalyst was initially used for alkane dehydrogenation. In these reactions it was proposed that C-H oxidative addition was the first step. Since AB has a heteroactomic backbone other reaction pathways are possible.

A theoretical investigation performed by Musgrave and co-workers[45b] has shown that, in contrast to the example described previously, AB dehydrogenation by iridium pincer catalysts proceeds through a concerted removal of hydrogen. The starting complex is the 16 e$^-$ dihydride iridium specie that is shown in scheme 3.8. The release of a hydogen molecule leads to the formation of the 14 e$^-$ iridium complex. Both these species are able to assist AB dehydrogenation but higher energy barriers are calculated when the 14 e$^-$ system is taken into account and too high for the reaction to occur at room temperature. The proposed mechanism for the 16 e$^-$ complex corresponds to a concerted transfer of hydride from boron to the iridium center and a simultaneous transfer of a proton from the nitrogen end to a hydride bound to the iridium center leads to the formation of the most stable intermediate caractherized by the presence of 4 hydrogen atoms coordinated to the Iridium center. This species subsequently undergoes further dehydrogenation regenerating the 16 e$^-$ starting iridium complex.



Scheme 3.8. Pathway for AB dehydrogenation by 16 e$^-$ complex.

3.2. Alkali-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

Although the majority of this research has concentrated upon the use of homogeneous mid- or later transition metal catalysts for the dehydrogenation and dehydrocoupling reactions of amine-boranes, recently, great interest has been aimed to d^0 redox-inactive species derived from the elements of group 2[8a-b,54,55] or group 3[8c] of the periodic table in their highest oxidation states that

were found to be able to dehydrogenate amine-boranes in a similar way to those postulated for transition-metal-catalysis. However, their use preclude the possibility of B-H oxidative addition, via B-H σ-borane complexes, and/or B-N reductive elimination as observed with transition metal catalysts, that have low oxidation state or more electronic-rich catalytic centers[8a-b]. In this case the formation of an amidoborane complex occurs, in which the chelating anion $NR_2BH_3^-$ is coordinated to the metal center through formally deprotonated nitrogen atom and the BH hydride from the BH_3 component of amine-borane.

Hill *et al.,* for example, have undertaken a systenatic program of study of the reactions of alkali amidoborane with secondary amine-boranes, R_2NHBH_3, in the expectation that extra substitution of the amine will provide more mechanistically amenable intermediates[8a-b]. They have also extended their study to a wider range of alkylamine-boranes. During the course of these reactions they observe the presence of the unsatured species $BH_2{=}NMe_2$ alongside the formation of the metal hydride. The production of the complex containing the $\{H_3BNMe_2BH_2Me_2N\}^-$ anion depends on the formation and insertion of the unsatured species in the M-L bond of the amido-borane species. Subsequent β-hydride elimination produce the cyclic dimer $[BH_2{=}NMe_2]_2$. All these observations led them to propose a preliminary mechanism that accounts for the observed reactivity of these more substituted amine-containing substrates.

What emerges from these studies is that the dehydrocoupling activity is also dependent upon the identity of the metal employed. In order to establish the role of the metal in the dehydrocoupling reactions they have consider the reactions of group 2 sylylamides $[HC\{(Me)CN(2\text{-}6^iPr_2C_6H_3)\}_2M(THF)_n\{N(SiMe_3)_2\}]$ (M = Mg, n = 0; M = Ca, Sr, n = 1), with secondary amine-boranes. The sterically encumbered β-diketiminate ligand, $[HC\{(Me)CN(Dipp)\}_2$ (Dipp=2,6-di-iso-propylphenyl), DiPP-nacnac, that is used in the synthesis of catalysts based on alkaline metals such as Mg and Ca. This ligand is essential for the stability of this heteroleptic complex. It prevents ligand exchange and formation of homoleptic species, such as $[Ca(DIPP\text{-}nacnac)_2]$ and polymeric, insoluble $(CaH_2)_n$. Moreover, the use of the bulky DIPPnacnac ligand seems to effectively prevent formation of coordination polymers with bridging BN ligands .

Notably, they found that an increase of cation charge density and a decrease of radius produces a consequent and resultant ability of cation center to mediate each step involved in the catalytic cycle. On the basis of their observations, they propose a preliminary mechanism of reactions highlighting the generality of the dehydrocoupling chemistry induced in dialkylamine boranes with group 2-centred reagents.

3.3. Objective of the work

As previously underlined, there is a growing number of transition metal systems that have been reported to effect the dehydrocoupling of amine–boranes (H_3BNR_2H) following different routes. However, in many cases, the mechanistic details are not well understood. Having a unified model broadly applicable to many of the used catalysts is absolutely necessary in order to comprise all such mechanistic possibilities, together with the role played by the metal in each of the involved steps.

With the aim to provide additional details to the general context of metal-assisted amine-boranes dehydrogenation processes, we have firstly focused our attention on Rh-based catalysts.

In 2008 Weller and co-workers[39a] reported that addition of 2 equiv of DMAB to the 12-electron complex $[Rh(P^iBu_3)_2][BAr^F_4]$ in 1,2-difluorobenzene results in the immediate formation of a Rh(I) species $[Rh(PiBu_3)_2(\eta^2\text{-}H_3BNHMe_2)][BAr^F_4]$ that is short-lived and evolves to give Rh(III) $[Rh(H_2)(PiBu_3)_2(\eta^2\text{-}H_3BNHMe_2)][BAr^F_4]$ and the cyclic dimer $[BH_2NMe_2]_2$.

The same authors have studied a further example of intermediate σ-amine–borane complexes, using a significantly more open transition-metal fragment, $[Rh\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}(\eta^2\text{-}H_3B{\cdot}NRR'Me)(\eta^1\text{-}H_3B{\cdot}NRR'Me)]BAr^F_4$ which contains a bis(σ-amine–borane) binding motif[16]. These complexes provide new insight into bonding modes of mono(amine–borane) ligands at transition-metal centers, an area that has until this point been limited to complexes in which one amine–borane binds to the metal center. These complexes also proceed to dehydrocouple to form cyclic products, and they may therefore help to elucidate further mechanistic details of the catalytic dehydrocoupling of amine–boranes. At the beginning of our research project, we have used Density functional theory (DFT) to evaluate possible mechanistic routes of the dehydrocoupling reaction of the bis(σ-amine-borane) complex formed by the displacement of the labile fluoroarene ligand in the phosphine/alkene complex $[Rh(\eta^6\text{-}C_6H_5F)\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}]\ BAr^F_4$ and coordination of two DMAB ligands.

A class of low coordinate cationic Rh complexes that has shown exceptional reactivity contains chelating diphosphines. In literature are present several studies relative to the effects of changing of bite-angle of chelating disphophines in catalysis reactions relative to hydroformylation[24-26], hydrocyanation[27,28] and cross-coupling reactions[29-31] but no one is referred to dehydrogenation and dehydrocoupling catalysis of amine-boranes. Recently, Weller and co-workers have noted a dependency of the rate of dehydrocoupling of H_3BNMe_2H on the P–Rh–P bite angle, β, in the complexes Rh-based complexes[32]. A systematic Density Functional Theory (DFT) investigation of the possible mechanistic routes of dehydrocoupling of the prototypical secondary dimethylamine-borane **A** assisted by Rh-chelating bis-phosphine complexes $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ (n = 3–5) was also object of our study. Details concerning the obtained outcomes are reported in *Paper I*.

In a second part of our research program we have investigated the ability of alkali metal compounds, e.g. Mg and Ca, to dehydrogenate secondary amine-boranes.

Our aim is to use Density Functional Theory (DFT) to explore, according to the catalytic regime proposed by Hill and co-workers[8a-b], the mechanistic routes of the dehydrocoupling reaction of three different bulky amine–boranes, dimethylamine-borane, DMAB, pyrrolidine-borane, PB, and di-*iso*-propylamine-borane, $^iPr_2$, in order to:

1) prove the viability of the pathways of the mechanistic scheme proposed by Hill and coworkers;

2) compare the behaviors of Mg and Ca complexes to assess whether differences in radius and charge density can be considered responsible of the observed differences in reactivity.

The knowledge of the dehydrocoupling process mechanistic aspects is indispensable for the improvement of the operative conditions and the application of such chemistry to a broader array of catalytic reactions. All the results of our rigorous DFT investigation are presented in *Paper II*.

Referents

(1) L. Schlapbach, A. Züttel, *Nature*, **2001**, 414, 353.

(2) G. Sandrock, S. Suda, L. Schlapbach, *Top. Appl. Phys.*, **1992**, 67, 197.

(3) B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.*, **1997**, 253, 1.

(4) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.*, **2007**, 107, 4111.

(5) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.*, **2007**, 2613.

(6) T. B. Marder, *Angew. Chem., Int. Ed.*, **2007**, 46, 8116.

(7) (a) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, 128, 12048; (b) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.,* **2003**, 125, 9424; (c) Y. Chen,; J. L. Fulton , J. L. Linehan, T. Autrey, *J. Am. Chem. Soc.,* **2005**, 127, 3254; (d) T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.,* **2006**,128, 9582; (e) Q. Xu, M. Chandra, *J. Power Sources,* **2006**, 163, 364; f) T. J. Clark, K. Lee, I.Manners, *Chem. Eur. J.,* **2006**, 12, 8634.

(8) a) J. D. Liptrot, M. S. Hill, M. F. Mahon, Dugald J. MacDougall, *Chem. Eur. J.*, **2010**, 16, 8508 b) M. S. Hill, M. Hodgson, D. J. Liptrot, M. F. Mahon, *Dalton Trans.*, **2011**, *40*, 7783; c) M. S. Hill, G. Kociok-Köhn, Thomas P. Robinson, *Chem. Commun.,* **2010**, 46, 7587.

(9) C. A. Jaska, I. Manners, *J. Am. Chem. Soc.,* **2004**, 126, 9776.

(10) Y. Chen, J. L. Fulton, J. C. Linehan, T. Autrey, *J. Am. Chem. Soc.,* **2005**, 127, 3254.

(11) a) C. M. Jensen, *J. Chem. Soc., Chem. Commun.,* **1999**, 2443; b) D. Morales-Morales, R. Redon, C. Yung, C. M. Jensen, *Inorg. Chim. Acta,* **2004**, 357, 2953; c) R. T. Baker, S. Maguire, J. C. Gordon, M. Murugesu, C. W. Hamilton, B. L. Scott, N. J. Henson, N. C. Smythe, P. Lin, *J. Am. Chem. Soc.*, **2012**, 134, 5598.

(12) K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord, A. S Goldman,. *J. Am. Chem. Soc.,* **2002**, 124, 11404.

(13) I. Göttker-Schnetmann, P. White, M.Brookhart, *J. Am. Chem. Soc.,* **2004**, 126, 1804.

(14) A. B. Chaplin, Andrew S. Weller, *Angew. Chem. Int. Ed.,* **2010**, 49, 581.

(15) R. Dallanegra, A. B. Chaplin, J.r Tsim, A. S. Weller, *Chem. Commun.*, **2010**, 46, 3092.

(16) R. Dallanegra, A. B. Chaplin, A. S. Weller, *Angew. Chem. Int. Ed.*, **2009**, 48, 6875.

(17) C. N. Muhoro, X. He, J. F. Hartwig, *J. Am. Chem. Soc.,* **1999,** 121, 5033.

(18) M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, H. Ogino, *J. Am. Chem. Soc.,* **1999,** 121, 11704.

(19) A. B. Chaplin, Andrew S. Weller, *Inorg. Chem.*, **2010**, 49, 1111.

(20) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals, Fourth Edition;* John Wiley & Sons: Hoboken, NJ, **2005**.

(21) a) G. Schwarzenbach, *Helv. Chim. Acta*, **1952**, 35, 2344; b) R. D. Hancock, A. E. Martell, *Comments Inorg. Chem.*, **1988**, 6, 237.

(22) a) Z. Freixa, P. W. N. M. Van Leeuwen, *Dalton Trans.*, **2003**, 1890; b) P.W. N. M. Van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Pure Appl. Chem.*, **1999**, 71, 1443; c) B. Breit, *Angew. Chem., Int. Ed.*, **2005**, 44, 6816; d) O. Delacroix, J. A. Gladysz, *Chem. Commun.*, **2003**, 665.

(23) C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney, D. R. Powell, *J. Am. Chem. Soc.*, **1992**, 114, 5535.

(24) R. H. Crabtree, *Acc. Chem. Res.,* **1979,** 12, 331.

(25) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.,* **2005,** 127, 3516.

(26) P. H. M. Budzelaar, N. N. P. Moonen, R. de Gelder, J. M. M. Smits, A. W. Gal, *Eur. J. Inorg. Chem.,* **2000,** 753.

(27) P. Zhao, C. Krug, J. F. Hartwig, *J. Am. Chem. Soc.,* **2005,** 127, 12066.

(28) P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.,* **2002,** 124, 14416.

(29) M. Brookhart, B. Grant, A. F. Jr. Volpe,. *Organometallics,* **1992,** 11, 3920.

(30) M. D. Butts, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.,* **1996,** 118, 11831.

(31) S. T. H. Willems, P. H. M. Budzelaar, N. N. P. Moonen, R. de Gelder, J. M. M. Smits, A. W. Gal, *Chem. Eur. J.,* **2002,** 8, 1310.

(32) R. Dallanegra, A. P. M. Robertson, A. B. Chaplin, I. Manners, A. S. Weller, *Chem. Commun.,* **2011**, *47*, 3763.

(34) M. Zahmakiran, S. Ozkar, *Inorg. Chem.*, **2009**, 48, 8955.

(35) M. E. Sloan, T. J. Clark, I. Manners, *Inorg. Chem.*, **2009**, 48, 2429.

(36) R. Rousseau, G. K. Schenter, J. L. Fulton, J. C. Linehan, M. H. Engelhard, T. J. Autrey, *Am. Chem. Soc.*, **2009**, 131, 10516.

(37) Y. Jiang, O. Blacque, T. Fox, C. M. Frech, H. Berke, *Organometallics,* **2009**, 28, 5493.

(38) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem., Int. Ed.*, **2008**,47, 6212.

(39) a) T. M. Douglas, A. B. Chaplin, A. S. Weller, *J. Am. Chem. Soc.*, **2008**, 130, 14432; b) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.*, **2008**, 130, 14034.

(40) D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Commun.*, **2007**, 3297.

(41) Y. Jiang,; H.Berke, *Chem. Commun.*, **2007**, 3571.

(42) J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.,* **2007**, 129, 11936.

(43) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa, H. Ogino, *J. Am. Chem. Soc.*, **2009**, 131, 14946.

(44) R. J. Keaton, J. M. Blacquiere, R. T.Baker, *J. Am. Chem. Soc.*, **2007**, 129, 1844.

(45) a) X. Yang, M. B. Hall, *J.Organomet. Chem.*, **2009**, 694, 2831. b) P. M. Zimmerman, A. Paul, Z. Y. Zhang, C. B. Musgrave, *Angew. Chem., Int. Ed.* **2009**, 48, 2201.

(46) P. M. Zimmerman, A. Paul, Z. Y. Zhang, C. B. Musgrave, *Inorg. Chem.,* **2009**, 48, 1069.

(47) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Z. Yang, M. B. Hall, *J. Am. Chem. Soc.*, **2009**, 131, 15440.

(48) A. Paul, C. B. Musgrave, *Angew. Chem., Int. Ed.*, **2007**, 46, 8153.

(49) Y. Luo, K. Ohno, *Organometallics,* **2007**, 26, 3597.

(50) V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant, D. A. Dixon, *Chem. Commun.*, **2008**, 6597.

(51) A. Friedrich, M. Drees, S. Schneider, *Chem. Eur. J.*, **2009**, 15, 10339.

(52) M. Kass, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem., Int. Ed.,* **2009**, 48, 905.

(53) X. Z.; Yang, M. B. Hall, *J. Am. Chem. Soc.,* **2008**, 130, 1798.

(54) J. Spielmann, G. Jansen, H. Bandmann, S. Harder, *Angew. Chem. Int. Ed.*, **2008**, 47, 6290.

(55) J. Spielmann, S. Harder, *J. Am. Chem. Soc.*, **2009**, 131, 5064.

Appendix A

Paper I

The role of chelating phosphine rhodium complexes in dehydrocoupling reactions of amine-boranes. A theoretical investigation attempting to rationalize the observed behaviors

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Submitted

The role of chelating phosphine rhodium complexes in dehydrocoupling reactions of amine-boranes. A theoretical investigation attempting to rationalize the observed behaviors

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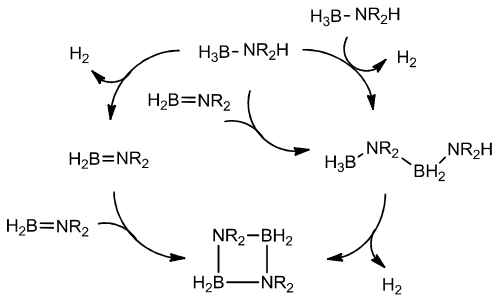
ABSTRACT: A quantum-chemical investigation of the dehydrocoupling reaction of the secondary amine-borane Me_2HNBH_3 assisted by phosphine chelating $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ (n = 3–5) complexes to ultimately afford the cyclic dimer $[Me_2NBH_2]_2$ is reported. The hypothesis, proposed on the basis of experimental evidences, that the catalytic efficiency of such systems is due to formation of Rh(III) dihydride complexes, which rapidly lose H_2 and re-form Rh(I) species has been explored together with the influence that the structure of the ligand, namely the chelating phosphine P-Rh-P bite angle, has on the rate of the reaction. Along the pathway that our computational analysis has indicated as the most likely, the first step of the dehydrogenation reaction is the concerted B–H hydride and N–H proton transfer from an additional amine-borane molecule to the rhodium centre of the formed $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ complexes. The reaction proceeds by formation of dihydrogen complexes, which eliminate molecular hydrogen and restore the σ-amine-borane complexes. The impact of the bite angle on the kinetics has been rationalized in terms of both the distortions to the geometry of stationary points around the metal centre and the strength of the Rh-B interaction with the amine-borane ligand. The final cyclic dimer is formed by off-metal coupling of the released aminoboranes.

1. INTRODUCTION

The potential use of hydrogen as a clean and abundant fuel source for energy generation has driven a recent intense research effort toward the use of ammonia-borane (AB), H_3NBH_3, and related amine-boranes (R_2HNBH_3) as safe and easily manipulated compounds for chemical storage of H_2.[1-4] Although the combination of hydridic B–H and protic N–H bonds within the AB and amine-borane molecules mean that they are susceptible to thermally induced hydrogen release, the temperatures at which this occurs are impractically high (110–200 ◦C). This factor has, in turn, resulted in a focus upon the use of catalytic methods to cause hydrogen evolution and concomitant B–N bond formation for the AB molecule itself, and for a wide variety of di- and mono-alkylamine borane molecules. Experimental and theoretical investigations carried out so far have shown that metal-mediated dehydrocoupling reactions of amine-boranes are very complex processes and both the mechanism and the final outcome depend on the nature of the catalyst in terms of identity of the metal centre, ligands and bonding modes. The nature of the amine-borane alkyl groups also influences the course of the process. In this respect, mechanistic investigations are more undemanding when secondary amine-boranes are used because of the limited number of possible products that can be formed on dehydrogenation. This is the reason why there is today a great number of catalytic systems of elements from different zones of the periodic table, which have been proved to be able to assist the dehydrocoupling of the secondary amine-borane Me_2HNBH_3 (**A**) to give the cyclic dimer $[Me_2NBH2]_2$ (**C**).[5-25] According to the schematic representation given in Scheme 1, a number of mechanistic regimes has been suggested by the detection of several boron-nitrogen intermediates: formation of the aminoborane $H_2B{=}NMe_2$ (**Z**) by dehydrogenation of **A**; coupling of **A** and **Z**, or of two **A** to form, by elimination of H_2, the intermediate linear diborazane **B**; and formation of the dimeric final product **C** by both dimerization of **Z** and dehydrocyclization of **B**. Diborazane **B** can be consumed also by B-N bond cleavage.

Scheme 1. Hypothesized intermediates and products of the dehydrocoupling reaction of amine-boranes assisted by metal catalysts.



Neither the explicit role played by the metal in each step is given in such scheme, nor all the sketched pathways are operative for each catalytic system. Concerning the role of the metal complex in such transformations, two are the viable general pathways. The so called on-metal, in which the amine-borane coordinates to the metal centre and undergoes H transfers with or without the direct involvement of the metal by a variety of mechanistic steps. BH and NH hydrogen atoms can be eliminated from the same molecule when the mechanism is intramolecular, whereas the process is intermolecular when the two

hydrogen atoms belong to different molecules. The mechanistic steps are defined off-metal if the metal complex does not participate in the reaction.

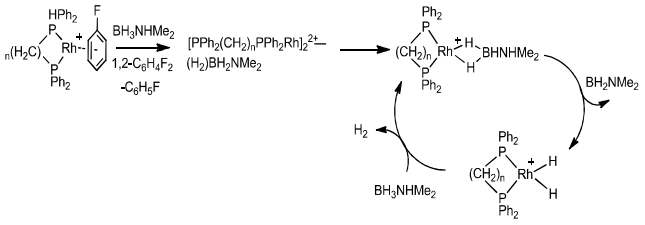
It should be desirable to comprise all such mechanistic possibilities, together with the role played by the metal in each of the involved steps, in a unified model broadly applicable to many of the used catalysts. Very recently Weller and co-workers, on the basis of the outcomes of a detailed study of isolated intermediates, catalysis, stoichiometric reactivity, and kinetic simulation using a rhodium catalyst system, have postulated a simplified and largely applicable mechanistic scheme that should be helpful in rationalizing the behavior of many transition-metal and main-group systems that catalyze the dehydrocoupling of **A** to afford the cyclic amino-borane dimer **C**.[26] A key aspect of such multifaceted and complex mechanistic scheme is the possibility for the involved cationic rhodium catalyst to shuttle between a fast Rh(I)/Rh(III) regime and a slower constant oxidation state rhodium(III) dihydride regime. Indeed, by dehydrogenation of bound **A** a dihydride intermediate $M(H)_2$ can be formed to give **Z**. If H_2 loss from the dihydride complex is slow, this species becomes the resting state of the process. In this mechanistic scenario **C** is invoked as a modifier, which acts in an autocatalytic way moving the system between the slow rhodium(III) dihydride regime and the fast Rh(I) regime by promoting reductive elimination of H_2.

[Rh(chelating bis-phosphine)] systems have been proved[27] to be extremely efficient catalysts for the dehydrogenation of **A** to ultimately form **C**. When systems such as $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)]^+$ are used to assist the dehydrocoupling process, turnover rates are two orders of magnitude faster than reported for monodentate phosphine catalysts. To explain such behaviour the authors have postulated that the Rh(III) dihydride complex formed by dehydrogenation of bound **A**, with concomitant change of the oxidation state, rapidly loses H_2 and re-form a Rh(I) species. The combined effects of relative instability of Rh(III) dihydride intermediates, lack of ligand flexibility and P-Rh-P bite angle, defined as the preferred chelation angle determined by the ligand backbone only,[28] have been considered to be responsible of the observed efficiency. In particular, the influence of the chelate ligand backbone on reactivity has been investigated by considering the relative rates of dehydrocoupling of **A** assisted by the bis-phosphine chelating complexes $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)][BAr^F{}_4]$ with n = 3–5. A structural analysis carried out on a great number of bi-dentate ligands in order to parametrize their coordinating properties,[29] has allowed the estimation of bis-phosphine ligand bite angle and *bite*, given as the distance between the two donor atoms when coordinated, for the involved complexes. The catalyst with n=3, corresponding to the estimated smallest chelate bite-angle, is found to be the fastest, while the catalyst with n=5 is the slowest. Moreover, there is an inducion period associated with this catalysis, that the authors suggest can be due to the formation of an inactive dimeric species (Scheme 2) possibly in equilibrium with mono-metallic active species.

In this paper the outcomes of a systematic Density Functional Theory (DFT) investigation of the possible mechanistic routes of dehydrocoupling of the prototypical secondary dimethylamine-borane **A** assisted by Rh-chelating bis-phosphine complexes $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ (n =

3–5) are reported. Even thought such complexes are the organometallic precatalysts in $1,2\text{-}C_6H_4F_2$ solvent, the mechanistic investigation really starts from the corresponding $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ complexes that are formed by displacement of the labile fluoroarene ligand and η_2 coordination of Me_2HNBH_3.

Scheme 2. Proposed mechanism for the dehydrogenation of A assisted by bidentate phosphine complexes $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)][BAr^F{}_4]$ (n = 3–5). $[BArF_4]^-$ anions are not shown.



Calculations have been carried out with the support of the experimental observations and hypotheses concerning the reaction mechanism. The assumption that in going from n=3 to n=5 the enlargement of the P-Rh-P bite angle corresponds to tighter Rh---B interactions and, as a consequence, to slower catalysis, has been tested with the aim to confirm the supposed relationship between structure and reactivity, very helpful for the development of tailored catalysts. Such a correlation between the bite angle of bi-dentate ligands, specifically bi-dentate phosphines, and the catalytic activity of their complexes has been previously explored both theoretically and experimentally, and the advantages deriving from the use of di-phosphine chelating ligands in homogeneous catalysis is still matter of debate.[30-36] The results of the rigorous computational analysis reported here of the mechanistic scheme suggested on the basis of experimental evidences aims to establish how bi-dentate phosphine ligand bite angles affect the performance in catalysis of their complexes. Moreover, the present computational exploration of the mechanistic aspects of the amine-boranes dehydrocoupling process catalyzed by Rh(chelating bis-phosphine) complexes furnishes additional details to the more general context of metal-assisted amine-boranes dehydrogenation processes.

2. COMPUTATIONAL DETAILS

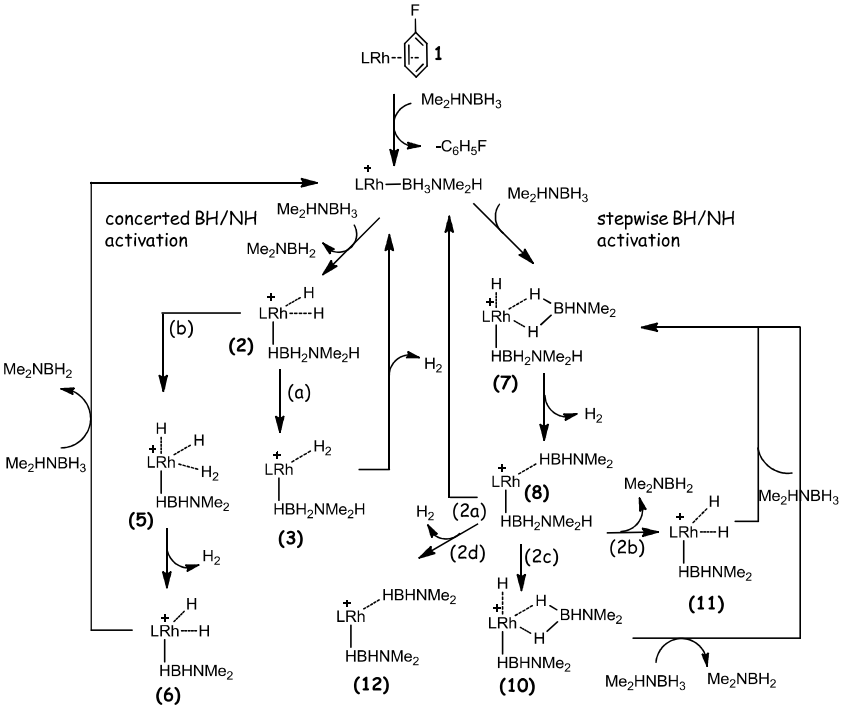
All density functional theory calculations in this study have been performed using the Gaussian 03 suite of ab initio programs[37] employing the hybrid XC functional B3PW91.[38] For Rh the relativistic compact Stuttgart/Dresden effective core potential[39] has been used in conjunction with its split valence basis set. The standard 6-311G* basis sets of Pople and co-workers have been employed for the rest of the atoms, except C and H atoms of phenyl rings for which the smaller 6-31G basis sets have been used. A series of preliminary calculations has been carried out to ascertain whether weak dispersion interactions can have an influence on the shape of the calculated energy profiles. The energetics of critical regions of Potential Energy Surfaces (PESs) re-calculated by using the ωB97XD functional,[40] a range-separated version of Becke's 97 functional,[41] do not show any significant change when dispersion corrections are accounted for. The geometric structures of all complexes studied in this paper have been optimized as gas-phase as the cation only. Calculating the harmonic vibrational frequencies at the optimized structures and not-

ing the number of imaginary frequencies have confirmed the nature of all intermediates (no imaginary frequency) and transition states (only one imaginary frequency), which also have been confirmed to connect reactants and products by the intrinsic reaction coordinate (IRC)[42] calculations. The zero-point energy (ZPE) and entropic contribution have been estimated within the harmonic potential approximation. The enthalpies, H, and free energies, G, have been calculated for T=298.15 K. Since the real entropic cost under catalytic conditions is not properly reproduced by using this method and the effects are particularly relevant for the substrate association and dissociation,[43] following a common approach in theoretical catalysis, the solvation entropy has been estimated as two/third of its gas-phase value.[43,44] All relative energies are reported in kcal/mol. Since preliminary calculations have clearly shown that geometry relaxation effects are not significant, the solvation Gibbs free energies have been calculated in implicit isoquiniline (ε=11.0), as a mimic of the 1,2-$F_2C_6H_4$ solvent, using the integral equation formalism polarizable continuum model (IEFPCM),[45] performing single point calculations on gas-phase optimized structures. Reaction Gibbs free energies in solution, ΔG_{sol}, have been calculated for each process as the sum of two contributions: a gas-phase reaction free energy, ΔG_{gas}, and a solvation reaction free energy term calculated with the continuum approach, ΔG_{solv}. In the beginning, an exploration of all the plausible reaction pathways, with the purpose to identify the most favorable one, has been carried out, by using a simplified model of the $[Rh(Ph_2P(CH_2)_2\text{-}PPh_2)(C_6H_5F)]^+$ complex. Indeed, in order to reduce the required computational effort, at this stage of the computational analysis, the phenyl rings of phosphine ligands have been replaced with less demanding methyl groups. For the studied complexes from now on we will adopt the same nomenclature used originally by the authors.[27] In particular, $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ complexes will be labeled **1b**, **1c** and **1d** for n=3, n=4 and n=3, respectively. The corresponding $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ complexes formed by addition of Me_2HNBH_3, and displacement of the labile fluoroarene ligand, will be labeled **2b**, **2c** and **2d**. The simplified model of **2b**, used to predict the lowest energy pathway, will be indicated as **2b(Me)**.

3. RESULTS

All the energy profiles describing the results of our computational analysis carried out by focusing on the simplified catalyst model **2b(Me)** are reported in terms of relative gas-phase zero-point corrected energies. Free energy profiles in solution, instead, are reported to illustrate the outcomes of the investigation of the dehydrogenation reaction for **2b**, **2c** and **2d** complexes. Along the reaction pathways the optimized structures of intercepted intermediates and transition states are shown, whereas complete geometric information is reported in the Supporting Information (SI). Scheme 3 provides an overview of all the possible reaction routes that appear to be viable on the basis of both experimental findings and computational results and have been selected as a function of the energetics of the intercepted minima and transition states. Even though complex **1** is the organometallic precatalyst in fluorobenzene solvent, the mechanistic investigation really starts from complex formed by addition and coordination of the Me_2HNBH_3 substrate which causes the displacement of the bound arene solvent in **1**.

Scheme 3. Overview of the all selected viable dehydrocoupling pathways.



3.1 Formation of dimeric species. At the very beginning of our investigation the attention has been focused on the hypothesis that the formation of a dinuclear metal-metal bonded complex in equilibrium with the mono-nuclear active species (see Scheme 2) could be responsible of the observed induction period. Experimental findings confirm an inverse relationship between the induction period and the catalyst loading, at constant substrate concentration. Such hypothesis is supported by the isolation of a dicationic dimer formed from two monodentate phosphine fragments bridged by three H_3BNMe_3 ligands,[45] as well as by the observation of induction periods in homogeneous systems that invoke equilibria between active monomeric species and inactive polymetallic species.[47] The authors also suggest that formation of dicationic dimer requires prior substrate activation and, anyhow, experiments do not allow to draw firm conclusions.

All the suitable computational strategies and all the possible starting assemblies of monomers (e.g. with and without fluoroarene units) have been employed to examine this hypothesis. All the attempts to model a pathway that from monomeric species leads to the formation of the dimer have been unsuccessful. The monomers tend, unavoidably, to stay apart and, plausibly, particular experimental conditions are required to form a dinuclear complex. Moreover, we have investigated what might happen once formed, whatever the mechanism, the dimeric complex.

The energy profile reported in Figure 1 shows minima and connecting transition states intercepted along a viable dehydrogenation pathway. The optimized structure of the dicationic dimeric species, **Rh_2**, formed from two $[Rh(Me_2P(CH_2)_3PMe_2)]^+$ fragments bridged by two **A** ligands, is reported in Figure 1. Full details of the optimized structures are reported in the Supporting Information (Table S1). The two rhodium atoms are bridged by two activated B-H hydrogen atoms for each **A** ligand. The Rh-Rh bond length is 2.515 Å consistent, even if shorter, with that for a single bond distance. Both rhodium centers adopt a distorted bipyramidal trigonal geometry. With respect to the monomeric rhodium sigma complex of $H_3B{\cdot}NMe_3$ **2b(Me)** the **Rh_2** complex is calculated to be more stable by 59.8 kcal/mol. Very similar values of the stabilization energy of dimeric species formed by two $[Rh(Ph_2P(CH_2)_nPPh_2)]^+$ fragments bridged by two **A** ligands have been calculated for n=1-3. Calculated values are 61.3, 60.9 and 58.6 kcal/mol for n=1, n=2 and n=3, respectively. Therefore, the **Rh_2** complex, once formed, is very stable and, as suggested by experiments, very inactive. As expected, all the attempts to locate a low energy practicable route leading from the intercepted dimeric species to the formation of separate **2b(Me)** fragments have failed.

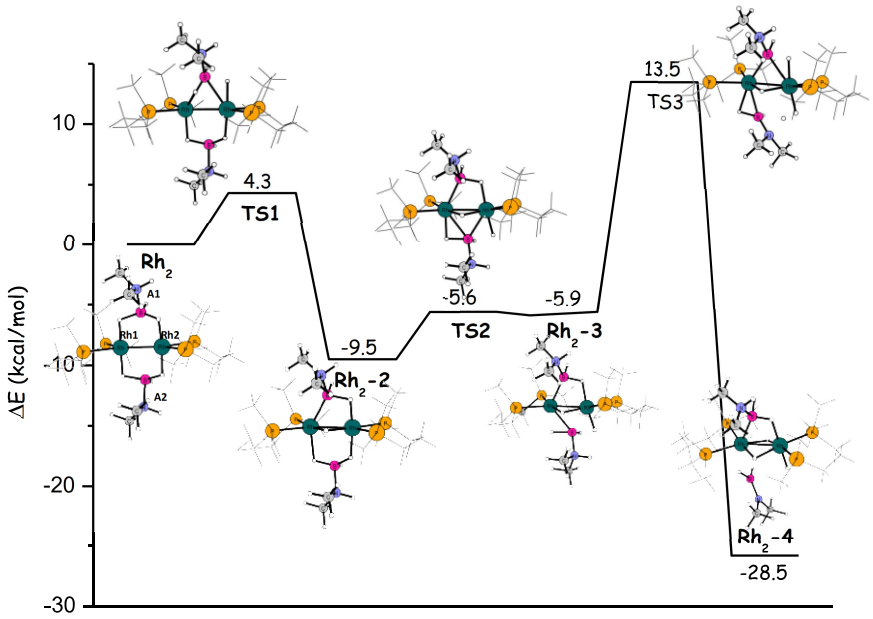


Figure 1. Calculated B3PW91 gas-phase zero-point corrected energy profile for the dehydrogenation reaction of amine-borane ligands in the dicationic dimeric complex labeled Rh_2. Energies are in kcal/mol and relative to reactants' asymptote.

Along the pathway sketched in Figure 1 the first step, which occurs by surmounting an energy barrier of about 4 kcal/mol, is the shift of a hydrogen from the dimethylamine-borane ligand, labeled **A1**, to rhodium. In the formed intermediate the hydrogen atom occupies a bridged position between the two rhodium atoms. The next step consists of another hydrogen atom shift from the **A** molecule, labeled **A2**, to **Rh_2** with concomitant detachment of the ligand **A1** from **Rh_2**. The barrier height is 3.9 kcal/mol and the formed intermediate is only slightly more stable. The height of the barrier for the last step of the process, which leads to the elimination of an amino-borane molecule is 19.4 kcal/mol. As a result of the interaction of the hydride on **Rh2** and a NH proton of ligand **A2**, which seems to prelude to the formation of a H_2 molecule, a very stable dimer is formed. The molecular structure of such complex, which lies about 26 kcal/mol below the entrance channel of the reaction, consists of one distorted octahedral rhodium centre linked to a pseudo-square pyramidal rhodium centre. The two Rh atoms lie at distance of 2.621 Å and are bridged by two hydride ligands in equatorial positions. In conclusion, an aminoborane molecule is eliminated, but neither molecular hydrogen is formed, nor separate **2b(Me)** fragments are formed. Thus the potential formation of the dimeric species inhibits the dehydrogenation reaction. In the next sections the most plausible reaction mechanism will be illustrated and a tentative explanation will be given of the observation of an induction period.

3.2 Selection of the Me_2HNBH_3 dehydrogenation reaction pathway. Experimental findings suggest that when [Rh(chelating bis-phosphine)] catalysts assist the dehydrocoupling process, the formation of **Z** occurs by dehydrogenation of **A** with formation of a Rh(III)-dihydride intermediate and change in oxidation state at Rh, followed by rapid loss of H_2 to re-form a Rh(I) species. Experiments have also shown that linear dimer $Me_2HNBH_2NMe_2BH_3$ is not an intermediate. Given the potential complexity of the reaction steps required to afford the final product **C**, an initial exploration of all the plausible reaction pathways has been carried out by using the catalyst model **2b(Me)**. All the Cartesian coordinates of stationary point along the examined reaction pathways illustrated in Figures 2-4 are given in Table S2 of SI. According to clues coming from experiments, at first, all the efforts have been devoted to compute a path leading to the formation of a Rh-dihydride complex. Direct transfer of hydrogen atoms from the coordinated **A** molecule to the rhodium centre in complex **2b(Me)** does not occur. Geometric constraints imposed by the presence of the chelating diphosphine ligand hamper the hydrogen atoms transfer. Only when a second amine-borane molecule interacts with the **2b(Me)** complex the dehydrogenation process starts and the reaction pathway bifurcates as we are going to illustrate. The first step of the pathways shown in Figure 2 is the concerted BH/NH activation of the second amine-borane molecule approaching the complex. The dehydrogenation proceeds by hydrogen transfer to the metal centre through the transition state **$TS_{1\text{-}2}$**, with an energy barrier of 8.1 kcal/mol, to afford the Rh-dihydride intermediate (**2**) that is more stable by 4.3 kcal/mol than **2b(Me)+A**. A $H_2B{=}NMe_2$ molecule is eliminated and the Rh centre assumes a pseudo-octahedral geometry thanks to the η^2-coordinatation of the remaining amine-borane ligand. Along an alternative and less productive dehydrogenation pathway, which is shown in Figure 3, the second amine-borane molecule can assist the stepwise NH and BH bonds activation of the bound **A** molecule. The first H-transfer from the N atom to the Rh centre occurs

through the transition state $\mathbf{TS_{1\text{-}5}}$ by overcoming a high energy barrier of 33.1 kcal/mol. In the formed intermediate

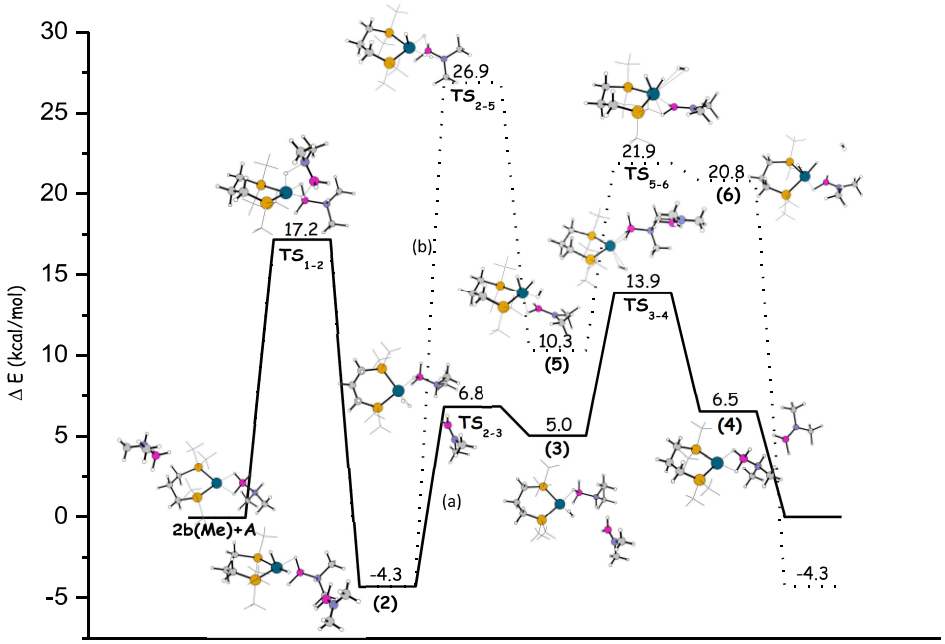


Figure 2. Calculated B3PW91 zero-point corrected energy profiles for the dehydrogenation reaction, which involves concerted NH/BH activation as the first step, of a dimethylamine-borane molecule A assisted by the model catalyst 2b(Me). Along the path labeled (a) a dihydrogen ligand in equatorial position coordinated with the Rh centre is formed, whereas hydrogen transfer from the bound A molecule occurs along path (b). Energies are in kcal/mol and relative to reactants' asymptote.

(7), which lies 5.1 kcal/mol below the reactants' asymptote, the second **A** molecule is η^1-coordinated to the metal centre in axial position. The subsequent BH hydride shift does not lead to the formation of a dihydride complex. Indeed, the two H atoms interact to directly produce and release molecular hydrogen. The intermediate **(8)** is formed that is less stable by 12.6 kcal/mol than the previous intermediate. The geometry at the Rh centre in the intermediate **(8)** is pseudo square planar, with the ligands **A** and formed **Z** coordinated in η^1 fashion. Such intermediate is afforded through the transition state $\mathbf{TS_{6\text{-}7}}$ by surmounting an energy barrier of 22.9 kcal/mol.

The outcomes of the computational analysis carried out so far clearly show that the pathway for the concerted dehydrogenation leading to the formation of intermediate (**2**), is more favorable and accessible in practice than the stepwise dehydrogenation affording intermediate **(8)**. Nevertheless, all the accessible routes from both intermediate (**2**) and **(8)** have been examined. The two non-competitive pathways that begin with formation of (**2**) are shown in Figure 2. After formation of the dihydride complex, the reaction proceeds along the low-energy path labeled (a) by formation of a dihydrogen ligand in equatorial position coordinated with the Rh centre that has a pseudo-square planar geometry. The minimum **(3)** lies 5.0 kcal/mol above the reactants' dissociation limit and the height of the barrier leading to it is 11.1 kcal/mol. The next step, that is loss of molecular hydrogen, regenerates the **2b(Me)** complex and the addition of a new **A** molecule restarts the catalytic cycle. Alternatively, along the second pathway labeled (b) the reaction mechanism involves the concerted NH proton and BH hydride shifts from the bound amino-borane to the metal centre in axial and equatorial positions, respectively. As a consequence, the geometry at the Rh centre of the formed **(5)** intermediate becomes pseudo-octahedral with the formed hydrogen molecule as the sixth ligand in equatorial position and the dehydrogenated amino-borane molecule adopting a η^1 coordination. Intermediate **(5)** , which is less stable by 14.6 kcal/mol than the preceding intermediate, can be accessed through $\mathbf{TS_{2\text{-}5}}$, by overcoming an energy barrier of 31.2 kcal/mol. The loss of the H_2 molecule from intermediate **(5)** occurs with a barrier of 11.6 kcal/mol and leads to the formation of an intermediate, **(6)**, which is more stable than $\mathbf{TS_{5\text{-}6}}$ by only 1.1 kcal/mol. Release of the formed amino-borane molecule and simultaneous coordination of a new **A** molecule restore the intermediate **(2)**. Along the (b) pathway, therefore, the **2b(Me)** complex plays the role of precatalyst and the catalytic cycle starts from the dihydride intermediate **(2)**.

Calculations carried out to explore the viable alternative pathways from intermediate **(8)** are illustrated in Figures 3 and 4. The pathway, labeled (2a), that involves the lowest energy barrier is reported in Figure 3, whereas three alternative non

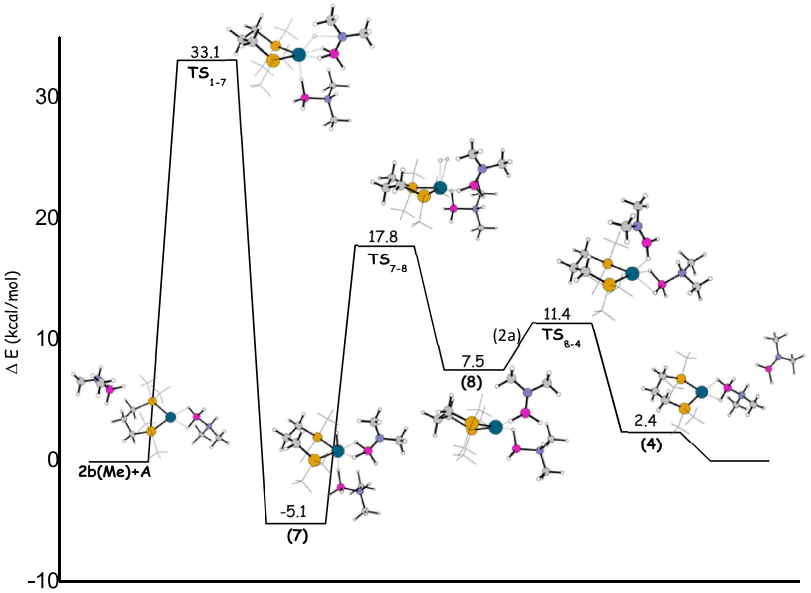
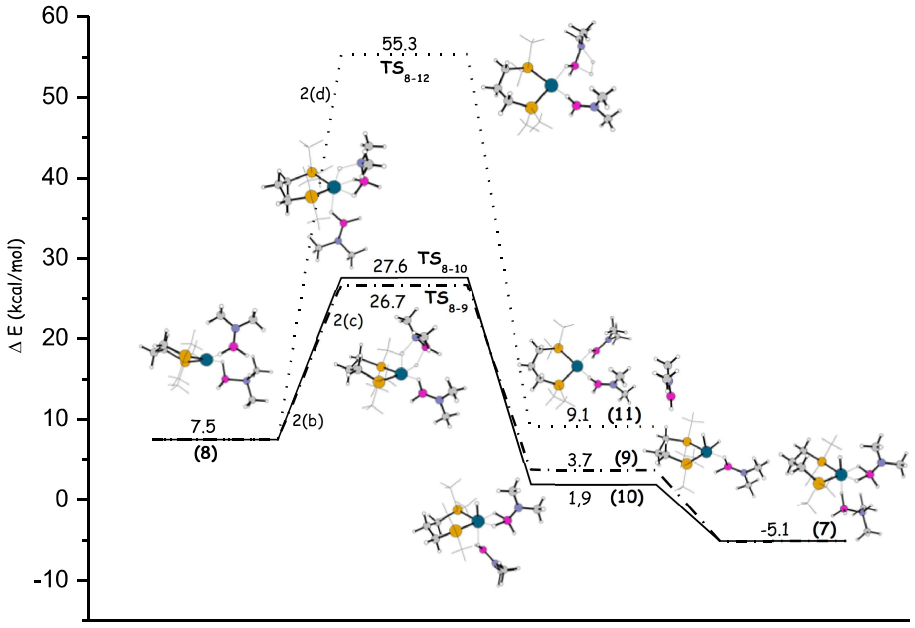


Figure 3. Calculated B3PW91 zero-point corrected energy profiles for the dehydrogenation reaction, which involves stepwise NH/BH activation as the first step, of the bound dimethylamine-borane molecule A in model complex 2b(Me) assisted by a second A molecule. Energies are in kcal/mol and relative to reactants' asymptote.

competitive pathways (2b-2c) are shown in Figure 4. Along the (2a) reaction path the **2b(Me)** complex is restored by the loss of the aminoborane molecule induced by the coordination



of a new **A** ligand. The height of the calculated barrier for the

Figure 4. . Calculated B3PW91 zero-point energy profiles for the different dehydrogenation pathways that from intermediate (8) lead to the regeneration of intermediate (7) along (2b) and (2c) and formation of the di-aminoborane intermediate (11) along (2d). Energies are in kcal/mol and relative to reactants' asymptote.

corresponding transition state, $\mathbf{TS_{1\text{-}4}}$, is 3.9 kcal/mol. Alternatively, along the (2b) pathway two hydrogen atoms from the ligated amine-borane molecule are transferred to the metal centre by overcoming an energy barrier of 19.2 kcal/mol for the $\mathbf{TS_{8\text{-}9}}$ transition state. The di-hydride intermediate **(9)** is formed, stabilized by 3.8 kcal/mol with respect the previous minimum, from which the intermediate labeled **(7)** in Figure 3 should be formed by coordination of a new **A** molecule and a hydride transfer from the Rh centre to the dehydrogenated dimethylammine-borane ligand. A very similar value of the energy barrier, 20.1 kcal/mol, has been calculated along the (2c) path for the $\mathbf{TS_{8\text{-}10}}$ transition state that corresponds to the shift of a NH proton from the amine-borane to the metal centre.

The esa-coordinated minimum **(10)** is formed that is calculated to be more stable by 5.6 kcal/mol than intermediate **(8)**. Displacement of the **Z** molecule in axial position and coordination of an additional amine-borane molecule regenerates the same **(7)** complex. Finally, through the very high $\mathbf{TS_{8\text{-}10}}$ transition state (47.8 kcal/mol) associated to the intramolecular elimination of a H_2 molecule from the dimethylamine-borane molecule the complex labelled **(11)** is formed, less stable by 1.6 kcal/mol than **(8)**. Although the complex **(11),** which has two aminoborane molecules coordinated to the Rh atom, does not lie on a competitive pathway, its formation is noteworthy for reasons that will be illustrated below.

As a general rule, if the possibility of the formation of borazane **B** can be excluded, such as in the present case, subsequent oligomerization, polymerization or dimerization of $R_2N{=}BH_2$ can occur either on or off the metal with or without the further involvement of R_2HNBH_3. Since the observed final product of the process under investigation is the cyclic dimer **C**, the possibility that formed $Me_2N{=}BH_2$ monomers undergo further reactivity on the metal to afford **C** has been explored. Calculations carried out to model both a concerted and stepwise rearrangement mechanism leading to the formation of the **C** dimer have been unsuccessful. Although intermediate **(11)** should be a promising starting point for the formation of the cyclic dimer directly on the metal centre, no pathway has been calculated leading to such product. According to our previous conclusions,[19] uncatalyzed dimerization in solution of the free **Z** monomers is the only way to form the dehydrocyclization product **C**.

Overall, these preliminary calculations suggest the most favorable reaction path to be that shown in Figure 2, which starts with the concerted dehydrogenation of the second non-coordinated amine-borane to yield the dihydride complex **(2)** and proceeds, along the pathway labeled (a), with the elimination of a H_2 molecule and regeneration of the initial complex **2b(Me)**. The consequence of such a result will be discussed in the next sections.

Minima and transition states along analogous pathways have been intercepted by considering the real catalytic systems **2a**, **2b** and **2c** with the aim to prove the suggested relationship between the amplitude of the P-Rh-P bite angle and the rate of the reaction.

3.3 Mechanistic aspects of the Me_2HNBH_3 dehydrogenation assisted by 1b, 1c and 1d and bite angle effect. The DFT optimized structure of the cationic portion of the reference complex **2b** formed by addition of Me_2HNBH_3 to the $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ complex **1b** and displacement of the fluoroarene ligand is shown in Figure 5. Calculations confirm the square-planar geometry at the Rh(I) centre and the η^2 coordination of the **A** ligand. Comparison with relevant available structural features extracted from crystallographic characterization of the complex[27] as well as with the estimated values of the bis-phosphine ligand bite angle and *bite*,[29] shows a good agreement, indicating a good modeling of the catalyst.

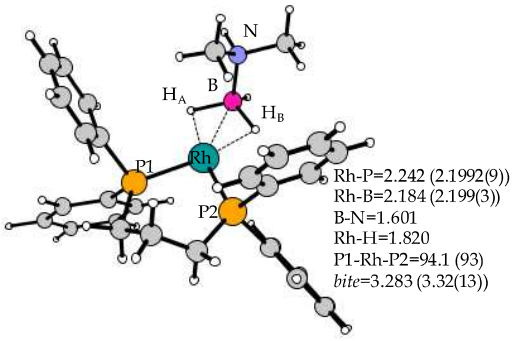


Figure 5. DFT optimized geometrical structure of cationic portion of 2b. Selected structural parameters (bonds in Å and angles in degrees) are compared with available experimental values (in parentheses).

The outcomes of the calculations for the dehydrogenation reaction are summarized in Figure 6, where the free energy profile is shown together with the fully optimized structures of

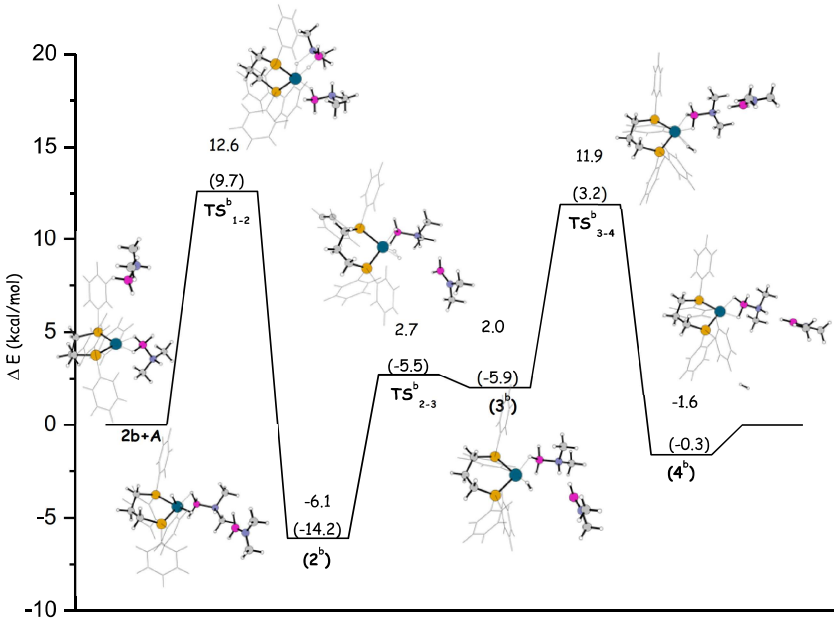


Figure 6. Calculated B3PW91 free energy profile for the dehydrogenation reaction along the selected dehydrogenation pathway starting from the 2b complex. Energies are in kcal/mol and relative to reactants' asymptote.

stationary points. More detailed geometrical information on intercepted stationary points can be found in Table S3 of the SI. Gas-phase zero-point corrected relative energies are also reported in parentheses to highlight the effects on the energetics of the replacement on the diphosphine ligand of the methyl groups, used to reduce the preliminary calculation computational efforts, with phenyl rings.

Concerted BH hydride and NH proton transfer to the Rh centre from the second **A** molecule approaching the **2b** complex occur by overcoming an energy barrier, $\mathbf{TS^b_{1-2}}$, of 9.7 kcal/mol in gas-phase and 12.6 kcal/mol along the free energy profile. The formed dihydride **(2^b)** complex, from which an aminoborane molecule is released, lies 6.1 kcal/mol (14.2 kcal/mol in gas-phase) below the reference energy of separated reactants **2b** + **A**. A free energy barrier of 8.8 kcal/mol for the $\mathbf{TS^b_{2-3}}$, comparable to the calculated gas-phase barrier of 8.7 kcal/mol, separates the **(2^b)** intermediate from the next minimum **(3^b)** and corresponds to the interaction between the two hydrogen ligands to form a H_2 molecule. The formed intermediate **(3^b)** is only slightly more stable than the previous transition state, by 0.7 and 0.4 kcal/mol in solution and gas-phase, respectively and, as a consequence it results to be less stable than intermediate **(2^b)** by 8.1 kcal/mol in solvent. The elimination of the hydrogen molecule coordinated to the Rh atom from the pseudo-square planar complex **(3^b)** occurs by overcoming a free energy barrier of 9.9 kcal/mol for the $\mathbf{TS^b_{3-4}}$. The corresponding barrier in gas-phase is calculated to be 9.1 kcal/mol. The elimination of the H_2 molecule along with the coordination mode switch from η^1 to η^2 of the amine-borane ligand leads to the restoration of the initial complex **2b** that is poised to react with a new **A** molecule. The qualitative behaviors of the **2b(Me)** and **2b** complexes are in agreement as can be inferred form a comparison of the data reported in Figures 2 and 6. From a quantitative viewpoint, instead, the presence of phosphine ligands bearing the more electron-donating phenyl substituents increases the stability of dihydride and dihydrogen complexes according with previous investigations,[31,35] which have demonstrated how strongly donating bidentate phosphines are able to stabilize complex structures containing hydride and hydrogen ligands. The most important conclusion that we can draw from the outcomes of the present computational investigation is that the active catalyst is the complex formed by displacement in the precatalyst of the fluoroarene ligand and coordination of one substrate molecule. Reaction with a second amine-borane molecule allows the catalytic cycle to start. Release of an aminoborane molecule and molecular hydrogen restore the catalyst that is poised to further react. Off-metal dimerization in solution of released aminoboranes leads to the formation of the cyclic dimer observed product. As underscored above, the first step of the process for the formation of the active catalyst is the displacement of the arene ligand caused by the coordination of the substrate. We have calculated the energetic cost of this step

Let us describe what happens when the dimethylamine-borane **A** is added to the $[Rh(Ph_2P(CH_2)n\text{-}PPh_2)(C_6H_5F)]^+$ (n=4, 5) precursors **1c** and **1d** to yield the corresponding **2c** and **2d** complexes and ultimately afford the cyclic aminoborane dimer **C**. The calculated structures of the cationic portion of the **2c** and **2d** complexes are shown in Figure 7. Fully optimized geometrical structures of all the minima and transition states are given in Table S4 of SI along with Cartesian coordinates. The pseudo-square planar geometry of such complexes is confirmed, with the dimethylamine-borane ligand coordinated to the metal centre in an η^2 fashion. As suggested, the increased length of the ligand backbone corresponds to wider P-Rh-P bite angles. The value of 94.1° calculated for the bis-phosphine ligand when the number of CH_2 units is equal to 3 (n=3) becomes 97.6° and 99.5° for n=4 and n=5, respectively. Calculated values reproduce the trend of estimated values of bites and bite angles for such complexes.[29] The Rh-B distances, instead, do not follow the surmised trend. Indeed, the Rh-B bond length decreases in going from n=3 to n=4 and increases again in **2d** becoming slightly longer than that in **2b**.

The corresponding calculated free energy profiles corrected for the solvent effect are reported in Figure 8 for both **2c** and **2d** complexes. Relative energies in gas-phase, reported in parentheses, are not commented. Supporting Information give geometrical structures of minima and transition states. The dehydrogenation reaction proceeds by following the same sequence of steps, but the relative stabilities of the intercepted stationary points change as it appears by comparison of the energy profiles in Figures 5 and 8.

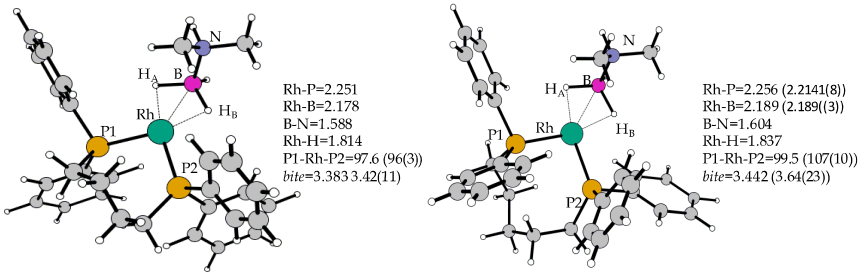
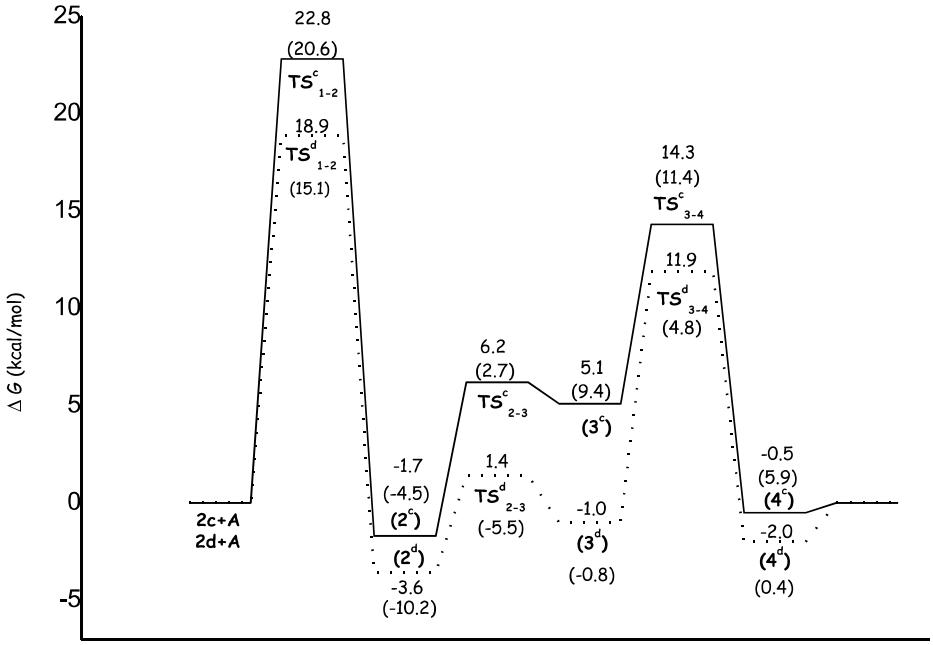


Figure 7. DFT optimized geometrical structure of cationic portion of 2c and 2d. Selected structural parameters (bonds in Å and angles in degrees) are compared with available experimental and estimated values (in parentheses).

We are going to establish whether these quantitative differences are in agreement with the experimentally observed catalytic behaviors and support the assumed relationship between structure and reactivity.

After the formation of the **2c** and **2d** σ complexes, the concerted B–H hydride and N–H proton transfer from the second amine-borane molecule **A** to rhodium center occurs through the $\mathbf{TS}^{c}_{1\text{-}2}$ and $\mathbf{TS}^{d}_{1\text{-}2}$ transition states by overcoming barriers of 22.8 and 18.9 kcal/mol, respectively. The corresponding barrier for the **2b** complex is 12.6 kcal/mol. This first barrier is the highest calculated barrier along the dehydrogenation pathways for all the three studied complexes. This means that the concerted NH/BH activation of the second **A** molecule at the metal center, with formation of the corresponding dihydride complex, represents the rate-determining step of the whole process. Experimental findings,[27] rationalized by invoking the correlation between the bite angle and the strength of the Rh---B interaction, give **2b** as the fastest and **2d** as the slowest.

On the basis of the calculated activation barriers along the pathway that our computational analysis has indicated as the most likely, the dehydrogenation rate of **2b**, corresponding to the narrowest bite angle, should be the fastest. The rate decreases in going from **2b** to **2c** and increase again for **2d**. These results, only partially in agreement with experimental results, can be explained by focusing on the effects of the bite angle on the stability of the involved transition states and intermediates. To this aim in Figure 9 are sketched the fully optimized structures of the dihydride intermediate $(\mathbf{2}^{b})$ and the transition state $\mathbf{TS}^{b}_{1\text{-}2}$ leading to it. The reported labels have to be used to read the geometrical information given in Table 1. In this table the values of some geometrical parameters for both dihydride complexes $[RhH_2(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ (n = 3–5) and corresponding transitions states are given, which can help us to rationalize the computed behaviours. Due to the simultaneous B–H hydride and N–H proton transfer from the second amine-borane molecule **A** to the rhodium center and the switching from a η^2 to η^1 coordination mode of the bound amine-borane molecule, the pseudo-square planar geometry of the initial complexes **2b**, **2c** and **2d** becomes square pyramidal in the transition states. Since one of the transferred H atoms (H_A) occupies an axial position, the angle they form with the Rh centre (H_A-Rh-H_B) does not change appreciably with the increasing of the diphosphine bite angle (P1-Rh-P2).



Larger bite angle, instead, causes a compression of the angle, in equatorial position, that the second H atom (H_B) forms with the phosphorus labelled P2. At the same time, as the partial detachment of the coordinated amine-borane molecule is required, the strength of the Rh—B bond in **2b**, **2c** and **2d** complexes has an influence on the height of the barrier for the transition states. The values of

Figure 8. Calculated B3PW91 free energy profiles for the dehydrogenation reaction along the selected dehydrogenation pathway starting from the 2c (solid line) and 2d (dashed line) complexes. Energies are in kcal/mol and relative to reactants' asymptote.

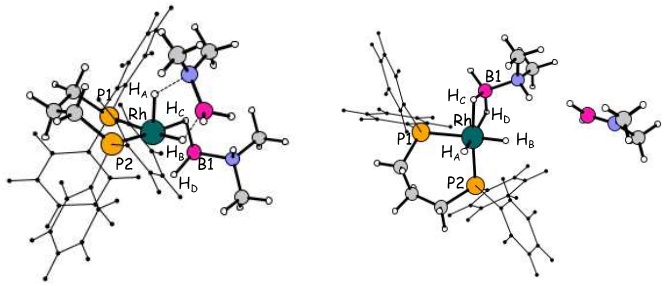


Figure 9. Optimized geometrical structure of cationic portion of (2^c). Labels have to be used to read the geometrical information given in Table 1.

Rh-B bond length (Rh-B1) are also reported in Table 1 to show the evolution of this geometrical parameter along the reaction coordinate. Since in square-planar 2b, 2c and 2d the values of the Rh-B distance are 2.184, 2.178 and 2.189 Å, respectively, the observed trend in the barrier heights results from a balance between the geometrical distortion caused by the bite angle enlargement and the influence the bite angle has on the Rh---B interaction strength. The calculated stability ordering of the corresponding minima (**(2^b)** > **(2^d)** > **(2^c)**) can be rationalized in terms of distortion of the octahedral geometry caused by the widening of the P-Rh-P angle, but compensated by the elongation of the Rh-P bond in axial position (Rh-P2). The Rh-P bond length in the **(2^d)** intermediate stretched to 2.45 Å indicates that one of the arms of the diphosphine ligand is detached and, consequently, the complex assumes a square pyramidal geometry. The next step of the process is the transformation of dihydride complexes into the corresponding $[Rh(H_2)(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ dihydrogen complexes. This transformation proceeds through **$TS^c_{2\text{-}3}$** and **$TS^d_{2\text{-}3}$** transition states with barriers of 7.9 and 5.0 kcal/mol, respectively, which are both lower than the analogous barrier of 8.8 kcal/mol calculated along the reaction path for **2b**.

Table 1. Calculated key geometrical parameters for (2^b), (2^b) and (2^d) intermediates and transition states leading to them.

Parameter	$TS^b_{1\text{-}2}$	(2^b)	$TS^c_{1\text{-}2}$	(2^c)	$TS^d_{1\text{-}2}$	(2^d)
P1-Rh-P2	92.5	95.7	98.3	98.5	103.8	106.8
H_A-Rh-H_B	81.1	87.88	80.0	83.3	79.7	83.0
H_A-Rh-P2	85.1	171.7	82.5	173.7	80.0	168.2
Rh-B1	2.343	2.227	2.335	2.221	2.332	2.218
Rh-P2	2.291	2.389	2.305	2.399	2.347	2.450

This trend should indicate an enhancing effect of larger bite angles on the rate of a reaction. Relative energies reported in Figures 6 and 8 show that the formed dihydrogen complexes are less stable than the corresponding dihydride complexes. Finally, molecular hydrogen release occurs by overcoming the barriers of 9.2 kcal/mol for **$TS^c_{3\text{-}4}$** and 12.9 kcal/mol for **$TS^d_{3\text{-}4}$**. The corresponding energy barrier for the **$TS^b_{3\text{-}4}$** transition state is 9.9 kcal/mol. Even though the intermediate **(4^d)**, possessing the largest bite angle, appears to be the most reluctant to lose molecular hydrogen, the calculated values of the height of the energy barriers for such and the previous step support the conclusion that, unlike monodentate phosphine systems, Rh(III) chelating-phosphine catalysts rapidly lose hydrogen to reform initial Rh(I) species. The computational exploration carried out in this work supports and reinforces the assumption the use of bidentate chelating phosphine ligands can be beneficial in homogeneous catalysis.

4. CONCLUSIONS

In the framework of a more general project aiming to understand the mechanistic scenario for amine-boranes dehydrogenation in more detail, a rigorous quantum-mechanical investigation of the dehydrocoupling reaction of the secondary amine-borane Me_2HNBH_3 assisted by phosphine chelating $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(C_6H_5F)]^+$ (n = 3–5) complexes to ultimately afford the cyclic dimer $[Me_2NBH_2]_2$ has been reported. An accurate exploration of all the viable dehydrocoupling pathways has been carried out. The dehydrogenation pathway that, on the basis of the computed results, appears to be the most viable involves, as the first step, the concerted B–H hydride and N–H proton transfer from an additional amine-borane molecule to the rhodium centre of the formed $[Rh(Ph_2P(CH_2)_n\text{-}PPh_2)(\eta_2\text{-}Me_2HNBH_3)]^+$ complexes. The reaction proceeds by formation of dihydrogen complexes, which eliminate molecular hydrogen and restore the σ-amine-borane complexes, which are poised to react with a new dimethylamine-borane molecule. Off-metal coupling of the released aminoborane molecules leads to the formation of the final cyclic product. The step that gives the formation of dihydride complexes has been calculated to be the rate determining step of the whole process and the calculated barrier heights have been rationalized by considering how the amplitude of the P-Rh-P bite angle influences the stability of the involved transition states. The impact that the length of the diphosphine ligand backbone has on every step of the process has been equally examined. According to conclusions coming from experimental evidences, the elimination of molecular hydrogen from the studied complexes is calculated to involve energy barriers low enough to allow the restoration of initial Rh(I) catalysts.

The trends observed for the systems studied above provide additional information to the more general context of metal-assisted amine-boranes dehydrocoupling processes. Future studies will address the influence that the identity of the metal has on both the rate of catalysis and the intermediates in order to supply yet more information on this important transformation.

SUPPORTING INFORMATION.

Complete reference 37, atomic coordinates and absolute energies of all optimized stationary points and transition states.This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Clark, T. J.; Lee, K.; Manners, I. *Chem. Eur. J.* **2006**, *12*, 8634-8648.
(2) Staubitz, A; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079-4124;
(3) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279-293.
(4) Staubitz, A.; Soto, A. P.; Manners, I. *Angew. Chem.* **2008**, *47*, 6212 –6215.
(5) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844.
(6) Hill, M. S.; Hodgson, M.; Liptrot, D. J.; Mahon, M. F. *Dalton Trans.* **2011**, *40*, 7783.
(7) Kawano, Y.; Uruichi, M.; Shimoi, M.; Taki, S.; Kawaguchi, T.; Kakizawa, T.; Ogino, H. *J. Am. Chem. Soc.* **2009**, *131*, 14946.
(8) Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 8826.
(9) Hill, M. S.; Kociok-Koehn, G.; Robinson, T. P. *Chem. Commun.* **2010**, *46*, 7587.
(10) Miyazaki, T.; Tanabe, Y.; Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2011**, *30*, 2394.
(11) Sloan, M. E.; Staubitz, A.; Clark, T. J.; Russell, C. A.; Lloyd Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 3831.
(12) Pun, D.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2007**, 3297.
(13) MacInnis, M. C.; McDonald, R.; Ferguson, M. J.; Tobisch, S.; Turculet, L. *J. Am. Chem. Soc.* **2011**, *133*, 13622.
(14) Vance, J. R.; Robertson, A. P. M; Lee, K.; Manners, I. *Chem. Eur. J.* **2011**, *17*, 4099.
(15) Ledger, A. E. W.; Ellul, C. E.; Mahon, M. F.; Williams, J. M. J.; Whittlesey, M. K. *Chem. Eur. J.* **2011**, *17*, 8704.
(16) Alcaraz, G.; Grellier, M.; Sabo-Etienne, S. *Acc. Chem. Res.* **2009**, *42*, 1640.
(17) Jiang, Y.; Hess, J.; Fox, T.; Berke, H. *J. Am. Chem. Soc.* **2010**, *132*, 18233.
(18) Zimmerman, P. M.; Paul, A.; Zhang, Z. Y.; Musgrave, C. B. *Inorg. Chem.* **2009**, *48*, 1069.
(19) Butera, V.; Russo, N.; Sicilia, E. *Chem. Eur. J.* **2011**, *17*, 14586.
(20) Sloan, M. E.; Clark, T. J.; Manners, I. *Inorg. Chem.* **2009**, *48*, 2429.
(21) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
(22) Vogt, M.; de Bruin, B.; Berke, H.; Trincado, M.; Grutzmacher, H. *Chem. Sci.* **2011**, *2*, 723.
(23) Tang, C. Y.; Thompson, A. L.; Aldridge, S. *J. Am. Chem. Soc.* **2010**, *132*, 10578.
(24) Rousseau, R.; Schenter, G. K.; Fulton, J. L.; Linehan, J. C.; Engelhard, M. H.; Autrey, T. *J. Am. Chem. Soc.* **2009**, *131*, 10516.
(25) Fulton, J. L.; Linehan, J. C.; Autrey, T.; Balasubramanian, M.; Chen, Y.; Szymczak, N. K. *J. Am. Chem. Soc.* **2007**, *129*, 11936.
(26) Sewell, L. J.; Lloyd-Jones, G. C.; Weller, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 3598.
(27) Dallanegra, R.; Robertson, A. P. M; Chaplin, A. B.; Manners, I.;Weller, A. S. *Chem. Commun.* **2011**, *47*, 3763.
(28) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.*, **1990**, *30*, 299.
(29) Aguilà, D.; Escribano, E.; Speed, S.; Talancón, D.; Yermán L.; Alvarez, S. *Dalton Trans.*, **2009**, 6610.
(30) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.*, **1977**, *99*, 8055.
(31) Marcone, J. E.; Moloy, K. G.*J. Am. Chem. Soc.*, **1998**, *120*, 8527.
(32) Wilson, A. D.; Miller, A. J. M.; DuBois, D. L.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.*, **2010**, *49*, 3918.
(33) Birkholz, M. N.; Freixa, Z.; van Leeuwen, P. W. N. M. *Chem. Soc. Rev.* **2009**, *38*, 1099.
(34) van Zeist, W. J.; Visser, R.; Bickelhaupt, F. *Chem. Eur. J.* **2009**, **15**, 6112.
(35) Freixa, Z.; van Leeuwen, P. W. N. M. *Dalton Trans.* **2003**, 1890.
(36) Lovitt, C. F.; Frenking, G.; Girolami, G. S. *Organometallics* **2012**, *31*, 4122.
(37) Frisch, M. J.; et al. *Gaussian03, Revision B.04*; Gaussian, Inc.:Pittsburgh, PA, 2003.
(38) a) Becke, A. D. *J. Chem. Phys.,* **1993**, *98*, 5648; b) Perdew, J. P.; Wang, Y. *Phys. Rev. B,* **1992**, *45*, 13244.
(39) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß *Teor. Chim. Acta* **1990**, *77*, 123.
(40) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.
(41) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**,*10*, 6615.
(42) a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161; b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.
(43) Cooper, J.; Ziegler, T. *Inorg. Chem.* **2002**, *41*, 6614.
(44) Tobisch, S. *Chem.-Eur. J.* **2005**, *11*, 3113.
(45) a) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997,** *107*, 3032; b) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253; c) Mennucci B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.
(46) Chaplin, A. B.; Weller, A. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 581.
(47) a) Liu, J.; Wang, H.; Zhang, H.; Wu, X.; Deng, Y.; Yang, Z.; Lei, A. *Chem.–Eur. J.* **2009**, *15*, 4437; b) Conley, B. L.; Williams, T. J. *Chem. Commun.*, **2010**, *46*, 4815.
(48) R. Dallanegra, A. B. Chaplin, A. S. Weller *Angew. Chem. Int. Ed.* **2009**, *48*, 6875.
(49)

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The role of chelating phosphine rhodium complexes in dehydrocoupling reactions of amine-boranes. A theoretical investigation attempting to rationalize the observed behaviors

Valeria Butera, Nino Russo, Emilia Sicilia*

Supporting Information

CONTENTS:

S-1

Cartesian coordinates (Å) and absolute energies, (Hartrees) of optimized structures for the dehydrogenation reaction of amine-borane ligands in the dicationic dimeric complex

Rh_2: E(B3PW91) = -2464.9472248
Gas-phase zero-point energy = -2464.205106
Gas-phase free energy = -2464.282777

Rh	1.20594300	0.02795200	-0.04851100
C	4.51819700	-0.85940000	-1.05182400
H	4.21106700	-1.90615800	-1.15864600
H	5.28686400	-0.68022300	-1.81171800
C	5.10685800	-0.62826400	0.34313900
H	5.37886200	0.42532600	0.47172200
H	6.05321700	-1.17494900	0.39934400
C	4.22651400	-1.09948900	1.50391800
H	4.79886100	-1.06576900	2.43758900
H	3.93882200	-2.14622800	1.35183500
H	-0.05431200	-2.38166900	1.25170300
H	-1.25643600	-1.60746200	-0.35330200
H	1.15016300	-1.60236000	-0.36232800
H	-0.93602400	-3.85427200	-0.46426300
B	-0.04920100	-1.98761600	0.12034500
N	-0.06168900	-3.40506600	-0.73823700
C	1.03014600	-4.32007500	-0.30931400
H	0.94806900	-5.27508200	-0.83079200
H	1.98769500	-3.85826900	-0.55073500
H	0.96360400	-4.47600700	0.76611900
C	-0.08369700	-3.25499600	-2.21326600
H	-0.21152600	-4.22663300	-2.69360200

H	-0.89402900	-2.58475400	-2.49201500
H	0.85886200	-2.81097200	-2.52938900
P	2.66296500	-0.15755800	1.77854400
P	3.05528800	0.18110700	-1.48207200
Rh	-1.30874600	0.01908300	-0.04485100
P	-2.75264000	-0.17438900	1.79153100
P	-3.17190100	0.17667500	-1.46472300
C	-4.30859500	-1.13008000	1.52408300
C	-4.62107600	-0.88024500	-1.02930500
C	-5.20177500	-0.66318600	0.37133600
H	-6.14118600	-1.22131900	0.43120600
H	-5.48518600	0.38640000	0.50742200
H	-5.39734900	-0.70369900	-1.78207800
H	-4.30392400	-1.92321600	-1.14480700
H	-4.01099900	-2.17324900	1.36562800
H	-4.87489800	-1.10601800	2.46173100
C	1.97021100	-1.02278900	3.24111000
H	2.72367200	-1.13065600	4.02950000
H	1.12797600	-0.44950100	3.63676600
H	1.60548100	-2.01428800	2.96021500
C	3.24470300	1.42194500	2.51438000
H	2.37977000	2.02543900	2.80591300
H	3.86011300	1.24071700	3.40272600
H	3.83620500	1.99527200	1.79493600
C	2.74992200	-0.30371200	-3.22957000
H	3.63129600	-0.11230100	-3.85254500
H	2.51066900	-1.36913100	-3.29268200
H	1.90254200	0.26042400	-3.62974300
C	3.80648600	1.84786800	-1.69334000
H	4.71855300	1.79152300	-2.29810800
H	3.10256000	2.51109100	-2.20539900
H	4.05605800	2.29069200	-0.72546600
C	-2.04788900	-1.02842700	3.25471300
H	-1.20278400	-0.45213000	3.63964700
H	-2.79514200	-1.13128000	4.04959900
H	-1.68542000	-2.02200000	2.97816300
C	-3.34074200	1.40609600	2.52006200
H	-3.95804400	1.22732700	3.40751400
H	-2.47831300	2.01338100	2.81219600
H	-3.93178100	1.97504500	1.79672000
C	-2.89169000	-0.27883500	-3.22470600
H	-3.78272800	-0.07691800	-3.83042800
H	-2.05129400	0.29297100	-3.62893500
H	-2.65481900	-1.34326100	-3.31095900
C	-3.93236300	1.84389800	-1.63888400
H	-3.23984100	2.51760600	-2.15315500
H	-4.85454800	1.79323900	-2.22853700
H	-4.16572700	2.27294700	-0.66088100
B	-0.06116300	1.99477900	0.51489800
H	1.12427900	1.69471900	-0.01865400
N	-0.09950400	3.52957500	-0.09702200
C	-0.10073500	3.61447200	-1.57798200
H	-0.87471700	2.95887300	-1.97250600
H	-0.27122300	4.64338500	-1.89956500
H	0.86522400	3.27148900	-1.94524700
C	0.96286500	4.39063000	0.48964800
H	1.93474300	3.98725500	0.20622300
H	0.87039300	5.41100500	0.11417200
H	0.86949200	4.38353300	1.57427500
H	-1.25402000	1.67641400	0.00183400
H	-0.06334600	2.18134500	1.69952500
H	-0.98889000	3.90841100	0.22976000

TS1: E(B3PW91) = -2464.9382249
Gas-phase zero-point energy = -2464.198297
Gas-phase free energy = -2464.274354

Rh	1.21661400	0.01592500	-0.05619000
C	4.46145600	-0.88273700	-1.14565900
H	4.08857700	-1.89574500	-1.33447700
H	5.22563200	-0.67989400	-1.90405500
C	5.08424500	-0.80822100	0.25155200
H	5.42613000	0.21138500	0.46132000
H	5.99302600	-1.41798400	0.24592200
C	4.18656700	-1.31372800	1.38390700
H	4.76425000	-1.36855300	2.31319300
H	3.84982600	-2.33357300	1.16492100
H	-0.11521700	-2.54665100	0.98994400
H	-1.23437800	-1.49136000	-0.50330800
H	1.03539200	-1.68230600	-0.55042700
H	-1.21401500	-3.80198100	-0.79813700
B	-0.10750300	-2.08774700	-0.11501500
N	-0.31492800	-3.40556500	-1.07272200
C	0.71051200	-4.44333400	-0.77610700
H	0.52354100	-5.33759600	-1.37274300
H	1.69302300	-4.04032700	-1.02139900
H	0.67491400	-4.68802300	0.28413100
C	-0.38038700	-3.12363600	-2.52707600
H	-0.59746300	-4.03713100	-3.08339400
H	-1.15281300	-2.37982000	-2.71265100
H	0.58044400	-2.72074600	-2.84440000
P	2.67180800	-0.31287700	1.72765200
P	3.05471000	0.27106000	-1.44444600
Rh	-1.30881900	0.11410100	0.02372400
P	-2.71846600	-0.32936100	1.78693100
P	-3.19055400	0.48523000	-1.38309500
C	-4.26900200	-1.24644000	1.38785000
C	-4.62370700	-0.64205300	-1.09991600
C	-5.18341900	-0.63073400	0.32573200
H	-6.11724600	-1.20127000	0.32364300
H	-5.47142800	0.38585000	0.61478500
H	-5.41361400	-0.37096500	-1.80888200
H	-4.29702000	-1.65455600	-1.36373100
H	-3.96999100	-2.25726400	1.08619000
H	-4.82252600	-1.35687200	2.32720900
C	1.94522500	-1.23456300	3.14039800
H	2.69982800	-1.43864400	3.90853400
H	1.14481200	-0.63917200	3.58731700
H	1.52106600	-2.18216000	2.79815500
C	3.35715800	1.16776500	2.57189100
H	2.53780500	1.80295000	2.92035700
H	3.96430300	0.87650300	3.43625100
H	3.98090300	1.75477000	1.89223900
C	2.67542000	-0.03861900	-3.21671500
H	3.55987300	0.11759900	-3.84492200
H	2.33029400	-1.06741600	-3.35230100
H	1.88011200	0.63384700	-3.55143900
C	3.89436100	1.90434400	-1.53028200
H	4.76002100	1.86187800	-2.20089400
H	3.20361600	2.66030400	-1.91587600
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C	-2.02027700	-1.35036500	3.13783700
H	-1.18553400	-0.81971000	3.60135100
H	-2.77769200	-1.55101600	3.90403600

H	-1.64898400	-2.30145900	2.74857300
C	-3.30196400	1.15921700	2.68501600
H	-3.94937200	0.88146800	3.52380900
H	-2.43958000	1.70666200	3.07823300
H	-3.85733200	1.82783900	2.02156400
C	-2.90454000	0.28624900	-3.19032200
H	-3.80556200	0.53634800	-3.76208400
H	-2.08841400	0.93815200	-3.51536500
H	-2.62621700	-0.74578800	-3.42255100
C	-3.98942900	2.14307600	-1.32381500
H	-3.30197000	2.90872500	-1.69627900
H	-4.89027800	2.16611100	-1.94748700
H	-4.26857000	2.40805500	-0.30045500
B	0.14688400	1.85299500	0.66330100
H	0.39338500	1.34395400	-0.63849100
N	0.16450500	3.43454000	0.18827100
C	-0.10066800	3.70400100	-1.24561000
H	-1.01265100	3.18920600	-1.54131700
H	-0.20102900	4.77706200	-1.41761700
H	0.72937400	3.31581100	-1.83455500
C	1.41044700	4.11488300	0.63545900
H	2.26049000	3.62857400	0.16037800
H	1.38256900	5.16939800	0.35548800
H	1.49851700	4.02028100	1.71612200
H	-1.24312300	1.67771300	0.58324900
H	0.39034900	1.94380200	1.83593200
H	-0.59562200	3.86238600	0.71753500

Rh_2-2: E(B3PW91) = -2464.9623629
Gas-phase zero-point energy = -2464.220251
Gas-phase free energy = -2464.294179

Rh	-1.21021600	-0.05700900	-0.04742200
C	-4.34397600	1.18922700	-0.97301000
H	-3.86134300	2.16919800	-1.05840200
H	-5.13573100	1.15644800	-1.72943500
C	-4.95060700	1.02530200	0.42339900
H	-5.42912600	0.04443100	0.51717600
H	-5.76382500	1.75060600	0.52413800
C	-3.97470700	1.25228900	1.58085000
H	-4.52420400	1.25588200	2.52848200
H	-3.50043200	2.23574800	1.48730600
H	0.13938100	2.52329600	1.38128400
H	1.22392900	1.59859900	-0.14806100
H	-0.97955900	1.87537000	-0.23079600
H	1.36793200	3.90402400	-0.31402700
B	0.13398500	2.23098300	0.22002400
N	0.42554300	3.61738900	-0.57900300
C	-0.48940100	4.70167900	-0.12712400
H	-0.26113800	5.62968100	-0.65412100
H	-1.51482700	4.40198100	-0.34296300
H	-0.37343200	4.84321700	0.94598200
C	0.40353200	3.48755800	-2.05662000
H	0.72111200	4.42016700	-2.52617700
H	1.06057200	2.67219300	-2.35297100
H	-0.61445600	3.25345100	-2.36587600
P	-2.60970100	0.02062800	1.74142100
P	-3.07316100	-0.07260600	-1.41909300
Rh	1.31243400	-0.14114100	-0.01938200
P	2.75053400	-0.04044700	1.78298400
P	3.18676000	-0.33105800	-1.44911900
C	4.33580700	0.86406600	1.53280900

C	4.70238600	0.62468500	-1.00785200
C	5.24028100	0.36753400	0.40163700
H	6.20190100	0.88132400	0.49427300
H	5.46988300	-0.69547100	0.53367200
H	5.47558900	0.39473800	-1.74893800
H	4.45906000	1.68698200	-1.12622800
H	4.07533900	1.91642400	1.37047400
H	4.87739300	0.81942700	2.48384700
C	-1.78458300	0.54842400	3.28847900
H	-2.51645900	0.70318700	4.08905000
H	-1.08232700	-0.22832100	3.60301500
H	-1.23188400	1.47640700	3.12310600
C	-3.47454400	-1.50410600	2.27956600
H	-2.73568200	-2.26237700	2.55156000
H	-4.10121600	-1.29938000	3.15463900
H	-4.10807000	-1.90981900	1.48720100
C	-2.65455200	0.38608400	-3.14877700
H	-3.55258900	0.41618500	-3.77587500
H	-2.17749600	1.36966000	-3.17174300
H	-1.95367500	-0.33992400	-3.57122500
C	-4.10107300	-1.57692500	-1.67875500
H	-4.94395200	-1.34819300	-2.34098800
H	-3.51011700	-2.36894700	-2.14701000
H	-4.50096200	-1.95765600	-0.73526200
C	2.06794000	0.79996800	3.25827100
H	1.20865100	0.23937200	3.63227500
H	2.82094700	0.86158300	4.05175200
H	1.73534500	1.80910400	3.00287600
C	3.26760600	-1.66661800	2.45129200
H	3.92160100	-1.54034100	3.32097700
H	2.38239900	-2.23136100	2.75931100
H	3.80088900	-2.25183200	1.69738800
C	2.90444200	0.19440000	-3.18822700
H	3.77652000	-0.02907700	-3.81307700
H	2.03361000	-0.32359200	-3.60057200
H	2.71653600	1.27084800	-3.23615000
C	3.84396700	-2.03379000	-1.68063300
H	3.09100100	-2.66160600	-2.16706300
H	4.74082100	-2.02748200	-2.31016000
H	4.09336900	-2.49032800	-0.71904800
B	-0.31641800	-1.84533900	0.55738800
H	0.11514500	-0.23953900	-1.30957400
N	-0.40762400	-3.24104600	-0.29651000
C	-0.27252100	-3.14004800	-1.76840600
H	0.63502600	-2.58803400	-2.00195000
H	-0.24008700	-4.13680600	-2.21292500
H	-1.12317100	-2.58412700	-2.15608900
C	-1.61979700	-4.01952500	0.07653700
H	-2.50030600	-3.43438400	-0.18014100
H	-1.63563500	-4.96856500	-0.46212300
H	-1.60650900	-4.20457200	1.14909900
H	1.12262500	-1.72367000	0.31170600
H	-0.40606200	-2.23851800	1.69821400
H	0.38692700	-3.79047800	0.03440000

TS2: E(B3PW91) = -2464.9558537
Gas-phase zero-point energy = -2464.214583
Gas-phase free energy = -2464.286524

Rh	-1.20798600	-0.02985500	0.07232200
C	-4.38671000	-0.47883200	1.32808500
H	-3.93230500	-1.28988700	1.90702900

H	-5.18641400	-0.05345600	1.94402600
C	-4.97488100	-1.02810600	0.02529800
H	-5.41480500	-0.21663400	-0.56424400
H	-5.81435200	-1.68029200	0.28493700
C	-4.00151800	-1.83953000	-0.83474500
H	-4.54047700	-2.28858400	-1.67595900
H	-3.57886500	-2.66491300	-0.25153800
H	0.11693100	-2.81115700	-0.05183500
H	1.73633300	-1.20020900	1.03388600
H	-1.24407400	-1.62470400	0.95975800
H	1.33526300	-2.86653200	2.12582900
B	0.01626500	-1.89353300	0.71450900
N	0.36068700	-2.57057000	2.17422600
C	-0.44415700	-3.80678900	2.38058000
H	-0.16863600	-4.28023500	3.32469600
H	-1.49937800	-3.53470700	2.40445700
H	-0.26821200	-4.49206700	1.55338700
C	0.23479300	-1.67125900	3.34569100
H	0.56222600	-2.18157700	4.25330900
H	0.82905500	-0.77692400	3.17253800
H	-0.81266900	-1.38871500	3.44537900
P	-2.57265600	-0.90486700	-1.52782600
P	-3.08867700	0.81502300	1.11107000
Rh	1.34370200	-0.01832500	0.07910500
P	2.72719700	-1.03882000	-1.45643500
P	3.19097100	1.14197700	0.98848700
C	4.42790700	-1.45397800	-0.88182200
C	4.78589500	0.22345500	1.03562200
C	5.26744700	-0.30819500	-0.31593100
H	6.28997500	-0.67570000	-0.18757500
H	5.34479200	0.50620300	-1.04443300
H	5.53985000	0.89209800	1.46449100
H	4.66102000	-0.60579200	1.74083500
H	4.32147700	-2.24605700	-0.13165700
H	4.94497200	-1.90311700	-1.73671100
C	-1.73146200	-2.16031300	-2.55919700
H	-2.44133500	-2.64913300	-3.23578600
H	-0.95588400	-1.67394900	-3.15768300
H	-1.26555700	-2.91685700	-1.92265200
C	-3.33785100	0.17583900	-2.79416000
H	-2.55658600	0.69879500	-3.35127700
H	-3.92306400	-0.42700500	-3.49738500
H	-4.00038700	0.91953600	-2.34566700
C	-2.72488300	1.30830000	2.84325500
H	-3.64078200	1.61655400	3.35992500
H	-2.27993200	0.47233300	3.38848200
H	-2.01530800	2.14050400	2.86142200
C	-4.09204900	2.24952800	0.53612000
H	-4.96912000	2.37510300	1.18148400
H	-3.51035200	3.17456600	0.57896400
H	-4.44097300	2.10974900	-0.49009500
C	2.17328800	-2.65871600	-2.10252900
H	1.18820700	-2.56657800	-2.56317800
H	2.88175300	-3.03123100	-2.85052900
H	2.10140100	-3.38917200	-1.29255600
C	2.99597900	-0.05639700	-2.97934700
H	3.64291600	-0.59361900	-3.68130000
H	2.03479700	0.13841200	-3.46406500
H	3.45771400	0.90696300	-2.74511700
C	2.96830900	1.62018600	2.74705900
H	3.83162500	2.18764100	3.11228200
H	2.07033200	2.23442500	2.86236100

H	2.85366500	0.72753000	3.36885300
C	3.67710900	2.73823300	0.21142800
H	2.86006900	3.46173900	0.29033000
H	4.55607700	3.16269000	0.70948600
H	3.91050400	2.60012400	-0.84824000
B	-0.29291000	1.32916700	-1.26993900
H	0.11570400	0.63233100	1.17854300
N	-0.37462200	2.96273500	-1.18736200
C	-0.32467300	3.55497600	0.16893400
H	0.49926500	3.10632100	0.71956300
H	-0.20185000	4.63830100	0.10601200
H	-1.25161300	3.31915800	0.68624400
C	-1.50983800	3.51042800	-1.97592800
H	-2.43809600	3.11361600	-1.57236100
H	-1.51801800	4.60051300	-1.91905400
H	-1.40422600	3.19583500	-3.01269400
H	1.03493500	1.24539100	-1.04585100
H	-0.41273800	1.11418000	-2.45368800
H	0.46994200	3.27031400	-1.67045500

Rh_2-3: E(B3PW91) = -2464.956148
Gas-phase zero-point energy = -2464.213988
Gas-phase free energy = -2464.286734

Rh	-1.21587200	-0.03222600	0.09133200
C	-4.41140500	-0.42922100	1.29120300
H	-3.96230700	-1.21514700	1.90745600
H	-5.22276700	0.01445900	1.87820300
C	-4.97689000	-1.03094000	0.00156800
H	-5.41090600	-0.24494600	-0.62583600
H	-5.81742000	-1.67665500	0.27353500
C	-3.98587800	-1.87102800	-0.80966500
H	-4.50723200	-2.35188500	-1.64437100
H	-3.57110100	-2.67247300	-0.18906400
H	0.05034200	-2.80286800	0.06535500
H	1.91512200	-0.98633800	1.23057800
H	-1.30805200	-1.59420100	1.03486100
H	1.35369800	-2.66265900	2.20509000
B	-0.04205700	-1.84903200	0.78721500
N	0.36012100	-2.44213700	2.25991600
C	-0.35093600	-3.72587500	2.51658200
H	-0.04293200	-4.13923500	3.47871500
H	-1.42363000	-3.53222300	2.53054600
H	-0.12411600	-4.42883400	1.71735600
C	0.18075500	-1.52099500	3.40760700
H	0.55181800	-1.98260600	4.32456100
H	0.70809900	-0.59204800	3.20466500
H	-0.88380300	-1.31337700	3.51219500
P	-2.55040100	-0.95258700	-1.50748600
P	-3.11705100	0.86448500	1.05135000
Rh	1.35643400	-0.02726900	0.13475300
P	2.70640000	-1.18980800	-1.33384600
P	3.19203700	1.26159100	0.85989500
C	4.43921400	-1.49192800	-0.78444500
C	4.80835500	0.38537400	0.93620700
C	5.25940200	-0.26913500	-0.37117000
H	6.29673000	-0.59262800	-0.24264000
H	5.28817900	0.46778100	-1.18119600
H	5.55840400	1.11007700	1.27063400
H	4.72566800	-0.37101700	1.72468600
H	4.38829100	-2.20408500	0.04699900
H	4.94209100	-2.01050000	-1.60783900

C	-1.68521200	-2.22714200	-2.49410100
H	-2.37248100	-2.70685400	-3.19983300
H	-0.87381500	-1.75769100	-3.05774300
H	-1.26410700	-2.98863500	-1.83279800
C	-3.30349600	0.09319100	-2.80949200
H	-2.51832100	0.59369500	-3.38097500
H	-3.89099500	-0.52809200	-3.49468200
H	-3.96211300	0.85424800	-2.38550300
C	-2.77668000	1.40772100	2.77294700
H	-3.70035400	1.73092900	3.26627500
H	-2.34197400	0.58623900	3.34767700
H	-2.06643600	2.23937300	2.77985100
C	-4.11632700	2.27642300	0.41724400
H	-4.99925200	2.41989400	1.05076900
H	-3.53855700	3.20467900	0.43434100
H	-4.45714800	2.09963900	-0.60590100
C	2.19312500	-2.88291100	-1.80345500
H	1.20303300	-2.86766400	-2.26303800
H	2.90833800	-3.30649400	-2.51715500
H	2.14943800	-3.52971700	-0.92371500
C	2.89626700	-0.35980600	-2.95747800
H	3.53959300	-0.94538200	-3.62306700
H	1.91555000	-0.24290300	-3.42770100
H	3.33207400	0.63561700	-2.83526200
C	3.01303100	1.88663600	2.57579100
H	3.87915700	2.49080500	2.86797100
H	2.11139800	2.49929100	2.66716300
H	2.92388300	1.04642300	3.27071400
C	3.60349400	2.78870500	-0.08109400
H	2.78087100	3.50709400	-0.01338500
H	4.50250500	3.26729100	0.32367300
H	3.77587600	2.56201200	-1.13731100
B	-0.28492100	1.26280400	-1.30169000
H	0.11204900	0.66504600	1.18852600
N	-0.34273500	2.89694100	-1.26160100
C	-0.30720700	3.52356300	0.07965200
H	0.49283400	3.07053300	0.66076200
H	-0.16006900	4.60211300	-0.00891100
H	-1.25057800	3.32150500	0.58154900
C	-1.46357000	3.43602000	-2.07593900
H	-2.39715700	3.04622800	-1.67769200
H	-1.47009700	4.52687000	-2.03628400
H	-1.34507600	3.10451000	-3.10596300
H	1.02479000	1.12403900	-1.12146600
H	-0.43158100	1.01138800	-2.47492000
H	0.51141300	3.18304700	-1.74062400

TS3: E(B3PW91) = -2464.9186526
Gas-phase zero-point energy = -2464.183647
Gas-phase free energy = -2464.255997

Rh	-1.23312900	-0.03921300	0.13809300
C	-4.52966800	-0.30687100	1.31956600
H	-4.11212600	-1.00520300	2.05278000
H	-5.37575900	0.19314300	1.80299800
C	-5.02277200	-1.07184500	0.08765400
H	-5.44815000	-0.37846200	-0.64602200
H	-5.86201400	-1.69862600	0.40475500
C	-3.99146400	-1.98776900	-0.57985500
H	-4.48386800	-2.58157900	-1.35737500
H	-3.58218500	-2.69624600	0.14827000
H	-0.92986200	-2.91188700	0.58897400

H	1.93124100	-0.84201700	1.33145800
H	-1.70229900	-1.14058500	1.54921200
H	1.07660800	-1.31020700	1.52960200
B	-0.77316800	-1.95049800	1.27441200
N	0.20768300	-2.10373800	2.35605700
C	0.80148300	-3.42223200	2.61120600
H	1.81648300	-3.31196200	3.00461000
H	0.20971700	-3.97527300	3.34692700
H	0.83251100	-4.00195500	1.68966600
C	0.11904400	-1.28167000	3.56779100
H	1.08890100	-1.25032100	4.07212600
H	-0.17058100	-0.26597200	3.29863800
H	-0.61492500	-1.69702100	4.26487600
P	-2.55543500	-1.14334500	-1.36894100
P	-3.23210600	0.96871400	1.00739300
Rh	1.38076200	0.08420700	0.07932600
P	2.72783900	-1.24830400	-1.24203700
P	3.23952400	1.39250700	0.71722900
C	4.42522400	-1.55992300	-0.59992000
C	4.81633000	0.46904400	0.94156500
C	5.28162600	-0.33319300	-0.27643100
H	6.29766000	-0.68552800	-0.07468500
H	5.37475100	0.31579200	-1.15416300
H	5.58633400	1.19378800	1.22737600
H	4.67689100	-0.19759100	1.80002600
H	4.31322600	-2.18289400	0.29478200
H	4.93463100	-2.17799200	-1.34731800
C	-1.73228500	-2.49796900	-2.28644000
H	-2.44856800	-3.00685900	-2.94114000
H	-0.93067000	-2.08306600	-2.90393200
H	-1.30984800	-3.22756000	-1.59227800
C	-3.33188100	-0.20520200	-2.73943400
H	-2.55739000	0.21781300	-3.38324000
H	-3.95696800	-0.87437900	-3.34134500
H	-3.95815400	0.60843000	-2.36794900
C	-2.93563800	1.63827300	2.69240300
H	-3.87009900	1.99655200	3.13919000
H	-2.51770900	0.85945700	3.33628800
H	-2.22523000	2.46977400	2.65723900
C	-4.20431700	2.33104000	0.23572600
H	-5.08361500	2.55086100	0.85202600
H	-3.60910000	3.24586700	0.16355400
H	-4.55156400	2.06468200	-0.76614900
C	2.10063700	-2.94883100	-1.49160100
H	1.12414600	-2.91480400	-1.97823200
H	2.78956100	-3.53057500	-2.11460400
H	1.98804400	-3.45394800	-0.52852200
C	2.98390300	-0.63173100	-2.94624800
H	3.56198100	-1.34969100	-3.53770000
H	2.01590500	-0.47392100	-3.43107800
H	3.51895000	0.32197300	-2.93795600
C	3.01794800	2.20561900	2.34590100
H	3.90686900	2.78411600	2.62154400
H	2.15610500	2.87926900	2.32179200
H	2.83567400	1.45234200	3.11791100
C	3.72249000	2.78335100	-0.38191500
H	2.90697600	3.50921600	-0.45579200
H	4.60432100	3.30290500	0.00976600
H	3.95033100	2.42130100	-1.38843200
B	-0.22677900	0.97439000	-1.40520400
H	0.11449000	0.80456900	1.08688600
N	-0.37514900	2.61052100	-1.56093900

C	-0.33149900	3.41050800	-0.31510700
H	0.55041200	3.13256000	0.25758300
H	-0.31603700	4.47659600	-0.55124200
H	-1.21083700	3.17158800	0.27875800
C	-1.55948400	2.97305100	-2.38144900
H	-2.44888600	2.60351900	-1.87663000
H	-1.61997900	4.05649600	-2.49988900
H	-1.47350000	2.50079000	-3.35828700
H	1.13995500	1.00682800	-1.27753300
H	-0.31794000	0.58466600	-2.54621400
H	0.43829100	2.88408500	-2.11271700

Rh_2-4: E(B3PW91) = -2464.9830334
Gas-phase zero-point energy = -2464.246164
Gas-phase free energy = -2464.321973

Rh	-1.16440900	-0.02411800	0.03074600
C	-4.30726900	0.79732700	-1.12850100
H	-3.86602100	1.77881300	-1.33003200
H	-5.05905900	0.62000800	-1.90496700
C	-4.97866100	0.79208000	0.24839900
H	-5.40854100	-0.19273500	0.46076300
H	-5.83443600	1.47233000	0.20061800
C	-4.08775600	1.24851500	1.40759900
H	-4.68328300	1.32332200	2.32383800
H	-3.68723100	2.24747800	1.20709900
H	-1.46724300	3.16421600	0.88185000
H	1.74388700	1.32681600	-0.47623000
H	-1.48324400	1.77437500	-0.71557600
H	0.16335400	0.61027200	0.99013600
B	-1.18096300	2.86979300	-0.23532600
N	-0.58748800	3.78314400	-1.07770800
C	-0.29311400	5.15223400	-0.66141300
H	0.77810300	5.35861400	-0.75718200
H	-0.83255300	5.86666300	-1.29115300
H	-0.59316000	5.30005700	0.37461700
C	-0.21732400	3.51410900	-2.45877800
H	0.84630900	3.72309000	-2.61526400
H	-0.40595900	2.46857300	-2.69915000
H	-0.78631000	4.15159400	-3.14380400
P	-2.65000700	0.15960300	1.77207500
P	-2.97134800	-0.45311900	-1.37530200
Rh	1.45528800	-0.11443500	0.03538000
P	2.97543000	0.35308600	1.69352500
P	3.15877900	-0.63330500	-1.41080800
C	4.53015400	1.17566400	1.16495600
C	4.65537600	0.42500700	-1.29055400
C	5.33378600	0.45592500	0.08072000
H	6.28900700	0.97749000	-0.02976200
H	5.59528300	-0.55756000	0.40398600
H	5.36177700	0.06831100	-2.04756600
H	4.35369500	1.43536300	-1.58668100
H	4.25255400	2.17898300	0.82415800
H	5.14612400	1.30501900	2.06120000
C	-1.88529600	0.92809500	3.24611500
H	-2.62525000	1.06872800	4.04175200
H	-1.08812000	0.27833000	3.61905000
H	-1.45525200	1.89799100	2.98394100
C	-3.41966500	-1.34874600	2.47244000
H	-2.64259600	-2.01770300	2.85059700
H	-4.08178600	-1.08056800	3.30322700
H	-4.00679600	-1.88600200	1.72395500

C	-2.51164500	-0.20760000	-3.13451000
H	-3.38913000	-0.30400900	-3.78344500
H	-2.08138200	0.78795100	-3.27112800
H	-1.76486600	-0.94582400	-3.44069600
C	-3.93736400	-2.01678300	-1.44928600
H	-4.77194500	-1.89293100	-2.14882000
H	-3.32602100	-2.84971700	-1.80580900
H	-4.35206400	-2.28156900	-0.47365900
C	2.29459800	1.52852700	2.91760300
H	1.43365800	1.08383800	3.42317500
H	3.04875800	1.78703500	3.66926900
H	1.96556700	2.44119800	2.41339400
C	3.51931400	-1.06951300	2.70996800
H	4.16611500	-0.73839300	3.52983000
H	2.64556200	-1.57237000	3.13512500
H	4.06936700	-1.79638500	2.10568700
C	2.65816900	-0.43269900	-3.16005200
H	3.49203700	-0.65961900	-3.83354500
H	1.82367000	-1.09902100	-3.39594600
H	2.33057800	0.59616400	-3.33225300
C	3.83275700	-2.33923600	-1.34463000
H	3.04593300	-3.06883800	-1.55682100
H	4.62854100	-2.46919300	-2.08649900
H	4.24121900	-2.56088400	-0.35466500
B	-0.21292900	-1.79965900	0.78962000
H	0.17235100	-0.15451000	-1.18522600
N	-0.38116200	-3.28270000	0.12150000
C	-0.25846900	-3.35302600	-1.35288000
H	0.62828300	-2.80071200	-1.65665000
H	-0.19250700	-4.39272200	-1.67969600
H	-1.12857600	-2.88027600	-1.80051200
C	-1.56232100	-4.04114100	0.61171100
H	-2.47000700	-3.52551300	0.31076200
H	-1.55928200	-5.04961900	0.19377900
H	-1.51930400	-4.09488600	1.69798400
H	1.09667800	-1.73184200	0.69062800
H	-0.40999600	-1.97908800	1.96499000
H	0.42953600	-3.77544300	0.49785900

Cartesian coordinates (Å) and absolute energies, (Hartrees) of optimized structures for the dehydrogenation reaction of a dimethylamine-borane molecule A assisted by the model catalyst 2b(Me)

BH_2NHMe_2: E(B3PW91) = -160.6336578
Gas-phase zero-point energy = -160.529183
Gas-phase free energy = -160.556459

H	1.04568300	2.11816600	0.00014100
H	-1.04659700	2.11767400	0.00047400
B	-0.00031700	1.53713300	0.00006900
N	-0.00001900	0.14881600	-0.00049200
C	1.21364100	-0.64914100	0.00009700
H	1.25755900	-1.29425400	0.88662600
H	1.25726000	-1.29603100	-0.88513700
H	2.08403500	0.00578900	-0.00066700
C	-1.21337300	-0.64960200	0.00007100
H	-1.25735200	-1.29440900	0.88682800
H	-2.08402400	0.00498500	-0.00124200

H	-1.25645000	-1.29683800	-0.88493500

BH_3NHMe_2: E(B3PW91) = -161.816812
Gas-phase zero-point energy = 161.690137
Gas-phase free energy = -161.717945

H	1.55727100	-0.00093000	1.33068300
B	1.57362100	-0.00150800	0.11645200
H	2.04916200	-1.01382500	-0.35419500
H	2.05125800	1.00956900	-0.35483100
N	0.00274800	-0.00002800	-0.34087400
H	0.01496200	0.00001200	-1.35855200
C	-0.69904500	1.22107400	0.10139600
H	-1.73971900	1.22336400	-0.23660200
H	-0.66272800	1.25693800	1.19055400
H	-0.17155000	2.08880500	-0.29201700
C	-0.70145600	-1.21973300	0.10141000
H	-0.17682100	-2.08848100	-0.29357200
H	-0.66350200	-1.25669000	1.19048700
H	-1.74266600	-1.21907900	-0.23493300

H_2: E(B3PW91) = -1.1785766
Gas-phase zero-point energy = 1.168520
Gas-phase free energy = 1.180015

H	0.00000000	0.00000000	0.49000000
H	0.00000000	0.00000000	-0.49000000

2b(Me)+A: E(B3PW91) = -1394.3098957
Gas-phase zero-point energy = -1393.810050
Gas-phase free energy = -1393.874404

Rh	-1.52769400	0.01841600	-0.29152500
C	0.74201500	-0.69664000	2.31875200
H	-0.00143800	-0.49127000	3.10149500
H	1.39066900	-1.50054700	2.69175800
C	1.58102500	0.56384900	2.05025500
H	2.30945600	0.37818200	1.25115200
H	2.18024100	0.77073200	2.94604200
C	0.74354800	1.81608800	1.73918000
H	1.39568200	2.69949200	1.71619000
H	0.00624900	1.97939700	2.53732100
H	-3.30388100	-0.52726900	-2.68156200
H	-2.77747000	0.89845000	-1.28439500
H	-2.78017000	-1.20112200	-0.79967400
B	-3.30652800	-0.25900900	-1.51301200
N	-4.83865300	-0.15708600	-1.04530400
C	-5.54131700	-1.45225500	-1.25496600
H	-5.10245800	-2.19479800	-0.58868200
H	-6.60435200	-1.34357800	-1.03420600
H	-5.40195400	-1.76836600	-2.28772700
C	-5.03541600	0.34969700	0.33711300
H	-4.52574900	-0.32328200	1.02599900
H	-4.58540500	1.33738400	0.41967500
H	-6.10085400	0.39753100	0.57153200
P	-0.18023300	1.75348800	0.14607300
P	-0.17317200	-1.34397700	0.85619900
C	-1.11871200	3.33105700	0.17548000
H	-1.60788600	3.48404400	-0.79293500
H	-1.88922000	3.29319100	0.95297100
H	-0.45228000	4.18034300	0.37336400
C	1.10443700	2.06341900	-1.12548500

H	1.86226400	1.27482700	-1.12041900
H	0.64105500	2.08234400	-2.11637000
H	1.60457400	3.02220900	-0.94657300
C	1.12083200	-2.15552300	-0.15832300
H	0.65823800	-2.61800400	-1.03527100
H	1.86169000	-1.43076300	-0.50753500
H	1.63980900	-2.92730500	0.42150900
C	-1.08520900	-2.77049500	1.57239000
H	-1.57897200	-3.33185600	0.77327800
H	-0.40277700	-3.44349700	2.10419500
H	-1.84914200	-2.41671700	2.27086100
H	4.47949000	1.10850500	-0.04106700
B	4.61669000	-0.01198000	-0.48995600
H	4.51234900	-0.87254700	0.36166000
H	3.89755300	-0.21643200	-1.44988500
N	6.14126000	-0.10006400	-1.03735800
C	6.42727000	-1.39640100	-1.69075700
H	7.44902000	-1.42085800	-2.07795800
H	6.29349900	-2.18729300	-0.95244800
H	5.71516400	-1.54682100	-2.50084700
C	7.12904800	0.19688200	0.02410000
H	7.01957800	-0.55056100	0.81004300
H	8.14714200	0.17095800	-0.37257500
H	6.91303700	1.17947300	0.44091100
H	6.22747600	0.62558100	-1.74657800
H	-5.26710200	0.51581400	-1.68165300

$TS_{1\text{-}2}$: E(B3PW91) = -1394.2762003
Gas-phase zero-point energy = -1393.782660
Gas-phase free energy = -1393.839400

Rh	-0.16149900	-0.03692800	-0.18004400
C	2.77638200	-1.08435200	1.45906500
H	2.67568800	-0.29611400	2.21754800
H	3.25744700	-1.94024800	1.95115300
C	3.66085800	-0.58494200	0.30360200
H	3.69239800	-1.32975000	-0.50324300
H	4.69092900	-0.51050400	0.67390500
C	3.26042200	0.79158800	-0.25378300
H	4.04629400	1.15785600	-0.92820000
H	3.18462400	1.51670000	0.56803000
H	-1.45348100	3.06282600	-0.85708400
H	-1.00516000	1.21336900	-0.96456600
H	-2.82587000	1.74122400	-0.17217900
B	-1.68065200	2.14290300	-0.11497900
N	-1.14650900	2.30869800	1.29477000
C	-0.50663900	3.57849000	1.61720900
H	-1.24551600	4.38151700	1.75354400
H	0.07315200	3.49517200	2.54272800
H	0.16199900	3.88158500	0.81158400
C	-1.99004300	1.84318300	2.38601300
H	-2.87623500	2.48053300	2.51771300
H	-2.33024500	0.82400000	2.19039400
H	-1.43390900	1.84217900	3.32953900
P	1.66853500	0.85017400	-1.17944400
P	1.07480600	-1.59692200	0.97887500
C	1.59397000	2.59810400	-1.71138800
H	0.71144900	2.76239000	-2.33500100
H	1.51743400	3.25722500	-0.84318800
H	2.49089700	2.86654500	-2.27994300
C	2.03475000	-0.03444300	-2.74619600
H	2.18911900	-1.10154700	-2.56393900

H	1.18664600	0.07111100	-3.42940300
H	2.92839700	0.37522100	-3.23065700
C	1.31068200	-3.20494400	0.13104500
H	0.33253300	-3.64115900	-0.09208400
H	1.84153500	-3.07090900	-0.81596700
H	1.87671500	-3.90347500	0.75693900
C	0.32941300	-2.06722200	2.58427100
H	-0.66067000	-2.50134100	2.41874500
H	0.95403100	-2.79860700	3.10863700
H	0.21387200	-1.18146000	3.21578800
H	-1.16384800	-1.47024800	-1.27725400
B	-2.00308900	-1.45322200	-0.36232000
H	-2.21620600	-2.55209300	0.07555700
H	-1.65274300	-0.71958700	0.63551700
N	-3.35392600	-0.81407300	-0.90967800
C	-4.47957200	-0.98824700	0.04261400
H	-5.37097300	-0.48226600	-0.33245300
H	-4.67820000	-2.05316800	0.16087800
H	-4.19840000	-0.56564000	1.00639900
C	-3.71118900	-1.31513200	-2.25997200
H	-3.83727700	-2.39725200	-2.21176000
H	-4.63999000	-0.85235000	-2.59884700
H	-2.90527200	-1.07811100	-2.95282100
H	-3.17647400	0.19566600	-0.97331700
H	0.01019200	1.08039700	0.91377500

(2): E(B3PW91) = =-1394.3118133
Gas-phase zero-point energy = -1393.816857
Gas-phase free energy = -1393.816857

Rh	0.67159100	0.24044900	-0.37652600
C	4.14999500	-0.53279100	-0.37109700
H	4.18141500	-0.72248400	-1.45271200
H	5.14987300	-0.18301500	-0.08164700
C	3.81971500	-1.83964300	0.37372300
H	3.64636100	-1.64101100	1.44093700
H	4.70746200	-2.48365900	0.33736500
C	2.64453800	-2.63530000	-0.22451700
H	2.64364500	-3.65512800	0.18452300
H	2.78041600	-2.73156100	-1.31048900
H	-3.87158700	-0.34732500	1.10856200
H	-0.81878000	-0.20630300	-0.73616900
H	-4.16598500	0.74082600	-0.65679200
B	-4.52265200	-0.08999800	0.13555600
N	-5.71257100	-0.75401500	-0.08674800
C	-6.23876800	-1.77212700	0.81138600
H	-7.22114400	-1.47671800	1.19621900
H	-6.35720000	-2.72640700	0.28594000
H	-5.55980000	-1.91258400	1.65135300
C	-6.56752800	-0.50640200	-1.23897600
H	-7.56057800	-0.17279900	-0.91800600
H	-6.12495200	0.26116500	-1.87245000
H	-6.69468800	-1.42121400	-1.82847600
P	0.95785400	-1.94294800	0.04931300
P	2.95075700	0.83895100	-0.08672700
C	-0.09957200	-3.09478400	-0.89614000
H	-1.15063100	-2.87470500	-0.69066900
H	0.06917200	-2.95736000	-1.96786000
H	0.11012300	-4.13611700	-0.62955300
C	0.58172000	-2.33651400	1.79885800
H	1.23603500	-1.76935800	2.46649100
H	-0.45252200	-2.05615400	2.01802000

H	0.70965300	-3.40621400	1.99871700
C	3.44215600	1.49501200	1.55659500
H	2.83780100	2.37636300	1.79207500
H	3.25828000	0.74741400	2.33411000
H	4.50094100	1.77542300	1.57934000
C	3.54070800	2.13660500	-1.24070800
H	2.98348100	3.06223100	-1.06624000
H	4.60928300	2.33924800	-1.10983800
H	3.36130100	1.82387000	-2.27375000
H	0.05788400	1.16132100	1.15885400
B	-0.18455000	2.14599500	0.38076700
H	0.32274200	3.15619600	0.78515200
H	0.23630700	1.92641500	-0.83174800
N	-1.75935000	2.34457900	0.30839600
C	-2.14341800	3.37369200	-0.69136000
H	-3.22922500	3.47592700	-0.72111600
H	-1.68854800	4.32318300	-0.40838600
H	-1.77488200	3.07211800	-1.67117000
C	-2.33121000	2.65209400	1.64382000
H	-1.90634300	3.59112300	1.99891600
H	-3.41640400	2.73716700	1.57257500
H	-2.07086200	1.85209300	2.33561500
H	-2.15602400	1.45324100	-0.00058800
H	1.01668300	-0.30843400	-1.77486900

$TS_{2\text{-}3}$: E(B3PW91) = -1394.2953129
Gas-phase zero-point energy = -1393.803297
Gas-phase free energy = -1393.868751

Rh	0.56336600	0.11669100	-0.23400000
C	4.11904400	-0.09746600	-0.65200000
H	4.04216700	-0.24345400	-1.73793500
H	5.06259700	0.43371700	-0.46810100
C	4.14321000	-1.46403100	0.05341100
H	4.11873800	-1.33386900	1.14447400
H	5.10664700	-1.94252200	-0.16308500
C	3.02831700	-2.42310600	-0.39837800
H	3.23501900	-3.43420900	-0.02172600
H	3.01880900	-2.48778000	-1.49482600
H	-3.98892600	-0.06923900	1.03860600
H	-0.91211100	-0.50738200	-0.58832100
H	-4.08869100	0.37696000	-1.00577900
B	-4.52456300	-0.17275600	-0.03098500
N	-5.66845900	-0.93662800	-0.14387700
C	-6.27731900	-1.63723600	0.97815600
H	-7.30222100	-1.28616300	1.14136300
H	-6.31886500	-2.71471300	0.78335900
H	-5.69702200	-1.46416700	1.88348100
C	-6.38983300	-1.11850800	-1.39580400
H	-7.41797100	-0.75108700	-1.30497500
H	-5.88993900	-0.57376300	-2.19557100
H	-6.43507900	-2.17989100	-1.66403600
P	1.32172500	-1.97827700	0.13616500
P	2.73553600	1.01460900	-0.15347300
C	0.32715200	-3.32436700	-0.61074200
H	-0.70993100	-3.24748800	-0.27122800
H	0.33719300	-3.23604500	-1.70120100
H	0.71900000	-4.30813000	-0.33132900
C	1.30096900	-2.39468300	1.92471700
H	1.94624800	-1.71443900	2.48730700
H	0.28290400	-2.28641100	2.31055100
H	1.63650700	-3.42391300	2.09573600

C	3.29817300	1.69378300	1.45816200
H	2.57307000	2.43229200	1.81348200
H	3.36369500	0.90061800	2.20946800
H	4.27865000	2.17448500	1.36836000
C	2.94653800	2.43392800	-1.29535400
H	2.26848700	3.24190400	-1.00639600
H	3.97555000	2.80973200	-1.27572700
H	2.69746500	2.12715800	-2.31527000
H	-0.12931200	1.34519300	1.33162900
B	-0.38410300	2.12967300	0.40964400
H	0.12287100	3.21136000	0.55431100
H	-0.00366100	1.72085600	-0.76295100
N	-1.96506100	2.32200100	0.31399400
C	-2.36337100	3.16097100	-0.84400300
H	-3.44924100	3.26264500	-0.87995800
H	-1.90109200	4.14237900	-0.73678900
H	-2.00755100	2.69345400	-1.76137600
C	-2.50940200	2.86929000	1.58299300
H	-2.06015100	3.84638100	1.76074000
H	-3.59438300	2.96499100	1.51542500
H	-2.24670500	2.19884600	2.39997400
H	-2.38497300	1.39962500	0.18014600
H	-0.22107900	-0.54766500	-1.43325900

(3): E(B3PW91) = -1394. 3032809
Gas-phase zero-point energy = -1393.802092
Gas-phase free energy = -1393.867626

Rh	0.54110100	0.10368800	-0.18154400
C	4.08521500	-0.04071200	-0.62164400
H	4.03267200	-0.17131000	-1.71102300
H	5.00548700	0.52133900	-0.41302100
C	4.14473700	-1.41645000	0.06135100
H	4.09723700	-1.30591800	1.15372300
H	5.12660800	-1.85955600	-0.14724000
C	3.06526400	-2.39591200	-0.42741300
H	3.28984600	-3.40869200	-0.06632100
H	3.07519000	-2.43923400	-1.52478900
H	-3.89160800	-0.03603700	1.03048300
H	-1.04276500	-0.54694100	-0.26669000
H	-4.07162100	0.38621700	-1.01365500
B	-4.44475400	-0.18525000	-0.02527700
N	-5.53097200	-1.03219400	-0.10602800
C	-6.06232800	-1.76440000	1.03531800
H	-7.10385000	-1.48143500	1.22313300
H	-6.03668300	-2.84344800	0.84675200
H	-5.47219600	-1.54645500	1.92445600
C	-6.26869400	-1.27291200	-1.33859000
H	-7.31781900	-0.97965500	-1.22270300
H	-5.83005000	-0.69807700	-2.15306700
H	-6.24416900	-2.33643400	-1.60077900
P	1.34394800	-1.99310600	0.09538700
P	2.66133500	1.02366000	-0.13281300
C	0.38171100	-3.31266600	-0.74326100
H	-0.65540900	-3.29717800	-0.39424300
H	0.38244900	-3.14594100	-1.82455500
H	0.80469000	-4.30178600	-0.53666400
C	1.30600900	-2.52398400	1.85500000
H	1.95230800	-1.88438600	2.46257700
H	0.28696800	-2.42905000	2.24157800
H	1.63181700	-3.56460700	1.96438000
C	3.17084500	1.70666300	1.49242500

H	2.42022600	2.42539400	1.83422300
H	3.23897400	0.91124900	2.24059500
H	4.14111200	2.21086500	1.42349600
C	2.84529400	2.44957700	-1.26941300
H	2.14275500	3.23814900	-0.98740300
H	3.86437900	2.85050400	-1.23513900
H	2.61820200	2.13771800	-2.29286300
H	-0.21317100	1.48690200	1.36969700
B	-0.42009200	2.19391600	0.39119600
H	0.11287400	3.27157300	0.46325700
H	-0.04282000	1.70175700	-0.74256100
N	-1.99571700	2.43258900	0.24772300
C	-2.34607000	3.20910500	-0.96761300
H	-3.42709700	3.34531300	-1.03162300
H	-1.85218600	4.17926000	-0.91183500
H	-1.98897000	2.67497300	-1.84725600
C	-2.54099100	3.07996900	1.46848000
H	-2.05443000	4.04708800	1.59523000
H	-3.61971800	3.21644200	1.37227200
H	-2.32060700	2.45259600	2.33078900
H	-2.45330000	1.52246600	0.16777100
H	-0.68900400	-0.58371900	-1.07943000

$TS_{3\text{-}4}$: E(B3PW91) = -1233.6360077
Gas-phase zero-point energy = -1233.250596
Gas-phase free energy = -1233.301183

Rh	-0.37904800	-0.23460500	0.11928100
C	2.28689500	1.76462800	-0.92770600
H	1.93682000	1.73163600	-1.96806500
H	2.73872100	2.75351800	-0.77025700
C	3.34344100	0.67088500	-0.69971800
H	3.68590000	0.68332400	0.34418000
H	4.22675500	0.91681100	-1.30235600
C	2.87534100	-0.74072400	-1.09294000
H	3.72159400	-1.43964800	-1.05647600
H	2.50697300	-0.73355200	-2.12743800
H	-1.10754300	-1.58833500	1.93030400
P	1.52365000	-1.42303600	-0.04681700
P	0.79368200	1.64966900	0.14907700
C	1.17329400	-3.04234700	-0.83752200
H	0.44108100	-3.59715500	-0.24300800
H	0.75754800	-2.88556900	-1.83701400
H	2.08435700	-3.64565900	-0.92107600
C	2.36369400	-1.89703600	1.51472600
H	2.72166500	-1.01225800	2.04828600
H	1.65471900	-2.41532500	2.16756400
H	3.21396800	-2.55997300	1.32006800
C	1.41728800	2.21774900	1.78407200
H	0.58204700	2.28654700	2.48751700
H	2.14004900	1.50666300	2.19400900
H	1.89613700	3.20092900	1.70636800
C	-0.18969300	3.09570200	-0.41267400
H	-1.04302000	3.24555200	0.25526100
H	0.41728500	4.00809800	-0.41638900
H	-0.57045300	2.91243600	-1.42118700
H	-1.75131400	-1.20345200	-0.93674500
B	-2.37507500	-0.11063300	-0.91565200
H	-1.92643900	0.68374200	0.01284100
H	-2.45477200	0.44122000	-1.97736400
N	-3.88562400	-0.42293300	-0.44760000
C	-4.71211200	0.81338700	-0.40543900

H	-5.75415400	0.56401800	-0.19813200
H	-4.32785300	1.46018500	0.38352500
H	-4.63124300	1.32552800	-1.36281000
C	-4.01316800	-1.19656700	0.81149800
H	-3.59599500	-0.60560000	1.62635100
H	-5.06295700	-1.41534300	1.01537600
H	-3.45098900	-2.12459300	0.71850600
H	-4.26248900	-1.00249200	-1.19826500
H	-0.68438100	-0.93388600	1.93055500

(4): E(B3PW91) = -1393.1096278
Gas-phase zero-point energy = -1392.631743
Gas-phase free energy = -1392.697337

Rh	0.84635200	-0.21828000	-0.19280300
C	3.36139900	2.20363300	-0.57031900
H	3.20339200	2.23746300	-1.65695200
H	3.64621200	3.21681200	-0.25596400
C	4.49598000	1.21773000	-0.24201100
H	4.64553700	1.15614000	0.84488400
H	5.43094000	1.62846900	-0.64366200
C	4.29842000	-0.18803200	-0.83649300
H	5.21261700	-0.78143800	-0.70045000
H	4.12508800	-0.10948700	-1.91837500
H	-1.52103900	-0.96602500	-1.88472800
H	-0.11294700	-1.71248600	-0.55977800
H	-0.88624300	0.28526400	-0.36673700
B	-1.13318200	-0.93005200	-0.75182000
N	-2.29598600	-1.47977200	0.19071300
C	-2.67088000	-2.86907600	-0.18644500
H	-1.82439300	-3.52648700	0.01377500
H	-3.53452300	-3.19233900	0.39621200
H	-2.90575500	-2.89703400	-1.24936200
C	-2.02352500	-1.37126700	1.64561300
H	-1.13723900	-1.96106800	1.87950200
H	-1.82688700	-0.32923500	1.89189300
H	-2.88101500	-1.73612700	2.21384700
P	2.88488200	-1.13974200	-0.13153200
P	1.73440500	1.79815100	0.19875900
C	2.94076700	-2.69727700	-1.10167300
H	2.22966000	-3.41720800	-0.68581400
H	2.65649200	-2.49760300	-2.13884900
H	3.94289400	-3.14039900	-1.08519600
C	3.49978000	-1.66324200	1.51882900
H	3.61844000	-0.80118000	2.18072400
H	2.77534000	-2.34039700	1.98064800
H	4.46304300	-2.17941800	1.43568700
C	1.96934000	2.25241800	1.96343200
H	1.02030900	2.14741100	2.49717200
H	2.69548200	1.58908400	2.44136400
H	2.31814400	3.28679200	2.06133900
C	0.65713000	3.14425800	-0.43132200
H	-0.31670200	3.10092200	0.06529300
H	1.10357300	4.12831200	-0.24902500
H	0.49782400	3.01810400	-1.50605500
B	-5.48719600	-0.03479900	0.07394000
N	-6.68978900	0.60213400	-0.14588100
H	-3.11419800	-0.89423700	-0.00843400
H	-4.51829800	0.33313900	-0.54021600
H	-5.42336400	-0.93493500	0.86362300
C	-7.92235500	0.23796600	0.54021600
H	-8.68728000	-0.06805000	-0.18172500

H	-7.73595700	-0.58570400	1.22780400
H	-8.31397200	1.09075100	1.10542500
C	-6.85692300	1.70035300	-1.08748000
H	-5.90753800	1.92180200	-1.57335800
H	-7.59482100	1.44022400	-1.85413900
H	-7.21047800	2.59958200	-0.57113200

$TS_{2\text{-}5}$: E(B3PW91) = -1233.6201259
Gas-phase zero-point energy = -1233.238014
Gas-phase free energy = -1233.286478

Rh	-0.41775700	-0.05979400	-0.43832900
C	2.71558400	1.48148300	-0.28500100
H	2.82349600	1.46488000	-1.37772500
H	3.22784100	2.38605100	0.06968300
C	3.38303000	0.23788100	0.32806100
H	3.21359400	0.20436700	1.41279600
H	4.46754200	0.34703300	0.20584100
C	2.97006000	-1.09206200	-0.32689500
H	3.63064000	-1.89662600	0.02272700
H	3.09963800	-1.02578300	-1.41554400
H	-1.33880100	-1.38115400	-1.21861800
P	1.23771700	-1.62280600	-0.01712700
P	0.92912700	1.70097300	0.08066800
C	1.06961000	-3.14046600	-1.02189100
H	0.11290400	-3.62717900	-0.80948200
H	1.09766800	-2.89142600	-2.08660000
H	1.87659500	-3.84698800	-0.80045100
C	1.22608800	-2.22271600	1.71207200
H	1.43107700	-1.40455700	2.40835300
H	0.23828600	-2.62693600	1.95245100
H	1.97384000	-3.00940900	1.86147300
C	0.84484700	2.19940800	1.83525300
H	-0.18829300	2.45775800	2.08491200
H	1.15464500	1.38108700	2.49070500
H	1.48363900	3.06878600	2.02532400
C	0.47431900	3.20341700	-0.84858500
H	-0.54987000	3.49458600	-0.59887500
H	1.14844900	4.03095700	-0.60272900
H	0.52205400	3.01003900	-1.92375200
H	-1.37688600	0.12088900	1.11759900
B	-2.30954900	0.73719500	0.40898700
H	-2.54221400	1.83573300	0.84859000
H	-1.63101600	1.06818400	-0.82359500
N	-3.40166300	-0.23082200	0.09010400
C	-4.53143400	0.35844800	-0.62349000
H	-5.21025500	-0.42885600	-0.96475700
H	-5.10500200	1.05822300	0.00249900
H	-4.17582300	0.90193100	-1.50287500
C	-3.84141000	-1.06791700	1.20434300
H	-4.36991900	-0.49728900	1.98239700
H	-4.52021000	-1.84447100	0.83861700
H	-2.98147900	-1.55590100	1.67188700
H	-2.00423700	-1.06497700	-0.79278800
H	0.28373600	-0.02578300	-1.82524700

(5): E(B3PW91) = 1233.6483176
Gas-phase zero-point energy = -1233.264460
Gas-phase free energy = -1233.314998

Rh	-0.33669900	-0.04915500	-0.71130300
C	2.68419500	1.53614800	-0.10552500

H	2.92547700	1.47800600	-1.17509500
H	3.13810000	2.46247300	0.27261000
C	3.29198400	0.33195300	0.63696900
H	2.98556900	0.33734200	1.69185700
H	4.38045000	0.46925500	0.65032600
C	3.00405500	-1.03882900	-0.00056800
H	3.65210900	-1.79862900	0.45649500
H	3.25389200	-1.00982600	-1.06980600
H	-1.06988100	-1.49706100	-1.40931200
P	1.26289500	-1.62823100	0.12700800
P	0.86114600	1.74286500	0.03326500
C	1.32291900	-3.21734300	-0.78688500
H	0.37383500	-3.75192700	-0.67774100
H	1.48889500	-3.02939400	-1.85207200
H	2.12717500	-3.86046600	-0.41351100
C	1.09750200	-2.15964000	1.87569300
H	1.16191800	-1.29952600	2.54824800
H	0.12006700	-2.62783200	2.02825000
H	1.87720700	-2.87919000	2.14879600
C	0.59132700	2.19069300	1.78595700
H	-0.45539200	2.46373600	1.94111600
H	0.82267200	1.35051600	2.44611000
H	1.22188700	3.04228000	2.06386300
C	0.54189900	3.29313500	-0.87555300
H	-0.51057700	3.57055300	-0.76848400
H	1.16694800	4.10847700	-0.49617400
H	0.74650000	3.14731000	-1.93976500
H	-1.37143500	-0.25891400	0.76474800
B	-2.36875600	0.51074000	0.56612900
H	-2.34048000	1.66146300	0.86150400
H	-1.20553300	1.05920100	-1.43955900
N	-3.58550300	-0.13129800	0.41926100
C	-4.84832200	0.59622600	0.49851000
H	-5.39710300	0.51261000	-0.44573000
H	-5.47679000	0.18463100	1.29512800
H	-4.65985400	1.64858000	0.70382900
C	-3.76378900	-1.55090900	0.16311900
H	-4.45869700	-1.98130900	0.89143400
H	-4.17924000	-1.72112100	-0.83693100
H	-2.81143100	-2.07414100	0.24471600
H	-1.38424600	-0.85240500	-1.84457400
H	0.58047600	0.11454900	-1.95152500

$TS_{5\text{-}6}$: E(B3PW91) = -1233.6236624
Gas-phase zero-point energy = -1233.246023
Gas-phase free energy = -1233.300627

Rh	0.36940400	-0.05280800	-0.46548300
C	-2.74488400	-1.36622200	-0.19101500
H	-2.96471700	-1.26865800	-1.26223700
H	-3.27677400	-2.26196100	0.16071400
C	-3.26816400	-0.13233500	0.56713900
H	-2.94983700	-0.16204700	1.61836200
H	-4.36251500	-0.20635000	0.59247200
C	-2.90290000	1.22078300	-0.07079100
H	-3.53268700	2.01271500	0.35555000
H	-3.11355500	1.19159700	-1.14826700
H	1.46074400	1.04016000	-3.15151300
P	-1.13731900	1.71024700	0.12936600
P	-0.95344600	-1.75215500	-0.03832200
C	-1.00053700	3.20320000	-0.92957900
H	-0.02328700	3.67708200	-0.79487600

H	-1.10171700	2.92616100	-1.98294800
H	-1.77655900	3.93482200	-0.67923200
C	-1.06340300	2.38930500	1.83293400
H	-1.24778600	1.59905500	2.56709800
H	-0.06598700	2.79607500	2.02665100
H	-1.80114900	3.18573100	1.97979100
C	-0.73403000	-2.36351600	1.66769100
H	0.29936700	-2.68705400	1.81612900
H	-0.95081800	-1.57617400	2.39431100
H	-1.40166400	-3.21253900	1.85376300
C	-0.73740700	-3.21985300	-1.09590900
H	0.27016700	-3.62321600	-0.96364600
H	-1.46939400	-3.99358300	-0.83957600
H	-0.85705200	-2.94412400	-2.14684200
H	1.31179600	0.12271300	1.05102300
B	2.32006400	-0.62470600	0.76283300
H	2.37236700	-1.72581400	1.21007700
H	1.28227500	-1.19728600	-1.07736700
N	3.48534500	0.05585300	0.43734700
C	4.79717300	-0.57575300	0.50140900
H	5.25164200	-0.62653800	-0.49410800
H	5.46461900	0.00107100	1.15086300
H	4.70447900	-1.58531800	0.89822200
C	3.52749600	1.42049300	-0.05857900
H	4.23278500	2.02068400	0.52626700
H	3.84489000	1.45065600	-1.10659100
H	2.53819500	1.88041700	0.01776800
H	1.79227900	1.65979400	-3.40534700
H	-0.42960900	-0.14717900	-1.80084700

(6): E(B3PW91) = -1233.6242466
Gas-phase zero-point energy = -1233.247773
Gas-phase free energy = -1233.307262

Rh	-0.38923500	-0.07752000	0.36413000
C	2.77718700	-1.30123200	0.29739400
H	2.93022000	-1.21326000	1.38116200
H	3.35462900	-2.17645800	-0.03351000
C	3.30881600	-0.04086100	-0.41010900
H	3.05503900	-0.06133000	-1.47908800
H	4.40441200	-0.08364800	-0.37039300
C	2.86644300	1.28940900	0.22788300
H	3.50001600	2.10605500	-0.14249100
H	3.01002300	1.24368900	1.31582800
H	-3.57807200	0.53712600	5.52724000
P	1.10449300	1.73824100	-0.07500200
P	1.00963000	-1.73614600	0.03549900
C	0.85481000	3.19084500	1.01883500
H	-0.12106400	3.64806100	0.82733200
H	0.88597800	2.88036000	2.06737600
H	1.62816000	3.94831300	0.85052000
C	1.12336600	2.47234900	-1.75693700
H	1.37150600	1.71114800	-2.50271300
H	0.13120900	2.86468400	-2.00073400
H	1.85059100	3.28839900	-1.83011200
C	0.90460300	-2.35310200	-1.67853600
H	-0.11378500	-2.69193900	-1.88594200
H	1.15126200	-1.56180300	-2.39132100
H	1.59446000	-3.19191200	-1.82521200
C	0.77197900	-3.20784300	1.08295800
H	-0.21294500	-3.64147600	0.89010100
H	1.54106100	-3.95962600	0.87435900

H	0.81888200	-2.92737200	2.13844200
H	-1.21273500	0.07937700	-1.21886800
B	-2.25523900	-0.63859600	-0.96944800
H	-2.33205100	-1.70797400	-1.48497000
H	-1.31113400	-1.26284500	0.87820700
N	-3.40034200	0.06080900	-0.60883500
C	-4.73653900	-0.50670100	-0.72981400
H	-5.19616700	-0.63505000	0.25646800
H	-5.37764000	0.15673500	-1.32047900
H	-4.68422300	-1.47617400	-1.22253300
C	-3.37951400	1.36782800	0.02274000
H	-4.06915200	2.05463400	-0.47984600
H	-3.67184000	1.30491700	1.07714000
H	-2.37199500	1.79678100	-0.03385900
H	-3.33540700	-0.10848000	5.24417900
H	0.29620800	-0.16078900	1.76301200

$TS_{1\text{-}7}$: E(B3PW91) = -1394.3122086
Gas-phase zero-point energy = -1393.817253
Gas-phase free energy = -1393.876186

Rh	-0.06515300	0.33531600	-0.01350200
C	3.19331500	0.57074100	1.27537400
H	3.14808200	1.66492600	1.18873600
H	3.83392300	0.34590300	2.13894600
C	3.81984400	-0.02476400	0.00167200
H	3.81913100	-1.12209700	0.05326300
H	4.87807300	0.26530500	-0.01506700
C	3.18340900	0.45092700	-1.31721500
H	3.82688200	0.16099400	-2.15886900
H	3.12205600	1.54751900	-1.32535500
H	-3.00860900	0.41897300	0.00934700
H	-1.21308000	0.84898800	-1.11933200
H	-1.19458800	0.97901400	1.04665900
H	0.52135100	1.75080600	-0.18754200
B	-2.10895400	1.21769500	-0.04093900
N	-2.54540900	2.55888800	-0.10643500
C	-3.95637900	2.90685100	-0.13296200
H	-4.21417700	3.55474100	0.71408300
H	-4.20846100	3.44840900	-1.05328600
H	-4.56870600	2.00749900	-0.08118500
C	-1.68199500	3.72109100	-0.16540300
H	-1.88255800	4.39687000	0.67538100
H	-0.63609500	3.42064500	-0.12661900
H	-1.84981900	4.28499400	-1.09171200
P	1.49039500	-0.19486100	-1.65640600
P	1.48842700	-0.00596000	1.66979400
C	1.09185400	0.53137800	-3.28882800
H	0.13968500	0.12546400	-3.64315000
H	0.98666700	1.61623400	-3.19808700
H	1.87004000	0.30692500	-4.02645100
C	1.77359500	-1.96167400	-2.04201900
H	2.08494600	-2.51074500	-1.14976500
H	0.84461400	-2.41266000	-2.39890500
H	2.54356800	-2.06954000	-2.81391100
C	1.72414600	-1.73114300	2.24426600
H	0.77975000	-2.11743300	2.63834700
H	2.02384200	-2.37823900	1.41546700
H	2.48385100	-1.78510900	3.03182700
C	1.11272900	0.90308100	3.21566100
H	0.15164400	0.56937000	3.61804500
H	1.88859000	0.74279100	3.97231100

H	1.03661300	1.97367400	3.00442400
H	-1.38277100	-1.98262600	-1.68287800
B	-1.33204100	-2.23304700	-0.50954500
H	-0.77590800	-3.26461400	-0.22695500
H	-0.76117700	-1.34501200	0.19300200
N	-2.82735400	-2.28532500	0.05186500
C	-2.89954300	-2.56716700	1.50403800
H	-3.93760300	-2.56665600	1.84282900
H	-2.45112500	-3.54297800	1.69150600
H	-2.33835900	-1.80214000	2.03925500
C	-3.65272600	-3.24243400	-0.72571300
H	-3.22273800	-4.23863300	-0.61968000
H	-4.68056100	-3.24341900	-0.35713800
H	-3.63219700	-2.95667800	-1.77616600
H	-3.21041200	-1.34785700	-0.09341800

(7): E(B3PW91) = -1394.3131973
Gas-phase zero-point energy = -1393.818187
Gas-phase free energy = -1393.877295

Rh	-0.08041400	0.33118400	0.01365500
C	3.16400600	0.48461800	1.34609200
H	3.10730300	1.58150800	1.36700200
H	3.79977900	0.18252800	2.18942800
C	3.80912700	0.02553600	0.02613600
H	3.82289200	-1.07140000	-0.03196400
H	4.86343200	0.32913800	0.04979100
C	3.17782300	0.62136600	-1.24570900
H	3.83323100	0.42571900	-2.10514400
H	3.09898900	1.71233200	-1.14645800
H	-3.02498300	0.37567100	-0.01662000
H	-1.21990900	0.93473300	-1.06656600
H	-1.23107900	0.86485200	1.10089700
H	0.51824300	1.75293700	0.07195400
B	-2.13592400	1.18802300	-0.00432400
N	-2.59139200	2.52391100	0.03020000
C	-4.00661000	2.85263300	0.06818700
H	-4.25246200	3.41925000	0.97510500
H	-4.28692500	3.46973000	-0.79444500
H	-4.60629800	1.94341300	0.05372800
C	-1.74266100	3.69836600	0.04260700
H	-1.90030500	4.28405600	0.95720600
H	-0.69393700	3.40966500	-0.00781200
H	-1.96835600	4.34921200	-0.81125700
P	1.49909200	-0.01542500	-1.66019200
P	1.46214200	-0.14401400	1.67203200
C	1.09818300	0.86234500	-3.21629900
H	0.15219600	0.48348400	-3.61448900
H	0.98042200	1.93191100	-3.02011200
H	1.88185500	0.72037300	-3.96846200
C	1.81998300	-1.73042900	-2.21755800
H	2.15020300	-2.35700700	-1.38473300
H	0.89891400	-2.16723100	-2.61159100
H	2.58690800	-1.74548100	-3.00000100
C	1.70681900	-1.91270600	2.08341200
H	0.76863500	-2.33415600	2.45578500
H	1.99009500	-2.47987500	1.19299000
H	2.47933800	-2.03813600	2.84985200
C	1.06613800	0.61446200	3.29164700
H	0.10982000	0.22833600	3.65653400
H	1.84223800	0.39828100	4.03396100
H	0.97154500	1.69828300	3.17881700

H	-1.28104600	-1.81608800	-1.76306200
B	-1.24120900	-2.17383900	-0.61811700
H	-0.67144200	-3.22200000	-0.43929100
H	-0.69721500	-1.38012500	0.21302900
N	-2.74794300	-2.31919600	-0.10024100
C	-2.84607200	-2.74219500	1.31549400
H	-3.89141700	-2.80407100	1.62527000
H	-2.37276000	-3.71862300	1.42065700
H	-2.32240100	-2.01711300	1.93746700
C	-3.52852500	-3.21717800	-0.98653900
H	-3.07348300	-4.20766200	-0.96591200
H	-4.56420100	-3.28001100	-0.64626900
H	-3.49207800	-2.83081100	-2.00385100
H	-3.15384800	-1.38213800	-0.16582300

TS_{7-8}: E(B3PW91) = -1394.2733797
Gas-phase zero-point energy = -1393.781737
Gas-phase free energy = -1393.841251

Rh	0.00088900	0.14297500	-0.10752300
C	-3.03346400	-1.09990900	-1.36099500
H	-2.91009300	-0.46875200	-2.25174100
H	-3.53672900	-2.01982800	-1.68789900
C	-3.90715300	-0.37411000	-0.32436600
H	-4.00702100	-0.98316800	0.58453900
H	-4.92189800	-0.29032500	-0.73387100
C	-3.41929800	1.03884100	0.03215100
H	-4.16122700	1.53178000	0.67513900
H	-3.33605300	1.64268100	-0.88213700
H	2.81197200	1.04956900	0.91974100
H	0.76557400	1.52790500	0.66421600
H	0.72937500	0.49602100	-2.12867000
H	0.02983500	0.79796600	-1.91903200
B	1.96271400	1.58784100	0.27581900
N	2.32584500	2.61338000	-0.57770400
C	3.71779000	2.99029600	-0.79144900
H	3.99843800	2.84756000	-1.84095900
H	3.86941200	4.04562800	-0.54191600
H	4.37092700	2.38602500	-0.16361800
C	1.39779200	3.40656400	-1.36750300
H	1.57478800	3.25223200	-2.43798500
H	0.37355300	3.11564600	-1.14300400
H	1.53020700	4.47216400	-1.15238200
P	-1.78363200	1.12918200	0.88563600
P	-1.34681900	-1.56241700	-0.77869100
C	-1.65134300	2.94265100	1.16950700
H	-0.75690800	3.16950600	1.75718700
H	-1.58234400	3.47319300	0.21534700
H	-2.52826300	3.31393600	1.71166600
C	-2.16425200	0.52708100	2.58073900
H	-2.37066300	-0.54599400	2.57239600
H	-1.29369700	0.68826900	3.22360400
H	-3.02574000	1.05415300	3.00741400
C	-1.66889500	-2.91028400	0.42008700
H	-0.71966800	-3.31447800	0.77984400
H	-2.22435800	-2.53606100	1.28342500
H	-2.24699800	-3.71470800	-0.04828600
C	-0.66243300	-2.44721400	-2.23062400
H	0.30753700	-2.87865500	-1.96959300
H	-1.33404100	-3.25060700	-2.55226500
H	-0.52068100	-1.74955600	-3.06108200
H	1.21623700	-1.59877600	1.75756600

B	1.69197800	-1.83837800	0.68098600
H	1.48936700	-2.95915800	0.27976000
H	1.39057600	-1.05456200	-0.28922400
N	3.28543700	-1.66239400	0.79053600
C	3.98825200	-1.93183500	-0.48512600
H	5.06261000	-1.76916000	-0.37467800
H	3.80107200	-2.96724900	-0.76988400
H	3.59002700	-1.27297600	-1.25617100
C	3.83640700	-2.48669600	1.89421700
H	3.62455300	-3.53484400	1.68248600
H	4.91521300	-2.33840900	1.97862000
H	3.34469600	-2.20652100	2.82433700
H	3.44429900	-0.68233200	1.02780500

(8): E(B3PW91) = =-1393.1089345
Gas-phase zero-point energy = -1392.629582
Gas-phase free energy = -1392.687471

Rh	0.08120700	0.03213100	0.20701000
C	-2.74920600	-1.13791900	-1.56493900
H	-2.58344800	-0.42128600	-2.38074700
H	-3.17589400	-2.04294900	-2.01840200
C	-3.74447600	-0.54813200	-0.55261400
H	-3.86601500	-1.22324000	0.30565900
H	-4.73093100	-0.50239100	-1.03136700
C	-3.38349300	0.86624700	-0.07097800
H	-4.21173400	1.27990000	0.52033500
H	-3.24756000	1.52861700	-0.93687200
H	2.80146700	1.50468600	0.79609600
H	0.71620000	1.48810000	0.90624000
B	1.76842500	1.70702000	0.22037400
N	1.80053300	2.59844700	-0.83945400
C	3.03332800	3.24899900	-1.26590500
H	3.27351400	2.98194200	-2.30111900
H	2.92493500	4.33795400	-1.21643200
H	3.85851700	2.95318700	-0.61964300
C	0.65405500	2.97050500	-1.65311100
H	0.85174600	2.74536400	-2.70687400
H	-0.21295200	2.38967300	-1.33991300
H	0.45173800	4.04454500	-1.56968900
P	-1.85240800	0.97586600	0.95046000
P	-1.08970000	-1.58911000	-0.89364600
C	-1.81177200	2.76752300	1.35777600
H	-1.01877500	2.96590800	2.08511900
H	-1.61019200	3.36066600	0.46155100
H	-2.76746700	3.09035600	1.78503700
C	-2.36660600	0.23527800	2.55391500
H	-2.53740700	-0.83918400	2.44616500
H	-1.56914000	0.37240100	3.29018100
H	-3.28201600	0.70611000	2.93025400
C	-1.42097200	-3.13953700	0.03121200
H	-0.47629100	-3.54657400	0.40235900
H	-2.06190300	-2.94069600	0.89465000
H	-1.90783200	-3.88661400	-0.60539900
C	-0.23958400	-2.18352200	-2.40700300
H	0.71762900	-2.63590300	-2.13649500
H	-0.85051700	-2.92721500	-2.93070700
H	-0.04725300	-1.34248500	-3.07921600
H	1.22010300	-1.50993000	1.50224900
B	1.86934800	-1.56565700	0.47846700
H	1.88810100	-2.65406400	-0.03826600

H	1.54284900	-0.73340100	-0.47056300
N	3.38574000	-1.17199500	0.81658800
C	4.27262600	-1.21723800	-0.37057500
H	5.28821800	-0.91989800	-0.10097400
H	4.27762900	-2.23511900	-0.76026100
H	3.88013900	-0.54516300	-1.13310200
C	3.91701900	-2.01320200	1.91805000
H	3.88683800	-3.05666200	1.60386900
H	4.94504200	-1.72769600	2.15030000
H	3.28561800	-1.88795500	2.79623200
H	3.36603600	-0.20422500	1.14297100

$TS_{8\text{-}4}$: E(B3PW91) = -1393.1009211
Gas-phase zero-point energy = -1392.623308
Gas-phase free energy = -1392.680663

Rh	-0.29770700	-0.49528800	-0.08480400
C	2.65521600	0.49918100	1.53233000
H	2.41741200	1.56083600	1.38236100
H	3.17502500	0.41835300	2.49655400
C	3.58133500	0.00976500	0.40515000
H	3.79643600	-1.06061300	0.52680300
H	4.54809600	0.51798400	0.51029800
C	3.04858900	0.28544200	-1.01214400
H	3.81434500	0.02560300	-1.75510400
H	2.83562700	1.35615900	-1.12786400
H	-2.09104800	1.59953500	0.51051100
H	-1.16594000	1.01307200	-1.30992200
B	-1.22890100	1.74009200	-0.31585700
N	-0.60102100	2.99055800	-0.33289000
C	-0.85094100	4.00345800	0.68012900
H	0.07500500	4.27682900	1.20168000
H	-1.25465600	4.91622900	0.22595500
H	-1.56929700	3.63213100	1.41014100
C	0.32450500	3.43624400	-1.35547600
H	1.31682400	3.64346300	-0.93456900
H	0.41997600	2.67808000	-2.13043500
H	-0.03253400	4.36164800	-1.82279800
P	1.50288400	-0.62404400	-1.42817800
P	1.05019200	-0.39914200	1.67775300
C	1.16863800	-0.13109100	-3.16438200
H	0.31888600	-0.70389400	-3.54870100
H	0.91696900	0.93026000	-3.22471600
H	2.03893000	-0.32549700	-3.80098800
C	2.05805600	-2.36301600	-1.63007500
H	2.38226800	-2.78290400	-0.67494200
H	1.22217700	-2.96938400	-1.99150400
H	2.88349400	-2.43179000	-2.34791400
C	1.53796700	-2.00315700	2.43288100
H	0.63738300	-2.57350800	2.67879700
H	2.12681800	-2.60093100	1.73199900
H	2.12475700	-1.85148900	3.34668800
C	0.24891500	0.46588000	3.08442200
H	-0.65587400	-0.07348400	3.37976800
H	0.92266900	0.52278000	3.94689900
H	-0.03603900	1.47712100	2.78293500
H	-1.69350200	-1.64521800	-0.94891700
B	-2.34437200	-1.51120900	0.11333900
H	-2.67130200	-2.55551100	0.60466000
H	-1.70497700	-0.82974000	1.00522800
N	-3.65919300	-0.66016600	-0.20149900
C	-4.49513200	-0.46640100	1.00969000

H	-5.36382800	0.15173600	0.77540300
H	-4.81961000	-1.44299200	1.36804200
H	-3.89520500	0.01844800	1.77918800
C	-4.44402000	-1.25574400	-1.31212900
H	-4.73745100	-2.26651800	-1.02846800
H	-5.33349800	-0.65470700	-1.51040100
H	-3.82029800	-1.30136800	-2.20396200
H	-3.33827200	0.26448700	-0.49919200

$TS_{8\text{-}9}$: E(B3PW91) = -1393.0675953
Gas-phase zero-point energy = -1392.598531
Gas-phase free energy = -1392.656752

Rh	0.22447400	0.00177700	-0.25805000
C	-3.29109000	0.22509300	-0.34556200
H	-3.33866500	1.09735500	0.32063200
H	-4.13311100	0.31632000	-1.04525100
C	-3.44646400	-1.06631000	0.47722200
H	-3.35848200	-1.94670100	-0.17394300
H	-4.47272200	-1.09176900	0.86457200
C	-2.48758500	-1.18726100	1.67532000
H	-2.82648100	-1.99508900	2.33769400
H	-2.51247900	-0.26144300	2.26605200
H	0.67870500	3.23168100	-1.24634600
H	2.38630200	2.39606200	-0.44529100
H	0.79944100	1.23395100	-1.20786700
H	-0.03180300	1.25731100	0.68564200
B	1.20852700	2.59032700	-0.38532900
N	0.61613100	2.70791600	0.98443700
C	-0.44395500	3.68538400	1.20934800
H	-1.01775900	3.43528900	2.10792500
H	-0.03234100	4.69428100	1.34189200
H	-1.11917100	3.71126100	0.35464900
C	1.51196600	2.59268300	2.13064300
H	0.94260900	2.40946300	3.04774200
H	2.20611200	1.76547000	1.97892300
H	2.09837400	3.50920100	2.27331100
P	-0.72729400	-1.51373100	1.24036700
P	-1.74084200	0.37450500	-1.33111800
C	-1.97717400	1.96129300	-2.20742400
H	-1.97661300	2.79628500	-1.50301200
H	-1.15509300	2.11868200	-2.91074500
H	-2.92500200	1.96224500	-2.75642500
C	-1.94024600	-0.85740400	-2.67735400
H	-1.90766800	-1.87786900	-2.28607400
H	-2.89005400	-0.71091500	-3.20404200
H	-1.12100900	-0.74433200	-3.39381400
C	0.09165200	-1.55434300	2.88019200
H	1.13577300	-1.86093200	2.76588200
H	0.07698200	-0.55831900	3.33204200
H	-0.40879000	-2.25656000	3.55592100
C	-0.72158900	-3.27805600	0.73396100
H	0.30847800	-3.60597500	0.56329400
H	-1.17051900	-3.91338100	1.50552300
H	-1.27445700	-3.41689500	-0.19961900
B	2.23053900	-0.84623600	-0.57518800
N	3.59432300	-0.91964300	-0.73177800
H	1.84918200	-0.22986900	0.48039100
H	1.47145800	-1.48346100	-1.28090300
C	4.55688500	-0.21505500	0.10498600
H	5.23505800	-0.92593600	0.58864000

H	5.15624800	0.47221800	-0.50039000
H	4.04063600	0.35972900	0.87260000
C	4.21466600	-1.70525000	-1.79390600
H	4.80089200	-1.05614800	-2.45246000
H	4.88622400	-2.45875500	-1.36945100
H	3.44952800	-2.20703900	-2.38478300

(9): E(B3PW91) = -1393.1065871
Gas-phase zero-point energy = -1392.635665
Gas-phase free energy = -1392.702868

Rh	-1.10055000	-0.26714100	-0.26012000
C	1.33895500	2.21852000	-0.59032700
H	2.20197000	1.54155300	-0.53947000
H	1.62925200	3.05101300	-1.24606400
C	1.01339800	2.75405100	0.81541700
H	0.07375800	3.32455200	0.80494300
H	1.79293300	3.47830500	1.08220900
C	0.98056500	1.67101700	1.90947300
H	1.04854800	2.13931900	2.90032700
H	1.85724000	1.01771100	1.80564500
H	4.05247000	-0.22220400	-1.09697000
H	3.87733300	-0.69493600	0.93406100
H	-1.28808000	-0.93306900	-1.69345700
H	0.29528000	-0.91207500	-0.32170000
B	4.48284800	-0.73259900	-0.10044900
N	5.70543900	-1.37610700	-0.14741200
C	6.51363500	-1.47230100	-1.35382100
H	7.49263500	-1.00355600	-1.20230800
H	6.68209700	-2.52087800	-1.62453900
H	6.00836400	-0.97250700	-2.17924600
C	6.31394300	-2.02477800	1.00433000
H	7.28780200	-1.57633100	1.23151700
H	5.66657800	-1.91944200	1.87395200
H	6.47338200	-3.09127000	0.80837100
P	-0.51578500	0.59558100	1.88602800
P	-0.00950600	1.31164500	-1.45070000
C	0.79817800	0.73471100	-2.98184400
H	1.54513600	-0.02725800	-2.74236700
H	0.05414300	0.28586400	-3.64532600
H	1.28894700	1.56473800	-3.50133700
C	-1.17053200	2.61101200	-2.01337800
H	-1.63875800	3.10805400	-1.15895500
H	-0.64892300	3.36122600	-2.61795300
H	-1.96006200	2.15748600	-2.61971400
C	-0.11608600	-0.69516100	3.12349300
H	-0.99387600	-1.32384100	3.30183200
H	0.68771800	-1.33383200	2.74558900
H	0.19821800	-0.25275200	4.07492400
C	-1.79322000	1.61146400	2.72733200
H	-2.70284100	1.01846500	2.86505600
H	-1.44894300	1.95868800	3.70768600
H	-2.05043800	2.48112700	2.11512400
B	-2.98011000	-1.11276200	-0.17676900
N	-4.12178500	-1.84191700	-0.38580000
H	-1.97363600	-1.68350800	0.41550400
H	-2.96719300	0.15283900	-0.25156000
C	-4.18564100	-3.28846600	-0.20619300
H	-4.95520800	-3.54768200	0.52781700
H	-4.43435200	-3.77627600	-1.15407800
H	-3.22495400	-3.66921500	0.13947900
C	-5.36722800	-1.24363300	-0.85392500

H	-5.65328100	-1.66974200	-1.82096500
H	-6.17442600	-1.43713500	-0.14030600
H	-5.24979200	-0.16610800	-0.96699200

$TS_{8\text{-}10}$: E(B3PW91) = -1393.0644948
Gas-phase zero-point energy = -1392.595162
Gas-phase free energy = -1392.655966

Rh	0.32788600	-0.45364700	-0.06587200
C	-0.69793100	2.61606700	1.38436700
H	-1.76677000	2.43415700	1.20861000
H	-0.62375400	3.19778200	2.31291500
C	-0.10868100	3.42178900	0.21347400
H	0.97601300	3.54242200	0.33948100
H	-0.52405000	4.43618100	0.25510500
C	-0.42478700	2.83274700	-1.17218400
H	-0.16735300	3.56002200	-1.95389100
H	-1.50333800	2.64371000	-1.25946100
H	0.89193700	-3.60626300	-0.26008500
H	0.43034700	-1.94393400	0.88880900
H	0.68479100	-1.77184600	-1.20595100
H	1.92886600	-0.60159900	0.11331500
B	1.18309600	-2.44688000	-0.13538400
N	2.64735600	-2.04499900	0.07546100
C	3.50318700	-2.32886600	-1.07175900
H	4.50479200	-1.92107700	-0.90723100
H	3.59463900	-3.40915400	-1.25521200
H	3.08240500	-1.87136700	-1.97123700
C	3.21592100	-2.54594700	1.32217900
H	4.21745000	-2.13337400	1.47518100
H	2.58331300	-2.25074800	2.16373000
H	3.28870000	-3.64310900	1.32532400
P	0.44938000	1.25881300	-1.56481500
P	0.10393400	0.98469100	1.68367300
C	2.15540500	1.79147100	-1.96466700
H	2.73929000	0.92960900	-2.29942200
H	2.15466700	2.54775000	-2.75732900
H	2.64834500	2.20588200	-1.08080100
C	-0.25445700	0.78534200	-3.18647900
H	-0.19214400	1.61368100	-3.90085300
H	0.29114100	-0.07214500	-3.59090300
H	-1.30218000	0.49440300	-3.06832500
C	-0.90353000	0.26492900	3.03209300
H	-0.42564300	-0.64683100	3.40220600
H	-1.01299500	0.96993900	3.86361800
H	-1.89570300	-0.00218200	2.65743200
C	1.68329400	1.41781300	2.50363000
H	1.50792100	2.03742000	3.38999600
H	2.20001800	0.50337800	2.80796700
H	2.34005000	1.95934800	1.81698300
B	-2.46608700	-1.58299400	-0.46608700
H	-2.01265900	-2.64235100	-0.75800200
H	-1.76330600	-0.58188900	-0.35524800
N	-3.82193900	-1.42869600	-0.25250100
C	-4.46746800	-0.17147200	0.08778400
H	-4.98489700	-0.24764700	1.05082800
H	-3.72543300	0.62497200	0.14648800
H	-5.21193400	0.09870500	-0.66939800
C	-4.75981900	-2.54105500	-0.36678300
H	-4.22261500	-3.45258800	-0.62282600
H	-5.28946500	-2.69450300	0.57966400
H	-5.50477900	-2.33687300	-1.14340000

(10): E(B3PW91) = -1393.1111575
Gas-phase zero-point energy = -1392.638434
Gas-phase free energy = -1392.697403

Rh	-0.15754500	-0.37633100	0.00057800
C	2.81119500	1.01579200	1.32384000
H	2.36789700	2.02080500	1.28887500
H	3.50128500	1.00468900	2.17861900
C	3.60075000	0.75493300	0.02571700
H	4.00738100	-0.26563800	0.02393300
H	4.47724300	1.41531300	0.03528800
C	2.82907000	1.02754200	-1.28120500
H	3.53023100	1.01452400	-2.12688400
H	2.38956900	2.03392100	-1.25050400
H	-3.03599600	0.09084400	-0.03021000
H	-1.37384700	-0.80503700	1.06435400
H	-1.33482800	-0.73202000	-1.11332700
H	0.18644200	-1.86402800	-0.05350700
B	-2.33635500	-0.87578300	-0.02852000
N	-2.98947600	-2.12168400	-0.07338600
C	-2.34418900	-3.41893700	-0.07259800
H	-2.71046600	-4.03219400	0.75972000
H	-2.55487500	-3.96170100	-1.00269200
H	-1.26541400	-3.30794100	0.02734300
C	-4.43985000	-2.21223700	-0.14527500
H	-4.83671900	-2.77297200	0.70973200
H	-4.87850200	-1.21565700	-0.14458700
H	-4.75228700	-2.73233000	-1.05911600
P	1.46707400	-0.15709600	-1.65583400
P	1.43997500	-0.16327300	1.68826900
C	2.33863000	-1.71822500	-2.05980000
H	1.61434100	-2.44996900	-2.43023900
H	3.09882500	-1.55432000	-2.83113800
H	2.81879300	-2.14325000	-1.17485100
C	0.86610400	0.38554900	-3.29876700
H	1.69178900	0.45228200	-4.01576200
H	0.13200100	-0.33582500	-3.67014300
H	0.37788600	1.36019300	-3.22735900
C	0.77891200	0.47112900	3.27526100
H	0.00740000	-0.20879800	3.64855100
H	1.56913900	0.55795200	4.02917200
H	0.32449700	1.45519000	3.12724900
C	2.28469500	-1.71032600	2.18469100
H	3.00674200	-1.52495600	2.98711200
H	1.54125900	-2.43060300	2.53921400
H	2.80743200	-2.16071200	1.33687700
B	-0.94145900	2.21237200	-0.44825400
H	-0.39459900	2.48339700	-1.46646400
H	-0.47875500	1.41649300	0.38595800
N	-2.03580200	2.92679900	-0.01749500
C	-2.73504400	2.69705200	1.23798600
H	-3.78414400	2.44663900	1.05101600
H	-2.27353500	1.87363400	1.78081800
H	-2.70708300	3.59900600	1.85875700
C	-2.61150600	4.01091400	-0.80684600
H	-2.04482800	4.14435500	-1.72693800
H	-3.65240900	3.78426100	-1.06011500
H	-2.59467100	4.94701800	-0.23927200

$TS_{8\text{-}11}$: E(B3PW91) = -1393.0296206
Gas-phase zero-point energy = -1392.557766

Gas-phase free energy = -1392.616748

Rh	-0.00759600	0.21254900	-0.11154400
C	-2.78390600	-1.91117300	-0.70227600
H	-2.65292800	-1.86713000	-1.79194400
H	-3.17322300	-2.91113100	-0.46785600
C	-3.79470000	-0.84260100	-0.25947800
H	-3.89451100	-0.83795800	0.83448500
H	-4.78203100	-1.12723400	-0.64436900
C	-3.46892400	0.56762200	-0.77373000
H	-4.31875700	1.23771900	-0.58629200
H	-3.31675800	0.54051300	-1.86114400
H	0.78287600	2.19182400	1.52511900
H	0.68229400	1.68885400	-0.66095800
B	1.22669800	2.12356100	0.42026100
N	2.36639100	2.83451500	0.08480300
C	3.08951800	3.64457300	1.05943500
H	4.12839100	3.30690900	1.14171200
H	3.09934700	4.69577600	0.75248600
H	2.61328200	3.56528000	2.03533000
C	2.95200400	2.88081700	-1.24778600
H	3.98771800	2.52358200	-1.22574800
H	2.37735400	2.25907500	-1.93412500
H	2.96237700	3.90824000	-1.62691400
P	-1.97412000	1.34681200	-0.02740100
P	-1.10566200	-1.78422600	0.05227800
C	-1.93792800	2.97080000	-0.88180000
H	-1.18258700	3.61806000	-0.42513300
H	-1.67904800	2.83205700	-1.93553900
H	-2.91008300	3.47198100	-0.81809400
C	-2.53312600	1.79552900	1.66414400
H	-2.71799600	0.89977200	2.26348600
H	-1.75244100	2.37548200	2.16487500
H	-3.45129800	2.39277000	1.62925000
C	-1.36966900	-2.37586500	1.77186000
H	-0.40624500	-2.46298700	2.28215900
H	-1.97924600	-1.66419300	2.33589900
H	-1.86606800	-3.35285600	1.78222100
C	-0.26168800	-3.20676900	-0.74173800
H	0.72924300	-3.34472500	-0.30232600
H	-0.83738100	-4.12941500	-0.60922300
H	-0.13996900	-3.01555200	-1.81202000
H	3.07575100	0.18500400	0.29624900
B	2.18948800	-0.87051000	0.34869500
H	1.79530000	-0.82126900	1.47511000
H	1.47529200	-0.60276700	-0.67296600
N	3.14324500	-2.04570300	0.05563700
C	3.43877400	-2.41495000	-1.32008800
H	4.41972200	-2.89573700	-1.38341300
H	2.69330100	-3.10597200	-1.73633100
H	3.45716800	-1.52437400	-1.95400700
C	3.33172200	-3.10687800	1.03264000
H	2.60812800	-3.92493300	0.90404000
H	4.33486700	-3.53430700	0.93842500
H	3.22290500	-2.70947900	2.04220200
H	3.53298100	-0.65791300	0.25671600

(11): E(B3PW91) = -1391.9153777
Gas-phase zero-point energy = -1391.458578
Gas-phase free energy = -1391.517536

Rh	-0.02979700	0.13035100	-0.12594800

C	-3.05776400	-1.56569900	-0.78980300
H	-2.89592900	-1.47855500	-1.87281900
H	-3.58677600	-2.51375300	-0.62197400
C	-3.92703400	-0.39581800	-0.29947600
H	-4.05655800	-0.44531200	0.79033200
H	-4.93249200	-0.52379600	-0.71997600
C	-3.41269500	0.99191400	-0.71662000
H	-4.17008100	1.75204800	-0.48217100
H	-3.25921500	1.01885700	-1.80383900
H	1.09615500	2.13717200	1.40262500
H	0.81136900	1.49951000	-0.72105400
B	1.50288400	1.82566300	0.32555500
N	2.78163700	2.18424600	-0.06307900
C	3.69113300	2.89472000	0.82871700
H	4.61653700	2.32444800	0.96308100
H	3.95410800	3.87167600	0.40908800
H	3.22154400	3.04151300	1.79998600
C	3.34644300	1.93971300	-1.38218000
H	4.26034400	1.34142900	-1.30323100
H	2.62802300	1.41040000	-2.00729600
H	3.60689100	2.88627700	-1.86798300
P	-1.83169800	1.52144400	0.06697100
P	-1.39548300	-1.71086100	-0.00568900
C	-1.58738800	3.18424300	-0.66837500
H	-0.74510500	3.68655600	-0.18273900
H	-1.36370400	3.09163300	-1.73511300
H	-2.48178700	3.80462500	-0.54544900
C	-2.30892600	1.90756800	1.79712500
H	-2.61187500	1.00132100	2.32868600
H	-1.44997700	2.33182100	2.32524100
H	-3.13442900	2.62758600	1.82746000
C	-1.75929000	-2.31361500	1.68983400
H	-0.82031600	-2.52056900	2.21232600
H	-2.29910300	-1.55659900	2.26534100
H	-2.35940000	-3.22988600	1.66276300
C	-0.72592600	-3.20711100	-0.83056400
H	0.21320100	-3.50676600	-0.35562900
H	-1.43256700	-4.04183400	-0.76672700
H	-0.52473100	-2.99325100	-1.88437800
B	1.82233900	-1.14318400	0.42927300
H	1.49584200	-0.91537300	1.55705400
H	1.24882300	-0.88277200	-0.69021300
N	2.96024700	-1.88463600	0.16903900
C	3.43320600	-2.24760200	-1.16043300
H	4.43882500	-1.84976100	-1.33312900
H	3.48268600	-3.33672000	-1.26683500
H	2.76322400	-1.84999700	-1.92255800
C	3.82062100	-2.38364800	1.23750100
H	3.88221300	-3.47664800	1.20154100
H	4.83497700	-1.98489900	1.12985500
H	3.42427300	-2.08255000	2.20594500

Cartesian coordinates (Å) and absolute energies, (Hartrees) of optimized structures for the dehydrogenation reaction of a dimethylamine-borane molecule A assisted by the real catalytic systems **2a**, **2b** and **2c.**

2b+A: E(B3PW91) = -2160.7588778
Gas-phase zero-point energy = -2160.041498

Gas-phase free energy = -2160.128127

Rh	-0.66859000	0.02463300	0.58081100
P	-0.73283700	1.72359600	-0.87676700
P	-0.89772900	-1.54760900	-0.99445600
B	-0.50242000	-0.08735300	2.75710000
N	-1.80800600	-0.08941200	3.68726800
H	-0.58190800	-1.12356600	1.98912600
H	0.45563700	-0.17083400	3.47317800
H	-0.48114700	1.02468600	2.10269300
C	-1.90066600	-1.36195500	4.45283500
H	-2.06962300	-2.17494800	3.74676400
H	-0.96219200	-1.52918300	4.97964200
H	-2.72830200	-1.31377000	5.16258500
C	-3.08153700	0.20875000	2.97992200
H	-3.24021800	-0.55864800	2.22237900
H	-2.99502700	1.17478500	2.48565300
H	-3.90912400	0.21621800	3.69303200
H	-1.65392000	0.65552900	4.36715500
B	5.73560200	-0.23478000	1.07030700
N	7.27269900	-0.25147700	1.60794500
H	5.22353100	0.75564700	1.55264600
H	5.80602300	-0.18912800	-0.14162400
H	5.22707900	-1.26072200	1.47634300
H	7.21060800	-0.28587900	2.62357300
C	8.00178900	0.98301000	1.24723300
C	8.00501000	-1.45687600	1.16461800
H	7.45748400	1.83985800	1.64162000
H	9.02000200	0.96751800	1.64519800
H	8.03149200	1.05530100	0.15971400
H	9.02399800	-1.46426200	1.56079900
H	8.03245100	-1.45664800	0.07471900
H	7.46438600	-2.33992300	1.50209400
H	-2.47304200	0.28623100	-3.93472600
C	-1.36603900	-1.11314900	-2.73626000
H	-0.43139500	-1.08962000	-3.31102000
C	-1.19029900	1.44071400	-2.64937700
H	-1.96685400	-1.93494900	-3.14410000
H	-1.65019800	2.35824200	-3.03571000
H	-2.98410300	0.26659200	-2.25323200
C	-2.10028700	0.22741200	-2.90361500
H	-0.24612300	1.31011700	-3.19336500
C	0.83099200	2.66007700	-1.00463400
C	0.86953000	3.91689400	-1.63819100
C	2.02031700	2.10193500	-0.50832500
C	2.08255800	4.59235600	-1.77841200
H	-0.04359200	4.37290000	-2.01027900
C	3.23401100	2.78172400	-0.65096400
H	1.98947100	1.13888400	-0.00726000
C	3.26429800	4.02479500	-1.28758600
H	2.10624900	5.56082800	-2.26763500
H	4.14339800	2.33426700	-0.26381000
H	4.20491700	4.55439400	-1.40003900
C	-1.94621000	2.96253400	-0.27249500
C	-3.24356000	3.06254700	-0.80435700
C	-1.58640900	3.79956000	0.80132100
C	-4.15799100	3.97973800	-0.27768700
H	-3.55045000	2.43364600	-1.63367300
C	-2.50158100	4.71568700	1.32343300
H	-0.58299200	3.74764100	1.21419000
C	-3.79047100	4.80681800	0.78673700
H	-5.15306100	4.05196300	-0.70487200

H	-2.20506900	5.36685100	2.13966000
H	-4.49901200	5.52324700	1.18928600
C	0.58503000	-2.59300700	-1.21278900
C	0.53940700	-3.75685800	-2.00434300
C	1.79878600	-2.21408300	-0.61601500
C	1.69348500	-4.51700900	-2.19829900
H	-0.39446700	-4.07566700	-2.45875300
C	2.95361100	-2.97748300	-0.81383900
H	1.83345600	-1.32333000	0.00483800
C	2.90046900	-4.12678100	-1.60593000
H	1.65190400	-5.41289400	-2.80943500
H	3.88423400	-2.66620300	-0.35090800
H	3.79548800	-4.72041000	-1.76199700
C	-2.20251400	-2.71713400	-0.44595600
C	-3.54351700	-2.55637300	-0.83798700
C	-1.87610200	-3.75569900	0.44645900
C	-4.53271600	-3.41708300	-0.35414800
H	-3.82550700	-1.76460600	-1.52476700
C	-2.86763200	-4.61426700	0.92758000
H	-0.84380700	-3.90494900	0.74892100
C	-4.19810700	-4.44650500	0.53015300
H	-5.56165100	-3.28745100	-0.67420800
H	-2.59857700	-5.42229600	1.60063300
H	-4.96608200	-5.11859200	0.89878600

TS$^{b}_{1\text{-}2}$: E(B3PW91) = -2160.7382041
Gas-phase zero-point energy = -2160.025984
Gas-phase free energy = -2160.100314

Rh	0.03295700	-0.71982900	0.37840500
C	-1.11933000	0.76265600	-2.55819400
H	-1.01804700	-0.22285300	-3.03187100
H	-1.95943100	1.25367200	-3.06419300
C	0.17491900	1.57072300	-2.74669600
H	0.14463500	2.49890100	-2.16215000
H	0.22745200	1.87669200	-3.79971500
C	1.46306700	0.79596200	-2.42509200
H	2.32737000	1.36452800	-2.78919600
H	1.45621800	-0.16725800	-2.95182800
H	2.60526100	-2.93281300	0.76788300
H	1.28197100	-1.61545000	1.08882100
H	0.89413700	-3.55081000	1.66373200
B	1.40593900	-2.98429100	0.71790200
N	0.82629200	-3.39867300	-0.62121900
C	1.78251300	-3.70153300	-1.68044700
H	2.26109700	-4.67944600	-1.52376600
H	1.28345600	-3.72520200	-2.65573300
H	2.56791000	-2.94683800	-1.70039900
C	-0.26543700	-4.35950800	-0.58743900
H	0.06970900	-5.34639100	-0.23591600
H	-1.05426600	-4.01050100	0.08265100
H	-0.69505400	-4.49105600	-1.58643400
P	1.71897500	0.45956100	-0.62889400
P	-1.61784000	0.42325300	-0.81365900
H	-0.60051100	-0.15383900	2.30144300
B	-1.29502800	-1.17635200	2.25398300
H	-2.45364400	-0.96544300	2.48925400
H	-1.27359800	-1.75560800	1.10380900
N	-0.72314400	-2.23333000	3.29831100
C	-1.65545800	-3.36862900	3.50557000
H	-1.20392800	-4.11052900	4.16704100
H	-2.57850700	-2.99036700	3.94443200

H	-1.87936700	-3.82419400	2.54186900
C	-0.34530800	-1.60622700	4.58737600
H	-1.22577000	-1.12782000	5.01798500
H	0.03438000	-2.36295600	5.27678000
H	0.41979100	-0.85282300	4.40593500
H	0.12337800	-2.62374900	2.86422300
H	0.24882700	-1.78068800	-0.76084400
C	-3.13871900	-0.56993200	-1.06391400
C	-3.00582200	-1.90742600	-1.47964000
C	-4.42462800	-0.02751600	-0.90560700
C	-4.13636400	-2.68366100	-1.73854000
H	-2.01699000	-2.34204600	-1.59363800
C	-5.55417200	-0.81205400	-1.15822700
H	-4.54912900	1.00096300	-0.58555500
C	-5.41364900	-2.13748800	-1.57533800
H	-4.02208800	-3.71276900	-2.06373000
H	-6.54285200	-0.38364800	-1.03039800
H	-6.29274900	-2.74208400	-1.77250200
C	-2.21979200	2.02617500	-0.16190700
C	-2.41072600	3.15248200	-0.98217400
C	-2.54523300	2.12265900	1.20448100
C	-2.90333800	4.34591200	-0.44632600
H	-2.18566700	3.11462600	-2.04156200
C	-3.04598800	3.31336100	1.73390100
H	-2.41719700	1.26295900	1.85322000
C	-3.22130100	4.43004200	0.91083600
H	-3.04153100	5.20627000	-1.09282700
H	-3.30098000	3.36790500	2.78737000
H	-3.60717000	5.35652500	1.32304700
C	3.40769000	-0.24593200	-0.55285900
C	4.10989200	-0.67701400	-1.69042400
C	4.03283500	-0.32827400	0.70476600
C	5.40957700	-1.18172200	-1.56972300
H	3.66220600	-0.62135900	-2.67675100
C	5.32964100	-0.82757000	0.82060400
H	3.50556000	0.00549100	1.59394900
C	6.02081000	-1.25785700	-0.31716200
H	5.94189800	-1.50887700	-2.45689800
H	5.80076200	-0.88178600	1.79643000
H	7.02933800	-1.64719000	-0.22653700
C	1.97131400	2.12874900	0.08869100
C	3.02884200	2.93550000	-0.37470100
C	1.13298100	2.61767700	1.10169100
C	3.22875900	4.20891800	0.15814000
H	3.70977200	2.56274600	-1.13442800
C	1.33866700	3.89364000	1.63637700
H	0.31947200	2.00342700	1.47309700
C	2.38290900	4.69050600	1.16405600
H	4.04728400	4.82201200	-0.20445100
H	0.68180000	4.26114400	2.41768100
H	2.54319500	5.68012800	1.57917200

(2[b]): E(B3PW91) = -2160.7382041
Gas-phase zero-point energy = -2160.064113
Gas-phase free energy = -2160.146078

Rh	0.07712100	0.53891900	-0.29401200
C	2.73539900	-1.10373500	-1.93241800
H	2.39138600	-0.67250800	-2.88022100
H	3.81868900	-1.24800000	-2.01705200
C	2.04366200	-2.45723900	-1.68845200
H	2.24248800	-2.79604100	-0.66354900

H	2.51382900	-3.19957600	-2.34671900
C	0.53472800	-2.47225300	-1.99300300
H	0.16537800	-3.50521900	-2.03577500
H	0.35869200	-2.04999000	-2.99177100
H	-4.25375200	1.66725400	2.05903700
H	-1.47201900	0.89625600	-0.32117600
H	-3.85466800	3.20223000	0.69074200
B	-4.62929000	2.50257500	1.28554800
N	-5.98280500	2.67612900	1.07338600
C	-7.00419200	1.88557600	1.74499000
H	-7.67206400	2.53165100	2.32577600
H	-7.61390900	1.34150900	1.01485300
H	-6.53532800	1.16801700	2.41687300
C	-6.53093800	3.66402500	0.15580400
H	-7.18428400	4.36486800	0.68753100
H	-5.72294700	4.22291100	-0.31459300
H	-7.12592800	3.17738000	-0.62523900
P	-0.59841400	-1.52769500	-0.87879300
P	2.41155800	0.11574600	-0.57951500
H	0.07560200	0.80193800	1.59813600
B	0.28125800	2.03203700	1.34642300
H	1.24219100	2.45241900	1.92701200
H	0.43168300	2.25718000	0.07610800
N	-1.00489800	2.84861100	1.80587800
C	-0.90013600	4.28381700	1.44009600
H	-1.79887300	4.81604700	1.75532500
H	-0.02370800	4.70579400	1.93220000
H	-0.78181100	4.36680500	0.36025800
C	-1.26417200	2.68047600	3.25728800
H	-0.40773500	3.06618600	3.81061000
H	-2.16750500	3.22237300	3.54119000
H	-1.38692800	1.62049600	3.47612500
H	-1.80367400	2.46043500	1.29826900
H	-0.00495700	0.67709900	-1.82435600
C	3.31459700	1.61761900	-1.11285300
C	3.13474800	2.11125600	-2.41879100
C	4.11368300	2.34763500	-0.21545600
C	3.76029000	3.29231900	-2.82286000
H	2.50189100	1.58324500	-3.12575500
C	4.73290900	3.53246000	-0.62306900
H	4.25930200	1.99058700	0.79851900
C	4.56210700	4.00531100	-1.92654000
H	3.62033900	3.65500400	-3.83607000
H	5.35266100	4.08174600	0.07837800
H	5.04889200	4.92220800	-2.24214300
C	3.40084900	-0.57860600	0.79569200
C	4.79289600	-0.75861600	0.67204000
C	2.76272400	-0.99721900	1.97424200
C	5.52431700	-1.33941700	1.70849900
H	5.30917000	-0.43164300	-0.22599300
C	3.49841800	-1.58152100	3.01045200
H	1.69053000	-0.86721100	2.07820400
C	4.87796100	-1.75202000	2.87937900
H	6.59667100	-1.46920500	1.60452500
H	2.99317700	-1.90155700	3.91591500
H	5.44955100	-2.20320100	3.68391400
C	-2.17616600	-1.67000000	-1.79803800
C	-2.86490400	-2.89774500	-1.81169600
C	-2.67252600	-0.59790700	-2.55712200
C	-4.02392600	-3.04674600	-2.57556400
H	-2.50786600	-3.73301600	-1.21650300
C	-3.83016200	-0.75442200	-3.32425000

H	-2.16305300	0.35939400	-2.53520300
C	-4.50645900	-1.97686700	-3.33552000
H	-4.54986400	-3.99583900	-2.57501900
H	-4.20469000	0.08049200	-3.90756700
H	-5.40701900	-2.09515200	-3.92920800
C	-0.85281100	-2.55400400	0.61261700
C	-0.17834400	-3.76500100	0.84156700
C	-1.77845500	-2.09567600	1.57096300
C	-0.42203500	-4.49963000	2.00662700
H	0.53435400	-4.14807900	0.11990400
C	-2.02251200	-2.83508400	2.72818100
H	-2.31388500	-1.16599200	1.40036000
C	-1.34152300	-4.03728300	2.95031400
H	0.10434000	-5.43408700	2.17120400
H	-2.74658200	-2.47871200	3.45378300
H	-1.53146900	-4.61190600	3.85086000

$TS^{b}_{2\text{-}3}$: E(B3PW91) = -2160.75984
Gas-phase zero-point energy = -2160.050244
Gas-phase free energy = - 2160.136032

Rh	-0.05777200	0.53992200	-0.21541500
C	2.52689500	-0.95257100	-2.13289000
H	2.15160400	-0.42468000	-3.01824400
H	3.61017300	-1.06025800	-2.26223800
C	1.87152300	-2.33914700	-2.02412200
H	2.13958800	-2.80810600	-1.06814200
H	2.30249100	-2.97885100	-2.80540500
C	0.34695700	-2.33233000	-2.21765300
H	-0.02883300	-3.35203800	-2.36815700
H	0.09105100	-1.78221000	-3.13300400
H	-3.78816800	2.20881200	2.26442000
H	-1.63471400	0.95729200	-0.21710300
H	-3.66383800	3.38598700	0.53605700
B	-4.30653600	2.75371100	1.32879200
N	-5.67335400	2.65509900	1.16172300
C	-6.53902400	1.91650100	2.06939300
H	-7.28982600	2.58045400	2.51226300
H	-7.06826100	1.11962600	1.53483000
H	-5.94636300	1.47231300	2.86794200
C	-6.39191900	3.28056800	0.06119600
H	-7.14227900	3.98366600	0.43963000
H	-5.69483700	3.82036800	-0.57840100
H	-6.91131300	2.52493600	-0.53887500
P	-0.65403400	-1.54838700	-0.87916300
P	2.23256500	0.12885000	-0.66017500
H	0.17708000	1.09021400	1.83913400
B	0.39296400	2.20245800	1.35228300
H	1.44671200	2.67740100	1.67753500
H	0.39229400	2.23633600	0.05814700
N	-0.77277600	3.19787000	1.80303500
C	-0.64607500	4.53063000	1.16298200
H	-1.45985100	5.18311300	1.48447900
H	0.31384700	4.96104200	1.44830400
H	-0.67576500	4.40916800	0.08093700
C	-0.82315200	3.31867500	3.28132000
H	0.12944100	3.71879900	3.62876300
H	-1.63718300	3.98261400	3.57765100
H	-0.97491100	2.33057200	3.71342100
H	-1.66401300	2.79885100	1.50182600
H	-1.16667600	1.03376900	-1.21541400
C	-0.60640400	-2.70870800	0.53596700
C	-0.16304500	-4.03814100	0.42652700

C	-1.05177200	-2.24136600	1.78762400
C	-0.16045800	-4.87721400	1.54456100
H	0.17968300	-4.43213700	-0.52378000
C	-1.05727700	-3.08527300	2.89968100
H	-1.39608700	-1.21505000	1.88417300
C	-0.60762500	-4.40414300	2.78077300
H	0.18807100	-5.90009900	1.44693900
H	-1.41051900	-2.71506000	3.85679800
H	-0.60792400	-5.05956100	3.64550100
C	-2.34370300	-1.71903500	-1.57805600
C	-2.70948300	-0.91644700	-2.67495400
C	-3.26479700	-2.65550500	-1.08195100
C	-3.96642900	-1.05346800	-3.26498500
H	-2.01431300	-0.17860900	-3.06819700
C	-4.52709700	-2.78313800	-1.67094500
H	-3.00299100	-3.28482400	-0.23844900
C	-4.87935900	-1.98682800	-2.76218100
H	-4.23369400	-0.43224300	-4.11374900
H	-5.23078800	-3.50903000	-1.27663000
H	-5.85752900	-2.09156800	-3.21997100
C	3.09855500	1.67738400	-1.12086000
C	2.71562700	2.33781100	-2.30407700
C	4.08391000	2.25787400	-0.30569600
C	3.32547300	3.53713000	-2.67491100
H	1.93007900	1.92494200	-2.93096600
C	4.68623100	3.46379900	-0.67772500
H	4.38306200	1.77386000	0.61728600
C	4.31410500	4.10253700	-1.86250900
H	3.02852800	4.03027600	-3.59500000
H	5.44894500	3.89990400	-0.04064500
H	4.78846300	5.03465100	-2.15156500
C	3.27958500	-0.66025600	0.61727000
C	4.64292800	-0.92789700	0.38156600
C	2.71352800	-1.04632800	1.84286000
C	5.41614100	-1.56453800	1.35288800
H	5.10833700	-0.62647300	-0.55231900
C	3.49060500	-1.68615000	2.81358400
H	1.66429900	-0.84922700	2.03580100
C	4.84055600	-1.94579700	2.57019800
H	6.46589700	-1.76219600	1.16181100
H	3.03956000	-1.98169900	3.75508700
H	5.44404500	-2.44189600	3.32333100

(3^b): E(B3PW91) = -2160. 769242
Gas-phase zero-point energy = -2160.049256
Gas-phase free energy = -2160.134505

Rh	-0.10031200	0.47367900	-0.18621300
C	2.51951400	-0.85160700	-2.11733300
H	2.11264400	-0.30143400	-2.97577000
H	3.60549200	-0.87817800	-2.26522800
C	1.93784100	-2.27270800	-2.08142900
H	2.21728600	-2.78290800	-1.15027100
H	2.39982300	-2.84832900	-2.89415600
C	0.41593200	-2.31918600	-2.27542000
H	0.08809300	-3.34777000	-2.46581500
H	0.13293200	-1.73374900	-3.15944000
H	-3.75336900	2.27232100	2.13945600
H	-1.76489600	0.64499100	0.19803200
H	-3.94254500	3.23800600	0.28982500
B	-4.42999100	2.68043000	1.23449500
N	-5.79769200	2.50355300	1.28507800

C	-6.47925600	1.84257900	2.38884200
H	-7.19928100	2.52150800	2.85897600
H	-7.02853600	0.96428400	2.03174600
H	-5.75370600	1.52503300	3.13649600
C	-6.70211800	2.96026300	0.23959400
H	-7.43020100	3.67249000	0.64342400
H	-6.13663800	3.44584100	-0.55456600
H	-7.25685500	2.11621700	-0.18518100
P	-0.56021300	-1.65474800	-0.85451600
P	2.16576000	0.19778900	-0.63832900
H	0.08770500	1.46408900	1.89692700
B	0.25232400	2.43201600	1.17517700
H	1.29155200	3.00839300	1.35645400
H	0.21731400	2.21662800	-0.09386500
N	-0.94000800	3.46931700	1.44378300
C	-0.89926400	4.62994300	0.52048300
H	-1.71652200	5.31923100	0.74105100
H	0.05904900	5.13450800	0.64377600
H	-0.98393800	4.27186700	-0.50461700
C	-0.93053200	3.91648000	2.85909800
H	0.01878900	4.41350000	3.05856400
H	-1.75759600	4.60495700	3.04324600
H	-1.02121900	3.04541200	3.50634600
H	-1.83034800	2.99205600	1.29209500
H	-1.67585000	0.87240100	-0.63717700
C	-0.35726800	-2.91539000	0.45689800
C	-0.39781800	-4.29612600	0.18317400
C	-0.16654100	-2.48965100	1.78249700
C	-0.24758800	-5.22464200	1.21470000
H	-0.55934400	-4.65478100	-0.82865300
C	-0.02080100	-3.42176600	2.81355100
H	-0.12603400	-1.42461500	1.99549500
C	-0.05889100	-4.78904900	2.53069500
H	-0.27995100	-6.28627600	0.99243600
H	0.12735800	-3.08055700	3.83281000
H	0.05753100	-5.51364100	3.32999900
C	-2.28094100	-1.86119900	-1.46293900
C	-2.67097300	-1.17079800	-2.62704400
C	-3.22507300	-2.65677600	-0.79442100
C	-3.97164000	-1.29022300	-3.11880500
H	-1.96191600	-0.53158600	-3.14714600
C	-4.52965200	-2.76748700	-1.28737000
H	-2.94632100	-3.19191600	0.10685300
C	-4.90422800	-2.09006400	-2.44939900
H	-4.25690000	-0.76034100	-4.02197700
H	-5.24902600	-3.38833800	-0.76315700
H	-5.91493900	-2.18360400	-2.83298000
C	3.18697400	-0.50932600	0.70650600
C	4.29371200	-1.34198200	0.45823100
C	2.87592000	-0.17584700	2.03735100
C	5.06508800	-1.82972300	1.51628800
H	4.56835300	-1.61447100	-0.55469300
C	3.65547600	-0.65657500	3.09128300
H	2.02656600	0.46618800	2.24528200
C	4.74919500	-1.48760800	2.83364100
H	5.91355000	-2.47368900	1.30925500
H	3.40709600	-0.38436500	4.11205000
H	5.35188100	-1.86568800	3.65287800
C	3.00884400	1.75490100	-1.11692000
C	2.42808400	2.54372800	-2.12778400
C	4.22081600	2.16505500	-0.53988800
C	3.05598900	3.71235000	-2.56010700

H	1.47929800	2.24760400	-2.56885500
C	4.84109300	3.34275300	-0.97022700
H	4.68116200	1.57398000	0.24446300
C	4.26390400	4.11536000	-1.97991700
H	2.60403600	4.30885200	-3.34632100
H	5.77636700	3.65230400	-0.51523500
H	4.75033300	5.02601100	-2.31392900

$TS^{b}_{3\text{-}4}$: E(B3PW91) = -2160.7451429
Gas-phase zero-point energy = -2160.036310
Gas-phase free energy = -2160.120172

Rh	0.04056300	0.02708900	0.05880100
C	-2.31644500	-1.08649200	-2.23878300
H	-1.55371300	-1.14091300	-3.02681900
H	-3.01824200	-1.90378100	-2.44541900
C	-3.03131400	0.27186400	-2.30046000
H	-3.74744100	0.37149700	-1.47384000
H	-3.62619900	0.30081100	-3.22259200
C	-2.07179100	1.47422200	-2.31542900
H	-2.61754400	2.39113600	-2.56713800
H	-1.30391100	1.32817500	-3.08470800
H	0.38448700	1.28632300	2.11495400
P	-1.23590600	1.72547400	-0.68943800
P	-1.41904600	-1.47493100	-0.66851300
H	2.03452300	0.57762500	-0.05434800
B	2.23443600	-0.64314700	0.06131500
H	1.18372200	-1.28463100	0.47868100
H	2.68079500	-1.16979500	-0.91912200
N	3.30076900	-0.88312500	1.23710500
C	3.53211600	-2.33194400	1.47032700
H	4.34266500	-2.47279600	2.18728800
H	2.61361100	-2.77434500	1.85687000
H	3.78322200	-2.80554700	0.52259400
C	3.01643100	-0.17552400	2.50647200
H	2.07857600	-0.55100800	2.91519800
H	3.82532300	-0.34476800	3.21937800
H	2.91842600	0.89024300	2.30467800
H	4.18076400	-0.50430700	0.87525000
H	-0.13536200	0.74681400	1.92490500
C	-2.58481700	2.39613600	0.34925700
C	-3.22538900	3.60280400	0.00284600
C	-3.02283700	1.69181500	1.48168000
C	-4.27661000	4.09036000	0.77990300
H	-2.89425600	4.17116300	-0.86169200
C	-4.07887500	2.18260200	2.25615800
H	-2.54407000	0.75627600	1.74918800
C	-4.70499600	3.38066300	1.90772800
H	-4.75994300	5.02306600	0.50794100
H	-4.40998900	1.62703400	3.12725900
H	-5.52296500	3.76275900	2.50973900
C	-0.08942200	3.12825700	-0.95289900
C	0.73194700	3.15939600	-2.09612800
C	0.06305800	4.13015000	0.02337600
C	1.66684100	4.18145900	-2.26762400
H	0.65382300	2.38369200	-2.85137000
C	1.00460100	5.14771600	-0.15069600
H	-0.56055500	4.12301700	0.91150800
C	1.80520700	5.17755900	-1.29581200
H	2.28619400	4.19979200	-3.15844400
H	1.10694300	5.91931000	0.60551400
H	2.53133700	5.97235600	-1.43139700

C	-2.72354900	-1.93087100	0.54257100
C	-4.05829500	-2.18660500	0.18512500
C	-2.35328400	-2.04789000	1.89622600
C	-4.99757400	-2.54619200	1.15713200
H	-4.38086600	-2.11225300	-0.84735000
C	-3.28867000	-2.42024400	2.86297200
H	-1.32652400	-1.84018300	2.18611500
C	-4.61585800	-2.66653200	2.49507600
H	-6.02551900	-2.73517100	0.86525500
H	-2.98511900	-2.51442400	3.90077700
H	-5.34580600	-2.95044900	3.24598800
C	-0.65808400	-3.08555200	-1.12123200
C	0.42716300	-3.07919000	-2.01731700
C	-1.14731300	-4.31441000	-0.64833200
C	0.99994100	-4.27849600	-2.44272000
H	0.83269400	-2.13305200	-2.36496100
C	-0.56241000	-5.51339200	-1.06911900
H	-1.98253800	-4.34041700	0.04302200
C	0.50665000	-5.49875300	-1.96767800
H	1.83155300	-4.26137100	-3.13999200
H	-0.94817500	-6.45714700	-0.69722500
H	0.95390900	-6.43124700	-2.29638800
B	6.75763000	-0.13014700	1.02341000
H	6.43843700	-0.53177900	2.10689400
H	5.94272700	0.07461800	0.16165900
N	8.08858200	0.10500100	0.74686400
C	8.56685200	0.59212300	-0.53908000
H	9.26738200	-0.12246000	-0.98532400
H	7.72714500	0.73394500	-1.21819200
H	9.09106600	1.54663800	-0.41833100
C	9.15452300	-0.10829500	1.71578800
H	8.73663600	-0.47179200	2.65351900
H	9.87518600	-0.84297900	1.33988800
H	9.69395800	0.82602000	1.90646000

(4[b]): E(B3PW91) = -2160.7563816
Gas-phase zero-point energy = -2160.049869
Gas-phase free energy = -2160.142706

Rh	-0.01558800	-0.41841800	-0.39763900
C	-3.12502200	0.06838300	-1.90543300
H	-2.71753700	-0.33468800	-2.84235800
H	-4.17905600	-0.23426000	-1.87951300
C	-2.99547600	1.60002300	-1.89888100
H	-3.32464100	2.01207000	-0.93595800
H	-3.68417700	2.00136800	-2.65381600
C	-1.58133100	2.10409300	-2.22946900
H	-1.59631900	3.18504900	-2.41131200
H	-1.22047200	1.63393000	-3.15345400
H	2.83184800	3.91544400	4.88456600
P	-0.33464200	1.74227800	-0.91279500
P	-2.22022800	-0.81755400	-0.55998800
H	1.80656000	-0.39867600	-0.30602600
B	1.75441900	-1.68632500	-0.23236500
H	0.54642500	-2.10838700	-0.03129200
H	2.26261000	-2.21221900	-1.18276300
N	2.58752400	-2.10482000	1.06360300
C	2.56998700	-3.58024600	1.24827000
H	3.21278800	-3.85929500	2.08436300
H	1.54522800	-3.89555200	1.44648200
H	2.92091900	-4.05513800	0.33326700
C	2.19852300	-1.40026600	2.30943000

H	1.16731000	-1.66018100	2.54803400
H	2.85833900	-1.69610800	3.12720100
H	2.26343200	-0.32610900	2.14370800
H	3.55995200	-1.85005900	0.86279600
H	2.22990700	3.89958200	4.44517100
C	-0.81317700	2.85177200	0.45992700
C	-1.16295100	4.19916900	0.24614400
C	-0.83000200	2.34332600	1.76931000
C	-1.52002200	5.01420800	1.32189400
H	-1.14609000	4.62206700	-0.75379700
C	-1.18628300	3.16224900	2.84459500
H	-0.57567000	1.29923200	1.92845300
C	-1.53176200	4.49746300	2.62210500
H	-1.78724400	6.05117100	1.14636400
H	-1.20243200	2.75634300	3.85075800
H	-1.81129400	5.13362200	3.45558100
C	1.20664900	2.44778800	-1.61221100
C	1.72067900	1.88624500	-2.79728300
C	1.90576800	3.49792700	-0.99491300
C	2.89627000	2.38220300	-3.36196900
H	1.21144600	1.05062300	-3.26999800
C	3.08754200	3.98618200	-1.56104000
H	1.53081800	3.93791100	-0.07736500
C	3.58187300	3.43435600	-2.74501300
H	3.27869000	1.94641800	-4.27934600
H	3.61734700	4.80021100	-1.07685800
H	4.49622200	3.81907000	-3.18484200
C	-3.20123100	-0.54562800	0.96243000
C	-4.48214100	0.03208500	0.96509000
C	-2.64455100	-0.96226100	2.18674100
C	-5.18583000	0.19114700	2.16312100
H	-4.94481000	0.36016100	0.04093200
C	-3.35389400	-0.81500000	3.37910800
H	-1.65155800	-1.40340900	2.19627900
C	-4.62602400	-0.23322500	3.36991900
H	-6.17257600	0.64238200	2.14977700
H	-2.91631400	-1.15022600	4.31412800
H	-5.17682600	-0.11319000	4.29700500
C	-2.53623600	-2.56898400	-1.00734400
C	-1.70912200	-3.17473100	-1.97160200
C	-3.60371600	-3.30147400	-0.46105800
C	-1.95305800	-4.48491300	-2.38775200
H	-0.86871700	-2.62166600	-2.38407900
C	-3.83880700	-4.61551500	-0.87626000
H	-4.24690900	-2.85295100	0.28886200
C	-3.01771900	-5.20758600	-1.83947200
H	-1.31201400	-4.94170700	-3.13490700
H	-4.66419000	-5.17430100	-0.44714100
H	-3.20488900	-6.22713900	-2.16039300
B	6.09387500	-1.82118300	1.25401500
H	5.62939300	-2.23747400	2.27777300
H	5.39300500	-1.48598300	0.33409200
N	7.46196300	-1.71925400	1.11298700
C	8.10973600	-1.22764900	-0.09465800
H	8.76988600	-1.99358600	-0.51646500
H	7.35860400	-0.96160300	-0.83726500
H	8.71806000	-0.34390700	0.12739200
C	8.40169800	-2.09552600	2.16005700
H	7.86002300	-2.45464000	3.03394900
H	9.07284500	-2.88695400	1.80861700
H	9.01650500	-1.23692200	2.45182000

2^{c}+A: E(B3PW91) = -2200.0552312
Gas-phase zero-point energy = -2199.307741
Gas-phase free energy = -2199.392651

Rh	0.25463900	-0.17007800	0.21969200
P	0.07693500	2.04394300	-0.11636500
P	2.49977100	-0.30507900	0.12836700
B	-1.26037500	-1.64620200	0.73917700
N	-2.19347700	-2.46993800	-0.24752900
H	-0.03176600	-1.94878100	0.43538300
H	-1.53012200	-1.95607800	1.86534500
H	-1.50720400	-0.38660300	0.52348300
C	-1.97760600	-3.93012600	-0.08159500
H	-0.96317800	-4.17436400	-0.39875100
H	-2.09879700	-4.18963500	0.96922900
H	-2.69938300	-4.48071600	-0.68628300
C	-2.09988300	-2.07202200	-1.67369400
H	-1.08269000	-2.25703400	-2.01883000
H	-2.31778500	-1.00918200	-1.76125600
H	-2.81360400	-2.64929300	-2.26391800
H	-3.16095300	-2.28541700	0.05670900
B	-5.47692100	-2.20391500	-0.12188400
N	-6.94910900	-2.39955400	0.50969200
H	-4.75471500	-1.87016100	0.80637200
H	-5.15504600	-3.27801600	-0.59367700
H	-5.55715700	-1.33466700	-0.96023300
H	-7.20989700	-1.49538300	0.89972600
C	-6.96795700	-3.38184500	1.61794200
C	-7.95219700	-2.73834200	-0.52740800
H	-6.25793500	-3.06658600	2.38126400
H	-7.96933200	-3.46221200	2.04744000
H	-6.65869600	-4.34955100	1.22266700
H	-8.94878900	-2.82175300	-0.08765300
H	-7.66816300	-3.68775800	-0.98136800
H	-7.94206100	-1.96437500	-1.29319800
H	4.36287200	2.91625300	-0.66711500
C	3.59879800	1.17570600	0.32467200
H	3.17438800	1.77823100	1.13756600
H	2.02257200	1.60298700	-2.12750400
H	2.73962900	3.17383200	-2.43292100
C	1.47096600	3.13727500	-0.67295800
C	2.47878200	2.47087300	-1.63153200
H	4.57914500	0.82631100	0.67199500
H	1.01991800	4.02888500	-1.12491700
H	4.38670800	1.47014300	-1.66798800
C	3.77943000	2.02720800	-0.94422400
H	1.97347600	3.48510900	0.23781400
C	-0.54615100	2.93457100	1.35796300
C	-1.04748100	4.24585800	1.25890600
C	-0.47481500	2.31895100	2.61916100
C	-1.46067500	4.92810600	2.40439300
H	-1.12644600	4.72952600	0.28954300
C	-0.89195400	3.00579900	3.76357300
H	-0.10084600	1.30011500	2.68983600
C	-1.38202100	4.30985200	3.65736600
H	-1.84589300	5.93917700	2.32026400
H	-0.83659800	2.52190600	4.73340400
H	-1.70523100	4.84305400	4.54560500
C	-1.22144400	2.32610000	-1.38673900
C	-0.90450400	2.67586300	-2.71098300
C	-2.57245700	2.12825500	-1.04287700
C	-1.91417300	2.82448700	-3.66689800

H	0.12617900	2.83775600	-3.00819100
C	-3.57798500	2.28097900	-1.99910100
H	-2.83836100	1.86966800	-0.02202600
C	-3.25126700	2.62679400	-3.31479600
H	-1.65380800	3.10039800	-4.68377000
H	-4.61548300	2.13565400	-1.71588900
H	-4.03341400	2.74732200	-4.05716400
C	3.00607600	-1.36378500	1.53933300
C	3.20616000	-0.79351000	2.81025700
C	3.12322800	-2.75736400	1.39352600
C	3.52918500	-1.59819400	3.90476700
H	3.10679900	0.27800200	2.95410900
C	3.44363700	-3.55872500	2.49190000
H	2.97510000	-3.21575800	0.42071400
C	3.64821300	-2.98216700	3.74865500
H	3.68727200	-1.14427700	4.87776100
H	3.53895400	-4.63232400	2.36416700
H	3.90004800	-3.60621300	4.59981200
C	3.18622400	-1.14238500	-1.34888700
C	2.36579800	-1.35282200	-2.46959300
C	4.53347600	-1.54703600	-1.40066000
C	2.87996100	-1.95666400	-3.62126700
H	1.32663300	-1.03539100	-2.42590200
C	5.04386600	-2.14923900	-2.55215900
H	5.18079400	-1.40476200	-0.54019500
C	4.21836200	-2.35473800	-3.66331600
H	2.23844000	-2.11389600	-4.48256500
H	6.08335700	-2.45934700	-2.58263700
H	4.61873200	-2.82349700	-4.55638400

$TS^{c}_{1\text{-}2}$: E(B3PW91) = -2200.0158243
Gas-phase zero-point energy = -2199.274962
Gas-phase free energy = -2199.352092

Rh	0.09862000	-0.69312700	0.34151100
P	1.86553300	0.34923000	-0.70986600
P	-1.62036300	0.65399900	-0.47519400
B	1.08321200	-3.15875400	0.10407900
N	0.22015300	-3.24209800	-1.14045400
H	0.64975500	-3.78632100	1.04938100
H	2.26168500	-3.29714700	-0.08507300
H	1.27688500	-1.86404700	0.67975000
C	-1.08149300	-3.88450800	-1.01628500
C	0.88861300	-3.61774000	-2.38008000
H	0.27319500	-3.35651800	-3.24790700
H	1.85000000	-3.10970800	-2.45860900
H	1.08362800	-4.69956400	-2.42090600
H	-0.98464600	-4.96958600	-0.86766700
H	-1.62688300	-3.46557300	-0.16898500
H	-1.68074600	-3.71542900	-1.91616400
H	-0.02009300	-1.58221200	-0.95553800
B	-0.86225200	-1.20768100	2.40663200
N	-0.25158900	-2.46372300	3.17105700
H	-1.18872600	-1.62652500	1.22930600
H	-0.02020000	-0.29975600	2.38484700
H	-1.88505300	-0.87413600	2.93957400
C	0.48358500	-2.07224300	4.39763000
H	1.29996400	-1.40557200	4.12413700
H	-0.20033700	-1.54916300	5.06699800
H	0.88029600	-2.95833500	4.89710200
C	-1.28237800	-3.49012000	3.46199600
H	-1.76542300	-3.78043800	2.52961800

H	-0.82264000	-4.36585700	3.92393100
H	-2.02578000	-3.06140200	4.13384900
H	0.41248500	-2.89390400	2.51608600
C	-1.20304700	1.60670300	-2.00231400
H	-2.12858700	2.07191000	-2.36191900
H	-0.56196500	2.43120700	-1.66682300
C	-0.51599700	0.81826500	-3.14695500
H	-1.03760400	1.06755900	-4.07965100
H	-0.63919900	-0.26481800	-3.01203400
C	0.97975500	1.12292400	-3.34824500
H	1.17607500	2.18251200	-3.14012700
H	1.22392700	0.97367700	-4.40838600
C	1.95692000	0.24021500	-2.55418200
H	2.98406100	0.48764300	-2.85069000
H	1.78851600	-0.81153100	-2.81583400
C	-2.42001700	1.92572500	0.58713600
C	-3.50399900	2.66723100	0.07723000
C	-1.99614500	2.16579800	1.90333000
C	-4.12826400	3.63907100	0.85945600
H	-3.88011900	2.47414400	-0.92297400
C	-2.62710000	3.13749400	2.68722700
H	-1.18762000	1.58120000	2.32778400
C	-3.68889600	3.87872400	2.16585000
H	-4.96155900	4.20281400	0.45313500
H	-2.29187600	3.30772400	3.70532400
H	-4.17857400	4.63188100	2.77431900
C	-3.07041900	-0.37591800	-0.94854200
C	-3.46136500	-0.58204600	-2.28212900
C	-3.83492600	-0.96173900	0.07871800
C	-4.58007600	-1.36785300	-2.58062100
H	-2.91230700	-0.12880400	-3.09867800
C	-4.95264900	-1.74041600	-0.22268100
H	-3.56745900	-0.79238300	1.11716200
C	-5.32506400	-1.95144400	-1.55462900
H	-4.87104700	-1.51345600	-3.61596700
H	-5.53859200	-2.17456300	0.58109500
H	-6.19472200	-2.55649000	-1.78857300
C	2.10038200	2.13766700	-0.37115300
C	3.15924600	2.83023800	-0.99091800
C	1.26971300	2.82805300	0.52202800
C	3.36149200	4.18621100	-0.73238900
H	3.83798100	2.31164500	-1.66112800
C	1.47587700	4.18686600	0.78307400
H	0.45960300	2.30393900	1.01468300
C	2.51892900	4.86797000	0.15336400
H	4.17940900	4.70973500	-1.21640500
H	0.82063600	4.70630300	1.47446200
H	2.68045100	5.92211300	0.35304500
C	3.47859300	-0.33251400	-0.16162300
C	4.22878300	-1.22535600	-0.94355100
C	3.96323500	0.03569800	1.10746500
C	5.44191900	-1.73404600	-0.46814600
H	3.88187600	-1.53145300	-1.92452700
C	5.17235600	-0.47628200	1.57887500
H	3.40435700	0.73858100	1.71875000
C	5.91485000	-1.36307300	0.79171200
H	6.01402400	-2.41940300	-1.08481900
H	5.54087800	-0.17545900	2.55434700
H	6.85738800	-1.75715100	1.15694200

(2^c): E(B3PW91) = -2200.0570772
Gas-phase zero-point energy = -2199.314994

Gas-phase free energy = -2199.400296

Rh	-0.00081800	-0.44821900	-0.33339500
P	0.53956500	1.74286300	-0.61470000
P	-2.40280700	-0.21051300	-0.27845500
H	1.55363900	-0.66387400	-0.53084900
H	0.00608000	-0.30465400	-1.86259400
B	0.10263900	-2.20746300	1.01926800
N	1.52094200	-2.89649500	1.21768700
H	-0.73084600	-2.85837600	1.58073200
H	-0.16519700	-2.22191700	-0.26226100
H	0.14999600	-1.02000800	1.47686700
C	1.55662900	-4.25522500	0.61892300
H	1.33324300	-4.17878100	-0.44478100
H	0.79752000	-4.86906100	1.10409300
H	2.54377000	-4.69708500	0.75853700
C	1.91084100	-2.92708000	2.65034900
H	1.16707900	-3.50289200	3.20139100
H	2.89504000	-3.38457100	2.75772200
H	1.93333100	-1.90741700	3.03378900
B	5.27826200	-2.98233000	0.62342100
N	6.59680300	-2.72850400	0.29981100
H	4.44234500	-2.16705200	0.33963700
H	4.99683800	-4.00612400	1.17917400
C	7.03757700	-1.51628700	-0.37323400
H	6.18461100	-0.86725200	-0.56657900
H	7.52344200	-1.75875700	-1.32541600
H	7.76300700	-0.97452600	0.24459700
C	7.68316600	-3.65098300	0.59668700
H	8.18817100	-3.96216800	-0.32472000
H	8.42809900	-3.17499000	1.24430300
H	7.29244000	-4.53444000	1.09955100
H	2.20574100	-2.32258400	0.72046800
C	-1.65739100	3.13046900	-2.00717000
H	0.45382900	3.49731600	-2.25422700
H	-1.78325500	3.82251300	-1.16385800
H	-1.80215100	3.73528500	-2.91304000
H	-0.07560100	1.96247700	-2.92328600
C	-0.20202200	2.63700600	-2.06696700
C	-2.77065800	2.07174100	-1.96730300
H	-2.55376700	1.27211700	-2.68881200
H	-3.68809300	2.54961800	-2.33249000
C	-3.07880300	1.49005600	-0.56786700
H	-4.16225100	1.43908600	-0.40611800
H	-2.67594400	2.15164000	0.20845200
C	-3.28740500	-1.20156700	-1.54352800
C	-4.69465800	-1.26357500	-1.54608900
C	-2.57651600	-1.87931100	-2.54755800
C	-5.36896700	-1.98403900	-2.53227100
H	-5.26484100	-0.76291000	-0.76900900
C	-3.25548600	-2.60102400	-3.53528600
H	-1.49181500	-1.84245200	-2.55509700
C	-4.65052800	-2.65344600	-3.52949700
H	-6.45329800	-2.02586600	-2.52240000
H	-2.69375800	-3.11986100	-4.30536800
H	-5.17772100	-3.21346200	-4.29495700
C	-3.21583100	-0.70919800	1.28984700
C	-3.44373300	0.22099500	2.32036000
C	-3.56424600	-2.05584100	1.50508500
C	-4.01252500	-0.18561000	3.53058900
H	-3.18724000	1.26675000	2.18699900
C	-4.13111900	-2.45771800	2.71650800

H	-3.40622400	-2.78866500	0.72020300
C	-4.35680300	-1.52456700	3.73242500
H	-4.19439500	0.54647300	4.31109800
H	-4.40272300	-3.49821500	2.86305000
H	-4.80298100	-1.83716000	4.67082300
C	2.32681600	2.00411000	-0.94888300
C	2.86849900	1.50555100	-2.14853200
C	3.16489600	2.68738800	-0.05392400
C	4.21367600	1.71105900	-2.45581300
H	2.24614300	0.94207700	-2.83763900
C	4.51622400	2.88038500	-0.36083300
H	2.77090900	3.07315100	0.87976800
C	5.04123600	2.40156200	-1.56253000
H	4.61585700	1.33227200	-3.38992400
H	5.15308300	3.41169300	0.33904300
H	6.08648000	2.56473600	-1.80434300
C	0.17900100	2.80837100	0.82939300
C	0.26441700	4.21115800	0.72782600
C	-0.17507300	2.23736400	2.06282600
C	-0.00329400	5.01774900	1.83540000
H	0.55210200	4.67807500	-0.20890600
C	-0.43915000	3.04815000	3.17140600
H	-0.24775300	1.15783700	2.15442400
C	-0.35579900	4.43791500	3.05873500
H	0.06568500	6.09674600	1.74429100
H	-0.70803200	2.59314900	4.11915400
H	-0.56167400	5.06733400	3.91821800

$TS^{c}_{2\text{-}3}$: E(B3PW91) = -2200.0420139
Gas-phase zero-point energy = -2199.303364
Gas-phase free energy = -2199.388808

Rh	0.03274100	-0.39904600	-0.25300000
P	0.48645400	1.82653200	-0.45163400
P	-2.33325400	-0.11466400	-0.18682900
H	4.21093800	-2.17423200	0.25658900
H	1.61417800	-0.66696800	-0.53769900
H	4.68449000	-4.16598500	0.70588200
B	5.01419400	-3.05929400	0.38658900
N	6.34923300	-2.78829400	0.16090800
C	6.84673600	-1.47833400	-0.23111500
H	7.56069100	-1.09985100	0.50938500
H	7.36341600	-1.53553900	-1.19600900
H	6.01880600	-0.77572100	-0.31558300
C	7.39961400	-3.78789700	0.29268400
H	8.13012700	-3.48218900	1.05005800
H	6.96760400	-4.74373000	0.58556300
H	7.93199500	-3.91540400	-0.65655400
H	0.10156800	-1.45391400	1.59923100
B	-0.01433700	-2.43452000	0.85982800
H	-0.91199000	-3.16292400	1.17853200
H	-0.26719200	-2.14162300	-0.38505600
N	1.34224800	-3.27732500	0.88099000
C	1.31463100	-4.41080100	-0.07655800
H	2.25399800	-4.96387300	-0.03262600
H	0.48184200	-5.06324600	0.18618200
H	1.16117100	-4.02230700	-1.08284300
C	1.63720700	-3.74793100	2.25853100
H	0.81695700	-4.38475100	2.58973000
H	2.57513700	-4.30487700	2.27108900
H	1.70752600	-2.88473100	2.91918800
H	2.10819100	-2.66103700	0.60319200

H	1.03517100	-0.51010300	-1.46420600
H	-4.15769700	1.41640800	0.11403000
H	-2.66954800	2.11505900	0.73953700
C	-1.78612600	3.41362000	-1.42630600
H	-1.75379100	3.97847900	-0.48551400
H	-1.99289500	4.15306800	-2.21235400
C	-0.39428200	2.84010000	-1.74232400
H	0.28137700	3.67139500	-1.98267500
H	-0.44992200	2.21091200	-2.63992200
C	-3.09749800	1.57872100	-0.11640700
C	-2.96629700	2.43421400	-1.39354900
H	-3.88331400	3.03238000	-1.47372400
H	-2.95241400	1.79788700	-2.28839000
C	2.23994500	2.12522500	-0.92099400
C	2.63326100	1.97813400	-2.26436200
C	3.20860700	2.45798700	0.03944000
C	3.96369300	2.17490500	-2.63815800
H	1.90597100	1.70922800	-3.02530500
C	4.54101400	2.65257300	-0.33895100
H	2.92585700	2.57589800	1.08010000
C	4.92081100	2.51512500	-1.67627400
H	4.25148600	2.06800100	-3.67908500
H	5.27745000	2.92042200	0.41191100
H	5.95292600	2.67687800	-1.96969400
C	0.28998500	2.76272500	1.10850900
C	0.44946200	4.16145100	1.14410500
C	0.00129800	2.07855600	2.30078100
C	0.31051500	4.85639000	2.34675300
H	0.69499800	4.70827700	0.23861300
C	-0.13463700	2.77739200	3.50474100
H	-0.10645500	0.99692500	2.28486000
C	0.01605100	4.16598200	3.52781900
H	0.43470300	5.93419000	2.36356500
H	-0.35223700	2.23766300	4.42073400
H	-0.08969500	4.70923800	4.46110000
C	-3.15789200	-0.93985500	1.23116300
C	-3.28431200	-0.26659800	2.46078900
C	-3.62325600	-2.26305100	1.13357000
C	-3.87437400	-0.89762400	3.55838900
H	-2.92933800	0.75355900	2.57066600
C	-4.21348100	-2.88999000	2.23403200
H	-3.53436600	-2.80253700	0.19657300
C	-4.34200000	-2.21004300	3.44764100
H	-3.97464500	-0.36126500	4.49663100
H	-4.57586500	-3.90862500	2.13979100
H	-4.80515900	-2.69699000	4.29952500
C	-3.13972400	-0.84011900	-1.66448900
C	-2.36390400	-1.22828400	-2.76884200
C	-4.54101500	-0.95916900	-1.73764900
C	-2.97389600	-1.73198300	-3.92237100
H	-1.28314500	-1.12997300	-2.71447600
C	-5.14627800	-1.46229200	-2.89013500
H	-5.15994500	-0.67402500	-0.89209700
C	-4.36405300	-1.85015600	-3.98384600
H	-2.36390400	-2.03050300	-4.76892500
H	-6.22669700	-1.55340400	-2.93482500
H	-4.83818800	-2.24193600	-4.87782700

(3^{c}): E(B3PW91) = 2200. 050137
Gas-phase zero-point energy = -2199.292685
Gas-phase free energy = -2199.378769

Rh	-0.16603600	0.53817700	-0.36058600
P	-0.60285800	-1.64658900	-0.92614800
P	2.19527400	0.44918200	-0.60009200
H	-4.33731100	2.30955900	1.80080000
H	-1.84161200	0.73137100	-0.27734300
H	-4.10982700	2.77477100	-0.22897300
B	-4.79964600	2.46566300	0.70396500
N	-6.15503800	2.29044600	0.51087200
C	-7.07352800	1.91943200	1.57739800
H	-7.84981200	2.68263600	1.70165500
H	-7.56996500	0.97027900	1.34594100
H	-6.53017400	1.81416700	2.51553300
C	-6.80680700	2.45423700	-0.78044400
H	-7.57752000	3.23120200	-0.72801900
H	-6.07241700	2.73650100	-1.53363000
H	-7.28996000	1.52047700	-1.08927600
H	-0.14490700	1.41009500	1.72888500
B	-0.04424500	2.43324800	1.06989800
H	0.91488800	3.10476200	1.34228700
H	0.04535700	2.28225100	-0.21405800
N	-1.34939500	3.33258500	1.29918500
C	-1.35737000	4.54521300	0.44428000
H	-2.25277600	5.13874600	0.63772900
H	-0.46471700	5.12956400	0.66716000
H	-1.33425400	4.24255400	-0.60171600
C	-1.48375100	3.69296600	2.73333600
H	-0.60172500	4.25974800	3.03142200
H	-2.38250200	4.29264100	2.88825900
H	-1.53965700	2.78024900	3.32480700
H	-2.17478300	2.78386000	1.05221700
H	-1.58259100	0.85369200	-1.14150300
C	2.91309500	-0.35016200	-2.11789600
H	2.84559300	0.41582300	-2.90058300
H	3.98552600	-0.48774400	-1.93126400
C	2.24733100	-1.63997900	-2.61746700
H	2.12498600	-2.35679300	-1.79558000
H	2.93527200	-2.11839900	-3.32596100
C	-0.31856200	-2.07906800	-2.70164000
H	-0.23671500	-3.16566000	-2.82189400
H	-1.21775100	-1.76170700	-3.24343500
C	0.89332400	-1.36628500	-3.31450100
H	0.95411200	-1.65370100	-4.37182700
H	0.68891300	-0.28763500	-3.29814400
C	-2.37260700	-2.08005000	-0.64219800
C	-3.16959700	-2.74306500	-1.58954100
C	-2.92900700	-1.77584600	0.61484700
C	-4.49412800	-3.08077900	-1.29041600
H	-2.77355000	-3.01182000	-2.56240000
C	-4.24837100	-2.11921900	0.91238500
H	-2.32405000	-1.27740700	1.36785300
C	-5.03643600	-2.77007600	-0.04256600
H	-5.09626800	-3.59287100	-2.03401400
H	-4.65842400	-1.88457700	1.88941100
H	-6.06180400	-3.03989700	0.18809100
C	0.21454900	-2.94050900	0.08937500
C	0.29168400	-4.28205900	-0.32765700
C	0.65856600	-2.60262900	1.37854200
C	0.81690900	-5.25665300	0.52247700
H	-0.07074700	-4.58152200	-1.30559300
C	1.17485400	-3.58238900	2.23091500
H	0.60731800	-1.57046200	1.71106800
C	1.25833300	-4.90909900	1.80322500

H	0.87260400	-6.28765000	0.18850200
H	1.51780800	-3.30528200	3.22188100
H	1.66083700	-5.67028900	2.46355700
C	3.10646400	-0.29099400	0.80874100
C	3.98923700	-1.37366700	0.66499900
C	2.90309800	0.25247000	2.09286600
C	4.65776100	-1.89653200	1.77653000
H	4.16182800	-1.82564600	-0.30500700
C	3.57940200	-0.26601200	3.19801700
H	2.22475000	1.08978700	2.22540300
C	4.45873800	-1.34336600	3.04267100
H	5.33560800	-2.73404700	1.64817600
H	3.42302800	0.17233600	4.17857300
H	4.98550600	-1.74531400	3.90201200
C	2.94880600	2.11965500	-0.78548100
C	2.37706600	3.00927800	-1.71442100
C	4.11373000	2.50423700	-0.10414200
C	2.95818700	4.25508000	-1.95394200
H	1.47114300	2.72838700	-2.24641600
C	4.68790400	3.75819000	-0.33997400
H	4.57565600	1.83252400	0.61066300
C	4.11426200	4.63432900	-1.26289100
H	2.51070100	4.92920600	-2.67760200
H	5.58678400	4.04438100	0.19649800
H	4.56466600	5.60433800	-1.44646300

TS$^{c}_{3\text{-}4}$: E(B3PW91) = -2200.0272621
Gas-phase zero-point energy = -2199.289480
Gas-phase free energy = -2199.375713

Rh	-0.00873100	0.04523600	0.11560900
P	-1.26246900	1.75795300	-0.66766500
P	-1.33102700	-1.59383100	-0.59150400
H	1.99925400	0.63200000	0.01290400
B	2.19645700	-0.58299500	0.15354300
H	1.14854300	-1.21727800	0.60188400
H	2.63255800	-1.14093400	-0.81348200
N	3.26537700	-0.79252800	1.33287300
C	3.50862400	-2.23338000	1.59908700
H	4.32200400	-2.35206900	2.31706000
H	2.59467100	-2.67388200	1.99849900
H	3.76018700	-2.72683900	0.66162600
C	2.97660500	-0.05599100	2.58445600
H	2.04235500	-0.42948300	3.00326100
H	3.78702000	-0.20024800	3.30124900
H	2.86879300	1.00340100	2.35576800
H	4.14024700	-0.41481800	0.95757900
H	0.26498900	1.34858000	2.21679000
H	-0.23256100	0.81231800	1.97053700
C	-2.44776000	-1.33720800	-2.04890500
H	-1.80222100	-1.07394300	-2.89586900
H	-2.87540600	-2.31418700	-2.30271200
C	-3.31184700	1.05054700	-2.56125900
H	-4.06320200	1.77174100	-2.21786000
H	-3.48617700	0.90933600	-3.63683600
C	-1.91141500	1.66796600	-2.40167000
H	-1.91303000	2.68328200	-2.81744100
H	-1.16987300	1.09525600	-2.97204800
C	-3.54798400	-0.27915700	-1.82773500
H	-3.67872000	-0.08441100	-0.75496300
H	-4.50987800	-0.68448800	-2.16472700
C	-2.64651100	2.45050700	0.30551900

C	-3.23673300	3.67694400	-0.05738400
C	-3.14746800	1.75181900	1.41561500
C	-4.30588500	4.18821800	0.67967400
H	-2.85512100	4.23936100	-0.90475500
C	-4.21879600	2.26772700	2.15147700
H	-2.69989100	0.80339500	1.69665200
C	-4.79815800	3.48438000	1.78463900
H	-4.75336600	5.13475700	0.39448200
H	-4.59847500	1.71911300	3.00717900
H	-5.62909100	3.88526900	2.35584600
C	-0.03790300	3.12097300	-0.75071000
C	0.83828700	3.21347500	-1.84930700
C	0.10247400	4.03297700	0.31165300
C	1.81915700	4.20581400	-1.88991900
H	0.76274100	2.51030700	-2.67281600
C	1.08902800	5.02163400	0.26791200
H	-0.56906900	3.98227200	1.16291700
C	1.94731200	5.11108900	-0.83161400
H	2.48106900	4.27303300	-2.74723600
H	1.18023100	5.72598600	1.08850700
H	2.70830400	5.88382100	-0.86632000
C	-0.36839500	-3.05519800	-1.15809500
C	0.53495000	-2.88314200	-2.22391900
C	-0.51132800	-4.32983400	-0.58549700
C	1.26205600	-3.96669600	-2.71853200
H	0.68487200	-1.89587300	-2.65230300
C	0.22807600	-5.41092200	-1.07703900
H	-1.19890700	-4.48429400	0.23878900
C	1.11040300	-5.23394500	-2.14505800
H	1.94959400	-3.82179700	-3.54572800
H	0.10709300	-6.39139800	-0.62749700
H	1.67703800	-6.07619400	-2.52872900
C	-2.45452900	-2.26674700	0.70042400
C	-3.61377500	-3.00134000	0.38910600
C	-2.13106700	-2.06176500	2.05375700
C	-4.42628600	-3.51002900	1.40576800
H	-3.89030800	-3.18666700	-0.64313100
C	-2.93976000	-2.57756900	3.06939300
H	-1.24160000	-1.48826900	2.30142300
C	-4.09183800	-3.30011200	2.74660300
H	-5.31938200	-4.07060800	1.14934300
H	-2.67415700	-2.41216900	4.10872300
H	-4.72490000	-3.69701400	3.53343000
B	6.68904000	0.04501000	0.92270200
H	6.42825700	-0.27269300	2.04897200
H	5.83189900	0.16075300	0.08614800
N	8.00030100	0.28412300	0.56617700
C	8.40831500	0.67235100	-0.77620700
H	9.10614200	-0.06164100	-1.19434200
H	7.53583600	0.73894600	-1.42493300
H	8.91286800	1.64483000	-0.75969400
C	9.11339700	0.17417600	1.49859600
H	9.83425500	-0.57427800	1.15127200
H	9.63823600	1.13194200	1.58658800
H	8.74690600	-0.11832800	2.48154900

(4^{c}): E(B3PW91) = 2200.112245
Gas-phase zero-point energy = -2199.378458
Gas-phase free energy = -2199.472575

Rh	-0.07225500	-0.36107400	-0.33752700
P	-0.29104700	1.82071600	-0.86258000

P	-2.26701200	-0.85626100	-0.43857900
H	1.75498700	-0.35798900	-0.24938500
B	1.68538500	-1.64451800	-0.23402300
H	0.47690800	-2.05169600	0.01248700
H	2.13970300	-2.14513500	-1.22407900
N	2.56846600	-2.12714400	1.00585900
C	2.52915700	-3.60788100	1.13894700
H	3.20978900	-3.92941300	1.92858300
H	1.51008400	-3.91031600	1.38141300
H	2.81973000	-4.05559600	0.18973900
C	2.25618000	-1.46061500	2.29324400
H	1.23624800	-1.71687500	2.57847600
H	2.95377000	-1.79242600	3.06436700
H	2.32685600	-0.38224900	2.16063500
H	3.53538300	-1.88455400	0.76717300
H	2.74802700	3.88840700	4.97540300
H	2.13791800	3.90678500	4.54750400
C	-3.42236800	0.12501000	-1.49276800
H	-3.03916800	0.04390800	-2.51421900
H	-4.38001400	-0.40230600	-1.50322500
C	-2.86221500	2.60474200	-1.94256300
H	-2.92975800	3.58541400	-1.46292300
H	-3.39854800	2.69263300	-2.89457100
C	-1.39749000	2.30644100	-2.27454900
H	-0.94737800	3.17713000	-2.76022100
H	-1.32250300	1.48335400	-2.99184700
C	-3.57489600	1.58845700	-1.04976500
H	-3.22850700	1.71065500	-0.01765900
H	-4.63738800	1.84761300	-1.02563600
C	-0.69291100	3.00574200	0.46997800
C	-0.76186000	4.38926600	0.21618600
C	-0.94863400	2.53324100	1.76727900
C	-1.08383200	5.27774300	1.24368600
H	-0.55283200	4.77501500	-0.77769000
C	-1.27075900	3.42644100	2.79421200
H	-0.90252000	1.46485300	1.95883100
C	-1.33996600	4.79734500	2.53307600
H	-1.13458200	6.34237000	1.03999500
H	-1.47248400	3.05149600	3.79236200
H	-1.59270200	5.49041100	3.32887300
C	1.35457800	2.35694200	-1.47797300
C	1.77699400	1.93886100	-2.75431600
C	2.22875900	3.11992000	-0.68560200
C	3.03952400	2.29331400	-3.23210700
H	1.12619300	1.32835700	-3.37345100
C	3.49434500	3.46810000	-1.16684300
H	1.92084600	3.45123600	0.30053900
C	3.90106700	3.05893500	-2.43934400
H	3.35046000	1.97209100	-4.22099700
H	4.15752800	4.06534800	-0.54918700
H	4.88129600	3.33618500	-2.81325300
C	-2.45803400	-2.53889700	-1.14703200
C	-1.70352300	-2.86739300	-2.28947600
C	-3.35076200	-3.48721500	-0.62024000
C	-1.85221900	-4.11401200	-2.89988800
H	-0.98790600	-2.15089700	-2.68570400
C	-3.49050900	-4.73696800	-1.23144800
H	-3.93229100	-3.25717200	0.26628800
C	-2.74636000	-5.05103600	-2.37147400
H	-1.26788400	-4.35570400	-3.78190700
H	-4.18140200	-5.46325200	-0.81558600
H	-2.85927100	-6.02128500	-2.84411400

C	-3.10944800	-0.91726100	1.19086800
C	-4.49673000	-0.73755100	1.33757000
C	-2.33832200	-1.17613200	2.33884300
C	-5.09387400	-0.81833800	2.59887800
H	-5.12168900	-0.53354000	0.47475400
C	-2.93711200	-1.26408800	3.59708500
H	-1.26380200	-1.29815800	2.23297000
C	-4.31721000	-1.08368500	3.72952500
H	-6.16492500	-0.67391000	2.69606600
H	-2.32962000	-1.46798500	4.47321000
H	-4.78383600	-1.14704600	4.70704300
B	6.08687100	-1.91842500	1.14720100
H	5.62481600	-2.31830000	2.17849700
H	5.38387800	-1.58751800	0.22741700
N	7.45512500	-1.83044100	0.99792400
C	8.10096500	-1.35957400	-0.21895200
H	8.75102500	-2.13696100	-0.63543600
H	7.34833200	-1.09471000	-0.96047900
H	8.71951800	-0.47953700	-0.01068700
C	8.39694400	-2.20323500	2.04437300
H	9.05903200	-3.00476600	1.69871400
H	9.02114100	-1.34704100	2.32307700
H	7.85663700	-2.54731200	2.92513000

2[d]+A: E(B3PW91) = -2239.3252417
Gas-phase zero-point energy = -2238.549176
Gas-phase free energy = -2238.636771

Rh	-0.66624600	-0.22232700	0.78689900
P	-1.48582900	1.33997700	-0.61467700
P	0.67248800	-1.34197300	-0.64233900
B	-0.98703800	-0.42963000	2.94256300
N	-2.16525500	-1.28313900	3.61819700
H	-0.28730800	-1.25717000	2.25727600
H	-0.34727000	0.06808700	3.82687700
H	-1.55651000	0.47160200	2.21799400
C	-1.60481000	-2.35345400	4.48654400
H	-1.05958100	-3.05659900	3.85696900
H	-0.91647800	-1.90574100	5.20201000
H	-2.40880700	-2.87299600	5.01075900
C	-3.16229100	-1.82657800	2.66074900
H	-2.64511400	-2.49720100	1.97496400
H	-3.59202300	-1.00520700	2.08942400
H	-3.94337700	-2.36669300	3.20044500
H	-2.65426700	-0.62878600	4.22935600
B	5.35315200	1.14402500	0.32449900
N	6.89459000	1.66035100	0.25949700
H	5.24653400	0.53548000	1.37047500
H	4.66248200	2.14218200	0.28938400
H	5.19927900	0.42940600	-0.64698800
H	7.47106600	0.82138500	0.28188300
C	7.25486500	2.48073800	1.43577400
C	7.18991600	2.37055800	-1.00333200
H	7.07394800	1.89893600	2.33836200
H	8.30189200	2.79198700	1.39049500
H	6.60836700	3.35848900	1.44941900
H	8.23670500	2.68354900	-1.04145000
H	6.54022800	3.24409500	-1.06188400
H	6.96493200	1.70933900	-1.83889500
H	0.82914700	2.46258600	-3.26419300
H	-0.34696800	-0.37045200	-3.10454000
H	-0.75762000	0.77612800	-4.35165400

C	-1.59091300	1.28510500	-2.47176700
C	-0.43600700	0.70355100	-3.30283200
H	-2.49450400	0.70722400	-2.69884100
H	1.53931100	1.05964400	-4.04605400
C	0.93908000	1.37219600	-3.17922500
H	-1.79855500	2.31249200	-2.79741200
C	1.73800700	1.05123500	-1.90795800
H	1.27710700	1.51269500	-1.02818600
H	2.72400100	1.52534200	-1.99753300
C	1.97117500	-0.44613400	-1.63722600
H	2.11988100	-0.98985100	-2.57953200
H	2.90074800	-0.55605400	-1.06793400
C	-0.81076700	3.00440900	-0.22846800
C	-1.28292300	4.16216100	-0.87518600
C	0.18443900	3.13405400	0.75595100
C	-0.76252000	5.41604800	-0.54893600
H	-2.06964800	4.09714900	-1.62090700
C	0.70365700	4.39076300	1.08023700
H	0.55198400	2.24151800	1.25740100
C	0.23292100	5.53219300	0.42708300
H	-1.13513700	6.30110700	-1.05444400
H	1.47666300	4.47357700	1.83704100
H	0.63679800	6.50811600	0.67621200
C	-3.27248700	1.48959400	-0.16890200
C	-3.72490700	2.47587100	0.72555300
C	-4.19794600	0.54512100	-0.65471700
C	-5.06827900	2.52453500	1.11035400
H	-3.03090600	3.21217100	1.11663500
C	-5.54026900	0.59904100	-0.27207900
H	-3.87729400	-0.23917700	-1.33429400
C	-5.97981000	1.58990100	0.61199300
H	-5.40240300	3.30056600	1.79174300
H	-6.24274700	-0.12735800	-0.66866800
H	-7.02396600	1.63597900	0.90373800
C	1.67527600	-2.46896200	0.41184800
C	1.35981700	-3.83262900	0.54443200
C	2.72968200	-1.93551800	1.17823700
C	2.09071900	-4.64634100	1.41543300
H	0.55358800	-4.26474800	-0.03875700
C	3.45864300	-2.75357500	2.04297100
H	2.99098700	-0.88357200	1.11070900
C	3.14131200	-4.11029900	2.16493700
H	1.84476900	-5.70044800	1.49837500
H	4.27574100	-2.32796600	2.61603700
H	3.71188400	-4.74537200	2.83502600
C	-0.17656800	-2.49694600	-1.78919600
C	0.52916300	-3.25563900	-2.74131900
C	-1.56739200	-2.66472700	-1.68126600
C	-0.14846700	-4.14683600	-3.57602400
H	1.60797700	-3.16595100	-2.82578800
C	-2.24345200	-3.55984100	-2.51559800
H	-2.10333700	-2.08468800	-0.93316500
C	-1.53491700	-4.29849800	-3.46686700
H	0.40528000	-4.72585500	-4.30792300
H	-3.31830700	-3.68139900	-2.42392700
H	-2.05755500	-4.99196400	-4.11760100

$TS^{d}_{1\text{-}2}$: E(B3PW91) = -2239.295144
Gas-phase zero-point energy = -2238.525149
Gas-phase free energy = -2238.602634

Rh	0.12199500	-0.83800800	-0.06722200

P	-1.94086200	0.01958400	0.65416100
P	1.65914700	0.84494400	0.50586500
B	-0.64507800	-3.34007600	0.43882300
N	0.29286900	-3.22010100	1.64188200
H	-0.24556400	-4.09842900	-0.42647300
H	-1.79852300	-3.50558000	0.73037300
H	-0.86697200	-2.19582400	-0.32231800
C	1.60139200	-3.84226500	1.48796600
C	-0.28739500	-3.55212700	2.94058100
H	0.37626500	-3.23534800	3.75157000
H	-1.25070600	-3.05914100	3.06438400
H	-0.45336900	-4.63443800	3.04058300
H	1.51627200	-4.93280000	1.37994400
H	2.10468100	-3.44827800	0.60282600
H	2.23081000	-3.63871700	2.36042200
H	0.34672500	-1.61536400	1.30388100
B	1.28035900	-1.47184900	-1.98927900
N	0.86753700	-2.88228500	-2.60975800
H	1.54369200	-1.69227100	-0.73451600
H	0.36814300	-0.66327100	-2.17683500
H	2.33006800	-1.11640300	-2.45163600
C	0.13473300	-2.73623600	-3.89119000
H	-0.77934400	-2.17200400	-3.71335900
H	0.76442800	-2.19360800	-4.59720500
H	-0.10942000	-3.71971400	-4.29776900
C	2.02980200	-3.79259300	-2.75607200
H	2.53111300	-3.88908900	-1.79401300
H	1.69813600	-4.77483500	-3.09841600
H	2.72507800	-3.36192300	-3.47627300
H	0.23268400	-3.31694900	-1.92867000
C	-0.37629600	0.54738900	3.59161500
H	-0.04200600	0.57741400	4.63661800
H	-0.00370600	-0.39965900	3.17837400
C	-1.91210300	0.54799000	3.53219700
H	-2.27512700	1.58181600	3.46841500
H	-2.32415000	0.13975200	4.46405500
C	-2.51071100	-0.29249300	2.38761300
H	-3.60398100	-0.20005000	2.39867800
H	-2.28653100	-1.35065900	2.56699700
C	0.26042600	1.72948400	2.83295900
H	-0.40417300	2.05713100	2.02333300
H	0.33611800	2.58931200	3.51136800
C	1.65236100	1.39445500	2.27179300
H	2.35395300	2.23300800	2.35420600
H	2.10527100	0.57606900	2.84479600
C	-3.23455300	-0.83248000	-0.35086500
C	-4.07622600	-1.82742500	0.17386700
C	-3.36492000	-0.48459300	-1.70893700
C	-5.02623900	-2.45443700	-0.63942400
H	-4.00314700	-2.12876200	1.21212000
C	-4.31263500	-1.11379900	-2.51739400
H	-2.74149800	0.29674200	-2.13266900
C	-5.14652300	-2.10242100	-1.98461700
H	-5.67167500	-3.21686400	-0.21568600
H	-4.41038000	-0.82181200	-3.55831200
H	-5.88810300	-2.58691200	-2.61110300
C	-2.37218900	1.76969900	0.30775800
C	-3.43124800	2.40522600	0.98377200
C	-1.72851100	2.45431800	-0.73546200
C	-3.81757300	3.70015800	0.63402900
H	-3.97088100	1.89378000	1.77325600
C	-2.12490200	3.74691700	-1.09057000

H	-0.91229600	1.98280600	-1.27124600
C	-3.16584300	4.37410800	-0.40350100
H	-4.63351900	4.17838300	1.16601400
H	-1.61476500	4.25965300	-1.89873900
H	-3.47236900	5.37866500	-0.67586900
C	3.39896100	0.25792900	0.36225600
C	3.77267600	-0.88431100	1.09486200
C	4.37320600	0.92279600	-0.39864200
C	5.08745700	-1.35029500	1.06645000
H	3.03316600	-1.41244200	1.68981000
C	5.68895100	0.44803000	-0.43145600
H	4.11533400	1.81154100	-0.96272900
C	6.04958200	-0.68590100	0.29819500
H	5.36231700	-2.22746800	1.64372700
H	6.43130100	0.97263500	-1.02409900
H	7.07222300	-1.04766100	0.27441700
C	1.64727600	2.38897400	-0.48140700
C	1.61511300	3.66621200	0.10226400
C	1.69756100	2.28716500	-1.88611300
C	1.64185600	4.81295100	-0.69751100
H	1.56422400	3.78425900	1.17826100
C	1.73187200	3.43424300	-2.68106400
H	1.72014200	1.30977400	-2.35785500
C	1.70480100	4.70137700	-2.08793100
H	1.61685100	5.79185000	-0.23019600
H	1.78396300	3.33915200	-3.76095800
H	1.73498400	5.59301200	-2.70557700

(2^{d}): E(B3PW91) = -2239.3369619
Gas-phase zero-point energy = -2238.565442
Gas-phase free energy = -2238.651125

Rh	0.20287800	0.44951900	0.31117100
P	0.40937600	-1.79185600	0.76955400
P	-2.17153700	1.00713700	0.54061100
H	1.76635600	0.30566800	0.40238600
H	0.31011100	0.52843700	1.83675900
B	0.57842700	1.91435600	-1.31108700
N	2.08636800	2.19284700	-1.73524100
H	-0.13396200	2.68400000	-1.89331500
H	0.48424200	2.17268500	-0.03220800
H	0.29303200	0.70136100	-1.57797000
C	2.47590800	3.60014200	-1.46493600
H	2.32928300	3.81167300	-0.40637900
H	1.83770900	4.25721400	-2.05565100
H	3.52259600	3.75397700	-1.73048000
C	2.32660200	1.82820400	-3.15437700
H	1.66047500	2.41937600	-3.78334300
H	3.36552300	2.02896700	-3.41915900
H	2.10908400	0.76944200	-3.29000100
B	5.56799000	1.72435500	-0.52554500
N	6.83572500	1.86517800	0.00544900
H	4.61937200	1.76856700	0.20875300
H	5.44000900	1.56812300	-1.70762900
C	7.09169700	2.06657200	1.42397500
H	6.15035300	2.08461800	1.97183100
H	7.61735700	3.01346000	1.59129900
H	7.71909800	1.26104100	1.82237300
C	8.04872200	1.83178200	-0.79896300
H	8.60057800	2.77379100	-0.70468400
H	8.70920800	1.02185100	-0.46926100
H	7.79514100	1.67438900	-1.84638400

H	2.67588900	1.59333000	-1.15340000
C	-0.73408500	-2.41541700	3.41906900
H	1.04444500	-3.29435200	2.54383000
H	-1.38434800	-3.22090900	3.05372600
H	-0.39283200	-2.73263200	4.41338100
H	1.23215800	-1.60961300	3.00273900
C	0.53323400	-2.32300500	2.54657200
C	-1.54511500	-1.11530700	3.54110900
H	-0.86457400	-0.25748900	3.45252200
H	-1.98388100	-1.04704800	4.54496700
C	-2.67646600	-0.99460300	2.49851200
H	-3.58144400	-1.46875100	2.90065300
H	-2.42014600	-1.57417100	1.60185200
C	-2.98331400	0.46532700	2.11420500
H	-4.05841900	0.66277100	2.02907700
H	-2.61774400	1.14820500	2.89096500
C	2.02574200	-2.40824600	0.12543300
C	3.21947500	-2.01704800	0.76149900
C	2.09844600	-3.26024000	-0.98802200
C	4.45216300	-2.48261100	0.30338900
H	3.19191300	-1.33846400	1.60897400
C	3.33832900	-3.71334700	-1.45306400
H	1.19259200	-3.57929300	-1.49112600
C	4.51519900	-3.33105900	-0.80787200
H	5.36269600	-2.18253900	0.81198500
H	3.37809900	-4.37171100	-2.31488400
H	5.47472100	-3.69080800	-1.16464600
C	-0.78117900	-2.94048400	-0.01124000
C	-0.90905200	-4.26815000	0.44181500
C	-1.52281300	-2.52871400	-1.13005500
C	-1.77221600	-5.15404600	-0.20500100
H	-0.32887400	-4.62111100	1.28792900
C	-2.38110200	-3.42101200	-1.77982100
H	-1.43716800	-1.50894000	-1.48973100
C	-2.50993300	-4.73210500	-1.31618100
H	-1.86486900	-6.17348300	0.15502900
H	-2.95066600	-3.08575800	-2.63964100
H	-3.17867000	-5.42397400	-1.81772000
C	-3.32476500	0.47507300	-0.78453100
C	-4.46966400	-0.30095900	-0.54013700
C	-3.03230700	0.84779100	-2.11177100
C	-5.30565400	-0.68622300	-1.59356800
H	-4.72029700	-0.61589600	0.46620100
C	-3.87260300	0.46935800	-3.15984100
H	-2.15249800	1.44825400	-2.32219200
C	-5.01267500	-0.30067000	-2.90312300
H	-6.18726100	-1.28408000	-1.38614900
H	-3.64088900	0.77737700	-4.17450100
H	-5.66747700	-0.59354300	-3.71737700
C	-2.43280900	2.82628500	0.64477400
C	-1.58140600	3.57073000	1.48401300
C	-3.47913500	3.48762400	-0.01808500
C	-1.77540400	4.94237700	1.65598900
H	-0.76355500	3.07715500	2.00332700
C	-3.66343200	4.86408500	0.14830500
H	-4.15131000	2.93375700	-0.66411500
C	-2.81531800	5.59337300	0.98414100
H	-1.11643300	5.50219600	2.31225900
H	-4.47491300	5.36241000	-0.37225100
H	-2.96405100	6.66029400	1.11464300

$TS^{d}_{2\text{-}3}$: E(B3PW91) = -2239.3260025

Gas-phase zero-point energy = -2238.558001
Gas-phase free energy = -2238.646086

Rh	0.22379500	-0.44222000	-0.20746800
P	0.49610600	1.76027800	-0.82142800
P	-2.19497000	-0.54614400	-0.31297300
H	4.74474900	-1.75979700	1.42727200
H	1.84343600	-0.49469000	-0.23403400
H	4.62595100	-2.25508300	-0.60419900
B	5.27023900	-2.02319300	0.37929500
N	6.64944700	-2.06951100	0.31760400
C	7.51336200	-1.80487800	1.45889300
H	8.13710200	-2.67777000	1.68238100
H	8.18054300	-0.96088100	1.25070300
H	6.91029200	-1.56777000	2.33439400
C	7.38410000	-2.38435200	-0.89914700
H	8.01123300	-3.27105200	-0.75346100
H	6.68745300	-2.57606100	-1.71416500
H	8.04022300	-1.55290000	-1.18061100
H	0.27846000	-1.25505700	1.90321700
B	0.38726700	-2.28850800	1.26214700
H	-0.39865700	-3.14445700	1.57394300
H	0.20147200	-2.19208400	-0.01791200
N	1.85610800	-2.88680200	1.47089400
C	2.08795300	-4.11251900	0.66827700
H	3.09670200	-4.49224700	0.83961400
H	1.35131700	-4.86080300	0.96097100
H	1.95918100	-3.87630800	-0.38712100
C	2.11641200	-3.13465500	2.91138600
H	1.38888800	-3.86016800	3.27545000
H	3.12824400	-3.51971900	3.04973100
H	1.99535200	-2.20075400	3.45854000
H	2.53218300	-2.18696600	1.16047600
H	1.41222700	-0.67450000	-1.21489500
C	-0.97013400	2.03361100	-3.29767900
H	-1.71978600	2.61366500	-2.74381800
H	-0.90868000	2.50614700	-4.28641600
C	0.40068600	2.19519600	-2.62264100
H	0.77153900	3.22264500	-2.72834400
H	1.13568000	1.55325600	-3.12533200
C	-1.43030800	0.56618200	-3.45135600
H	-1.35469600	0.26429600	-4.50356600
H	-0.75021800	-0.09246200	-2.89230300
C	-2.86717000	0.31906000	-2.97301900
H	-3.55224000	0.97154500	-3.53343200
H	-3.16229100	-0.70982500	-3.21258500
C	-3.10575000	0.57945000	-1.47521400
H	-2.84130600	1.61166500	-1.21304100
H	-4.17462100	0.45240500	-1.26083900
C	2.20625100	2.33185300	-0.43166100
C	3.29264300	1.82373400	-1.16954000
C	2.45906700	3.26535000	0.58680800
C	4.59466700	2.24849100	-0.90180600
H	3.13235000	1.09223800	-1.95681100
C	3.76683800	3.68028400	0.85937600
H	1.63977600	3.67655800	1.16564400
C	4.83569100	3.17714000	0.11621300
H	5.41911200	1.85571000	-1.48815200
H	3.94462000	4.40284300	1.64924900
H	5.84827800	3.50650000	0.32468300
C	-0.55490300	2.98259300	0.04013400
C	-0.86353200	4.23826300	-0.51659200

C	-0.99506800	2.68852800	1.34297400
C	-1.60248000	5.17159100	0.21356000
H	-0.52156200	4.49971400	-1.51188100
C	-1.72305700	3.63028300	2.07561100
H	-0.76548500	1.72271900	1.78445200
C	-2.03010500	4.87088700	1.51083300
H	-1.83690500	6.13504000	-0.22714400
H	-2.05391200	3.38961500	3.08006400
H	-2.59743100	5.60162000	2.07795500
C	-3.07726200	-0.28174400	1.27921800
C	-3.94707400	0.80113400	1.49550000
C	-2.86818800	-1.19847400	2.32810700
C	-4.59228200	0.95959200	2.72663700
H	-4.12974200	1.53084400	0.71581200
C	-3.51550000	-1.03798100	3.55379200
H	-2.20807100	-2.04621200	2.18191400
C	-4.37989900	0.04243500	3.75754600
H	-5.26526800	1.79837600	2.87316400
H	-3.34933500	-1.75966000	4.34713400
H	-4.88620600	0.16450100	4.70950500
C	-2.79363200	-2.19515000	-0.85993900
C	-4.06379900	-2.66782100	-0.48440700
C	-2.01496100	-2.96357300	-1.74267100
C	-4.53604100	-3.88803000	-0.97369700
H	-4.67974400	-2.09109400	0.19792100
C	-2.49358200	-4.18048300	-2.23555800
H	-1.03295500	-2.60742900	-2.04062000
C	-3.75296600	-4.64649100	-1.84858600
H	-5.51488500	-4.24540700	-0.67069900
H	-1.88372600	-4.76319000	-2.91871400
H	-4.12272100	-5.59398000	-2.22683700

(3[d]): E(B3PW91) = -2239.3272277
Gas-phase zero-point energy = -2238. 550462
Gas-phase free energy = -2238. 636954

Rh	-0.15034600	0.56580700	-0.41424500
P	-0.37124400	-1.72957600	-0.38021600
P	2.23280800	0.68158800	-0.65857200
H	-4.38215500	2.07229400	1.39465100
H	-1.80777000	0.64431000	-0.33186900
H	-4.58300700	2.43881600	-0.65786700
B	-5.06478600	2.19922400	0.41488800
N	-6.43495900	2.07022400	0.52553500
C	-7.11478400	1.79117900	1.78259300
H	-7.81316900	2.59821100	2.03036400
H	-7.68971800	0.86092900	1.71280200
H	-6.38605200	1.69655800	2.58657400
C	-7.34511800	2.21151900	-0.60246900
H	-8.05018100	3.03194600	-0.42853200
H	-6.78151900	2.41692500	-1.51151600
H	-7.92655500	1.29401400	-0.74614100
H	-0.21036100	2.11317400	1.35054900
B	-0.26469100	2.83448900	0.37406100
H	0.55421000	3.71104000	0.37420200
H	-0.06942700	2.28185400	-0.78922400
N	-1.70809400	3.53228300	0.30307200
C	-1.89420400	4.32827900	-0.93419100
H	-2.87725000	4.80277300	-0.93725400
H	-1.11294400	5.08746600	-0.97488900
H	-1.79956200	3.67141300	-1.79810800
C	-1.92499300	4.36874400	1.51035700

H	-1.15575300	5.14034900	1.53841500
H	-2.91500200	4.82772900	1.47850100
H	-1.83299300	3.74215400	2.39619300
H	-2.42948100	2.81021600	0.31144400
H	-1.56201000	0.56236300	-1.22724000
C	2.64063000	0.73908200	-2.46677400
H	2.00613200	1.51779600	-2.90810700
H	3.67789900	1.08221100	-2.56640000
C	2.43112400	-0.58094600	-3.22972700
H	2.96475600	-1.39070900	-2.71517800
H	2.92730600	-0.47698900	-4.20317200
C	0.94899600	-0.95960600	-3.44473200
H	0.69134200	-0.85049000	-4.50593300
H	0.30663100	-0.25340700	-2.89623700
C	0.59505600	-2.38917800	-3.01281700
H	-0.42782000	-2.60840400	-3.34085900
H	1.24524100	-3.09717900	-3.54694600
C	0.73827600	-2.68950400	-1.50388800
H	0.58269500	-3.76191600	-1.33550100
H	1.75958700	-2.47416500	-1.16386400
C	2.96403600	2.24796300	-0.02803200
C	3.20305800	3.34968600	-0.86670600
C	3.27170200	2.35771600	1.33945400
C	3.74425800	4.52989400	-0.34886200
H	2.97119800	3.30365100	-1.92510400
C	3.80872200	3.53879700	1.85364800
H	3.10662200	1.51590200	2.00461200
C	4.04734100	4.62833500	1.01087400
H	3.93195400	5.36906100	-1.01115600
H	4.04760800	3.60473700	2.91017400
H	4.47127900	5.54394300	1.41007500
C	3.40223700	-0.55429800	0.03191400
C	3.08491600	-1.21900300	1.22783000
C	4.66065600	-0.78439900	-0.55697000
C	3.99675000	-2.10013600	1.81779100
H	2.12315500	-1.05431600	1.69971300
C	5.56540100	-1.67083300	0.02957600
H	4.94848800	-0.26939900	-1.46692800
C	5.23577600	-2.33136200	1.21753100
H	3.73258400	-2.60441400	2.74123500
H	6.53015900	-1.84002100	-0.43750900
H	5.94299300	-3.01725400	1.67221300
C	-2.06797500	-2.36480300	-0.73923200
C	-2.29841200	-3.49269300	-1.54574300
C	-3.16878100	-1.76650100	-0.09844500
C	-3.59378900	-3.98664700	-1.72951600
H	-1.47733200	-4.00399400	-2.03379100
C	-4.45969900	-2.26562400	-0.27560900
H	-3.01835900	-0.91689300	0.56151100
C	-4.67772600	-3.37361300	-1.09975600
H	-3.75031400	-4.85421800	-2.36229200
H	-5.29301300	-1.79208300	0.23331700
H	-5.68145100	-3.76011700	-1.24202900
C	-0.11144700	-2.44351500	1.29554700
C	0.18463900	-3.80107100	1.50431100
C	-0.30009800	-1.60902300	2.41256500
C	0.30323500	-4.30714500	2.80118300
H	0.31919800	-4.47557300	0.66551800
C	-0.18716500	-2.11927100	3.70844500
H	-0.52496900	-0.55557400	2.25940800
C	0.11774400	-3.46927900	3.90480100
H	0.53482800	-5.35705600	2.94856900

H	-0.33506200	-1.46448400	4.56134600
H	0.20604500	-3.86727100	4.91041000

$TS^{d}_{3\text{-}4}$: E(B3PW91) = -2239.3083855
Gas-phase zero-point energy = -2238.541535
Gas-phase free energy = -2238.628713

Rh	0.14108400	-0.01197200	-0.07807900
P	-1.04434400	-1.79641100	0.70269600
P	-1.26334100	1.65061500	0.46157800
H	2.09548300	-0.52697000	0.21795800
B	2.32093200	0.66460400	-0.06275000
H	1.28496000	1.25479000	-0.59139400
H	2.75045300	1.32161800	0.84287500
N	3.42640400	0.71855900	-1.22588800
C	3.69093500	2.11484200	-1.66015300
H	4.53918400	2.14119600	-2.34631400
H	2.80077700	2.50024100	-2.15798800
H	3.89806200	2.72409500	-0.78181000
C	3.18179800	-0.16745500	-2.38724500
H	2.28006000	0.16566200	-2.90023000
H	4.03067600	-0.12944400	-3.07235300
H	3.03554800	-1.18683200	-2.03268100
H	4.28450100	0.38838800	-0.77415400
H	0.37100700	-1.19360200	-2.05337800
H	-0.17504000	-0.65866500	-1.90642200
C	-2.25991500	1.70329400	2.02277500
H	-1.52268900	1.84956100	2.82171200
H	-2.83329200	2.63852800	1.98856200
C	-2.69125500	-0.30788400	3.55702100
H	-3.39648400	-1.13009800	3.74280500
H	-2.74863400	0.34787600	4.43753400
C	-3.16268600	0.49171300	2.33202500
H	-3.25095500	-0.16708500	1.46073000
H	-4.18334100	0.84483900	2.52885400
C	-1.26637700	-0.87127700	3.47322400
H	-0.55336100	-0.08216300	3.19798800
H	-0.97432000	-1.20222300	4.47953500
C	-1.06300200	-2.07523300	2.54086600
H	-0.08294200	-2.51426400	2.75999500
H	-1.80134600	-2.85549500	2.76440000
B	6.80278400	-0.12754800	-0.50930800
H	6.63728800	0.02293400	-1.68695600
H	5.88283500	-0.09150200	0.26617400
C	9.25660600	-0.41085500	-0.86340600
H	9.97762500	0.36244400	-0.57616900
H	9.74895500	-1.38444600	-0.76296000
H	8.97673600	-0.26301800	-1.90545100
C	8.36367900	-0.53699600	1.39641800
H	8.82777700	-1.51493700	1.56613600
H	9.05820100	0.23134700	1.75378400
H	7.44352400	-0.47747700	1.97627500
N	8.07295000	-0.34657900	-0.01739000
C	-2.71715500	-2.21924600	0.08405100
C	-3.46013900	-3.28411500	0.62921200
C	-3.25052700	-1.50511600	-1.00194100
C	-4.71338700	-3.61058800	0.10861100
H	-3.06335400	-3.87530500	1.44814300
C	-4.50441000	-1.83761600	-1.52375600
H	-2.68856800	-0.68181200	-1.42935000
C	-5.23892200	-2.88674900	-0.96700800
H	-5.27669300	-4.43221500	0.53885600

H	-4.90450900	-1.27257900	-2.35885800
H	-6.21370500	-3.14309000	-1.36892100
C	-0.02865400	-3.22567500	0.12449300
C	1.24857600	-3.44437600	0.67750900
C	-0.46867700	-4.06916900	-0.91124200
C	2.05291700	-4.49042700	0.22038600
H	1.62632000	-2.79734700	1.46426500
C	0.34101600	-5.11230600	-1.36914700
H	-1.44659000	-3.91911000	-1.35501200
C	1.60071500	-5.32777800	-0.80415600
H	3.02864200	-4.65344500	0.66702600
H	-0.01772000	-5.76005100	-2.16246800
H	2.22371200	-6.14348500	-1.15616300
C	-2.48651800	2.00306800	-0.86739400
C	-3.84342400	2.26424100	-0.61361700
C	-2.03860800	2.00907600	-2.20351100
C	-4.72708500	2.52487100	-1.66665000
H	-4.22659000	2.26118100	0.40004100
C	-2.91863200	2.27997200	-3.25200400
H	-0.99435000	1.79893500	-2.41784200
C	-4.26846300	2.53612500	-2.98539700
H	-5.77262400	2.72141200	-1.45227400
H	-2.55457100	2.28915600	-4.27448200
H	-4.95492900	2.74352300	-3.79975400
C	-0.37813900	3.25680500	0.65518800
C	0.64232600	3.33585600	1.62177500
C	-0.71834100	4.41058800	-0.06976100
C	1.30134400	4.54241800	1.86119400
H	0.93157300	2.44615600	2.17456100
C	-0.04724000	5.61576100	0.16529600
H	-1.50701800	4.37640200	-0.81300400
C	0.95970400	5.68571300	1.13016100
H	2.08097500	4.59030200	2.61491900
H	-0.32037500	6.49998600	-0.40176900
H	1.47318900	6.62375900	1.31483600

(4[d]): E(B3PW91) = -2239.3198096
Gas-phase zero-point energy = -2238.554699
Gas-phase free energy = -2238.649028

Rh	-0.03968900	0.43333100	-0.39759800
P	0.17006700	-1.76149400	-0.91720300
P	2.14817300	1.03259900	-0.40251700
H	-1.84913300	0.38461700	-0.35144600
B	-1.82699100	1.65917100	-0.16506400
H	-0.62728200	2.08207300	0.07987800
H	-2.34090000	2.25783900	-1.06824600
N	-2.67959800	1.93757800	1.15605400
C	-2.63796100	3.37944200	1.51656300
H	-3.31393800	3.57624900	2.35016300
H	-1.61771700	3.64014700	1.79875500
H	-2.93383700	3.96940000	0.65041600
C	-2.33033500	1.07646300	2.31302000
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H	-2.46115400	0.03344100	2.03024700
H	-3.65116900	1.72953300	0.90686500
H	-4.88352000	-2.99474400	3.50176900
H	-5.18065400	-2.96371700	4.18468000
C	3.41362700	0.42318000	-1.60949800
H	3.12690100	0.87418500	-2.56807300
H	4.35995900	0.90573100	-1.33256600

C	3.07796200	-1.62949100	-3.11407300
H	3.26469600	-2.71116900	-3.17065700
H	3.69170300	-1.17333900	-3.90397300
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H	3.07369300	-1.63675500	-0.94249700
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H	1.36719200	-0.29041100	-3.29279400
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H	-0.39632700	-2.10123800	-3.19718500
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H	4.01038400	5.65219900	0.00848300
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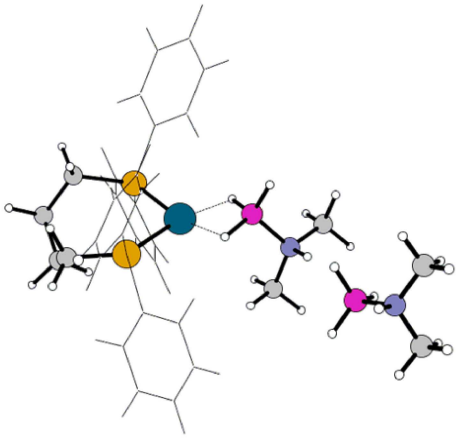
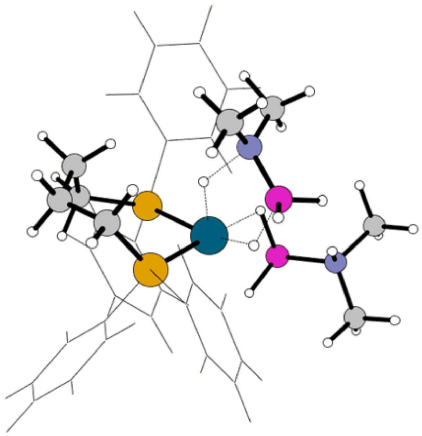
Optimized structures of minima and transition states along the selected dehydrogenation pathway starting from the **2c** and **2d** complexes



2c+A



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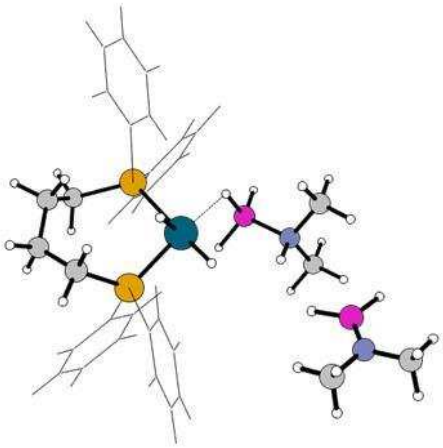
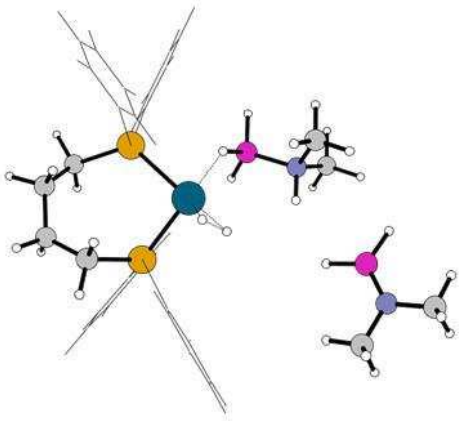


$(2)^{c}$



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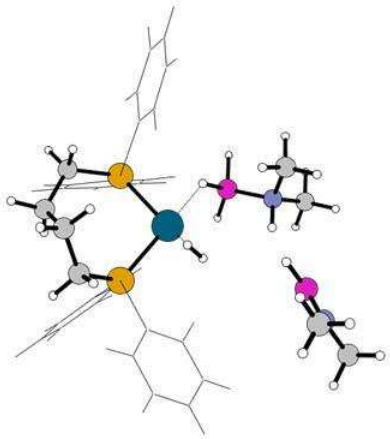
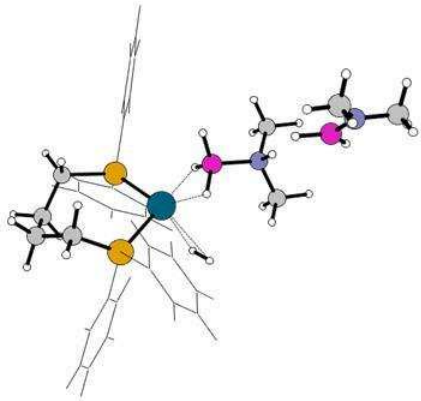
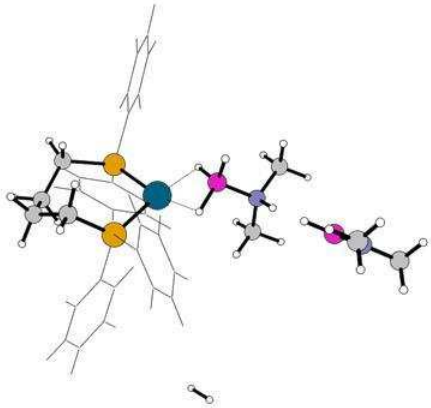


(3)^{c}



$TS^{c}_{3\text{-}4}$



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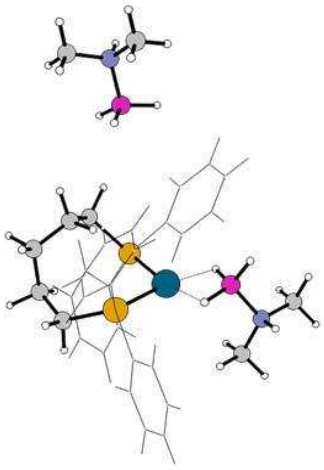
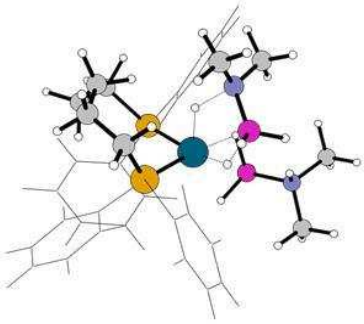


2d+*A*



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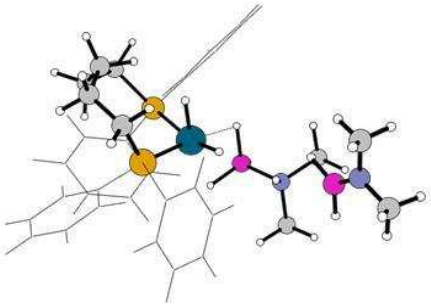

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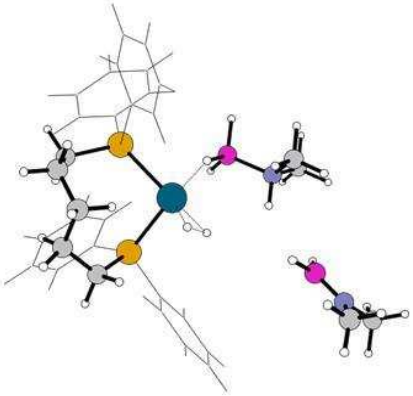

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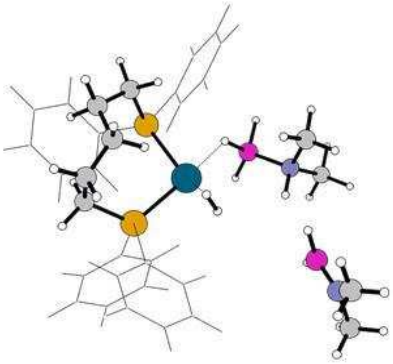

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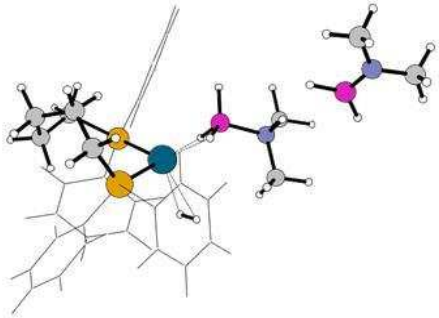
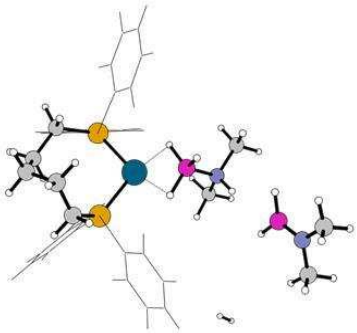


TS^{d}_{3-4}



(4)[d]

Reference (37) details

Paper II

Hydrogen release from dialkylamine-boranes promoted by Mg and Ca complexes: a DFT analysis of the reaction mechanism

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Hydrogen release from dialkylamine-boranes promoted by Mg and Ca complexes: a DFT analysis of the reaction mechanism

Valeria Butera,[a] Nino Russo[a] and Emilia Sicilia*[a]

Dedication ((optional))

Abstract: Mg and Ca β-diketiminato silylamides, [HC{(Me)CN(2,6-$^{i}Pr_2C_6H_3$)}$_2$M(THF)$_n${N(SiMe$_3$)$_2$}] (M = Mg, n = 0; M = Ca, n = 1) have been studied as precatalysts for the dehydrogenation/dehydrocoupling of secondary amine-boranes R_2HNBH_3. By reaction with equimolar quantities of amine-boranes the corresponding amidoborane derivatives are formed, which further react to yield dehydrogenation products such as the cyclic dimer [BH_2=NMe_2]$_2$. Density Functional Theory (DFT) has been used here to explore the mechanistic alternatives proposed on the basis of the experimental findings for both Mg and Ca amidoboranes. The influence the steric demand of amine-boranes can have on the course of the reaction has been likewise examined by performing calculations for the dehydrogenation of dimethylamine-borane, DMAB, pyrrolidine-borane, PB and di-*iso*-propylamine-borane. In spite of the analogies in amine-boranes dehydrocoupling catalytic activity between Mg- and Ca-based complexes, the outcomes of our computational analysis confirm the experimentally observed reduced reactivity of Ca complexes. Difference in catalytic activity of Mg- and Ca-based complexes has been examined and rationalized. As a consequence of the increase of the ionic radius in going from Mg to Ca the dehydrogenation mechanism changes and formation of a key metal hydride intermediate becomes inaccessible. Dimerization is likely to occur off the metal in solution for DMAB and PB, whereas steric hindrance of $^{i}Pr_2NHBH_3$ hamper formation of the cyclic dimer. Reported results are of particular interest because, although amine-borane dehydrogenation is now well-established, mechanistic insight is still lacking for many systems.

Keywords: amine-boranes • dehydrocoupling • Mg^{2+} • Ca^{2+} • density functional theory • catalysis

Introduction

The compound with the formal composition H_3NBH_3 (AB) has a long history.[1-6] First identified as a product of the reaction between ammonia and diborane, it may be prepared, depending on the conditions, in the form of a simple molecular adduct ammonia-borane, H_3NBH_3, and as a saltlike complex, the so-called 'diammoniate of diborane', $[(H_3N)_2BH_2]^{+}[BH_4]^{-}$. Ammonia-borane is a solid that at ambient temperatures is thermally stable enough to transport and store. Replacing the hydrogen atoms of the ammonia fragment by alkyl substituents gives in the alkylamine-boranes $R_nH_{3-n}NBH_3$, a series of molecular adducts which resemble ammonia-borane in being stable solids at ambient temperature. The coexistence of both hydridic B-H and protic N-H bonds in ammonia-borane and the alkylamine-boranes RH_2NBH_3 and R_2HNBH_3, associated to a relatively strong B-N coordinate link, causes dihydrogen loss favored over dissociation. When heated or subjected to acid hydrolysis, these compounds, indeed, release dihydrogen gas, but at a rate and with co-products that depend markedly on the precise operative conditions. Nevertheless, the combination of low molecular weight and high gravimetric hydrogen capacity (19.6 wt % for $H_3N{\cdot}BH_3$) has attracted intense interest in them as media for chemical hydrogen storage[7] alongside the potential reversibility of their dehydrogenation reactions.[8] In order to increase the hydrogen release rate at a relatively low temperature several strategies have been developed. In the last years a series of new and in many cases improved catalysts for AB and its derivatives mono- and di-alkylamine-boranes dehydrocoupling at room temperature based on a variety of early and late transition metals have been developed.[9] Cohomprensive and detailed reviews are available covering the chemistry of H_3NBH_3 and amine-borane derivatives and their potential as hydrogen storage materials.[10] In this context, great interest has been focused on the dehydrocoupling of secondary alkylamine-boranes in the hope that limiting the number of reactive, protic N-H residues would provide less ambiguous intermediate species and systems which are more amenable to mechanistic study. Following this line of reasoning, we have previously studied catalysts based on Rh metal that can be used for the dehydrocoupling of secondary amine-boranes.[11] However, more recently, a considerable number of d^0 complexes of the benign,

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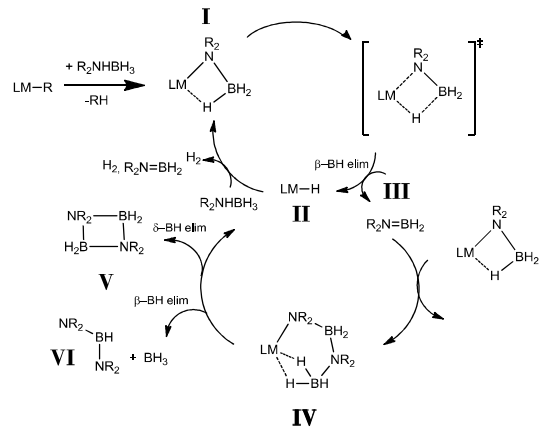
cheaper and more abundant group 2 and group 3/13 metals in their highest oxidation states has been found to be competent for the dehydrogenation of amine-boranes.[12] In contrast to the reactivity derived from low oxidation state or more electron-rich catalytic centers, for such series of metals the possibility of B-H oxidative addition and/or B-N reductive elimination is unavoidably excluded.

Hill and coworkers[12a-12e] have carried out a wide survey of the catalytic activity of Group 2 elements in amine-boranes dehydrocoupling reactions and suggested that the process that leads to the formation of ultimate products, such as the cyclic dimer $[BH_2{=}NMe_2]_2$, is predominantly metal-mediated according to the mechanism illustrated in Scheme 1, which accounts for the observed reactivity. The proposed mechanism is supported by the detection of the unsatured species $BH_2{=}NR_2$ during the course of the reaction and the formation of the $\{H_3BNR_2BH_2R_2N\}^-$ anion alongside the apparent metal hydride formation. The catalytic B-N bond formation and turnover depends on production and insertion of the unsaturated species $R_2N{=}BH_2$ to yield a key catalytic intermediate containing the $[H_3BNR_2BH_2R_2N]^-$ ion. Subsequent formation of the amidoborane products, $[H_2BNMe_2]_2$ and $HB(NR_2)_2$, is then dictated by the relative energetics of a sequence of metalated amidoborane β-hydride elimination, polarized aminoborane insertion and δ-hydride, eventually in competition with further β-hydride elimination, steps. What emerges from these studies is that an increase of the cation charge density as well as a decrease of the radius produces a consequent increase in dehydrocoupling activity and resultant ability of cation center to mediate each step involved in the catalytic cycle. Since the initial studies concerned primarily the dimethylamine borane (DMAB), the same authors have extended their studies to a wider range of alkylamine-boranes and demonstrated the proposed mechanism to be not restricted to DMAB substrate only.[12c]

Density Functional Theory (DFT) has been used here to explore the mechanistic routes of the dehydrocoupling reaction of several more or less bulky amine-boranes according to the catalytic regime pointed up in Scheme 1. Given that the first step of the process is likely to be formation of amidoborane derivatives as the true catalysts for the amine-borane dehydrocoupling, the mechanistic investigation really starts from such species, which are formed by loss of a RH unit due to a hydrogen atom transfer from the entering amine-borane to the R group of the metal complex. In particular, in the present computational exploration, amidoborane complexes **I** are Mg and Ca β-diketiminato amidoborane derivatives of the form $[HC\{(Me)CN(2,6\text{-}^{i}Pr_2C_6H_3)\}_2MNR_2{\cdot}BH_3$ (M = Mg, n = 0; M = Ca, n = 1) that are produced by reaction of the corresponding silylamides, $[HC\{(Me)CN(2,6\text{-}^{i}Pr_2C_6H_3)\}_2M(THF)_n\{N(SiMe_3)_2\}]$ with an equimolar quantity of amine-boranes R_2HNBH_3.[12b,12c] Further reaction of the amine-boranes with such derivatives induces the formation of species that are key intermediates in the proposed catalytic cycle in Scheme 1.

Scheme 1



Once that the metal amidoborane species **I** is formed, it can undergo a β-hydride elimination to form a metal hydride LM-H **II** together with an unsaturated aminoborane $R_2N{=}BH_2$ **III**. At this point the reaction pathway bifurcates. From one hand the metal hydride specie **II** can react directly with another amine-borane molecule with the consequent loss of molecular hydrogen and regeneration of the starting amidoborane compound **I**. Alternatively, an insertion reaction of the unsaturated species **III** into the M-N bond of LM-H **II** metal hydride could occur in order to obtain the anion $[H_3BNR_2BH_2R_2N]^-$ coordinated to the metal center, **IV**. Owing to the demonstrated olefin-like reactivity of aminoboranes,[13] the authors have hypothesized that the key B-N bond forming step is the insertion of the olefin isoelectronic aminoborane $R_2N{=}BH_2$ into the metal-N bond. The formed intermediate can be converted into the cyclic product $[R_2N\text{-}BH_2]_2$ **V** by a δ-hydride elimination. Alternatively, as a result of a further β-hydride elimination step minor quantities of diaminoboranes $HB(NR_2)_2$, **VI**, are formed. The metal hydride **II** is formed that is poised to react with an additional amine-borane molecule to restore the amidoborane complex **I** and restart the catalytic cycle.

To date, it is still a difficult challenge to obtain experimentally direct and accurate insight in the mechanistic pathways of chemical reactions. The most important limitation is the fact that key intermediates often have a very short lifetime. This limitation holds also for the metal catalyzed dehydrocoupling reactions of amine-boranes, such as those under examination in the present paper, that are today well established, but whose mechanism is very often unclear. Computational studies do not suffer from these limitations and provide therefore a valuable complementary approach to study these reactions.

With the present study we attempt to shed light on the dehydrocoupling process underlying mechanism, whose knowledge is indispensable for the improvement of the operative conditions and the application of such chemistry to a broader array of catalytic reactions.

Results and Discussion

The DFT investigation, whose results are reported here, was performed with a twofold purpose: to prove the viability of the pathways of the mechanistic scheme proposed by Hill and coworkers[12b-12e] and to compare the behaviors of Mg and Ca complexes to assess whether differences in radius and charge density can be considered responsible of the observed differences in reactivity. The influence that the steric demand of amine-boranes can have on the course of the reaction has been likewise examined by performing calculations for the dehydrogenation of dimethylamine-borane, DMAB, pyrrolidine-borane, PB and di-*iso*-propylamine-borane. In order to reduce the computational expense the β-diketiminato ligand was simplified by replacing the two ^{i}Pr substituents on N-aryls with H atoms. Unless otherwise noted, in what follows, the discussed energies are relative free energies calculated in THF solvent and with respect to amidoborane complex **I**.

Mechanism of hydrogen release from DMAB promoted by Mg amidoborane complex: The calculated B3PW91 free energy profiles relative to the reaction between the Mg complex $HC\{(Me)CN(2,6\text{-}C_6H_5)\}_2MgNMe_2{\cdot}BH_3$, **I-Mg$_{DMAB}$** and a DMAB molecule are sketched in Figure 1. Figure 2 shows the structure of the intercepted stationary points except that of the complex containing the anion coordinated to the metal centre, which is depicted in Figure 3. Supporting Information (SI) give the geometries of all the optimized structures shown here.

The amidoborane complex **I-Mg$_{DMAB}$** contains a pseudo-four-coordinate magnesium centre, where the coordination sphere of the

alkaline earth element is provided by the bidentate β-diketiminato ligand and the chelating anion of the DMAB molecule interacting with magnesium through formally deprotonated nitrogen atom and BH hydrides from the BH_3 component of DMAB. Transfer of an H atom from boron to the Mg centre occurs by overcoming a free energy barrier of 20.7 kcal/mol, corresponding to the **TS-$_{I\text{-}II}$Mg$_{DMAB}$** transition state for the BH/MgN σ-bond metathesis. The normal mode associated with the imaginary frequency calculated to be 140i cm^{-1}, corresponds to the stretching of the B-H bond that allows the transfer of the H atom to Mg. Boron hybridization changes from sp^3 to sp^2, whereas the nitrogen atom appears to be detached yet. The formed products the magnesium hydride, **II-Mg$_{DMAB}$**, and the aminoborane $Me_2N{=}BH_2$ **III$_{DMAB}$** are by only 1.3 kcal/mol more stable than the preceding transition state. As illustrated in Figure 1, the next step, along the pathway labeled (a), can be the reaction of the formed **II-Mg$_{DMAB}$** hydride with a second molecule of DMAB to release molecular hydrogen and regenerate the **I-Mg** complex that is poised to restart the catalytic cycle. Alternatively, the generated aminoborane **III$_{DMAB}$** can insert (pathway (b)) into the Mg-N bond of the unreacted amidoborane **I-Mg$_{DMAB}$** to form what is considered to be a key catalytic intermediate, that is the **IV-Mg$_{DMAB}$** complex containing the $[H_3BNR_2BH_2R_2N]^-$ anion.

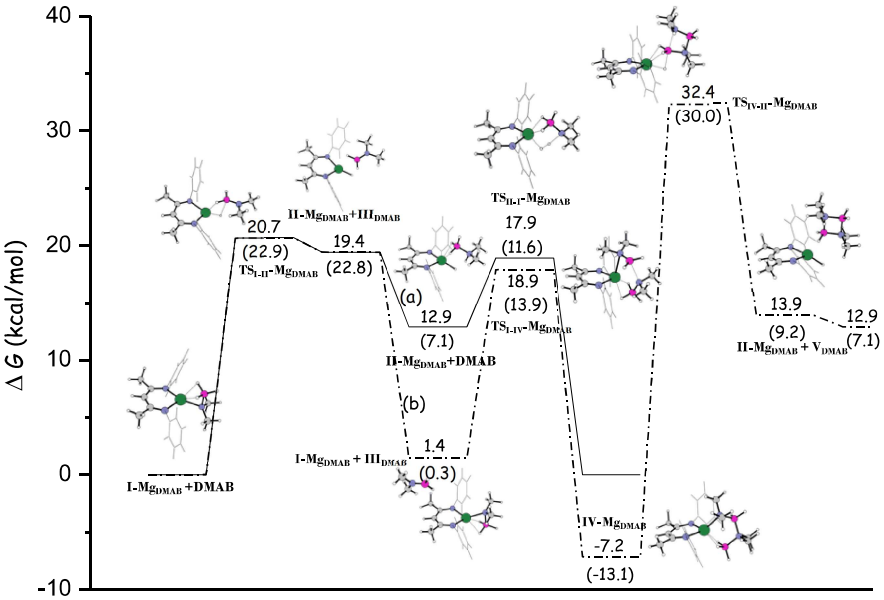


Figure 1. Calculated B3PW91 free energy profiles for the dehydrocoupling reaction of DMAB assisted by the amidoborane **I-Mg$_{DMAB}$** complex. Along the pathway named (a) (solid line) the formed hydride complex reacts with a second DMAB molecule and along pathway (b) (dot-dashed line) the released aminoborane molecule inserts into the Mg-N bond of unreacted amidoborane. Gas-phase zero-point corrected energy changes are reported in parentheses.Energies are in kcal/mol and relative to reactants' asymptote.

Interaction of the Mg hydride with a second DMAB molecule, pathway (a), causes a stabilization of 12.9 kcal/mol. From the formed adduct **II-Mg$_{DMAB}$+ DMAB** molecular hydrogen loss occurs through the **TS-$_{II\text{-}I}$Mg$_{DMAB}$** with a low free energy barrier of 5.3 kcal/mol. The intercepted transition state is characterized by an imaginary frequency of 210i cm^{-1} and the associated normal mode mainly corresponds to the stretching of the Mg-H and N-H bonds. As a result, the initial complex **I-Mg$_{DMAB}$** is regenerated and by reaction with a new DMAB molecule the catalytic cycle can restart.

Along the pathway labeled (b), instead, the released unsaturated aminoborane $R_2N{=}BH_2$ reacts with unreacted amidoborane complex **I-Mg$_{DMAB}$** to afford the **IV-Mg$_{DMAB}$** complex. The free energy barrier of the transition state, labeled **TS$_{I\text{-}IV}$**, which allows this transformation is 16.5 kcal/mol. The structure of the transition state and the calculated imaginary frequency reveal that the aminoborane coordinates to the Mg centre through the nitrogen atom and inserts into the Mg-N bond of the amido complex **I-Mg$_{DMAB}$**. The formed **IV-Mg$_{DMAB}$** complex, which lies 1.8 kcal/mol in solvent above the entrance channel of the reaction, contains a pseudo-four-coordinate magnesium center, in which the coordination sphere is provided by the bidentate β-diketiminato ligand and the chelated $[H_3BNMe_2BH_2Me_2N]^-$ ion. The anion interacts with the Mg centre primarily through the formally deprotonated nitrogen atom and the B-H hydrides of the BH_3 unit. Such compound has been characterized by a single-crystal X-ray diffraction experiment. The comparison between the computed and experimental values of the most relevant geometrical parameters is given in Figure 3. The very good agreement between theoretical and experimental values proves the reliability of the reported results and the suitability of the employed computational protocol. A BH hydride δ-elimination leads from intermediate **IV-Mg$_{DMAB}$** to the elimination of the cyclic dimer $[Me_2N\text{-}BH_2]_2$ **V$_{DMAB}$** and restoration of the **II-Mg$_{DMAB}$** intermediate. Nevertheless, for this elimination to occur it is necessary to surmount a high free energy barrier of 39.6 kcal/mol for the transition state **TS$_{IV\text{-}II}$Mg$_{DMAB}$**. The imaginary frequency of 628i cm^{-1}, which confirms the nature of transition state of the intercepted stationary point, corresponds to the transfer of a BH hydride to the Mg centre together with the formation of a new B-N bond. The reaction of the regenerated magnesium hydride complex with an additional amine-borane molecule, according to the description of the mechanistic steps along the pathway (a), yields again the initial Mg amidoborane complex.

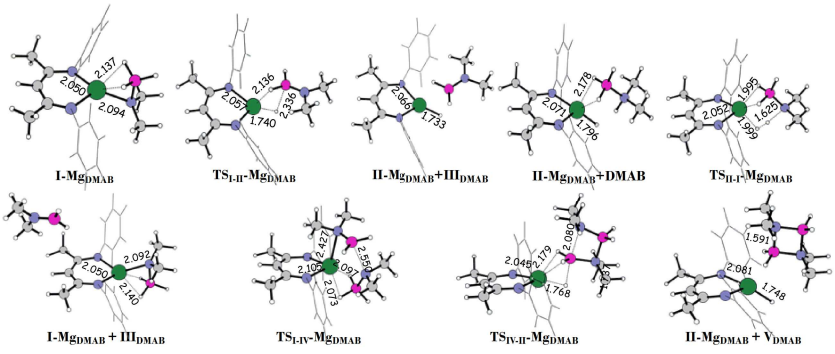


Figure 2. DFT fully optimized structures of stationary points intercepted along DMAB dehydrocoupling (a) and (b) pathways assisted by the β-diketiminato Mg amidoborane complex **I-Mg$_{DMAB}$**. Selected bond distances are provided in Å.

For the sake of completeness, the mechanism of the reaction that as a result of a further, eventually competitive, β-hydride

elimination step from the **IV-Mg$_{DMAB}$** intermediate can afford the observed diaminoborane species HB(NMe$_2$)$_2$ by loss of a BH$_3$ unit has been equally examined. The structures of the intercepted intermediates and transition states and their energetics are provided in Figure S2 of the Supporting Information. From the results of our calculations clearly appears that the pathway is not viable. The process is not concerted, but it should occur in two steps. In the first one the β-hydride is transferred to the terminal BH$_3$ group to form a BH$_4^-$ anion that coordinates to the metal centre and the formed aminoborane is simultaneously eliminated. In a second step an H atom from the anion should be transferred to metal atom to restore the **II-Mg$_{DMAB}$** intermediate. The first calculated barrier for the β-BH transfer, 55.3 kcal/mol, is very high. The situation is even worst for the formation of the final products: **II-Mg$_{DMAB}$** + BH$_3$ + HB(NMe$_2$)$_2$ that are calculated to be completely inaccessible as they lie 57.1 kcal/mol above the reference energy of the **IV-Mg$_{DMAB}$** intermediate. This reaction channel has been disregarded in the calculations reported below.

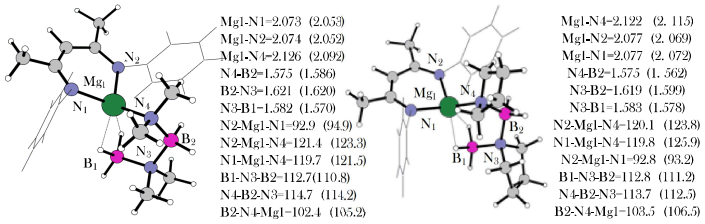


Figure 3. DFT optimized geometrical structure of β-diketiminato Mg complexes containing the [H$_3$BNMe$_2$BH$_2$Me$_2$N]$^-$ and [H$_3$BN(CH$_2$)$_4$BH$_2$(CH$_2$)$_4$N]$^-$ anions coordinated to the metal center. Selected bond lengths (Å) and angles (degrees) are compared with available experimental values (in parentheses).

The outcomes of our computational exploration of the surmised mechanism proposed to account for the experimental observations, show that the pathway that from the generated Mg-H hydride complex leads, by reaction with an additional DMAB molecule, to the elimination of a H$_2$ molecule and regeneration of the **I-Mg$_{DMAB}$** catalyst is the most favorable. Along the pathway that involves formation of the complex containing the anion [H$_3$BNR$_2$BH$_2$R$_2$N]$^-$ coordinated to the metal center, the rate determining step is represented by the elimination of the cyclic dimer **V$_{DMAB}$**. The high energy barrier that hampers the formation of **V$_{DMAB}$** makes the pathway named (b) impracticable, or, at least, it is unlikely that once intermediate **IV-Mg$_{DMAB}$** is formed, the reaction can proceed to form the final product. Intermediate **IV-Mg$_{DMAB}$** sits in a deep well and for that reason it should be detectable and characterizable. The barrier of 39.6 kcal/mol for the formation of the next minimum can be compared with the barrier calculated for the off-metal uncatalyzed dimerization.[11] The calculations show that the off-metal dimerization is exothermic (4.2 kcal/mol), as it should be,[9h] and give a free energy barrier of 20.5 kcal/mol, which is in good agreement with that experimentally determined of 18.2±2.9 kcal/mol.[14] As a consequence, free monomers, once released, should form the cyclic dimer [Me$_2$N-BH$_2$]$_2$ in solution without the involvement of the Mg complex. The possibility has been taken into consideration, that such independently formed cyclic dimer can react with the magnesium–hydride species **I-Mg$_{DMAB}$** to produce the **IV-Mg$_{DMAB}$** complex. Looking at the energy profile reported in Figure 1 from the right to the left side the calculated energetic cost of such transformation results to be about 18 kcal/mol, that is a value comparable with the energy barrier of 16.5 kcal/mol for the formation of the **IV-Mg$_{DMAB}$** complex by insertion of the aminoborane R$_2$N=BH$_2$ into the Mg-N bond of the amidoborane **I-Mg$_{DMAB}$** catalyst. However, the experiment carried out to prove whether the products of δ-hydride elimination could combine to form the anion observed in compound **IV-Mg$_{DMAB}$** did not give any corroboration of this hypothesis.

Alkylamine-boranes dehydrocoupling promoted by Mg β-diketiminato complex: In order to establish what is the influence of the identity of the substrate on the energetics of the process, mainly due to the steric hindrance of alkyl substituents, analogous calculation have been carried out for Mg β-diketiminato amidoborane derivatives of pyrrolidine-borane, PB, and di-*iso*-propylamine-borane. Both reaction pathways labeled (a) and (b) have been examined and the corresponding results are summarized in Figure 4 and 5, respectively. Fully optimized geometrical structures of stationary points together with Cartesian coordinates are given in the Supporting Information.

Dehydrocoupling reaction of the Mg β-diketiminato pyrrolidine-borane amidoborane derivative has been experimentally examined,[12c] whereas for the di-*iso*-propylamine-borane experimental information for the same process has been obtained by considering the magnesium amidoborane species formed by reaction with the homoleptic silylamide [Mg{N(SiMe$_3$)$_2$}$_2$]. In the former case different products are observed as a function of the reaction stechiometry. In presence of 1 equivalent of PB the complete consumption of the substrate leads to the formation of an apparent amidoborane complex, whereas when 2 equivalents of PB are used the formation of the complex containing the anion [H$_3$BN(CH$_2$)$_4$BH$_2$(CH$_2$)$_4$N]$^-$ has been detected indicating a behavior analogous to that of DMAB magnesium amidoborane. On the contrary, when the more sterically demanding ^{i}Pr$_2$NH·BH$_3$ amine-borane reacts with the magnesium silylamide [Mg{N(SiMe$_3$)$_2$}$_2$] the only observed product is the ^{i}Pr$_2$N=BH$_2$ aminoborane, while no evidence for the formation of the [H$_3$BN^{i}Pr$_2$BH$_2$^{i}Pr$_2$N]$^-$ anion exists. The outcomes of our theoretical exploration are in agreement with the experimental findings and are helpful to their rationalization. As illustrated in Figures 4 and 5 the

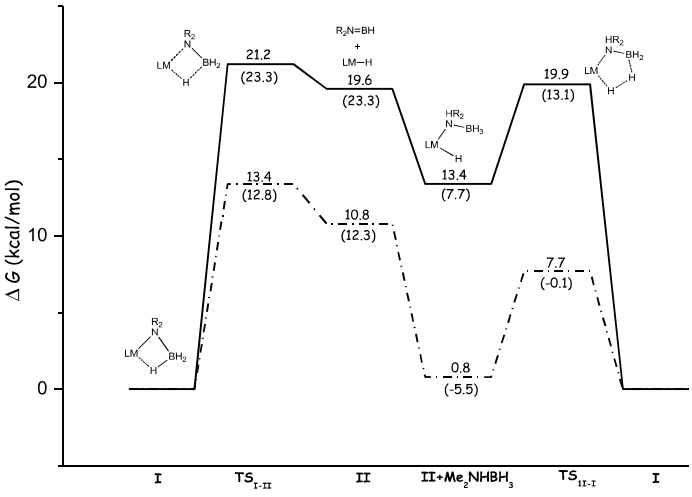


Figure 4. Calculated B3PW91 free energy profiles for the dehydrocoupling of pyrrolidine-borane (solid line) and di-*iso*-propylamine-borane (dot-dashed line) assisted by the corresponding Mg amidoborane complexes along the pathway named (a). Gas-phase zero-point corrected energy changes are reported in parentheses. Energies are in kcal/mol and relative to reactants' asymptote

first common step of both pathways (a) and (b), that is the BH/MgN σ-bond metathesis that leads to the formation of the β-diketiminato Mg hydride species, occurs by overcoming for the **TS-$_{I-II}$** transition state an energy barrier of 21.2 and 13.4 kcal/mol for PB and ^{i}Pr$_2$NH·BH$_3$ substrates, respectively. The height of the activation energy barrier calculated for PB is comparable to that of DMAB,

whereas the barrier for the β-hydride elimination from the $^{i}Pr_2NH{\cdot}BH_3$ amine-borane is lower by about 7 kcal/mol. This difference in behaviour can be ascribed to the presence of the more electron donating ^{i}Pr groups on nitrogen. Indeed, as it can be expected and it is confirmed by the NBO population analysis the charge density distribution (see Figure S5 of Supporting Information) is more favourable to the β-BH hydride release. Further support comes from the calculated values of the bond distance between the boron atom and the H atom that will be transferred to the Mg centre, which is 1.244 Å for DMAB and PB and 1.255 Å for $^{i}Pr_2NH{\cdot}BH_3$. The eliminated aminoborane **III** together with the formed magnesium hydride **II** are more stable, by only about 2 kcal/mol, than the preceding transition state in both cases. Interaction of complex **II** with a second amine-borane molecule causes a stabilization of 6.2 kcal/mol for PB and 10.0 kcal/mol for $^{i}Pr_2NH{\cdot}BH_3$.

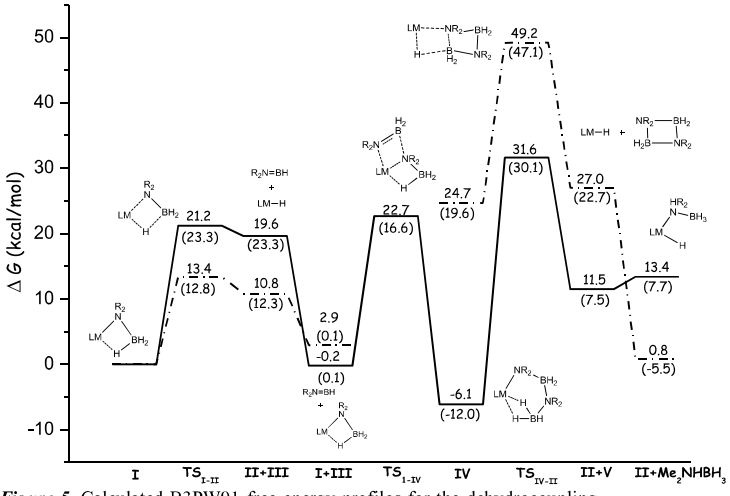


Figure 5. Calculated B3PW91 free energy profiles for the dehydrocoupling of pyrrolidine-borane (solid line) and di-*iso*-propylamine-borane (dot-dashed line) assisted by the corresponding Mg amidoborane complexes along the pathway named (b). Gas-phase zero-point corrected energy changes are reported in parentheses. Energies are in kcal/mol and relative to reactants' asymptote

From the adduct between intermediate **II** and an additional amine-borane a H_2 molecule is eliminated and the starting amidoborane complex is regenerated through the $\mathbf{TS_{II\text{-}I}}$ transition state with a barrier of about 7 kcal/mol for both PB and $^{i}Pr_2NH{\cdot}BH_3$ substrates. Along the pathway (b), the eliminated aminoborane **III**, alternatively, can react with the amidoborane catalyst **I**, to form the complex **IV**, containing the anion obtained by the insertion of the aminoborane **III** into the Mg-N bond of the amidoborane complex. The fully optimized structure of complex **IV** formed by reaction with PB is shown in Figure 3, where also calculated and experimental values of selected geometrical parameters are reported. The barrier for the transition state $\mathbf{TS_{I\text{-}IV}}$ is calculated to be 19.8 kcal/mol for PB. All the attempts, instead, to locate an analogous transition state for this transformation for $^{i}Pr_2NH{\cdot}BH_3$ have been unsuccessful, most likely because of the involved aminoborane greater steric demands, which hinder insertion into the Mg-N bond of the amidoborane. The formed intermediate **IV** along the dehydrocoupling pathway of PB is stabilized by 6.1 kcal/mol with respect to the entrance channel, whereas for $^{i}Pr_2NH{\cdot}BH_3$ an endothermicity of 24.7 kcal/mol has been calculated. Finally, in order to release the cyclic dimer and restore the corresponding Mg hydride it is required to overcome a barrier of 37.7 and 24.5 kcal/mol for PB and $^{i}Pr_2NH{\cdot}BH_3$, respectively. In analogy with DMAB, also for the PB and $^{i}Pr_2NH{\cdot}BH_3$ substrates the accessibility of self-dimerization in solution has been examined. The calculated pathways can be found Figure S6 of the Supporting Information. The $(CH_2)_4N{=}BH_2$ monomers can dimerize off the metal by overcoming an energy barrier of 24.4 kcal/mol and the reaction is thermoneutral. The aminoborane $^{i}Pr_2N{=}BH_2$ is experimentally demonstrated to resist to self-dimerization.[15] Calculations confirm that the energy barrier that is necessary to surmount is very high, 40.3 kcal/mol, and the cyclic dimer that should be produced lies 20.1 kcal/mol above the dissociation limit of reactants. Summarizing, from the illustrated results of our computational analysis it results that for the di-*iso*-propylamine-borane the only viable path is that involving release of the $^{i}Pr_2N{=}BH_2$ monomer and activation of a second amine-borane molecule assisted by the Mg hydride intermediate, whose formation is favoured by the electron-donating nature of the ^{i}Pr groups. Alternative reactions as well as self-dimerization are precluded by the steric hindrance of the same alkyl groups. For the less sterically demanding PB substrate, instead, although formation of the magnesium hydride and loss of the corresponding aminoborane molecule is less facile, the subsequent reaction with an additional substrate molecule is straightforward as well as the reaction with the unreacted amidoborane to yield the intermediate containing the $[H_3BN(CH_2)_4BH_2(CH_2)_4N]^-$ anion is not precluded. Our calculations, instead, do not support the hypothesis that the cyclic dimer could be released from the accessible intermediate **IV**. The height of the barriers for the dimerization of the aminoborane monomers and for the reaction of the magnesium hydride with the released $(CH_2)_4N{=}BH_2$ monomer to form intermediate **IV** are calculated to be 24.4 and 19.8 kcal/mol, respectively. According to experiments, for the $^{i}Pr_2NH{\cdot}BH_3$ neither the $[H_3BN\,{}^{i}Pr_2BH_2(CH_2)_4N]^-$ anion nor the cyclic dimer $[^{i}Pr_2N\text{-}BH_2]_2$ can be formed.

Mechanism of hydrogen release from dialkylamine-boranes promoted by Ca amidoborane complexes: Calcium based complexes, albeit less reactive than their magnesium counterparts, are found to show a similar reactivity in dehydrocoupling processes and yield similar products when thermally promoted catalytic conditions are employed.[12b, 12c] For that reason the general reactivity pattern shown in Scheme 1, assumed to describe the viable pathways for all Group 2-centred, should be valid also for amine-borane dehydrocoupling reactions assisted by Ca catalysts. Experiments carried out by employing the Ca β-diketiminato silylamide $[HC\{(Me)CN(2,6\text{-}{}^{i}Pr_2C_6H_3)\}_2Ca(THF)\{N(SiMe_3)_2\}]$ and DMAB clearly evidenced the formation of the corresponding amidoborane $[HC\{(Me)CN(2,6\text{-}{}^{i}Pr_2C_6H_3)\}_2CaNMe_2{\cdot}BH_3$.[12b] Further reactivity of the detected amidoborane has been suggested on the basis of NMR spectra and their similarities with analogous spectra of the dehydrocoupling reaction of DMAB assisted by Mg amidoboranes. Although NMR spectra support only the formation of the monomeric $Me_2N{=}BH_2$, the authors do not totally exclude that β-diketiminato calcium-hydride and dimeric $[Me_2N{=}BH_2]_2$ species could be formed. The reduced facility toward β-hydride elimination and B-N coupling for group 2 elements heavier than magnesium has been confirmed by these results. Analogous conclusions have been drawn on the basis of the experimental findings for the reaction of $[HC\{(Me)CN(2,6\text{-}{}^{i}Pr_2C_6H_3)\}_2Ca(THF)\{N(SiMe_3)_2\}]$ with PB and $[Ca\{N(SiMe_3)_2\}_2]$ with $^{i}Pr_2NH{\cdot}BH_3$. Overall, experiments support only formation of the corresponding Ca amidoborane complexes and, in appropriate conditions, of the aminoboranes. In particular, for $^{i}Pr_2NH{\cdot}BH_3$, clean and selective conversion to $^{i}Pr_2N{=}BH_2$ upon addition of 2 equivalents of the amine-borane has been assumed as an indication that that dehydrogenation should be assisted by coordination of a further molecule of $^{i}Pr_2NH{\cdot}BH_3$. The fully optimized structures of the Ca amidoborane complexes formed by reaction with DMAB and PB substrates are provided in Figure 6, where also the comparison between the calculated and experimental values of selected bond

lengths and angles is provided. The reproduction of the experimental geometrical parameters of the complex is good. Coordination to the Ca centre is provided by the β-diketiminato ligand, the dimethylamidoborane through formally deprotonated nitrogen atom and B-H hydrides of the BH_3 unit and a THF solvent molecule.

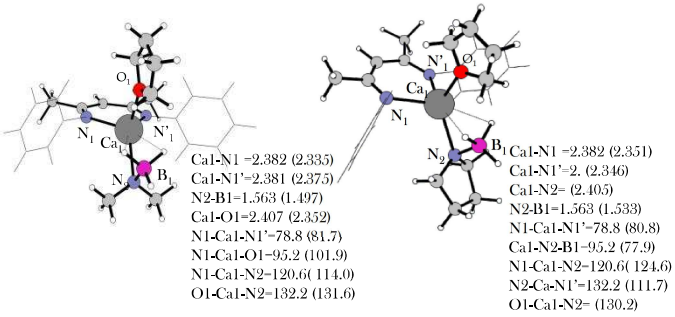


Figure 6. DFT optimized geometrical structure of β-diketiminato Ca amidoboranes of DMAB and PB. Selected bond lengths (Å) and angles (degrees) are compared with available experimental values (in parentheses).

At the beginning of our computational investigation, driven by the hypothesis that a calcium hydride should be formed, we have used all the suitable computational strategies to intercept the transition state that by BH β-elimination from the amidoborane **I** leads to the release of the aminoborane $R_2N{=}BH_2$ with concomitant formation of the calcium hydride **II**. All the attempts to computationally model the pathway that leads to the calcium hydride intermediate have been unsuccessful. Moreover, the optimized structures of the β-diketiminato Ca hydrides are calculated to be less stable. For example, the Ca-H compound lies about 35 kcal/mol above the reference energy of the Ca DMAB amidoborane derivative. Therefore, all the efforts have been concentrated on the search of a viable alternative pathway. The energy profiles for the only pathway that appears to be practicable are reported in Figure 7.

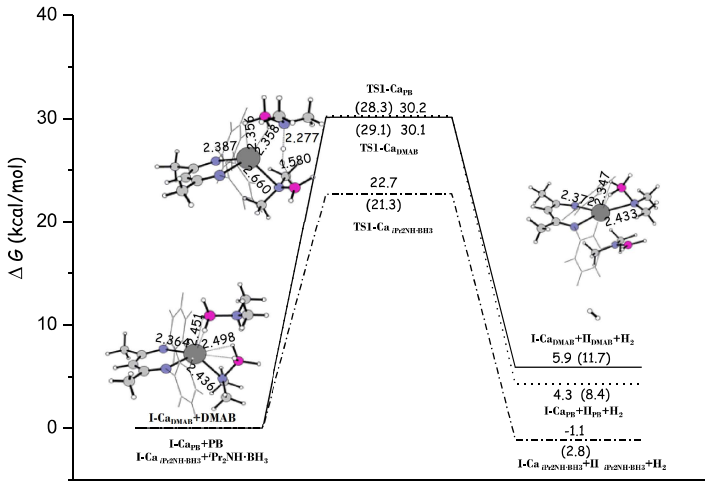


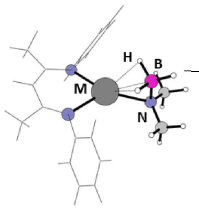
Figure 7. Calculated B3PW91 free energy profiles for the dehydrogenation of DMAB (solid line), PB (dashed line) and $^{i}Pr_2NH{\cdot}BH_3$ (dot-dashed line) promoted by the corresponding β-diketiminato Ca amidoboranes. Gas-phase zero-point corrected energy changes are reported in parentheses. Energies are in kcal/mol and relative to reactants' asymptote.

In the same figure are sketched the structures of the intercepted stationary points for the reaction of the DMAB substrate. Cartesian coordinates can be found in the Supporting Information along with the structures and Cartesian coordinates of the analogous stationary points for PB and $^{i}Pr_2NH{\cdot}BH_3$. According to the conclusion previously drawn[16] that calcium and magnesium β-diketiminato complexes catalytic activity is inhibited by Lewis bases such as THF as well as substrate or product binding to the metal center, only when the THF-free calcium catalyst **I-Ca$_{DMAB}$** coordinates a second DMAB molecule a reaction can take place. Intermolecular elimination of molecular hydrogen occurs by interaction of the NH proton of the aminoborane molecule and a BH hydride of the ligated amidoborane through the transition state TS1-Ca$_{DMAB}$ with a solvent corrected free energy barrier of 30.1 kcal/mol. As a consequence, also the aminoborane $Me_2N{=}BH_2$ molecule is eliminated and the THF-free amidoborane catalyst is regenerated. Coordination of a further DMAB molecule restarts the catalytic cycle. The reaction proceeds in a very similar way for the other two examined substrates and an energy barrier with the same height, 30.2 kcal/mol, has to be overcome when the involved aminoborane is PB. A change in behavior, in agreements with experimental evidence, occurs when the substrate is $^{i}Pr_2NH{\cdot}BH_3$. Both steric hindrance and electron-donating nature of the ^{i}Pr groups cooperate in lowering the activation barrier height that is calculated to be 22.7 kcal/mol. The charge induction enhances the charge polarization of the BH hydride and the acidity of the NH proton. The steric hindrance of the ^{i}Pr groups on the nitrogen atom of the amidoborane causes an elongation of the Ca-N bond favouring the release of the $^{i}Pr_2N{=}BH_2$ aminoborane. The difference in height of the activation barriers allows the rationalization of the experimental findings. Once the amidoborane complex is formed, in all cases further addition of a second amino-borane molecule is required for the dehydrogenation reaction to proceed. However, for DMAB and PB substrates, due to the barriers which hamper products formation, only by heating the sample the corresponding aminoboranes can be formed and detected.

Cation charge density and radius effects: The outcomes of our theoretical investigation clearly demonstrate that in spite of the apparent analogy in behaviors of the examined Mg- and Ca-based catalytic systems toward amine-borane dehydrocoupling, over-generalizations, as recommended by Hill and coworkers,[12c] have to be avoided. The observed difference in catalytic activity of Mg- and Ca-based systems has been assumed to depend on the decreased stability of formed amidoboranes toward β-hydride elimination in going from Mg to Ca. The products of such β-H elimination should be, according to Scheme 1, the corresponding metal-hydride and an aminoborane molecule, both poised to further react. Our calculations show that, when the metal is Ca, only after pre-coordination of an additional amine-borane molecule to the metal centre β-H elimination can occur to release molecular hydrogen, while formation of a Ca hydride intermediate is not accessible. That means that the reaction mechanism changes. The transfer of an H atom to the Ca centre does not occur and the increase of the ionic radius and the resultant charge density at the metal centre should be at the origin of this behavior. The NBO charge analysis results and the values of the most relevant bond distances are compared in Table 1. For Ca the calculated values of both THF-free and THF-solvated complexes are provided. The Ca cation bears a positive charge (+1.622, +1.540, respectively) greater than that on Mg (+1.483). Since the BH hydrogen that is transferred carries a partial negative charge, shift to the calcium centre should be more favorable. Nevertheless, as a consequence of the increase in ionic radius from 0.72 Å for Mg^{2+} to 1.00 Å for Ca^{2+} (in six-coordinate complexes), the bond distances between the metal centre and the nitrogen and boron atoms of coordinated amidoborane are

considerably longer for Ca than Mg. It can be proposed that, owing to the too long distance between the Ca centre and the BH hydride, transfer cannot occur.

Table 1. Selected values of NBO charges and bond distances of Mg and Ca β-diketiminato amidoborane derivatives.



	NBO		Distances (Å)		
	H	M	M-H	M-N	M-B
I-Ca_{DMAB} THF-free	-0.084	1.622	2.354	2.384	2.510
I-Ca_{DMAB} THF-solvated	-0.079	1.540	2.406	2.408	2.560
I-Mg_{DMAB}	-0.051	1.483	2.137	2.094	2.241

The Ca-hydride complex that should be formed by β-hydride transfer, as reported above, results to be significantly less stable than the corresponding amidoborane complex. Formation of the Mg-hydride complex, instead, is almost thermoneutral (see Figure 1). The calculated Mg-H bond length of 1.734 Å compares well with the values experimentally estimated[12j] that range from 1.72(3) to 1.90(3) Å as a function of the environment. The calculated Ca-H bond distance of 2.057 Å is significantly longer and in line with the hypothesis that the bonding interaction, at least in monometallic species, is too weak to have access to the hydride complex formation.

Conclusions

In an effort to establish whether proposed largely benign and inexpensive Group 2 complexes can function as catalysts for the dehydrocoupling of amine-boranes substrates equally well as electron rich mid- and late-transition metal species, a detailed theoretical exploration of the mechanistic scenario put forward on the basis of experimental evidences has been carried out. Catalytic activity of β-diketiminato Mg and Ca silylamides toward dehydrocoupling of dimethylamine-borane, pyrrolidine-borane, and di-*iso*-propylamine-borane substrates has been examined. The differences in catalytic activity of Mg and Ca complexes have been examined and rationalized, as well as the influence on the mechanism of the steric hindrance of the alkyl substituents on nitrogen. The formed Mg amidoboranes undergo BH/MgN σ-bond metathesis to form the corresponding hydrides. Reaction pathway, then, bifurcates. The hydride complex can react along a pathway denominated (a) with a second amine-borane molecule to eliminate molecular hydrogen and restore the amidoborane catalyst. Alternatively, along a pathway denoted as (b) the released aminoborane molecule can insert into the Mg-N bond of the unreacted amidoborane to form a complex containing the $[H_3BNR_2BH_2R_2N]^-$ anion. Loss of an H_2 molecule causes the release of the final cyclic dimer product and regeneration of the hydride complex. With respect to the mechanistic hypotheses formulated on the basis of experimental findings our calculation show that the pathway (a) is largely more favorable for all the examined amine-boranes and especially for the di-*iso*-propylamine-borane, due to the electron-donating nature of the ^{i}Pr substituents. The complex with the $[H_3BNR_2BH_2R_2N]^-$ anion coordinated to the metal centre is accessible for dimethylamine-borane and pyrrolidine-borane and inaccessible to the more sterically demanding di-*iso*-propylamine-borane, whereas the barrier to release the cyclic dimer is very high in all cases. The possibility exists that the $[Me_2N\text{-}BH_2]_2$ and $[(CH_2)_4N{=}BH_2]_2$ cyclic dimers, which can be formed off-metal in solution, react with the Mg hydride to yield the complex containing the corresponding anion.

In spite of the analogies in amine-boranes dehydrocoupling catalytic activity between Mg- and Ca-based complexes the outcomes of our computational analysis confirm the experimentally observed reduced reactivity of Ca complexes. The dehydrogenation reaction, when the involved metal is Ca, can proceed only once a second amine-borane molecule coordinates to the metal centre and intermolecular H_2 elimination occurs. Ca hydride formation is inaccessible very likely because of the increase of the cationic radius. The distance between the Ca centre and the BH hydride is too long to allow the transfer on the metal centre. Reported results are of particular interest as, although amine borane dehydrogenation is now well-established, mechanistic insight is still lacking for many systems. Future work will continue the theoretical exploration and rationalization of the catalytic behaviours toward dehydrogenation/dehydrocoupling of amine-boranes of a more extended range of Group 2 metals and d^0 species of the early transition metals.

Computational Details

Geometry optimizations as well as frequency calculations for all the reactants, intermediates, products and transition states have been performed at the Density Functional level of theory by using the B3PW91 functional[17] as implemented by GAUSSIAN03[18] code. For all the atoms, including Mg and Ca, all electron standard 6-311G** basis sets of Pople and co-workers were employed. For each optimized stationary point vibrational analysis was performed to establish its nature of minimum or saddle point and zero-point vibrational energy (ZPVE) corrections have been included in all relative energies (ΔE). For transition states it has been carefully checked that the vibrational mode associated to the imaginary frequency corresponds to the correct movement of involved atoms. Furthermore, the intrinsic reaction coordinate (IRC)[19] method has been used to asses that the localized TS's correctly connect to the corresponding minima along the imaginary mode of vibration. The free energies, *G*, have been calculated for T=298.15 K. All relative energies are reported in kcal/mol. Implicit solvent effects have been calculated through the integral equation formalism polarizable continuum model (CPCM).[20] Since preliminary calculations have clearly shown that geometry relaxation effects are not significant, single point calculations have been performed by using more extended 6-311+G** basis sets on fully optimized geometry of each stationary point along the reaction paths. Calculations have been carried out in THF solvent (ε=7.6). Reaction Gibbs free energies in solution, Δ*G*sol, have been calculated for each process as the sum of two contributions: a gas-phase reaction free energy, Δ*G*gas, and a solvation reaction free energy term calculated with the continuum approach, Δ*G*solv. NBO charge analysis[21] was carried out on the structures of some intercepted stationary points.

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[1] S. G. Shore, R. W. Parry, *J. Am. Chem. Soc.* **1955,** *77*, 6084-6085.
[2] A. B. Burg, H. I. Schlesinger, *J. Am.Chem. Soc.* **1937,** *59*, 780–787.
[3] A. Stock, E. Pohland, *Ber. Dtsch. Chem. Ges.* **1925,** 58, 657.
[4] R. D. Schultz, R. W. Parry, *J. Am.Chem. Soc.* **1958,** 80, 4-8.
[5] Shore, S. G.; Girardot, P. R.; Parry, R. W., *J. Am.Chem. Soc.* **1958,** 80, 20-24.
[6] R. W. Parry, *J. Chem. Educ.* **1997**, 74.
[7] U.S. DOE. Basic Research Needs for the Hydrogen Economy (http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf).
[8] a) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129, b) A. Staubitz, M. Besora, J. N. Harvey, I. Manners *Inorg. Chem.* **2008**, *47*, 5910-5918.
[9] Selection of papers reporting the use of transition metals for the H_3NBH_3 and amine-borane derivatives dehydrocoupling: (*a*) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Commun.*, **2001**, 962-963; (*b*) M. C. Denney, V. Pons, D.M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, **2006**, *128*, 12048-12049; (*c*) R. J. Keaton, J. M. Blacquiere and R. T. Baker, *J. Am. Chem. Soc.*, **2007**, *129*, 1844-1845; (*d*) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey, J. C. Linehan, *Inorg. Chem.*, **2008,** *47*, 8583-8585; (*e*) T.M. Douglas, A. M. Chaplin, A. S.Weller, *J. Am. Chem. Soc.*, 2008, **130**,

14432-14433; (*f*) N. Blacquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.*, **2008, *130,*** 14034-14035; (*g*) M. Kass, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem., Int. Ed.*, **2009**, ***48***, 905-907; (*h*) A. Friedrich, M. Drees and S. Schneider, *Chem.–Eur. J.*, **2009**, *15,* 10339-10342; (*i*) T. M. Douglas, A. M. Chaplin, A. S. Weller, X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, **2009, *131***, 15440-15456; (*j*) Y. Jiang, H. Berke, *Chem. Commun.*, **2007**, 3571-3573; (*k*) A. B. Chaplin and A. S. Weller, *Inorg. Chem.*, **2010**, *49*, 1111-1115; *(l)* Baker, R. T.; Gordon, J. C.; Hamilton, C. W.; Henson, N. J.; Lin, P.-H.; Maguire, S.; Murugesu, M.; Scott, B. L.; Smythe, N. C. *J. Am. Chem. Soc.* **2012**, 134, 5598-5609.

[10] *(a)* A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners *Chem. Rev.* **2010**, 110, 4023-4078, *(b)* A. Staubitz, A. P. M. Robertson, I. Manners *Chem. Rev.* **2010**, *110*, 4079 -4124.

[11] Butera V., Russo N., Sicilia E., *Chem. Eur J.* **2011**, *17*, 14586-14592.

[12] *(a)* M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics*, **2007**, *24*, 10410-10415; *(b)* D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem.–Eur. J.,* **2010**, *16*, 8508-8515; *(c)* M. S. Hill, M. Hodgson, D. J. Liprot and M. F. Mahon, *Dalton Trans.*, **2011**, 40, 7783-7790; *(d)* P. Bellham, , M. S. Hill, D. J. Liptrot, D. J .MacDougall, Mahon, M. F., *Chem. Commun*, **2011**, *47*, 9060-9062; *(e)* P. Bellham, , M. S. Hill, G. Kociok-Kohn, D.J. Liptrot, *Dalton Transactions*, **2013**, *42*, 737-745; *(f)* J. Spielmann, G. Jansen, H. Bandmann and S. Harder, *Angew. Chem., Int. Ed*., **2008**, *47*, 6290; *(g)* J. Spielmann and S. Harder, *J. Am. Chem. Soc.,* **2009**, *131*, 5064; *(h)* J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.,* **2009**, 6934; *(i)* J. Spielmann, D. F.-J. Piesik and S. Harder, *Chem.–Eur. J.,* **2010**, *16*, 8307-8318; *(j)* H. J. Cowley, M. S. Holt, R. L. Melen, J. M. Rawson and D. S. Wright, *Chem. Commun*., **2011**, *47*, 2682; *(k)* M. M. Hansmann, R. L. Melen and D. S. Wright, *Chem. Sci.,* **2011**, *2*, 1554; *(l)* R. J. Less, R. L. Melen and D. S. Wright, *RSC Adv*., **2012**, *2*, 2191.

[13] *(a)* G. Pawelke and H. Bürger, *Appl. Organomet. Chem*., **1996**, *10*, 147; *(b)* D. J. Brauer, H. Bürger, T. Dittmar, G. J. Pawelke, *J. Organomet. Chem*., **1995**, *493*, 167; (c) D. J. Brauer, S. Buchheim-Spiegel, H. Bürger, R. Gielen, G. Pawelke, J. Rothe, *Organometallics*, **1997**, *16*, 5321; (d) B. C. Dutmer, T. M. Gilbert, *Organometallics*, **2011**, 30, 778.

[14] C. J. Stevens, R. Dallanegra, A. B. Chaplin, A. S. Weller, S. A. Macgregor, B. Ward, D. McKay, G. Alcaraz,, S. Sabo-Etienne *Chem. Eur. J.* **2011**, *17*, 3011- 3020.

[15] (*a*) L. Euzenat, D. Horhant, Y. Ribourdouille, C. Duriez, G. Alcaraz, M. Vaultier, *Chem. Commun*., **2003**, 2280; (*b*) C. Y. Tang, A. L. Thompson and S. Aldridge, *Angew. Chem., Int. Ed.*, 2010, **49**, 2010.

[16] M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, G. Kaciock-Köhn, P. A. Procopiou, *Organometallics*, **2011**, *30*, 1493-1506.

[17] a) A. D. Becke, *J. Chem. Phys.,* **1993**, *98*, 5648–5652; b) J. P. Perdew, Y. Wang, *Phys. Rev. B,* **1992**, *45*, 13244–13249.

[18] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[19] *(a)* K.Fukui, *J. Phys. Chem.* **1970**, *74*, 4161-4163; *(b)* C. Gonzalez, H. B. Schlegel *J.Chem. Phys.* **1989**, *90*, 2154-2161.

[20] (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001; M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **2003**, *24,* 669-681.

[21] *(a)* J. E. Carpenter, F. Weinhold, *J. Mol Struct.* **1988**, *169*, 41. *(b)* J. E. Carpenter, F. Weinhold, *The Structure of Small Molecules and Ions*; Plenum: New York, 1988.

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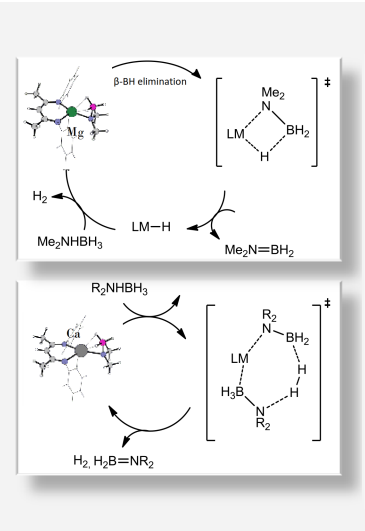
*Valeria Butera, Nino Russo, Sicilia Emilia** …….…. Page – Page

Hydrogen release from dialkylamine-boranes promoted by Mg and Ca complexes: a DFT analysis of the reaction mechanism



A DFT investigation of the dehydrocoupling reactions of amine-boranes assisted by Mg- and Ca-based complexes has been performed with a twofold purpose: to prove the viability of the pathways of the mechanistic scheme proposed on basis of the experimental evidence and to compare the behaviors of Mg and Ca complexes to assess whether differences in radius and charge density can be considered responsible of the observed differences in reactivity. The influence that the steric demand of amine-boranes can have on the course of the reaction has been likewise examined by performing calculations for the dehydrogenation of dimethylamine-borane, DMAB, pyrrolidine-borane, PB and di-*iso*-propylamine-borane.

Supporting Information

Hydrogen release from dialkylamine-boranes promoted by Mg and Ca complexes: a DFT analysis of the reaction mechanism

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S-1

Cartesian coordinates (Å) and absolute energies (Hartrees) of optimized structures for the dehydrocoupling reaction of DMAB assisted by the amidoborane I-Mg$_{DMAB}$ complex.

III-Mg$_{DMAB}$: E(B3PW91) = -160.6336578
Gas-phase zero-point energy= -160.529185
Gas-phase free energy = -160.556461

N	-0.00001500	0.14882000	-0.00004300
B	-0.00004100	1.53707500	-0.00002600
H	1.04590000	2.11817700	0.00008200
H	-1.04609400	2.11800100	0.00011800
C	-1.21357000	-0.64939700	0.00000800
H	-2.08429900	0.00518300	-0.00054600
H	-1.25696500	-1.29577000	-0.88561100
H	-1.25744200	-1.29493600	0.88622100
C	1.21369500	-0.64937300	0.00001300
H	1.25735700	-1.29493200	0.88618400
H	1.25689500	-1.29565100	-0.88566000
H	2.08421300	0.00543200	-0.00048700

DMAB: E(B3PW91) = -161.816812
Gas-phase zero-point energy= -161.690137
Gas-phase free energy = -161.717945

N	-0.00266500	-0.00000700	-0.34090300
B	-1.57358900	-0.00017200	0.11645800
H	-2.05032700	1.01137000	-0.35473500
H	-2.05001600	-1.01203600	-0.35435400
C	0.70036000	-1.22036700	0.10141600
H	0.17460300	-2.08862600	-0.29316200
H	1.74144700	-1.22096800	-0.23530600
H	0.66274900	-1.25702300	1.19051100
C	0.70008000	1.22051800	0.10141700
H	0.66227200	1.25727700	1.19049900
H	1.74122200	1.22128400	-0.23513900
H	0.17425200	2.08865600	-0.29333800
H	-1.55731800	0.00006900	1.33062700
H	-0.01492700	-0.00000200	-1.35856800

I-Mg$_{DMAB}$: E(B3PW91) = -1128.8082245
Gas-phase zero-point energy= -1128.395235
Gas-phase free energy = -1128.452613

N	-1.49829800	0.87410500	-0.12844400

N	1.49810000	0.87420200	-0.12806200
C	-2.44896300	3.13078900	0.05956600
C	-1.27581200	2.18427600	-0.04189300
C	-0.00015100	2.77486300	-0.04126900
C	1.27554600	2.18440200	-0.04192700
C	2.44868600	3.13097900	0.05891100
H	-2.94975100	3.02718900	1.02632900
H	-2.12619200	4.16548000	-0.05012200
H	-3.19640400	2.90711700	-0.70607700
H	-0.00020900	3.85600900	0.00054000
H	3.19501800	2.90811800	-0.70807000
H	2.12567300	4.16574300	-0.04933200
H	2.95095100	3.02642900	1.02479100
B	-0.00036400	-2.47190500	-1.46792100
N	0.00024600	-2.52519600	0.11108100
H	-1.00015700	-1.79958400	-1.77633400
H	-0.00007000	-3.52897100	-2.05109900
H	0.99881700	-1.79888600	-1.77704300
Mg	0.00001900	-0.49636500	-0.40895400
C	-2.83105300	0.38309100	-0.03109200
C	-3.44370800	0.22364200	1.21615100
C	-3.51968500	-0.02221500	-1.17775400
C	-4.72310600	-0.31224900	1.31075700
H	-2.90238900	0.51640000	2.11036200
C	-4.79915600	-0.55910000	-1.07855100
H	-3.04129800	0.08442600	-2.14552300
C	-5.40720000	-0.70450400	0.16404900
H	-5.18446100	-0.42940100	2.28618400
H	-5.32006500	-0.86863300	-1.97878400
H	-6.40374400	-1.12615600	0.23922200
C	2.83089500	0.38326400	-0.03089400
C	3.44367900	0.22380300	1.21629000
C	3.51944900	-0.02196800	-1.17762900
C	4.72309700	-0.31205800	1.31076500
H	2.90242600	0.51652700	2.11055200
C	4.79893900	-0.55884100	-1.07855500
H	3.04099000	0.08469600	-2.14536200
C	5.40709300	-0.70427900	0.16398400
H	5.18454600	-0.42922200	2.28614800
H	5.31977200	-0.86833600	-1.97884500
H	6.40364900	-1.12592200	0.23905400
C	-1.19709300	-3.16938800	0.64843700
H	-1.23653800	-4.23228900	0.36487100
H	-1.21727500	-3.10619300	1.74286300
H	-2.09490600	-2.68507400	0.25765500
C	1.19844800	-3.16862300	0.64751100
H	2.09566700	-2.68346200	0.25641400
H	1.21919700	-3.10578800	1.74194700
H	1.23857600	-4.23138800	0.36353900

$TS_{I\text{-}II}$-Mg_{DMAB}: E(B3PW91) = -1128.7675585
Gas-phase zero-point energy = -1128.358773

Gas-phase free energy = -1128.418913

N	-1.20920600	-1.27190400	0.19453700
N	1.76205700	-0.90330800	0.14314200
C	-1.88469300	-3.59790000	-0.24623500
C	-0.83604600	-2.52488500	-0.05812400
C	0.50064500	-2.94840600	-0.14975400
C	1.69687100	-2.20921600	-0.10101100
C	2.96911900	-2.99147500	-0.33361300
H	-2.33316100	-3.53977300	-1.24214000
H	-1.44477600	-4.58868800	-0.13357700
H	-2.69676400	-3.48310300	0.47566600
H	0.63027900	-4.00991900	-0.31580500
H	3.73816000	-2.71189200	0.39055800
H	2.78346200	-4.06287300	-0.26144900
H	3.37884400	-2.78346800	-1.32624900
B	-0.06243300	2.63517600	-0.49525700
N	-1.02372100	3.64030500	-0.42240000
H	1.10026500	2.87518100	-0.38398500
H	-0.41724000	1.56507800	-0.95944800
H	-0.02390700	1.65639900	1.62569000
Mg	0.12147400	0.23949700	0.62606000
C	-2.58190200	-0.91493200	0.15912800
C	-3.28657300	-0.85402400	-1.04925200
C	-3.23150000	-0.52546500	1.33504800
C	-4.61368700	-0.44158200	-1.07402200
H	-2.77787800	-1.12072900	-1.97003400
C	-4.55892400	-0.11134000	1.30527100
H	-2.68584700	-0.55510800	2.27260400
C	-5.25775000	-0.07108600	0.10318900
H	-5.14473600	-0.40266700	-2.01991600
H	-5.04788000	0.18166800	2.22876800
H	-6.29268100	0.25305300	0.08210800
C	3.01593300	-0.23461800	0.09485500
C	3.62557100	0.06911700	-1.12683600
C	3.61763500	0.20662700	1.27683400
C	4.82286900	0.77398700	-1.16115000
H	3.14356500	-0.24116100	-2.04840800
C	4.81470700	0.91356000	1.23779500
H	3.13799600	-0.01158400	2.22552400
C	5.42470400	1.19676000	0.02036200
H	5.28280700	1.00240000	-2.11736200
H	5.26956800	1.24662600	2.16507700
H	6.35659200	1.75116000	-0.00877800
C	-2.44455000	3.40029300	-0.57097000
H	-2.88951800	4.11383200	-1.27626200
H	-2.61923600	2.38986600	-0.93984700
H	-2.96460500	3.50863800	0.39028800
C	-0.70426600	4.97611400	0.04027000
H	0.37666200	5.09669500	0.10584600
H	-1.10314400	5.73357700	-0.64651600
H	-1.13522600	5.16211500	1.03354900

II-Mg$_{DMAB}$ +III-Mg$_{DMAB}$: E(B3PW91) = -1128.7677842
Gas-phase zero-point energy = -1128.358805
Gas-phase free energy = -1128.420597

N	1.18920500	-1.29926800	0.23689600
N	-1.77875600	-0.90861400	0.18202100
C	1.85194900	-3.59548500	-0.37048400
C	0.81177400	-2.52931900	-0.10539600
C	-0.52708800	-2.93960100	-0.22338200
C	-1.71919300	-2.19529900	-0.14834200
C	-2.99065700	-2.95480400	-0.45417100
H	2.70497300	-3.49174900	0.30354200
H	1.41781800	-4.58784900	-0.24630100
H	2.23778600	-3.52665900	-1.39173300
H	-0.66177700	-3.98897200	-0.45232300
H	-3.34523600	-2.73615100	-1.46555400
H	-2.82172600	-4.02931500	-0.38296800
H	-3.79180000	-2.67201400	0.23253600
B	0.11352800	2.58807800	-0.51762500
N	1.08558700	3.57182300	-0.46252800
H	-0.00470000	1.40625100	2.03514500
H	-1.04269500	2.84864700	-0.39238300
H	0.47077000	1.46791900	-0.81440400
Mg	-0.14198500	0.16470800	0.83314900
C	-3.01505700	-0.21274800	0.12441700
C	-3.60571500	0.25479100	1.30251000
C	-3.61699600	0.09856000	-1.09996200
C	-4.78398800	0.99208300	1.25705400
H	-3.13218200	0.03332800	2.25345500
C	-4.79574700	0.83328700	-1.14038500
H	-3.14174500	-0.22769900	-2.01940300
C	-5.38705700	1.28093900	0.03744200
H	-5.22996300	1.34389000	2.18173400
H	-5.24914100	1.06608000	-2.09873900
H	-6.30465100	1.85846900	0.00363700
C	2.55493700	-0.92700700	0.19558400
C	3.19981500	-0.52403000	1.37052900
C	3.25961600	-0.85555100	-1.01321200
C	4.52054700	-0.08989900	1.33967100
H	2.65513500	-0.55923000	2.30840000
C	4.58051300	-0.42372600	-1.03864500
H	2.75512500	-1.12792300	-1.93443100
C	5.21948000	-0.04148000	0.13770900
H	5.00468400	0.21158000	2.26299500
H	5.11057300	-0.37851800	-1.98489900
H	6.24979500	0.29708100	0.11620000
C	0.77579000	4.95670300	-0.15548400
H	-0.30257100	5.08461100	-0.07049300
H	1.24014000	5.25533900	0.79244300
H	1.15214400	5.62340900	-0.94117900
C	2.50736800	3.31090400	-0.59921200

H	2.93579800	3.91016500	-1.41222100
H	3.03719000	3.56891200	0.32552000
H	2.67844700	2.25601300	-0.81039100

II-Mg$_{DMAB}$+DMAB: E(B3PW91) = -1129.9771878
Gas-phase zero-point energy = -1129.544826
Gas-phase free energy = -1129.603003

N	1.49397100	-1.09613900	0.08468800
N	-1.49424000	-1.09596400	0.08457600
C	2.45037800	-3.33211600	-0.26175000
C	1.27560000	-2.39070000	-0.12291900
C	-0.00023200	-2.97604100	-0.20781500
C	-1.27599800	-2.39056500	-0.12293300
C	-2.45087800	-3.33187900	-0.26161300
H	3.16703400	-3.17942700	0.54970500
H	2.12141900	-4.37082600	-0.25282100
H	2.98996200	-3.15052100	-1.19557500
H	-0.00028800	-4.04783000	-0.35665900
H	-2.99063000	-3.15023400	-1.19532800
H	-2.12200300	-4.37061400	-0.25274600
H	-3.16736900	-3.17913800	0.54998300
H	0.00035300	1.55386500	1.64443600
Mg	-0.00007800	0.31447200	0.34447700
H	-1.01447100	1.63310100	-1.06245700
H	-0.00009300	2.78989600	-2.33790700
H	1.01317100	1.63187900	-1.06285900
H	0.00055800	2.85651700	0.77010500
N	0.00052400	3.43328200	-0.11494700
B	-0.00031100	2.29934500	-1.23763200
C	-2.82242800	-0.59687100	0.12368000
C	-3.54816600	-0.37401100	-1.05193300
C	-3.39423500	-0.22964600	1.34637600
C	-4.82224800	0.17946900	-1.00140600
H	-3.09498200	-0.62562100	-2.00528900
C	-4.66914200	0.32511500	1.39231600
H	-2.82585500	-0.38451800	2.25763900
C	-5.39045600	0.52903800	0.22029200
H	-5.37111200	0.34503800	-1.92319500
H	-5.09920800	0.59916400	2.35053000
H	-6.38454200	0.96192700	0.25735100
C	2.82221000	-0.59717900	0.12374700
C	3.54774900	-0.37403600	-1.05193700
C	3.39428400	-0.23039600	1.34644800
C	4.82190300	0.17928600	-1.00148400
H	3.09436400	-0.62534500	-2.00527800
C	4.66926500	0.32420100	1.39231500
H	2.82605100	-0.38547000	2.25776600
C	5.39038000	0.52840900	0.22021700
H	5.37061800	0.34506800	-1.92332400
H	5.09954600	0.59790600	2.35053000
H	6.38452200	0.96117400	0.25722400

C	1.22375000	4.25470600	-0.13513000
H	1.29734900	4.76891600	-1.09521800
H	1.20473600	4.98810300	0.67529100
H	2.08786200	3.60151800	-0.01559600
C	-1.22204000	4.25566200	-0.13457300
H	-1.29595800	4.76948900	-1.09484500
H	-2.08660300	3.60323500	-0.01411400
H	-1.20188900	4.98942700	0.67549400

$TS_{II\text{-}I}$-Mg_{DMAB}: E(B3PW91) = -1289.4222206
Gas-phase zero-point energy = -1288.902177
Gas-phase free energy = -1288.963717

N	1.42546000	-1.08371100	-0.02159400
N	-1.61012100	-0.96077100	-0.17194300
C	2.23563900	-3.39478900	0.18079600
C	1.12352100	-2.37112800	0.12224400
C	-0.18238200	-2.88837600	0.19483400
C	-1.42772600	-2.27074100	-0.01443700
C	-2.61018000	-3.21208100	-0.09980500
H	2.93512100	-3.17227200	0.99086000
H	1.83764800	-4.39841000	0.32536700
H	2.81847800	-3.38070700	-0.74466700
H	-0.23149100	-3.96137500	0.32360100
H	-3.19577600	-3.01281400	-1.00115500
H	-2.27847100	-4.24946400	-0.11881600
H	-3.28831600	-3.08328300	0.74807000
B	0.10978300	1.94141600	-1.78413700
N	0.68065000	2.64588200	-0.49694900
H	0.75998700	0.91081800	-1.97708400
H	0.11764200	2.62357600	-2.78222800
H	-1.05477900	1.62620000	-1.50377500
H	1.88407300	1.42586800	1.85964400
H	0.72703500	3.13761600	2.10598000
N	-0.31436800	1.11643300	2.18870100
B	0.82183200	1.96197300	1.95591900
C	2.79072900	-0.74025600	-0.24447100
C	3.27214200	-0.60874900	-1.55115700
C	3.66120800	-0.48674000	0.81935200
C	4.59199600	-0.23758900	-1.78473800
H	2.59691700	-0.79419200	-2.37924600
C	4.98045800	-0.11524800	0.58264100
H	3.29725800	-0.58315800	1.83642500
C	5.45192500	0.01191600	-0.71986400
H	4.94688100	-0.13909900	-2.80564300
H	5.64090600	0.07852400	1.42184200
H	6.47990700	0.30566400	-0.90343800
C	-2.92600700	-0.49230300	-0.45116100
C	-3.25291100	-0.05687600	-1.73918500
C	-3.90196500	-0.40998800	0.54852900
C	-4.52102100	0.44117700	-2.01805700
H	-2.50124600	-0.11393500	-2.51812600

C	-5.16945900	0.08828900	0.26698600
H	-3.66270400	-0.74862300	1.55171800
C	-5.48517200	0.51742100	-1.01807800
H	-4.75360800	0.77339000	-3.02464900
H	-5.91240900	0.14099800	1.05664200
H	-6.47288200	0.90846800	-1.23746600
Mg	-0.02936000	0.42833900	-0.12105700
C	-1.59960500	1.73261200	2.52960900
H	-1.66194500	2.72623100	2.08830200
H	-2.43217300	1.13223700	2.15571500
H	-1.70424800	1.82771100	3.61821000
C	-0.14850000	-0.19244300	2.83270400
H	0.82168300	-0.61292800	2.57263100
H	-0.20916200	-0.08835000	3.92336400
H	-0.92577700	-0.88839500	2.50617700
C	2.09470800	2.98927400	-0.65968000
H	2.48011600	3.48318300	0.23929000
H	2.68421300	2.08896500	-0.83917900
H	2.23537500	3.66650400	-1.51567100
C	-0.08856300	3.87741500	-0.29489400
H	0.27423300	4.44044500	0.57005000
H	-0.01722800	4.52221300	-1.18332500
H	-1.14538500	3.64176000	-0.14615600

I-Mg$_{DMAB}$ + III$_{DMAB}$: E(B3PW91) = -1289.4424591
Gas-phase zero-point energy = -1288.924320
Gas-phase free energy = -1288.998063

N	0.45778600	1.29729500	-0.90749000
N	-1.48089300	-0.98178000	-0.78523800
C	2.43740500	0.79293000	-2.26916000
C	1.09286200	0.42540500	-1.68659000
C	0.59650400	-0.84737100	-2.02236500
C	-0.55897100	-1.51685500	-1.58317700
C	-0.73405900	-2.93660000	-2.06890400
H	3.20139300	0.83188500	-1.48760200
H	2.74947500	0.06664500	-3.01901000
H	2.40498600	1.78547700	-2.72582500
H	1.22094500	-1.41440400	-2.70002500
H	-1.73243400	-3.08242200	-2.48966100
H	0.01005000	-3.18604400	-2.82458300
H	-0.63715600	-3.64458300	-1.24090900
B	-3.10749100	2.41981900	0.21425000
N	-2.34369500	1.85904700	1.47876600
H	-2.23182900	2.94047200	-0.49876000
H	-4.00753800	3.19783100	0.42079800
H	-3.52325100	1.41798700	-0.39355500
H	5.38935100	-1.82323300	3.00000100
H	3.74200900	-1.45344100	1.76386200
N	5.19332800	-3.02173500	1.12985100
B	4.75108800	-2.04660900	2.01296800
Mg	-1.43528500	0.97858900	-0.18809700

C	1.09901200	2.51900200	-0.55576800
C	2.04054300	2.55633800	0.47774200
C	0.73712700	3.71336500	-1.18481800
C	2.61968700	3.76111600	0.85978300
H	2.30609300	1.63320900	0.98312200
C	1.31805900	4.91674200	-0.79790400
H	-0.00494200	3.68911600	-1.97570000
C	2.26242900	4.94598800	0.22299800
H	3.34874600	3.77359000	1.66365100
H	1.02639600	5.83569300	-1.29597400
H	2.71172400	5.88590300	0.52517400
C	-2.56313700	-1.78685400	-0.32966300
C	-2.40332400	-2.63658800	0.76980700
C	-3.82363800	-1.68133300	-0.92401300
C	-3.47741200	-3.37636300	1.25162200
H	-1.43051500	-2.70338500	1.24682400
C	-4.89577800	-2.42255000	-0.43805200
H	-3.95503100	-1.01026800	-1.76613900
C	-4.72770200	-3.27396300	0.64904300
H	-3.33746800	-4.03024500	2.10652100
H	-5.86824700	-2.32876300	-0.91040400
H	-5.56617300	-3.84784100	1.02877900
C	6.40334900	-3.79790100	1.33957500
H	6.17573400	-4.86975900	1.39536200
H	7.11107000	-3.64994200	0.51429700
H	6.88007100	-3.49151400	2.26981900
C	4.49187100	-3.36797600	-0.09431900
H	5.13225700	-3.20527400	-0.97036100
H	4.19658100	-4.42472300	-0.08970800
H	3.59784000	-2.75368400	-0.19361900
C	-1.66974500	2.91260100	2.23612500
H	-1.07842000	2.48753000	3.05553900
H	-1.00045200	3.47831600	1.58404600
H	-2.39689200	3.61803300	2.66651900
C	-3.21983800	1.09042500	2.36193700
H	-3.71839200	0.29585100	1.80206600
H	-2.64906200	0.63430100	3.17933600
H	-3.99862500	1.73145200	2.80256100

$TS_{I\text{-}IV}$-Mg_{DMAB}: E(B3PW91) = -1289.4222206
Gas-phase zero-point energy = -1288.902177
Gas-phase free energy = -1288.963717

N	1.42546000	-1.08371100	-0.02159400
N	-1.61012100	-0.96077100	-0.17194300
C	2.23563900	-3.39478900	0.18079600
C	1.12352100	-2.37112800	0.12224400
C	-0.18238200	-2.88837600	0.19483400
C	-1.42772600	-2.27074100	-0.01443700
C	-2.61018000	-3.21208100	-0.09980500
H	2.93512100	-3.17227200	0.99086000
H	1.83764800	-4.39841000	0.32536700

H	2.81847800	-3.38070700	-0.74466700
H	-0.23149100	-3.96137500	0.32360100
H	-3.19577600	-3.01281400	-1.00115500
H	-2.27847100	-4.24946400	-0.11881600
H	-3.28831600	-3.08328300	0.74807000
B	0.10978300	1.94141600	-1.78413700
N	0.68065000	2.64588200	-0.49694900
H	0.75998700	0.91081800	-1.97708400
H	0.11764200	2.62357600	-2.78222800
H	-1.05477900	1.62620000	-1.50377500
H	1.88407300	1.42586800	1.85964400
H	0.72703500	3.13761600	2.10598000
N	-0.31436800	1.11643300	2.18870100
B	0.82183200	1.96197300	1.95591900
C	2.79072900	-0.74025600	-0.24447100
C	3.27214200	-0.60874900	-1.55115700
C	3.66120800	-0.48674000	0.81935200
C	4.59199600	-0.23758900	-1.78473800
H	2.59691700	-0.79419200	-2.37924600
C	4.98045800	-0.11524800	0.58264100
H	3.29725800	-0.58315800	1.83642500
C	5.45192500	0.01191600	-0.71986400
H	4.94688100	-0.13909900	-2.80564300
H	5.64090600	0.07852400	1.42184200
H	6.47990700	0.30566400	-0.90343800
C	-2.92600700	-0.49230300	-0.45116100
C	-3.25291100	-0.05687600	-1.73918500
C	-3.90196500	-0.40998800	0.54852900
C	-4.52102100	0.44117700	-2.01805700
H	-2.50124600	-0.11393500	-2.51812600
C	-5.16945900	0.08828900	0.26698600
H	-3.66270400	-0.74862300	1.55171800
C	-5.48517200	0.51742100	-1.01807800
H	-4.75360800	0.77339000	-3.02464900
H	-5.91240900	0.14099800	1.05664200
H	-6.47288200	0.90846800	-1.23746600
Mg	-0.02936000	0.42833900	-0.12105700
C	-1.59960500	1.73261200	2.52960900
H	-1.66194500	2.72623100	2.08830200
H	-2.43217300	1.13223700	2.15571500
H	-1.70424800	1.82771100	3.61821000
C	-0.14850000	-0.19244300	2.83270400
H	0.82168300	-0.61292800	2.57263100
H	-0.20916200	-0.08835000	3.92336400
H	-0.92577700	-0.88839500	2.50617700
C	2.09470800	2.98927400	-0.65968000
H	2.48011600	3.48318300	0.23929000
H	2.68421300	2.08896500	-0.83917900
H	2.23537500	3.66650400	-1.51567100
C	-0.08856300	3.87741500	-0.29489400
H	0.27423300	4.44044500	0.57005000
H	-0.01722800	4.52221300	-1.18332500

H	-1.14538500	3.64176000	-0.14615600

IV-Mg$_{DMAB}$: E(B3PW91) = -1289.4686558
Gas-phase zero-point energy = -1288.945262
Gas-phase free energy = -1289.006535

H	1.06829000	1.50982100	-1.28889100
B	0.00753200	1.94952900	-1.72931500
H	-0.88483800	1.09851400	-1.68343200
N	-0.44740100	3.17133600	-0.83344000
H	0.17244800	2.26699200	-2.88147000
N	0.05379000	1.61825900	1.30606900
B	-0.86836800	2.72413100	0.66656200
H	-1.97180700	2.23141000	0.55881200
H	-0.87498500	3.72954100	1.35995900
C	-1.14654700	-2.66710400	-0.43827600
C	0.14641500	-3.19320000	-0.60702000
C	1.40278500	-2.57615700	-0.49287600
C	-2.28400900	-3.65378800	-0.57101000
H	-3.03229000	-3.29060100	-1.28055400
H	-1.92165000	-4.62538000	-0.90476800
H	-2.79862200	-3.78601500	0.38485700
C	2.60195400	-3.48019400	-0.66635800
H	2.29930600	-4.46256800	-1.02735500
H	3.31740500	-3.04719600	-1.37042400
H	3.13361200	-3.61125500	0.28039100
N	1.58796500	-1.27837800	-0.25664900
H	0.17943100	-4.24999400	-0.83630200
N	-1.41499400	-1.38929300	-0.18162200
Mg	0.03548700	0.09315200	-0.17509700
C	2.91307600	-0.79379400	-0.08022000
C	3.57906600	-0.95789300	1.13958300
C	3.54900800	-0.08217200	-1.10223200
C	4.85283500	-0.43355600	1.32668300
H	3.08311600	-1.49710700	1.94073900
C	4.82320800	0.44285400	-0.91040800
H	3.03451300	0.05297600	-2.04748500
C	5.48114000	0.26949300	0.30281100
H	5.35512300	-0.57124000	2.27907100
H	5.30265000	0.98977000	-1.71603400
H	6.47415400	0.68024000	0.45087100
C	-2.77050800	-1.00142300	0.01484000
C	-3.38465500	-1.15524700	1.26191500
C	-3.49305000	-0.40401000	-1.02195900
C	-4.69266000	-0.72880400	1.46317800
H	-2.82351100	-1.61067100	2.07187200
C	-4.80128200	0.02113200	-0.81669100
H	-3.01796100	-0.27808100	-1.98907600
C	-5.40691900	-0.13855100	0.42526100

H	-5.15382300	-0.85484000	2.43764300
H	-5.34887100	0.48105300	-1.63320300
H	-6.42584700	0.19755900	0.58466800
C	0.60211100	4.21692200	-0.84784300
H	0.27373800	5.07568500	-0.25748800
H	1.52678000	3.83099400	-0.42430400
H	0.79766500	4.52816900	-1.87807400
C	-1.66208600	3.77185400	-1.43561200
H	-2.02903400	4.58004600	-0.79651900
H	-1.42418100	4.16351000	-2.42849600
H	-2.43542300	3.01031200	-1.52095800
C	1.40239300	2.08407000	1.66160600
H	2.00511500	2.25704500	0.76870200
H	1.35293000	3.01757300	2.24059500
H	1.92496500	1.33135100	2.26035000
C	-0.60961200	1.17816400	2.54614700
H	-0.68979400	2.00568900	3.26544900
H	-1.61924900	0.82739700	2.32678600
H	-0.04251300	0.36813300	3.01936900

$TS_{IV\text{-}II}$-Mg_{DMAB}: E(B3PW91) = -1289.3946795
Gas-phase zero-point energy = -1288.876629
Gas-phase free energy = -1288.942031

B	-0.01650600	1.96856500	-0.11258700
H	1.04636400	1.50840700	0.24619200
N	-0.06415800	3.30569900	1.47944100
H	-1.02667100	1.42374600	0.28810200
N	-0.07484100	3.27450800	-0.95502800
B	0.04406900	4.31405400	0.31694900
H	1.13279000	4.83977400	0.26633500
H	-0.87335500	5.10432600	0.25987300
C	1.34265400	-2.86824600	0.44883100
C	0.07809100	-3.44895500	0.64949200
C	-1.20850300	-2.92133100	0.44275500
C	2.53730300	-3.73865100	0.75808300
H	3.12973800	-3.30825000	1.57036200
H	2.22862500	-4.74270600	1.04627600
H	3.20056000	-3.80713400	-0.10855400
C	-2.36739500	-3.84125200	0.74501100
H	-3.03414200	-3.91911100	-0.11808800
H	-2.01869100	-4.83774300	1.01313800
H	-2.96936100	-3.44905500	1.56958100
N	-1.45303000	-1.69068900	-0.00251400
H	0.09835000	-4.46873100	1.01013600
N	1.53874800	-1.62838800	0.00473700
H	-0.01689700	1.02644700	-1.57179100
Mg	0.01671700	-0.34094100	-0.45063100
C	2.86649100	-1.14651300	-0.17803900
C	3.56253700	-0.54863600	0.87639700

C	3.46182100	-1.19215900	-1.44167700
C	4.83401300	-0.02368300	0.67291800
H	3.09306400	-0.49205200	1.85319900
C	4.73368200	-0.66578600	-1.64110900
H	2.91610200	-1.64310300	-2.26445000
C	5.42550000	-0.08143200	-0.58517000
H	5.36159200	0.43837500	1.50111700
H	5.18341300	-0.70987100	-2.62783500
H	6.41572800	0.33223500	-0.74287500
C	-2.79773800	-1.25882700	-0.18301400
C	-3.52578700	-0.71807000	0.88083000
C	-3.38096500	-1.29359000	-1.45269200
C	-4.81600000	-0.23998300	0.68053800
H	-3.06616700	-0.66834400	1.86270600
C	-4.67169200	-0.81398700	-1.64899200
H	-2.81120500	-1.69994300	-2.28233800
C	-5.39506500	-0.28742300	-0.58383500
H	-5.36837500	0.17737700	1.51628900
H	-5.11175300	-0.84975800	-2.64040800
H	-6.40034600	0.08927300	-0.73896900
C	-1.31332100	3.28025900	2.22049200
H	-2.16212800	3.34113100	1.53730400
H	-1.40688200	2.34814400	2.79482400
H	-1.39051100	4.12095600	2.92771500
C	-1.34823200	3.41715800	-1.68966000
H	-1.43454700	2.62837300	-2.44278800
H	-2.18266900	3.34267600	-0.99361500
H	-1.38192200	4.39832300	-2.16945700
C	1.04444000	3.42520600	-1.90614400
H	0.95870700	2.68743500	-2.70827600
H	1.02708800	4.43544000	-2.32330700
H	1.98746500	3.28089100	-1.38104100
C	1.06884500	3.20159800	2.38119000
H	1.11267200	4.04300700	3.09078800
H	1.01332500	2.27397200	2.96809800
H	2.00052300	3.19159200	1.81382500

II-Mg_{DMAB} + V_{DMAB}: E(B3PW91) = -1289.4303674
Gas-phase zero-point energy = -1288.909821
Gas-phase free energy = -1288.973870

H	0.04110100	0.35176400	-2.59939700
B	-0.02763900	1.93902400	0.18228700
H	-1.05657100	1.31998000	0.00733800
N	0.06496800	3.22220500	-0.74430100
H	0.97371600	1.25333400	0.11793500
N	-0.07280200	2.76241800	1.54404300
B	-0.00320400	4.08204000	0.61163400
H	-1.01962100	4.72306800	0.68577800
H	1.00939000	4.70451100	0.80478600
C	-1.27983600	-2.84709700	0.22028700
C	-0.00454300	-3.41622500	0.38533600

C	1.27430500	-2.84949400	0.23626600
C	-2.44532700	-3.74725000	0.57077800
H	-3.28177100	-3.59704700	-0.11495000
H	-2.13875400	-4.79298000	0.53460700
H	-2.81511000	-3.54474900	1.58019700
C	2.43430200	-3.74904400	0.60523700
H	2.12685500	-4.79466800	0.57414400
H	3.27795700	-3.60503700	-0.07301700
H	2.79404100	-3.53868000	1.61669500
N	1.49757200	-1.62103200	-0.21974800
H	-0.00763000	-4.44793200	0.71314800
N	-1.49665300	-1.61645000	-0.23550500
Mg	0.00619400	-0.41321000	-1.02805200
C	2.80742500	-1.08520800	-0.23660100
C	3.51217300	-0.81978200	0.94460900
C	3.38504300	-0.71495600	-1.45696100
C	4.76906400	-0.22813000	0.90219900
H	3.05812900	-1.07025800	1.89782500
C	4.64223700	-0.12144500	-1.49404200
H	2.83601300	-0.90042400	-2.37450000
C	5.34274600	0.12190800	-0.31690700
H	5.30118900	-0.03393300	1.82838400
H	5.07588900	0.15039500	-2.45115400
H	6.32371600	0.58392600	-0.34793700
C	-2.80580100	-1.07950500	-0.26339700
C	-3.52682700	-0.82847800	0.91117700
C	-3.36691200	-0.69368700	-1.48664700
C	-4.78271000	-0.23564800	0.85915700
H	-3.08607000	-1.09089000	1.86739500
C	-4.62286400	-0.09826500	-1.53339700
H	-2.80638300	-0.86875400	-2.39940600
C	-5.33938900	0.13059000	-0.36304800
H	-5.32725100	-0.05280900	1.78042600
H	-5.04305300	0.18618800	-2.49283500
H	-6.31942800	0.59399300	-0.40162300
C	1.32589100	3.35169200	-1.50131100
H	2.17340900	3.21018900	-0.83203200
H	1.35899200	2.59418700	-2.28856600
H	1.38915000	4.35113100	-1.94183800
C	1.08981000	2.57555300	2.42846500
H	2.00945800	2.66812900	1.85342600
H	1.08680100	3.33786500	3.21320200
H	1.05978700	1.58327900	2.88925100
C	-1.31546700	2.62271700	2.32149600
H	-1.35178500	3.38463200	3.10592800
H	-2.17574800	2.75071100	1.66707100
H	-1.36570900	1.63053700	2.78047300
C	-1.07548500	3.41206500	-1.66285700
H	-1.02667200	4.41057800	-2.10741400
H	-1.04321300	2.65078300	-2.44632300
H	-2.00954700	3.32035100	-1.11047300

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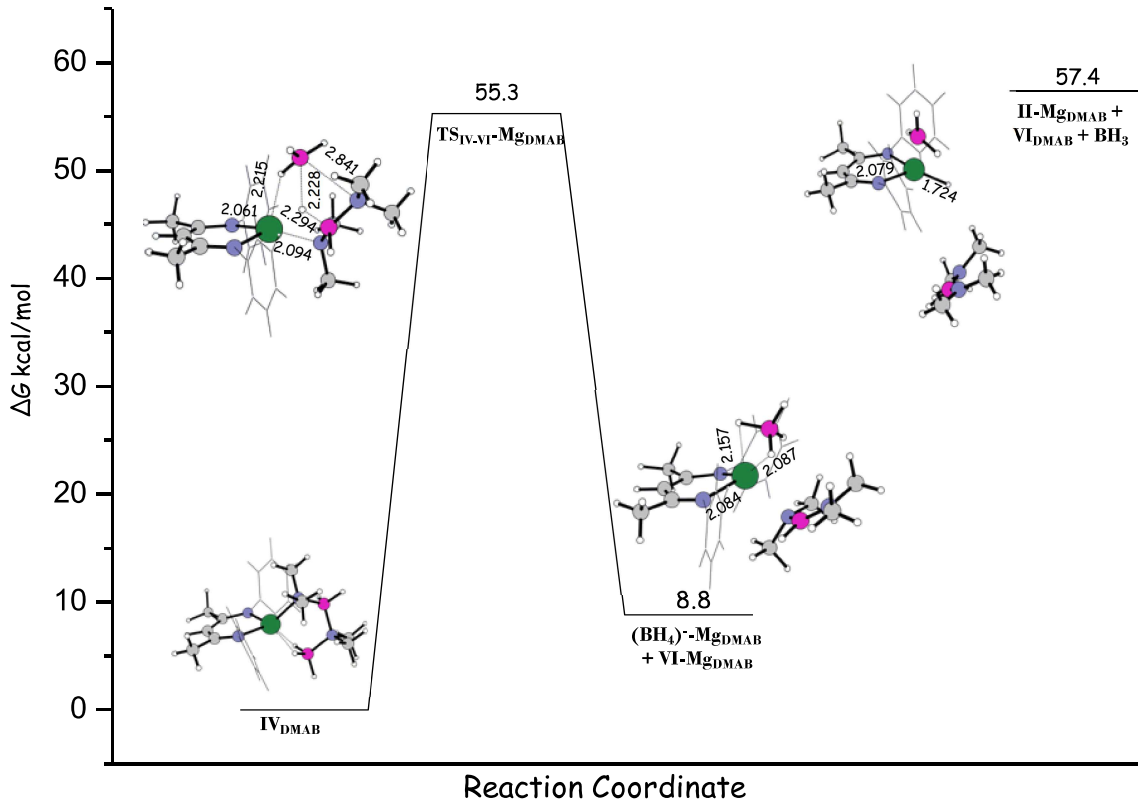
DFT zero-point corrected energy profile for the alternative pathway that from IV-Mg_{DMAB} intermediate leads by β-hydride elimination to the formation of BH_3 + $HB(NMe_2)_2$ products and relative cartesian coordinates (Å) and absolute energies (Hartrees) of optimized structures.



TS_{IV-VI}-Mg_{DMAB}: E(B3PW91) = -1289.3730899
Gas-phase zero-point energy = -1288.857068
Gas-phase free energy = -1288.922208

H	0.90927500	1.01282300	-1.94611800
B	0.24451900	1.82085400	-2.55332000
H	-0.68474200	1.42517400	-3.18255100
N	-1.13135100	3.49066800	-0.71252000
H	0.73759100	2.88172400	-2.75248500
N	0.16532000	1.82682200	0.90734600
B	-1.12257700	2.17780800	0.04687100
H	-1.17883000	1.31489600	-0.91524100
H	-2.09938500	1.93804700	0.74560400
C	-0.89286000	-2.81701100	-0.43247900

C	0.43483000	-3.23222600	-0.64116900
C	1.63674300	-2.52280300	-0.49668300
C	-1.95048600	-3.89001200	-0.54182700
H	-2.73728500	-3.59022400	-1.23903600
H	-1.51912700	-4.83243000	-0.87724700
H	-2.43637500	-4.05380000	0.42409100
C	2.90797800	-3.32491300	-0.64694900
H	2.69085600	-4.35179800	-0.93840900
H	3.56750800	-2.87599200	-1.39445500
H	3.46731900	-3.34162000	0.29296700
N	1.71568400	-1.21820100	-0.23027700
H	0.55037700	-4.27779700	-0.89347300
N	-1.25400300	-1.56946600	-0.14275800
Mg	0.06199400	0.00999600	-0.16185700
C	2.99659000	-0.64317200	0.00541700
C	3.53525600	-0.63164000	1.29628400
C	3.70633800	-0.02210900	-1.02604500
C	4.75833600	-0.01904100	1.54652500
H	2.98145100	-1.10653500	2.10015100
C	4.92879100	0.59139100	-0.77162900
H	3.28969700	-0.02293800	-2.02770900
C	5.46017300	0.59572000	0.51387300
H	5.16261400	-0.01940800	2.55380500
H	5.46651300	1.07023400	-1.58364300
H	6.41218500	1.07690600	0.71047400
C	-2.62387600	-1.30186000	0.14891200
C	-3.11001300	-1.46189500	1.44898500
C	-3.48195600	-0.81644500	-0.83969400
C	-4.43272200	-1.15651400	1.75004500
H	-2.43868300	-1.82479800	2.22119400
C	-4.80396100	-0.51191400	-0.53499800
H	-3.10086900	-0.67347900	-1.84535400
C	-5.28550000	-0.68182200	0.75890400
H	-4.79565000	-1.28487200	2.76483300
H	-5.45862800	-0.13272100	-1.31298300
H	-6.31569200	-0.43766500	0.99492200
C	-1.05863100	4.67540500	0.12349800
H	-1.96652600	4.80539300	0.74426600
H	-0.20182600	4.63409000	0.79676300
H	-0.95081200	5.57707700	-0.49279000
C	-2.27933000	3.61838700	-1.59498800
H	-3.22426800	3.75613700	-1.03697200
H	-2.15866300	4.48074700	-2.26308800
H	-2.39182700	2.72602500	-2.21403600
C	1.40970600	2.56459500	0.63855500
H	1.49787500	2.79369000	-0.42307800
H	1.43699800	3.51633100	1.18511500
H	2.28402200	1.98492200	0.95231500

C	-0.06333300	1.77476900	2.35485900
H	-0.21221000	2.77956900	2.77698100
H	-0.95503400	1.18609400	2.57655300
H	0.79650800	1.32283000	2.86424400

$(BH_4)^+$-Mg_{DMAB} + IV-Mg_{DMAB}: E(B3PW91) = - 1289.4507146
Gas-phase zero-point energy = -1288.931288
Gas-phase free energy = -1288.995773

H	-0.89315700	1.56894800	1.88737300
B	0.05517900	1.15752300	2.56948500
H	-0.14353700	-0.03331600	2.81498800
N	1.70852800	3.38101600	-0.16116000
H	0.16563800	1.80965700	3.56899700
N	0.00681800	1.61502200	-1.05465800
B	1.34088900	2.19137600	-0.79789200
H	1.07875400	1.24261800	1.87843400
H	2.23752100	1.50091600	-1.17879400
C	0.71617700	-2.78069900	0.10771400
C	-0.63837700	-3.16067000	0.12181000
C	-1.81052000	-2.38709300	0.13518100
C	1.70958600	-3.91874100	0.01784500
H	2.55307000	-3.75770500	0.69306100
H	1.23046100	-4.86543300	0.26654000
H	2.12179600	-4.00486100	-0.99162000
C	-3.10589800	-3.16817300	0.08217100
H	-2.92903900	-4.21775600	0.31607200
H	-3.83579600	-2.76435400	0.78786500
H	-3.56123900	-3.11670400	-0.91087700
N	-1.83999600	-1.05706400	0.21373700
H	-0.80527900	-4.22957800	0.09945400
N	1.14900600	-1.52576100	0.18762200
Mg	-0.12761100	0.05257200	0.65936500
C	-3.08869300	-0.38786700	0.13368400
C	-3.80577900	-0.32447000	-1.06847800
C	-3.58863500	0.29621400	1.24715100
C	-4.99322700	0.39393700	-1.15012200
H	-3.41708200	-0.83796200	-1.94240300
C	-4.77571700	1.01578900	1.15992100
H	-3.03528100	0.25660600	2.17882800
C	-5.48439700	1.06880600	-0.03620900
H	-5.53409700	0.43051400	-2.09065000
H	-5.14811900	1.53696300	2.03606100
H	-6.40934900	1.63176400	-0.10110000
C	2.54189400	-1.26723000	0.08822400
C	3.21972900	-1.39470500	-1.12985500
C	3.24868300	-0.80913900	1.20459500

C	4.57134900	-1.08565200	-1.22456400
H	2.67431100	-1.73282200	-2.00531200
C	4.60142400	-0.50062800	1.10542900
H	2.72602200	-0.70071900	2.14848800
C	5.26989500	-0.63771600	-0.10700500
H	5.08018100	-1.19125600	-2.17764400
H	5.13454400	-0.15251400	1.98440300
H	6.32503700	-0.39680200	-0.18154800
C	0.87640700	4.39897000	0.45918800
H	1.30485800	5.38923400	0.26731800
H	-0.13315500	4.39450100	0.06118300
H	0.82480600	4.25411500	1.54491600
C	3.11954300	3.61358700	0.12027400
H	3.43667000	4.58432600	-0.28105200
H	3.30193600	3.61857100	1.20206400
H	3.72755000	2.82947600	-0.32757600
C	-1.21838700	2.43002900	-0.98128900
H	-1.36384200	2.81985700	0.02493300
H	-1.19255900	3.26143200	-1.69725700
H	-2.08424900	1.80819400	-1.21776100
C	-0.02445500	0.78621100	-2.27821500
H	-0.08314200	1.41003500	-3.17948800
H	0.87711100	0.17722100	-2.33443400
H	-0.89446100	0.12443800	-2.25728000

II-Mg_{DMAB} + VI-Mg_{DMAB} + BH_3: E(B3PW91) = -1289.3674546
Gas-phase zero-point energy = -1288.853752
Gas-phase free energy = -1288.925819

H	1.15878100	1.24938400	2.03043000
B	0.11160700	1.50862400	2.59818300
H	-0.71286100	0.64692300	2.67000300
N	-5.84673600	-1.20555000	-0.29141900
H	0.25159500	2.25629400	3.52318900
N	-3.59396400	-2.34911300	-0.68653000
B	-4.74072200	-1.61977700	-1.08843300
H	0.48218300	-1.84116500	0.87258900
H	-4.77893900	-1.29065000	-2.24386900
C	1.13924000	2.12101200	-1.37456500
C	2.43387400	1.83193500	-1.81261100
C	3.35172300	0.87089100	-1.33018200
C	0.48434000	3.36413000	-1.93000700
H	0.48508600	4.17080900	-1.19052000
H	1.01518900	3.72237800	-2.81193100
H	-0.55795000	3.16989900	-2.19615900
C	4.72916300	0.90643500	-1.95156600
H	4.71963900	1.47413200	-2.88187700
H	5.44937600	1.37568200	-1.27492100

H	5.09398800	-0.10349900	-2.15210300
N	3.07437000	-0.01931400	-0.38891400
H	2.81579900	2.48048000	-2.59048800
N	0.45415200	1.34917900	-0.53015400
Mg	1.19561100	-0.33085400	0.44433200
C	4.10215400	-0.86787800	0.10887500
C	4.09975400	-2.22859600	-0.21034300
C	5.06954000	-0.38103700	0.99394700
C	5.06248000	-3.07780200	0.32457700
H	3.33552800	-2.61202400	-0.87813200
C	6.02931400	-1.23419600	1.52587400
H	5.05233900	0.66841400	1.27029700
C	6.03265600	-2.58491900	1.19087600
H	5.04876500	-4.13146700	0.06554500
H	6.77306400	-0.84241100	2.21239000
H	6.77970400	-3.24997200	1.61058300
C	-0.69132900	1.79196000	0.12681400
C	-1.91741100	1.14344700	-0.06379600
C	-0.59649100	2.77835400	1.14730700
C	-3.03389700	1.52420700	0.66512900
H	-1.98636900	0.34525700	-0.79400400
C	-1.75492200	3.17047300	1.85039400
H	0.29870500	3.38964300	1.20071600
C	-2.96260800	2.53735700	1.62493300
H	-3.97375500	1.01179300	0.48446200
H	-1.67582300	3.95544600	2.59478800
H	-3.84391300	2.81981500	2.18912000
C	-6.24128400	-1.73131100	0.99957300
H	-7.30178400	-2.01757400	0.97781500
H	-5.66905300	-2.62124500	1.25383400
H	-6.12167400	-0.99775400	1.81080000
C	-6.80648700	-0.25682800	-0.81924500
H	-7.81306200	-0.69638900	-0.87616700
H	-6.87945000	0.64167000	-0.18880800
H	-6.50983500	0.05608800	-1.82059200
C	-3.16965600	-2.65110000	0.66875400
H	-3.63609500	-1.97284700	1.38236900
H	-3.40284100	-3.68514200	0.96388000
H	-2.08476800	-2.52123200	0.75587100
C	-2.72120700	-2.93679300	-1.68635200
H	-2.76983700	-4.03516200	-1.67083600
H	-3.01625900	-2.60078100	-2.68128200
H	-1.67566400	-2.65364000	-1.50891300

S-3

Cartesian coordinates (Å) and absolute energies (Hartrees) of optimized structures for the dehydrocoupling reaction of pyrrolidine-borane and di-*iso*-propylamine-borane assisted by the amidoborane I-Mg$_{PB}$ and I-Mg$^{i}{}_{Pr2}$ complexs respectively.

III$_{PB}$: E(B3PW91) = -239.2289478
Gas-phase zero-point energy = -239.065639
Gas-phase free energy = 239.097600

H	2.79014000	1.00918000	-0.40482900
H	2.33454200	0.00422600	1.29543700
H	2.79078600	-1.01241400	-0.39791900
B	2.32122800	-0.00011000	0.08009400
C	-0.03340000	-1.16622200	0.15396300
C	-0.03185000	1.16890000	0.14169900
C	-1.50429700	-0.77588700	-0.02705300
H	0.23359700	-1.28971100	1.20583200
H	0.27532500	-2.06423000	-0.38074100
C	-1.50662900	0.77469600	-0.01167000
H	0.26808200	2.05727000	-0.41368400
H	0.24899000	1.31325900	1.18714300
H	-1.89268500	-1.15254100	-0.97707500
H	-2.12571500	-1.20214000	0.76258100
H	-1.92376400	1.16990600	-0.94145400
H	-2.10692900	1.18086800	0.80448500
N	0.74914500	-0.00201800	-0.33291700
H	0.71453000	-0.00791900	-1.35145100

PB: E(B3PW91) = -238.0450438
Gas-phase zero-point energy = -237.903738
Gas-phase free energy = -237.933902

H	-2.83290300	-1.04226100	-0.09337200
H	-2.83323300	1.04184600	0.09308700
B	-2.25043100	-0.00012800	-0.00002300
C	-0.01680300	1.19850700	0.12738100
C	-0.01671600	-1.19846100	-0.12720500
C	1.38641900	0.72417600	-0.24610100
H	-0.03429700	1.56068100	1.16247500
H	-0.38619900	2.00178000	-0.51305000
C	1.38655600	-0.72415000	0.24605200
H	-0.03429800	-1.56072300	-1.16223200
H	-0.38618000	-2.00153300	0.51341600
H	1.51826200	0.75046400	-1.33319600
H	2.17104500	1.33764300	0.20202900
H	2.17102600	-1.33745000	-0.20265000
H	1.51887100	-0.75084700	1.33303700
N	-0.86523900	0.00008700	-0.00002700

I-Mg$_{PB}$: E(B3PW91) = -1206.2209919

Gas-phase zero-point energy= -1205.771323
Gas-phase free energy = -1205.830894

N	-1.49641700	-1.16908900	0.11631800
N	1.49639300	-1.16911700	0.11630400
C	-2.44882000	-3.36602500	-0.42785700
C	-1.27533800	-2.45098300	-0.16818100
C	-0.00003200	-3.03712100	-0.24887500
C	1.27528600	-2.45100600	-0.16820600
C	2.44874200	-3.36609100	-0.42784600
H	-2.93436600	-3.11567700	-1.37552700
H	-2.12992900	-4.40688000	-0.47105100
H	-3.20737200	-3.25709800	0.35167900
H	-0.00004300	-4.09952300	-0.45359900
H	3.20728800	-3.25717800	0.35169900
H	2.12981700	-4.40693700	-0.47102700
H	2.93430900	-3.11577500	-1.37551200
B	0.00002900	1.85326800	2.07927400
H	-0.99825500	1.13204900	2.25453400
H	0.00006000	2.78038000	2.85294200
H	0.99827700	1.13199600	2.25452400
Mg	0.00000100	0.12514500	0.65003300
C	1.15106400	2.99689700	0.08311000
C	-1.15096900	2.99694200	0.08311500
C	0.77470200	3.43552200	-1.33879600
H	1.27889100	3.87582500	0.73493700
H	2.07417200	2.41410900	0.13417200
C	-0.77459600	3.43554800	-1.33879400
H	-2.07410000	2.41419100	0.13418200
H	-1.27875700	3.87587700	0.73494000
H	1.16255400	2.72758500	-2.07639600
H	1.19454500	4.41479600	-1.58094800
H	-1.16247200	2.72761800	-2.07639000
H	-1.19440700	4.41483400	-1.58095100
N	0.00003300	2.21086300	0.54692400
C	-2.82412400	-0.65870100	0.06675800
C	-3.54399400	-0.43941600	1.24451100
C	-3.39920400	-0.29257700	-1.15477300
C	-4.81733400	0.11862700	1.19785100
H	-3.09461100	-0.70645000	2.19497300
C	-4.67261500	0.26394700	-1.19688200
H	-2.83284700	-0.44258000	-2.06858700
C	-5.38798000	0.47020100	-0.02105500
H	-5.36316100	0.28245200	2.12132000
H	-5.10482500	0.54277000	-2.15262100
H	-6.37995500	0.90773500	-0.05433800
C	2.82410900	-0.65874900	0.06674400
C	3.54399500	-0.43951700	1.24449700

C	3.39916700	-0.29255600	-1.15477800
C	4.81733700	0.11852100	1.19784300
H	3.09462500	-0.70659300	2.19495300
C	4.67258000	0.26396500	-1.19687900
H	2.83279100	-0.44250000	-2.06858900
C	5.38796700	0.47015100	-0.02105400
H	5.36318000	0.28229700	2.12131300
H	5.10477300	0.54284000	-2.15261000
H	6.37994300	0.90768300	-0.05433000

$TS_{I\text{-}II}$-Mg_{PB} E(B3PW91) = -1206.1798271
Gas-phase zero-point energy= -1205.734248
Gas-phase free energy = -1205.796259

N	-0.56777500	-1.88097400	0.17142500
N	2.20518200	-0.75075200	0.12856300
C	-0.62396500	-4.28152600	-0.36395800
C	0.11423900	-2.98168900	-0.13764300
C	1.51338300	-3.03811200	-0.25680000
C	2.47821800	-2.01750200	-0.17099300
C	3.90799800	-2.43631500	-0.42705600
H	-1.12728900	-4.28338900	-1.33503400
H	0.06457000	-5.12586500	-0.33894700
H	-1.39743000	-4.42902600	0.39385000
H	1.91157200	-4.02120100	-0.47179400
H	4.58566100	-1.97745600	0.29676300
H	4.00808300	-3.52016800	-0.37233600
H	4.23879200	-2.11541200	-1.41912600
B	-0.36598300	2.22777200	-0.52101800
N	-1.54350700	2.95662600	-0.45749700
C	-1.62603800	4.35093900	-0.00025900
H	-0.92511800	4.52704300	0.81841400
H	0.69999500	2.73448400	-0.35019600
H	-0.43387300	1.09987600	-0.97926400
H	-0.18721400	1.19728300	1.69845100
Mg	0.32510800	-0.08295400	0.63865000
C	-1.98694900	-1.90248000	0.18472200
C	-2.72413300	-1.94445500	-1.00436600
C	-2.67464000	-1.78904100	1.39734200
C	-4.11318700	-1.90125600	-0.97674000
H	-2.19512900	-1.99821300	-1.95047800
C	-4.06466600	-1.74443500	1.42043300
H	-2.10708400	-1.73971600	2.32093500
C	-4.79073700	-1.80421500	0.23535900
H	-4.66883800	-1.93708300	-1.90856000
H	-4.58102200	-1.66192900	2.37145000
H	-5.87473500	-1.76883800	0.25495600
C	3.24137700	0.22202000	0.11366400

C	3.76763700	0.70110500	-1.09070100
C	3.68904900	0.78090200	1.31425200
C	4.73720300	1.69667600	-1.09011400
H	3.39711200	0.29544900	-2.02663700
C	4.65852900	1.77800800	1.31015300
H	3.26964700	0.42436300	2.24948200
C	5.18972600	2.23762200	0.10971400
H	5.13429100	2.05826800	-2.03334600
H	4.99658500	2.19900600	2.25153400
H	5.94321100	3.01793400	0.10797500
C	-2.89194700	2.40026000	-0.63623100
H	-2.96936100	1.86004100	-1.58288400
H	-3.11254100	1.69153000	0.17195000
C	-3.82296600	3.60966900	-0.56105200
H	-4.82933800	3.34323800	-0.23079500
H	-1.36830600	5.03460100	-0.81953800
C	-3.08636700	4.53465700	0.41006000
H	-3.23271600	4.18978000	1.43890600
H	-3.41229700	5.57574900	0.35313100
H	-3.90647100	4.08693800	-1.54371900

II-Mg$_{PB}$ +III-Mg$_{PB}$: E(B3PW91) = -1206.1799264
Gas-phase zero-point energy= -1205.734217
Gas-phase free energy = -1205.798186

N	0.46506300	-1.85877500	0.21920900
N	-2.27916600	-0.66136300	0.16139300
C	0.46332500	-4.25746800	-0.34986600
C	-0.23971900	-2.94022500	-0.10665000
C	-1.63960700	-2.96327200	-0.22656600
C	-2.57900800	-1.91764400	-0.15498900
C	-4.01260100	-2.29788000	-0.44863800
H	1.30285900	-4.38960400	0.33610300
H	-0.23230500	-5.08774600	-0.22613900
H	0.86637100	-4.30909000	-1.36547600
H	-2.06036500	-3.93616000	-0.44600400
H	-4.29834400	-1.99638900	-1.46065000
H	-4.14771500	-3.37654600	-0.36925700
H	-4.70008800	-1.79900500	0.23818600
B	0.51122200	2.19556700	-0.51969800
H	0.10346100	1.10987200	1.94261200
H	-0.49365700	2.82006000	-0.37094000
H	0.46779000	1.03615800	-0.88301600
Mg	-0.40102600	-0.06489600	0.76888800
C	-3.28291900	0.34284500	0.11502400
C	-3.73686400	0.92814700	1.30084900
C	-3.77022500	0.82565900	-1.10444200
C	-4.67597200	1.95330300	1.26726100

H	-3.34680400	0.56960000	2.24788800
C	-4.70970200	1.84926400	-1.13310300
H	-3.39380700	0.39961200	-2.02887500
C	-5.16986200	2.41568200	0.05200200
H	-5.01985600	2.39377200	2.19754400
H	-5.07721100	2.21245300	-2.08767500
H	-5.89996400	3.21754700	0.02752600
C	1.88088000	-1.88667600	0.19060100
C	2.60322900	-1.67498400	1.37071000
C	2.58713400	-2.02347000	-1.01130500
C	3.99329000	-1.62991300	1.35159700
H	2.06224600	-1.54994600	2.30301400
C	3.97606800	-1.98062100	-1.02504400
H	2.03430000	-2.14709400	-1.93672200
C	4.68732000	-1.78681300	0.15598500
H	4.53487500	-1.47203800	2.27873700
H	4.50550200	-2.09105600	-1.96625700
H	5.77139900	-1.75169000	0.14293700
C	1.97775400	4.18785200	-0.02921900
C	3.04627400	2.10632500	-0.61686800
C	3.47805400	4.41399600	-0.21223500
H	1.69249400	4.30993200	1.02210600
H	1.36514100	4.86917000	-0.62416400
C	4.05993100	3.02540000	0.05996400
H	3.27616700	2.00726700	-1.68544600
H	3.01622000	1.10434300	-0.18478600
H	3.69432900	4.71592600	-1.24286700
H	3.86765100	5.18847400	0.45203800
H	5.07244400	2.89229300	-0.32728200
H	4.08025000	2.83069200	1.13719100
N	1.75583700	2.79057900	-0.44044400

II-Mg$_{PB}$ + PB: E(B3PW91) = -1207.3899398
Gas-phase zero-point energy = -1206.920880
Gas-phase free energy = -1206.982157

N	1.36682500	-1.59625700	0.07743000
N	-1.61573900	-1.40681700	0.08630700
C	2.18064200	-3.89886600	-0.17793700
C	1.06720300	-2.88137700	-0.07685700
C	-0.24337100	-3.38745100	-0.13892200
C	-1.47903400	-2.72021100	-0.06904600
C	-2.71098200	-3.59211900	-0.15968700
H	2.89451100	-3.77469700	0.64100200
H	1.78661600	-4.91441400	-0.15286800
H	2.74379900	-3.76995800	-1.10655500
H	-0.31186600	-4.46189300	-0.24719900
H	-3.24946200	-3.41384400	-1.09482300

H	-2.44636500	-4.64801900	-0.11275700
H	-3.40714500	-3.36402200	0.65178800
H	0.09631300	1.21115600	1.50699600
Mg	-0.03456100	-0.07960900	0.26065900
H	-0.98363400	1.26854800	-1.16270600
H	0.08918200	2.25913500	-2.52831000
H	1.03024000	1.05623000	-1.23697600
B	0.08484000	1.82137800	-1.40577400
C	-2.91245700	-0.83007800	0.12473500
C	-3.64256500	-0.60729200	-1.04800300
C	-3.44459700	-0.39101100	1.34145200
C	-4.88439300	0.01535000	-0.99933500
H	-3.21820300	-0.91519100	-1.99810200
C	-4.68708800	0.23312900	1.38550900
H	-2.87134900	-0.54647700	2.24961600
C	-5.41420500	0.43609900	0.21700900
H	-5.43746800	0.17953500	-1.91885000
H	-5.08714900	0.56234400	2.33937500
H	-6.38275200	0.92358300	0.25241500
C	2.72413700	-1.18289500	0.11489100
C	3.46300300	-1.01605600	-1.06169400
C	3.31734300	-0.84262200	1.33515900
C	4.76959000	-0.54370000	-1.01428600
H	2.99548800	-1.24724200	-2.01326900
C	4.62466000	-0.36948900	1.37806400
H	2.73904500	-0.95211100	2.24668400
C	5.35812400	-0.22079400	0.20507500
H	5.32838200	-0.42096500	-1.93682500
H	5.07058500	-0.11509100	2.33449400
H	6.37746600	0.14902200	0.23972100
C	1.51474300	3.75035400	-0.38848800
C	-0.85215200	3.99657700	-0.31998300
H	0.22079800	2.45522500	0.57030900
C	1.24071400	4.95796100	0.49798900
H	1.70225100	4.03831800	-1.42705800
H	2.33154700	3.11033200	-0.05169500
C	-0.21749500	5.31714900	0.16282700
H	-1.64168700	3.62309700	0.33459600
H	-1.25966800	4.07932400	-1.32867600
H	1.33569300	4.67151300	1.54998300
H	1.93460300	5.78047100	0.31380700
H	-0.74531500	5.73703700	1.02108400
H	-0.25256400	6.06249900	-0.63583600
N	0.24573200	2.98721900	-0.34219700

$TS_{II\text{-}I}$-Mg_{PB}: E(B3PW91) = =-1207.3767635
Gas-phase zero-point energy = -1206.912328
Gas-phase free energy = -1206.974521

N	-1.47450100	-1.47144600	0.03430700
N	1.51424700	-1.44202400	0.03325800
C	-2.41030100	-3.72314900	-0.23856700
C	-1.24237000	-2.77406300	-0.11104400
C	0.03827200	-3.35162000	-0.15608400
C	1.30736100	-2.74908400	-0.11156300
C	2.49347600	-3.67536000	-0.23895200
H	-2.98452000	-3.51077800	-1.14483200
H	-2.07339400	-4.75839100	-0.27556900
H	-3.09971800	-3.60462700	0.60184300
H	0.04880900	-4.42846900	-0.25972900
H	3.18281700	-3.53994100	0.59889300
H	2.17702400	-4.71718500	-0.27107100
H	3.06074300	-3.45540300	-1.14780500
H	-0.01601100	1.15266300	-1.31400400
Mg	0.00652600	-0.06632600	0.25363700
H	1.01616900	1.23770000	1.37962500
H	-0.01004300	2.37786500	2.63347900
H	-1.02337700	1.20466600	1.39855100
H	-0.02877200	1.84529100	-0.80247600
B	-0.01420300	1.93737300	1.50716300
C	2.84504700	-0.93655300	0.01005400
C	3.53206600	-0.69088500	1.20216400
C	3.45482600	-0.60114500	-1.20279100
C	4.80777200	-0.13767100	1.17897400
H	3.05327400	-0.93244400	2.14548700
C	4.73082400	-0.04845000	-1.22159200
H	2.91462700	-0.77303100	-2.12844600
C	5.41354800	0.18327800	-0.03156200
H	5.32782000	0.04768100	2.11328500
H	5.19075900	0.20641000	-2.17107700
H	6.40744200	0.61752500	-0.04715100
C	-2.81454100	-0.99121400	0.01217800
C	-3.50537200	-0.75932200	1.20485600
C	-3.43074100	-0.66529100	-1.20002000
C	-4.79063200	-0.22862800	1.18286900
H	-3.02193300	-0.99342800	2.14767000
C	-4.71627400	-0.13518400	-1.21764000
H	-2.88794600	-0.82632700	-2.12608600
C	-5.40241800	0.08326600	-0.02703500
H	-5.31347800	-0.05364700	2.11762200
H	-5.18104200	0.11263600	-2.16663900
H	-6.40377200	0.50005600	-0.04170400
C	-1.21429800	3.81439500	0.26293400
C	1.10640700	3.84953800	0.24846200
C	-0.85577100	4.82199300	-0.83633300
H	-1.39720300	4.32996900	1.22032100

H	-2.10667200	3.22267400	0.03654500
C	0.68884400	4.90634400	-0.79010700
H	2.00103600	3.28845100	-0.03983200
H	1.31960500	4.32380600	1.21995500
H	-1.18958100	4.45370100	-1.81010800
H	-1.33582300	5.79003400	-0.67433000
H	1.11857400	4.68373300	-1.76995100
H	1.04020300	5.90076400	-0.50450800
N	-0.04078500	2.95060100	0.35920500

I-Mg$_{PB}$ + III$_{PB}$: E(B3PW91) = -1444.2664414
Gas-phase zero-point energy = -1443.674927
Gas-phase free energy = -1443.754341

N	-1.60278900	1.75088700	-0.98613000
N	-2.19969900	-1.18161500	-1.09823100
C	-1.24509000	2.73349400	-3.20838600
C	-1.58305900	1.57089000	-2.30503700
C	-1.85822900	0.34855100	-2.94332500
C	-2.09268600	-0.92648800	-2.40111100
C	-2.22522100	-2.05919600	-3.39188800
H	-0.18270900	2.98386200	-3.13552500
H	-1.46884000	2.49651900	-4.24807300
H	-1.80038100	3.62873500	-2.91746300
H	-1.83546000	0.38565800	-4.02442000
H	-3.10095900	-2.67359600	-3.16755100
H	-2.30784300	-1.67890400	-4.40953700
H	-1.35555800	-2.72104900	-3.34263400
B	-3.22792800	0.42664400	2.30545100
H	-3.32810400	1.49169200	1.67087600
H	-3.79882000	0.50589400	3.36675500
H	-3.73417000	-0.46194800	1.59785100
H	4.91539800	1.31094300	-1.84673500
H	3.67304900	-0.11800000	-0.95704900
B	4.76287900	0.32073500	-1.19047000
Mg	-2.17697400	0.28829600	0.32878300
C	-1.20735800	3.00595200	-0.44349400
C	0.14674700	3.32640000	-0.29941000
C	-2.16828500	3.90490800	0.02759900
C	0.52766900	4.52798000	0.28755600
H	0.89627300	2.62171900	-0.64561300
C	-1.78226200	5.10548100	0.61456200
H	-3.21868000	3.65154300	-0.06826100
C	-0.43437800	5.42326600	0.74559300
H	1.58237500	4.76200000	0.39151700
H	-2.54100800	5.79266500	0.97474100
H	-0.13532800	6.35841600	1.20681000
C	-2.32800500	-2.52762500	-0.65550500

C	-1.20003100	-3.34644700	-0.53592400
C	-3.57034900	-3.02734400	-0.25530400
C	-1.31716300	-4.64098600	-0.04251700
H	-0.23110700	-2.95237700	-0.82606500
C	-3.68284900	-4.32281600	0.23870300
H	-4.44404000	-2.38903400	-0.33215200
C	-2.55888000	-5.13546100	0.34558800
H	-0.43253200	-5.26387600	0.04440700
H	-4.65480800	-4.69544800	0.54536100
H	-2.64839800	-6.14420700	0.73423700
C	7.27131700	0.10638100	-0.86981000
C	5.84352700	-1.56175000	0.12402200
C	8.11993100	-1.05236700	-0.34695000
H	7.45599800	1.01267000	-0.28146600
H	7.46752300	0.34346600	-1.91749300
C	7.23339300	-1.64693400	0.74932700
H	5.66323900	-2.43181500	-0.51965900
H	5.03757600	-1.51654100	0.85869100
H	8.28198200	-1.79219700	-1.13830800
H	9.09874700	-0.72694300	0.01170500
H	7.50890900	-2.66624000	1.02834200
H	7.28134700	-1.02555600	1.65009700
C	-1.33206200	-1.17123400	2.98708700
C	-0.86276900	1.08274200	3.07488300
C	0.19180400	-1.10834500	3.16333700
H	-1.66959100	-2.01836600	2.38469800
H	-1.82913300	-1.24423200	3.96761700
C	0.50818300	0.40719900	3.21154700
H	-1.30077000	1.26928800	4.06859600
H	-0.83010700	2.03884600	2.54658600
H	0.51171300	-1.63226400	4.06740500
H	0.69883400	-1.58318000	2.31901600
H	1.01100800	0.70231800	4.13574200
H	1.16210200	0.69213700	2.38295500
N	5.87500900	-0.33262000	-0.68691000
N	-1.68854800	0.10526800	2.35367800

$TS_{I\text{-}IV}$-Mg_{PB}: E(B3PW91) = -1444.2425482
Gas-phase zero-point energy = -1443.648670
Gas-phase free energy = -1443.713702

N	1.14840800	-1.38680800	-0.64266300
N	-1.78074200	-0.83374200	-0.84255600
C	1.80653300	-3.32497900	-2.02688300
C	0.80188800	-2.28983400	-1.56660900
C	-0.46454600	-2.36872100	-2.16535500
C	-1.68551500	-1.80055500	-1.74686100
C	-2.93605500	-2.37038600	-2.37520200

H	1.80724900	-4.19824100	-1.36833300
H	1.55383600	-3.66913600	-3.03071000
H	2.82106600	-2.92131600	-2.03112800
H	-0.54713700	-3.08760900	-2.97024100
H	-3.56761500	-1.57451700	-2.77878800
H	-2.68946100	-3.06828500	-3.17455300
H	-3.53498200	-2.89910400	-1.62804700
B	-0.08429500	2.02813500	-2.09994300
H	0.10939400	0.87036500	-2.50774900
H	-0.30766000	2.72910400	-3.06140400
H	-1.07225800	2.02133800	-1.34923200
H	2.15718500	1.34856000	1.36839000
H	1.00715000	3.08999000	1.42686000
B	1.10540800	1.90930600	1.34421100
C	2.28642300	-1.66672700	0.15565500
C	3.43007000	-0.86422300	0.11794300
C	2.26247900	-2.74295400	1.05457400
C	4.51709000	-1.13484000	0.94326900
H	3.46851100	-0.02936300	-0.57095100
C	3.34925800	-3.01192500	1.87705500
H	1.37048200	-3.35955500	1.10742700
C	4.48488400	-2.20837900	1.82644600
H	5.39623000	-0.50051400	0.89083200
H	3.30622500	-3.85054400	2.56512200
H	5.33341600	-2.41591400	2.46946100
C	-3.06778200	-0.44710700	-0.38699300
C	-3.72684700	0.65251100	-0.94848000
C	-3.67863400	-1.12750000	0.67251500
C	-4.96563000	1.05635700	-0.46095900
H	-3.25513300	1.18669800	-1.76573500
C	-4.91904900	-0.72158800	1.15415900
H	-3.16980000	-1.98082800	1.11001000
C	-5.56768900	0.37353700	0.59128000
H	-5.46260700	1.91055700	-0.90976800
H	-5.38020900	-1.26460800	1.97335300
H	-6.53403800	0.69055100	0.96861400
Mg	-0.05543500	0.33643500	-0.59256600
C	0.00773100	-0.15061400	2.32658300
C	-1.35491900	1.76934600	1.92983800
C	-0.56986700	0.25342500	3.67813300
H	1.03836400	-0.50024100	2.36198800
H	-0.60699800	-0.93205800	1.86420100
C	-1.74674200	1.16119000	3.29443400
H	-2.13447100	1.58587800	1.18757600
H	-1.18339000	2.84537300	1.97456100
H	-0.87423900	-0.60590300	4.28007500
H	0.18481900	0.81099500	4.24230100
H	-2.66159900	0.57345200	3.18863900

H	-1.93710400	1.93217600	4.04397500
C	2.42574900	2.22630300	-1.94739700
C	1.17845900	3.89663700	-1.00938300
C	3.45054200	3.03988500	-1.15617600
H	2.35093400	2.61379100	-2.97781700
H	2.65571300	1.16086200	-2.02735400
C	2.62612500	4.23026100	-0.61293600
H	0.43661100	4.19049800	-0.26448900
H	0.91868000	4.41062700	-1.94833800
H	3.85271600	2.44782900	-0.33003000
H	4.29260000	3.35400000	-1.77790100
H	2.73555700	4.31772700	0.47017300
H	2.93913300	5.18188500	-1.04986800
N	1.15020100	2.44198300	-1.24852400
N	-0.07804400	1.10518800	1.53466100

IV-Mg$_{PB}$: E(B3PW91) = -1444.2915617
Gas-phase zero-point energy = -1443.694246
Gas-phase free energy = -1443.758792

H	1.04159400	1.06654300	-1.32459300
B	-0.00140200	1.61993000	-1.67423000
H	-0.95903500	0.84521300	-1.62840000
H	0.13578800	1.97888100	-2.81565300
B	-0.78466500	2.28370400	0.78745400
H	-1.92023600	1.88712600	0.62308100
H	-0.74086200	3.25324900	1.52618300
C	-1.29163300	-3.03916700	-0.63852500
C	-0.01894600	-3.60609400	-0.82967900
C	1.25929900	-3.03535400	-0.72172300
C	-2.46346000	-3.98124200	-0.79619000
H	-3.20027600	-3.57126800	-1.49208300
H	-2.13605200	-4.95453500	-1.15989700
H	-2.98032300	-4.12392400	0.15690800
C	2.42224300	-3.97299000	-0.95604400
H	2.07681800	-4.93246900	-1.33940100
H	3.13298400	-3.54164200	-1.66591200
H	2.97456000	-4.15215600	-0.02938700
N	1.49465800	-1.75333300	-0.44554300
H	-0.02565100	-4.65647200	-1.08877300
N	-1.51309900	-1.76071700	-0.34529600
Mg	-0.00869600	-0.33131000	-0.26201400
C	2.84142500	-1.32046300	-0.30144400
C	3.54914600	-1.55650100	0.88281200
C	3.46239800	-0.59030700	-1.31950300
C	4.84721800	-1.08384100	1.03852100
H	3.06694900	-2.11109100	1.68189500
C	4.76099000	-0.11716600	-1.15927400
H	2.91665700	-0.40066400	-2.23740400

C	5.45948900	-0.36142900	0.01849400
H	5.38108300	-1.27727700	1.96364300
H	5.22768900	0.44503800	-1.96190200
H	6.47152100	0.00905900	0.14202200
C	-2.85437200	-1.32895800	-0.14109300
C	-3.48410800	-1.50867200	1.09458900
C	-3.54533700	-0.66423900	-1.15815800
C	-4.77767900	-1.04372100	1.30301900
H	-2.94639300	-2.01465200	1.89012600
C	-4.83914500	-0.20038100	-0.94570800
H	-3.05730700	-0.51627700	-2.11554200
C	-5.46135000	-0.38778800	0.28404700
H	-5.25157800	-1.19143000	2.26833400
H	-5.36214000	0.31205300	-1.74692700
H	-6.46917900	-0.02210800	0.44908200
C	0.85385500	3.76026300	-0.63573200
C	-1.39718100	3.66474400	-1.19511600
C	0.73256700	4.61490800	-1.90119000
H	1.79580900	3.21447300	-0.58096700
H	0.74786500	4.37282600	0.26470300
C	-0.76967500	4.57570300	-2.25506500
H	-1.78703100	4.24918600	-0.35540900
H	-2.20037200	3.02948700	-1.56770200
H	1.09565800	5.62936500	-1.72021300
H	1.32923100	4.19315700	-2.71197600
H	-1.22841500	5.56695300	-2.22985700
H	-0.91893300	4.17163600	-3.25755500
C	-0.62438700	0.50203800	2.53751800
C	1.38011900	1.41781800	1.87769600
C	-0.20756800	1.39252600	3.72195300
H	-0.26496100	-0.52307300	2.70538700
H	-1.70296000	0.46327600	2.38123200
C	1.13531400	2.00955500	3.27809500
H	1.90483300	2.09862900	1.20842100
H	1.99126800	0.51139200	1.95980600
H	-0.95300600	2.17109900	3.89369700
H	-0.11901800	0.81146200	4.64354700
H	1.06188900	3.09749900	3.23156600
H	1.95637400	1.76385100	3.95651200
N	-0.29364100	2.80400500	-0.66480400
N	0.04558700	1.06285700	1.33673500

$TS_{IV\text{-}II}$-Mg_{DMAB}: E(B3PW91) = -1444.218809
Gas-phase zero-point energy = -1443.627086
Gas-phase free energy = -1443.696495

B	-0.40858000	-1.51443600	-0.08187600
H	-1.25893700	-0.68661800	0.18606400

H	0.71141900	-1.34019700	0.35305400
B	-0.82674700	-3.74496900	0.48546500
H	-1.78077700	-4.49473700	0.38970900
H	0.23428100	-4.31761300	0.59075300
C	-0.11921900	3.52214400	0.26493800
C	1.25769500	3.65953900	0.51167800
C	2.30562000	2.73317600	0.36707700
C	-0.96688100	4.74971700	0.50095200
H	-1.67050600	4.58452000	1.32176100
H	-0.34831900	5.61274200	0.74414600
H	-1.56731900	4.98126800	-0.38298100
C	3.69225900	3.23259200	0.69619000
H	4.37131300	3.06847400	-0.14493100
H	3.68055800	4.29442900	0.93887100
H	4.11021400	2.68477900	1.54545800
N	2.14611700	1.47712300	-0.04344900
H	1.56247200	4.64050100	0.85108300
N	-0.69816800	2.40241000	-0.16531800
H	-0.04060600	-0.69030800	-1.58489800
Mg	0.32818700	0.66528200	-0.51100700
C	-2.10320700	2.37915800	-0.39387900
C	-2.99902600	2.14762900	0.65410100
C	-2.60288600	2.51006100	-1.69255700
C	-4.36539300	2.06928400	0.40890700
H	-2.61233100	2.02175500	1.66020900
C	-3.97051900	2.42990000	-1.93402800
H	-1.90749400	2.67708400	-2.50906400
C	-4.85746200	2.21231300	-0.88482400
H	-5.04780400	1.88892400	1.23329800
H	-4.34271900	2.53665500	-2.94788400
H	-5.92351000	2.14752600	-1.07425900
C	3.28210100	0.62712500	-0.16918400
C	3.76235500	-0.09354600	0.92787500
C	3.88399100	0.44034000	-1.41673500
C	4.83459900	-0.96659000	0.78240400
H	3.28104900	0.03077400	1.89252100
C	4.95670900	-0.43386900	-1.55795700
H	3.50266300	0.98802900	-2.27275100
C	5.43819200	-1.13833800	-0.45937400
H	5.19447800	-1.52079200	1.64320200
H	5.41518200	-0.56627600	-2.53272000
H	6.27205200	-1.82284900	-0.57165300
C	-2.04484000	-2.70859900	-1.59943400
C	0.27390500	-3.28553700	-1.86180000
C	-1.90559700	-3.67354800	-2.76492300
H	-2.16120500	-1.68398000	-1.96727000
H	-2.86389600	-2.94558200	-0.92033700
C	-0.45988000	-3.42555700	-3.19408400

H	0.64902900	-4.24888600	-1.51253700
H	1.10278000	-2.57889900	-1.90518900
H	-2.03660500	-4.70462200	-2.42026000
H	-2.63584800	-3.48058400	-3.55456300
H	-0.04274300	-4.22668800	-3.80902600
H	-0.39697200	-2.49253000	-3.76299200
C	-2.31947600	-2.34285000	2.05876500
C	-0.03381800	-2.61419300	2.69481500
C	-2.10715700	-1.70600900	3.43005600
H	-2.91518400	-3.26269400	2.14841600
H	-2.84911100	-1.67542800	1.36869700
C	-0.89511400	-2.47580400	3.95131800
H	0.63576000	-1.74498900	2.59938000
H	0.59768000	-3.50587000	2.70664200
H	-1.85899600	-0.64376000	3.32135000
H	-2.98783400	-1.78120600	4.07318100
H	-0.37395300	-1.97298800	4.77054800
H	-1.20753200	-3.46352700	4.30784400
N	-0.97100700	-2.65625500	1.55879200
N	-0.74466200	-2.80662500	-0.86152900

II-Mg_{PB} + V_{PB}: E(B3PW91) = -1444.2569453
Gas-phase zero-point energy = -1443.663142
Gas-phase free energy = -1443.731602

H	-0.05135100	-0.15581000	-2.68060100
B	0.10251800	1.44552500	0.09732300
H	-0.94961400	0.84145700	0.00663900
H	1.08669600	0.74953600	-0.06028000
B	0.21130300	3.58316100	0.54186700
H	-0.77150400	4.26065000	0.71415800
H	1.26045100	4.16839400	0.64829100
C	-1.45845300	-3.26518400	0.16919100
C	-0.21162300	-3.90022700	0.31218100
C	1.09235900	-3.40133500	0.14199100
C	-2.66375600	-4.10435500	0.53620700
H	-3.49831200	-3.91531100	-0.14230600
H	-2.41113700	-5.16448400	0.50292000
H	-3.01310900	-3.87760900	1.54770500
C	2.20818000	-4.36540500	0.48454400
H	1.84742900	-5.39309800	0.43266400
H	3.05473400	-4.25001400	-0.19534900
H	2.58241400	-4.19655300	1.49856400
N	1.37266900	-2.18396700	-0.31279900
H	-0.26296000	-4.93176500	0.63660400
N	-1.61805900	-2.02397700	-0.28018100
Mg	-0.06712600	-0.89604500	-1.09524300
C	2.70748700	-1.71645200	-0.35022200

C	3.45462700	-1.51551800	0.81768100
C	3.27258600	-1.34541000	-1.57632500
C	4.73747700	-0.98474100	0.75611800
H	3.01311800	-1.76615700	1.77665400
C	4.55561300	-0.81213900	-1.63246800
H	2.69255400	-1.48156800	-2.48349700
C	5.29670200	-0.63208200	-0.46885400
H	5.30133200	-0.83926300	1.67242000
H	4.97767800	-0.53786900	-2.59406600
H	6.29777300	-0.21675000	-0.51465000
C	-2.89906600	-1.42242100	-0.29221800
C	-3.59155500	-1.13372000	0.89075700
C	-3.45724800	-1.01391500	-1.50941700
C	-4.81945700	-0.48389900	0.85295700
H	-3.15081500	-1.41365400	1.84202300
C	-4.68477900	-0.36104800	-1.54185100
H	-2.91666800	-1.21692000	-2.42836500
C	-5.37478000	-0.09625000	-0.36318700
H	-5.34243700	-0.27275700	1.78064300
H	-5.10374900	-0.05980500	-2.49672800
H	-6.33259700	0.41225400	-0.39070800
C	1.26285600	2.88319800	-1.76330100
C	-1.05039700	2.98959300	-1.68277500
C	0.90647600	4.12150700	-2.59089400
H	1.29750000	1.98402700	-2.38608200
H	2.19884400	2.97139500	-1.21179500
C	-0.63992300	4.19266300	-2.53692900
H	-1.93333300	3.16151700	-1.06728200
H	-1.21128600	2.09968400	-2.29903300
H	1.34576400	5.01904000	-2.14892700
H	1.28840500	4.03633300	-3.61035600
H	-0.96323000	5.12519700	-2.06818400
H	-1.09820700	4.14650400	-3.52701900
C	-0.95326200	2.13601400	2.40297000
C	1.35914900	2.03792100	2.32975600
C	-0.49706200	2.90550500	3.64692900
H	-1.10882000	1.07490000	2.62796300
H	-1.86205200	2.52581200	1.94570300
C	1.05006100	2.84534300	3.59415100
H	2.26706400	2.34781500	1.81361700
H	1.43711900	0.96762200	2.55084300
H	-0.84090300	3.94111400	3.60106200
H	-0.90595000	2.46472600	4.55865300
H	1.46857800	3.85095200	3.51350700
H	1.48553400	2.37914900	4.48055200
N	0.18112000	2.25149700	1.45800100
N	0.12829700	2.73138600	-0.81658300

III- $_{iPr2}$**:** E(B3PW91) = - 317.874265

Gas-phase zero-point energy = - 317.657121

Gas-phase free energy = - 317.691771

N	-0.00872400	-0.00050700	0.64496100
C	1.41880500	-0.00008500	0.27691700
H	1.95074000	-0.00043800	1.23202200
B	-0.40597100	-0.00156800	1.97664300
C	1.82408500	1.26737000	-0.47729000
H	1.56544200	2.15907500	0.09902100
H	2.90440700	1.27310400	-0.64885100
H	1.33825900	1.33752700	-1.45534600
C	1.82443500	-1.26667000	-0.47851700
H	2.90474000	-1.27187500	-0.65019500
H	1.56613400	-2.15901200	0.09695800
H	1.33852500	-1.33602000	-1.45657900
H	-1.56847700	-0.00186400	2.25877400
H	0.43081300	-0.00207400	2.83296800
C	-0.98224800	0.00028200	-0.47069300
H	-0.40127900	0.00093700	-1.39857300
C	-1.84052300	1.26448700	-0.46665500
H	-2.50540900	1.27906000	-1.33579200
H	-2.45728400	1.30815000	0.43467700
H	-1.21758600	2.16178600	-0.49596700
C	-1.84072400	-1.26376100	-0.46835900
H	-2.50572500	-1.27696200	-1.33742300
H	-1.21796900	-2.16113500	-0.49904000
H	-2.45738800	-1.30860900	0.43298000

iPr2: E(B3PW91) = -319.0467886

Gas-phase zero-point energy = -318.806964

Gas-phase free energy = - 318.841594

N	0.02806200	0.51690500	0.17836900
C	-1.34220100	0.08514500	-0.33267400
H	-1.49909800	0.73243500	-1.19894000
B	0.20676400	2.11445100	-0.20122600
H	-0.01451200	0.48278000	1.19614000
C	-2.37897400	0.41886400	0.73341800
H	-2.29440000	1.45842900	1.05179800
H	-3.38557300	0.26526100	0.33686100
H	-2.26474900	-0.23635800	1.60533700
C	-1.51650900	-1.36109500	-0.79194600
H	-2.47836800	-1.42061300	-1.30902300
H	-0.75573400	-1.69084700	-1.50122700
H	-1.55734800	-2.06929800	0.03938000
H	1.09037600	2.56047700	0.49409600
H	0.45688200	2.14227200	-1.38984300

H	-0.85592100	2.63864800	0.04704000
C	1.19978300	-0.35063200	-0.21667400
H	1.01446400	-0.63807200	-1.25442000
C	1.29049800	-1.58842800	0.67560900
H	0.38100600	-2.18690100	0.68982300
H	2.10654800	-2.23139500	0.33631300
H	1.52031100	-1.29116500	1.70528700
C	2.52936300	0.39484500	-0.17069700
H	2.53512900	1.25771400	-0.83291300
H	2.76041700	0.74086700	0.84022400
H	3.31855600	-0.29700800	-0.48060600

I-MgiPr2: E(B3PW91) = -1286.0335298
Gas-phase zero-point energy = -1285.506868
Gas-phase free energy = - 1285.568365

N	-1.34685200	-1.33592700	-0.19092700
N	1.65271200	-1.18677100	-0.14492500
C	-2.15115600	-3.51181800	-1.02156900
C	-1.05015100	-2.51337500	-0.74299000
C	0.25038400	-2.94242200	-1.04948400
C	1.49388200	-2.38642500	-0.70002500
C	2.69307400	-3.27743700	-0.93658400
H	-2.84180800	-3.14316000	-1.78436900
H	-1.73735000	-4.46064300	-1.36040300
H	-2.74522700	-3.68885500	-0.12083800
H	0.30642500	-3.91984300	-1.50937600
H	3.29009500	-3.36875600	-0.02533100
H	2.38024000	-4.27165700	-1.25304400
H	3.35318500	-2.86294600	-1.70283700
B	0.32021500	2.03113500	1.28952900
N	-0.25854300	2.27271600	-0.16741400
C	-1.58912800	2.94499800	-0.22940200
H	-1.40390400	4.03059600	-0.20709300
H	-0.37750200	1.12487300	1.80497600
H	0.36263600	2.95314000	2.06486900
H	1.43651000	1.54016900	1.12868600
Mg	0.07162000	0.14912500	0.10197500
C	-2.69165500	-1.09986000	0.21381200
C	-3.69129100	-0.77262300	-0.70748500
C	-3.01884000	-1.14346000	1.57255200
C	-4.98753200	-0.50727100	-0.28016200
H	-3.44269600	-0.72452000	-1.76266700
C	-4.31620200	-0.87633000	1.99704300
H	-2.24415800	-1.39024300	2.29118800
C	-5.30634500	-0.55823800	1.07315700
H	-5.75025700	-0.25328000	-1.00926200
H	-4.55153900	-0.91482300	3.05570100

H	-6.31702600	-0.34687600	1.40528600
C	2.95539000	-0.81168600	0.29573400
C	3.95649200	-0.42780300	-0.60184200
C	3.23138000	-0.77219400	1.66516200
C	5.20685500	-0.03164000	-0.13953700
H	3.74563100	-0.43361600	-1.66616800
C	4.48188500	-0.37500600	2.12447700
H	2.45308900	-1.05638900	2.36558800
C	5.47623300	-0.00473500	1.22484700
H	5.97159100	0.26343200	-0.85099200
H	4.67679100	-0.35089300	3.19171400
H	6.45058100	0.30867700	1.58404000
C	-2.49806100	2.63789200	0.95571000
H	-2.76600900	1.57938600	1.00279000
H	-2.03802300	2.91944400	1.90331400
H	-3.42712700	3.20491700	0.84440600
C	-2.32097800	2.61668500	-1.53300300
H	-3.22780400	3.22255500	-1.62460300
H	-1.71111500	2.80394000	-2.42020300
H	-2.62002600	1.56522200	-1.54184600
C	0.68361600	3.01299800	-1.06303300
H	0.07871000	3.41150000	-1.88388400
C	1.71448100	2.08765200	-1.69647800
H	2.33650000	2.63787200	-2.40927700
H	2.38506100	1.66027900	-0.94729100
H	1.23062800	1.27360000	-2.25034100
C	1.36562800	4.20503100	-0.38754600
H	2.07700100	3.87570200	0.37328900
H	1.90800300	4.79625200	-1.13230400
H	0.63938200	4.86204500	0.09767100

$TS_{I\text{-}II}$-$Mg^{i}{}_{Pr_2}$: E(B3PW91) = - 1286.0080122
Gas-phase zero-point energy = - 1285.486477
Gas-phase free energy = - 1285.552666

N	-2.09517800	-1.33799000	0.08427400
N	0.77366800	-2.20111300	0.12773400
C	-3.62815400	-3.16956000	-0.50142900
C	-2.24454000	-2.61975100	-0.23993700
C	-1.18589100	-3.53989400	-0.34536900
C	0.20066500	-3.35464400	-0.20800400
C	1.06141800	-4.57339400	-0.44921500
H	-4.01230200	-2.82467100	-1.46563000
H	-3.61608000	-4.25914900	-0.51119800
H	-4.33346700	-2.82708500	0.25993800
H	-1.48643200	-4.55074500	-0.58752400
H	1.81128400	-4.68326700	0.33841100
H	0.45322800	-5.47655600	-0.48949100

H	1.60650400	-4.48684400	-1.39352100
B	0.13639600	1.84839200	-0.37651200
N	1.05295400	2.90091500	-0.31312800
C	2.49155300	2.67248200	-0.51100700
H	2.57815500	1.61810900	-0.78867800
H	0.52844100	0.80665200	-0.87722600
H	-1.04159400	2.02280200	-0.28096300
H	0.09903200	0.85283000	1.61415600
Mg	-0.28574600	-0.49696100	0.58096900
C	3.29310200	2.86789900	0.77789300
H	3.28301600	3.91101900	1.11008200
H	2.88507800	2.24603700	1.57772800
H	4.33746900	2.58303100	0.62005800
C	3.05895600	3.49924800	-1.66684100
H	4.10942800	3.24292500	-1.83406900
H	2.50721300	3.30403500	-2.59001000
H	3.01390500	4.57373700	-1.46320800
C	-3.22208700	-0.47153600	0.09794600
C	-3.80351900	-0.01998700	-1.09151200
C	-3.70878200	0.01736500	1.31369300
C	-4.86127100	0.88082700	-1.06188000
H	-3.40586100	-0.36943600	-2.03891000
C	-4.76637600	0.92027300	1.33887300
H	-3.24922600	-0.31808500	2.23785100
C	-5.34951100	1.35344400	0.15280100
H	-5.29991600	1.22274400	-1.99395600
H	-5.13312700	1.28802400	2.29176200
H	-6.17231700	2.05996300	0.17370600
C	2.19002600	-2.10056500	0.17627700
C	2.94963700	-2.00766200	-0.99529800
C	2.84144500	-2.00583200	1.40984000
C	4.32956100	-1.85075600	-0.93140700
H	2.44501800	-2.04995900	-1.95529500
C	4.22190500	-1.84685300	1.46926000
H	2.25372300	-2.06160700	2.32044200
C	4.97270500	-1.77314700	0.30052300
H	4.90403200	-1.78281600	-1.84986200
H	4.71149000	-1.77930900	2.43544700
H	6.04921700	-1.64889700	0.34870500
C	0.63828300	4.25695000	0.09841900
H	1.54628400	4.86858200	0.12410900
C	0.03569900	4.27018200	1.50266000
H	-0.19889600	5.29515000	1.80753800
H	-0.88540300	3.68283800	1.53538100
H	0.72709000	3.84118300	2.23111500
C	-0.30597700	4.88654900	-0.92590000
H	-0.55235100	5.91446400	-0.64145300
H	0.14996500	4.90350100	-1.91906900

H	-1.23882100	4.31985000	-0.98992200

II-Mg^{i}$_{Pr2}$+III^{i}$_{Pr}$: E(B3PW91) = -1286.0088102
Gas-phase zero-point energy = -1285.487172
Gas-phase free energy = -1285.556263

N	0.77568900	-2.21737300	0.15939800
N	-2.09210200	-1.35324200	0.11364900
C	1.09347300	-4.49347500	-0.72857800
C	0.22353800	-3.31478800	-0.35173600
C	-1.15710200	-3.48269000	-0.55665100
C	-2.22179500	-2.57925000	-0.38575500
C	-3.58806800	-3.08659500	-0.78950600
H	1.89108700	-4.64359900	0.00255000
H	0.49627100	-5.40289300	-0.79602100
H	1.57384200	-4.33589800	-1.69857800
H	-1.44470600	-4.45622700	-0.93214700
H	-3.89753400	-2.66315400	-1.74934100
H	-3.58150300	-4.17212100	-0.88727300
H	-4.34477600	-2.79800100	-0.05615800
B	0.21556200	1.75610200	-0.38419800
N	1.07324600	2.84017500	-0.32618300
C	2.53490100	2.66841300	-0.42078400
H	2.68384100	1.59728400	-0.58024700
H	-0.02016900	0.44568200	2.21252700
H	-0.96885700	1.87793800	-0.29486100
H	0.69900600	0.67017800	-0.61302500
Mg	-0.31921400	-0.61545000	0.87396100
C	-3.21230800	-0.48237200	0.16538000
C	-3.74552100	-0.10899600	1.40306300
C	-3.74308300	0.09074600	-0.99585200
C	-4.79878000	0.79645100	1.47459800
H	-3.32497300	-0.53598700	2.30769900
C	-4.79738100	0.99299700	-0.91995700
H	-3.30905300	-0.16588600	-1.95678700
C	-5.33246200	1.34855000	0.31485400
H	-5.20169900	1.07172200	2.44395200
H	-5.19694200	1.42771300	-1.83082700
H	-6.15291300	2.05583400	0.37242900
C	2.18548200	-2.08958800	0.23130700
C	2.81070400	-2.00131700	1.47988600
C	2.96821100	-1.95235500	-0.92196500
C	4.18514300	-1.81047500	1.57079800
H	2.20686200	-2.08759500	2.37733700
C	4.34215100	-1.76471900	-0.82626000
H	2.48549700	-1.98198000	-1.89344600
C	4.95858200	-1.69645700	0.42002800
H	4.65254700	-1.75107300	2.54845300

H	4.93310600	-1.66458000	-1.73135300
H	6.03082000	-1.54915300	0.49312600
C	3.12686800	3.40238400	-1.62474700
H	3.02829200	4.48869900	-1.53556500
H	4.19390900	3.17789800	-1.71028800
H	2.63737800	3.08922400	-2.55048900
C	3.24061900	3.03851500	0.88415900
H	2.81662500	2.47751500	1.71989400
H	4.30467700	2.79577900	0.81323900
H	3.16170300	4.10733100	1.10649600
C	0.57356600	4.21528200	-0.09591600
H	1.45214100	4.86771800	-0.08365900
C	-0.32707600	4.67862300	-1.23968400
H	-1.23062300	4.06536100	-1.29201500
H	-0.63148000	5.71875500	-1.08856800
H	0.19017400	4.60781200	-2.19992400
C	-0.11823500	4.34149900	1.25997100
H	-0.41188800	5.38010600	1.44141300
H	-1.01614200	3.71981700	1.29802800
H	0.54182300	4.02146100	2.06892800

II-Mg^{i}$_{Pr2}$+ *i*Pr2: E(B3PW91) = - 1287.2109139
Gas-phase zero-point energy = - 1286.665426
Gas-phase free energy = - 1286.730444

N	1.64266000	-1.64499700	0.01945900
N	-1.34068900	-1.80588100	0.01216400
C	2.71680000	-3.78741900	-0.51764300
C	1.49317600	-2.92618200	-0.30130100
C	0.25128900	-3.56919500	-0.44525800
C	-1.05303500	-3.06326300	-0.30831200
C	-2.17709900	-4.04904100	-0.53239800
H	3.40969200	-3.69310900	0.32301900
H	2.44228100	-4.83546900	-0.63352000
H	3.26372600	-3.47316700	-1.41110200
H	0.30868500	-4.62024800	-0.69558900
H	-2.77090600	-3.77159900	-1.40802800
H	-1.79120600	-5.05681400	-0.68202500
H	-2.86180300	-4.05526600	0.32027700
C	0.90245900	3.84559000	0.26314100
H	0.61445400	4.44199300	1.13870400
H	-0.02155600	0.78319900	1.78960100
Mg	0.07602300	-0.33530700	0.39893800
H	-0.99787900	0.99435100	-0.96381300
H	0.01889600	2.21464900	-2.16312500
H	1.00120400	1.15126400	-0.81194000
H	-0.17770300	2.24415000	0.93763700

N	-0.22375900	2.85571900	0.08876100
B	-0.03742800	1.75035400	-1.05684300
C	1.05917700	4.78046800	-0.92812400
H	1.90560200	5.44769000	-0.74487400
H	1.26053600	4.21763000	-1.84194600
H	0.17810100	5.40514400	-1.08896900
C	2.20854700	3.13541500	0.59619300
H	2.93528800	3.87826600	0.93654600
H	2.07418900	2.39981700	1.39284500
H	2.62770400	2.62416600	-0.27170800
C	-2.69795100	-1.40434600	0.11895900
C	-3.43134500	-1.03254300	-1.01337400
C	-3.30201100	-1.29715500	1.37595500
C	-4.74441900	-0.59083800	-0.89126500
H	-2.95675800	-1.08794800	-1.98770100
C	-4.61550500	-0.85426300	1.49380400
H	-2.72756300	-1.56493800	2.25664700
C	-5.34404400	-0.50267700	0.36174400
H	-5.30014400	-0.31063200	-1.78073500
H	-5.06994200	-0.78268100	2.47696600
H	-6.36812000	-0.15702400	0.45514200
C	2.94710500	-1.09325800	0.11636100
C	3.64849700	-0.69323900	-1.02649200
C	3.51961000	-0.86209400	1.37140500
C	4.90225700	-0.10272700	-0.91576900
H	3.19386000	-0.84176300	-2.00063500
C	4.77355100	-0.26913900	1.47787700
H	2.96907000	-1.15388900	2.25986600
C	5.47259700	0.10947000	0.33619200
H	5.43373400	0.19818600	-1.81324200
H	5.20501000	-0.10259400	2.45993500
H	6.45057600	0.57133800	0.42094200
C	-1.58248200	3.52708500	0.12892000
H	-1.40847300	4.50228500	0.59889300
C	-2.19377600	3.75813400	-1.24803200
H	-2.48401000	2.81446100	-1.71306100
H	-3.09307900	4.36983800	-1.12999600
H	-1.51747200	4.27503900	-1.92913400
C	-2.53175400	2.73810800	1.02317200
H	-2.12503700	2.60429500	2.02852500
H	-3.47953500	3.27678400	1.10533500
H	-2.74390000	1.74927900	0.61000200

TS $_{II\text{-}I}$-Mg$^{i}{}_{Pr_2}$: E(B3PW91) = - 1287.1978334
Gas-phase zero-point energy = -1286.656942
Gas-phase free energy = -1286.722519

N	1.58249300	-1.67706000	-0.05580700

N	-1.40222600	-1.83549300	-0.06626200
C	2.65510300	-3.88449900	-0.01750500
C	1.43050900	-3.00039000	-0.04168200
C	0.18895900	-3.65809200	-0.05056200
C	-1.11560900	-3.13458400	-0.04508000
C	-2.24205700	-4.14026900	-0.01299700
H	3.21735700	-3.74302500	0.90979500
H	2.38214000	-4.93573700	-0.10048100
H	3.33360100	-3.62865400	-0.83585900
H	0.24586200	-4.73843500	-0.04819500
H	-2.92163700	-3.98851600	-0.85612100
H	-1.86036900	-5.16000900	-0.04704700
H	-2.84058700	-4.02072300	0.89457900
C	0.86508900	3.68745600	0.18940600
H	0.44625700	4.54003000	0.73479900
H	-0.16428500	0.76743000	1.48353500
Mg	0.01710600	-0.35074000	-0.13759500
H	-1.06241500	0.95450100	-1.14242600
H	-0.12864500	2.19499300	-2.33999900
H	0.96590300	1.12477400	-1.09532300
H	-0.18094700	1.49934400	1.03340000
N	-0.24487800	2.72550300	-0.02198200
B	-0.10747900	1.76094000	-1.21354000
C	1.48029000	4.23823600	-1.10147700
H	2.21405200	5.01424200	-0.85909300
H	1.99383200	3.45226300	-1.66114200
H	0.72512800	4.67473500	-1.75754800
C	1.95426000	3.08371000	1.07806500
H	2.75153900	3.81341800	1.25002500
H	1.55433100	2.78611100	2.05089500
H	2.41009000	2.20497700	0.61190200
C	-2.76193900	-1.41586700	-0.02514400
C	-3.45686000	-1.14293400	-1.20687600
C	-3.39693000	-1.18950400	1.19965500
C	-4.76405700	-0.67072700	-1.16249100
H	-2.95918300	-1.29830100	-2.15855700
C	-4.70451900	-0.71735000	1.23979100
H	-2.85223200	-1.38384200	2.11812200
C	-5.39410300	-0.45770900	0.05960900
H	-5.28992300	-0.46295500	-2.08884900
H	-5.18389300	-0.54751200	2.19861300
H	-6.41256300	-0.08576600	0.09188700
C	2.89452700	-1.12604300	-0.00352500
C	3.53589600	-0.71634700	-1.17588300
C	3.53065400	-0.91442000	1.22359200
C	4.79384900	-0.12559200	-1.12199600
H	3.03649800	-0.86337200	-2.12797300
C	4.78891700	-0.32427600	1.27312300

H	3.02592900	-1.21285400	2.13702200
C	5.42673200	0.07052400	0.10129500
H	5.27846600	0.18650600	-2.04147500
H	5.26974300	-0.16724200	2.23337900
H	6.40656600	0.53404400	0.14184300
C	-1.60152600	3.28906600	0.14390100
H	-2.27534100	2.44551500	-0.04820600
C	-1.95642800	4.38762900	-0.86271900
H	-3.01053100	4.66668900	-0.76527600
H	-1.36077600	5.29087000	-0.69462800
H	-1.78672400	4.04841200	-1.88707300
C	-1.87164200	3.75171200	1.57856800
H	-2.92804900	4.01209100	1.69348000
H	-1.63898000	2.96182500	2.29746000
H	-1.29051300	4.63931900	1.84731900

I-Mg^{i}$_{Pr2}$+III $_{iPr2}$: E(B3PW91) = - =-1603.9082509
Gas-phase zero-point energy = - 1603.163924
Gas-phase free energy = - 1603.247647

N	1.18980900	-1.25820300	-1.28908700
N	0.74239400	1.71653200	-1.17965800
C	-0.28768600	-2.35599800	-2.92308900
C	0.25736400	-1.12369600	-2.23749500
C	-0.28512500	0.09672400	-2.65925600
C	-0.10049800	1.39780300	-2.15659700
C	-0.94842800	2.47334400	-2.79701100
H	-0.76516600	-3.02247900	-2.19942400
H	-1.01963600	-2.08647700	-3.68331500
H	0.51351700	-2.93174500	-3.39393300
H	-0.99961000	0.02090500	-3.46769600
H	-0.33237300	3.31880400	-3.11352900
H	-1.48560900	2.08287700	-3.66065800
H	-1.67766600	2.86890800	-2.08450300
B	4.08112900	1.31721200	0.19159300
N	3.60820200	0.16162800	1.16929600
C	3.14581400	0.67296500	2.49561100
H	3.18538300	-0.17255000	3.18784200
H	4.01495000	0.85272800	-0.97320700
H	5.18157400	1.78636000	0.34887000
H	3.21895600	2.18460500	0.25183500
H	-4.98785000	0.34250500	3.09759600
H	-4.90625400	1.87767200	1.69532200
N	-5.76510300	-0.07328000	1.03439600
B	-5.19210000	0.75344200	1.99281100
C	-6.14611600	-1.47421300	1.32376000
H	-6.56405100	-1.88549900	0.39948000
C	-4.92934700	-2.32149600	1.69327000

H	-5.21888100	-3.36717500	1.83609100
H	-4.17085700	-2.27934100	0.90770600
H	-4.47865600	-1.96258400	2.62215500
C	-7.23440600	-1.55140100	2.39356400
H	-8.11242700	-0.96950200	2.10270500
H	-7.54633600	-2.58879300	2.54913500
H	-6.86711600	-1.15961700	3.34562700
C	4.02745100	1.77692800	3.08443600
H	3.94754600	2.70031000	2.50677200
H	3.72305400	1.98794100	4.11463200
H	5.07987800	1.48266600	3.10024800
C	1.68531900	1.11105600	2.43699700
H	1.54465200	1.97140500	1.77487500
H	1.04024100	0.28564900	2.10765600
H	1.32873300	1.41621000	3.42525300
Mg	2.13417600	0.36302900	-0.40408800
C	1.56007400	-2.58492100	-0.92427800
C	0.89153300	-3.24346600	0.11195800
C	2.60744400	-3.24315900	-1.57439800
C	1.25435800	-4.53472300	0.47958000
H	0.08228300	-2.73189500	0.62335800
C	2.96958100	-4.53411200	-1.20336500
H	3.13047400	-2.73500200	-2.37841600
C	2.29382300	-5.18642600	-0.17713800
H	0.72399700	-5.03167100	1.28563100
H	3.78517000	-5.03056000	-1.71926600
H	2.57806300	-6.19247100	0.11191400
C	0.74777900	3.06915100	-0.72702900
C	-0.17481500	3.49842800	0.23095400
C	1.70195300	3.97363700	-1.19939900
C	-0.15115200	4.80926700	0.69648100
H	-0.90960900	2.79411200	0.60835100
C	1.72184800	5.28304500	-0.73283200
H	2.43177500	3.63700000	-1.92767500
C	0.79605900	5.70724200	0.21546900
H	-0.87498800	5.12665800	1.44033200
H	2.47114700	5.97263900	-1.10792700
H	0.81670100	6.72830900	0.58121800
C	-6.02652300	0.41186500	-0.33301500
H	-5.67610900	1.44748400	-0.33128300
C	-5.21728800	-0.34862900	-1.38506800
H	-5.51490600	-1.39968900	-1.45275500
H	-5.37329800	0.09756900	-2.37159400
H	-4.14912000	-0.30840800	-1.15846100
C	-7.51912600	0.42998100	-0.66681700
H	-7.67850300	0.88247400	-1.64987700
H	-7.94676600	-0.57704300	-0.69863700
H	-8.07362000	1.01451700	0.07145900

C	4.62740600	-0.90642000	1.37394900
C	5.40323100	-1.24417200	0.10415000
H	6.13505800	-2.02493300	0.33123200
H	4.74032400	-1.63455400	-0.67395100
H	5.93535200	-0.38073100	-0.29436200
C	4.03125100	-2.19494400	1.94549600
H	3.37699100	-2.67425000	1.21403600
H	4.83344800	-2.89789600	2.19039900
H	3.45516700	-2.03687600	2.86008500
H	5.36196000	-0.51687300	2.09775400

IV-Mg^{i}$_{Pr_2}$: E(B3PW91) = - 1603.8835121
Gas-phase zero-point energy = - 1603.132702
Gas-phase free energy = - 1603.203271

H	-0.13030900	-1.00751100	-1.40060900
B	1.08683900	-0.84976900	-1.37794600
H	1.37521700	0.23208200	-0.89320700
N	1.80211600	-1.92734300	-0.43843200
C	3.29067600	-1.54451500	-0.46736000
H	3.24072600	-0.46331000	-0.32293900
H	1.45752600	-0.82833000	-2.51957400
N	-0.26062500	-1.30549000	1.37948700
B	1.28314200	-1.66123900	1.10233800
H	1.91568500	-0.69075100	1.45823300
H	1.56739000	-2.64913000	1.74121500
C	-0.34313200	-0.74645200	2.78386600
H	-1.40329800	-0.74909300	3.03712000
C	-0.28642700	3.48254800	0.41926900
C	-1.68658300	3.46617300	0.57140200
C	-2.61442000	2.50222000	0.14972400
C	0.38331100	4.82060000	0.63883100
H	0.81295400	5.19022400	-0.29685500
H	-0.32867600	5.55873300	1.00694800
H	1.20939800	4.73760200	1.34954300
C	-4.05254000	2.97298600	0.09347900
H	-4.10996100	4.04790600	0.26021400
H	-4.49380400	2.74522900	-0.88033500
H	-4.67315900	2.47694500	0.84420000
N	-2.29295700	1.26816400	-0.24507900
H	-2.11924500	4.40289000	0.89693800
N	0.43376900	2.42787000	0.06261900
C	0.38495500	-1.56171500	3.86053500
H	1.46581100	-1.41845800	3.80810100
H	0.04500400	-1.23550000	4.84949100
H	0.19230100	-2.63282600	3.77305200
C	0.07021100	0.71859800	2.88393600
H	1.10422000	0.87965000	2.57702000

H	-0.58597300	1.38368000	2.30950100
H	-0.02030900	1.04294500	3.92507500
C	4.17353600	-2.08352300	0.66543600
H	5.05976000	-1.44304000	0.71755000
H	3.67963100	-2.04624100	1.63413800
H	4.52346700	-3.10101400	0.48789200
C	3.99146300	-1.78518100	-1.80433900
H	4.95697900	-1.27141400	-1.77307200
H	4.19820000	-2.84339200	-1.98271400
H	3.42993300	-1.38549200	-2.64734400
Mg	-0.37756100	0.45051400	0.03832800
C	-3.31102600	0.44853300	-0.80131500
C	-4.34829500	-0.08421600	-0.02646500
C	-3.24461100	0.10239300	-2.15499200
C	-5.30078400	-0.92190800	-0.59538500
H	-4.39547400	0.15323300	1.03096000
C	-4.19468100	-0.74188800	-2.71975400
H	-2.43876000	0.50710600	-2.75864500
C	-5.22945700	-1.25542000	-1.94459200
H	-6.09702400	-1.32465600	0.02266900
H	-4.12491000	-0.99736600	-3.77224300
H	-5.97029400	-1.91349400	-2.38578500
C	1.80325800	2.64398900	-0.26556400
C	2.81208600	2.54046700	0.69558200
C	2.16339700	2.92165300	-1.58777900
C	4.14632500	2.72202900	0.34387500
H	2.54612700	2.32223400	1.72389800
C	3.49635000	3.10238800	-1.93663400
H	1.38326000	2.98352000	-2.33936400
C	4.49522600	3.00521300	-0.97223300
H	4.91554600	2.64101300	1.10547800
H	3.75575300	3.31586900	-2.96875600
H	5.53578400	3.14552100	-1.24506700
C	1.48898700	-3.36136800	-0.85415400
H	0.51400600	-3.54206700	-0.40679100
C	1.32099800	-3.58613500	-2.35804100
H	2.25210500	-3.45832200	-2.91143500
H	0.98340400	-4.61610900	-2.51151000
H	0.57649700	-2.92040200	-2.79452800
C	2.40701000	-4.43340800	-0.26822000
H	2.55106700	-4.30886700	0.80435200
H	1.93266500	-5.40615300	-0.43030800
H	3.38179100	-4.46724800	-0.75934800
C	-1.14806500	-2.53507000	1.26977200
H	-0.49207600	-3.39461400	1.47029700
C	-1.77701900	-2.72291800	-0.11331200
H	-2.23029000	-3.71798200	-0.16643600
H	-2.57278000	-1.99442900	-0.27991500

H	-1.07606700	-2.63664600	-0.93763700
C	-2.31046200	-2.63956200	2.26866300
H	-3.01934500	-1.81303500	2.15967100
H	-2.85797800	-3.55879900	2.04145500
H	-1.99948500	-2.70332000	3.31195600

TS $_{IV\text{-}II}$ **Mg**$^{i}{}_{Pr_2}$**:** E(B3PW91) = - 1603.8337374
Gas-phase zero-point energy = - 1603.088917
Gas-phase free energy = - 1603.163437

B	-1.10053900	-0.33743200	-0.25996000
H	-0.79038000	0.75246000	0.14600700
N	-2.55401900	-0.51577800	1.37778200
C	-2.68972200	0.82202600	1.99582000
H	-2.67629800	1.52522700	1.16346000
H	-0.43272700	-1.26146900	0.10055600
N	-2.33129400	-0.51519900	-1.17112900
B	-3.38638100	-0.77198200	0.09593600
H	-4.33991000	-0.03521300	-0.04679400
H	-3.69594900	-1.92880000	0.03111400
C	-2.59271600	0.72416400	-2.03481100
H	-1.70407600	0.78340300	-2.67366200
C	3.27132500	2.06384900	0.67796200
C	4.05980200	0.94657700	1.00230400
C	3.87517100	-0.41570400	0.70832100
C	3.82811900	3.41038200	1.07645100
H	3.18944500	3.89252400	1.82155900
H	4.83034700	3.31207600	1.49167500
H	3.86635400	4.08286300	0.21499500
C	4.99012600	-1.34463400	1.12765900
H	5.32034000	-1.95598500	0.28349000
H	5.84149000	-0.78482600	1.51280200
H	4.65204400	-2.03804300	1.90269800
N	2.81260200	-0.91083500	0.07672800
H	4.97954100	1.17674900	1.52318000
N	2.10627800	2.00057400	0.03527100
C	-3.82825100	0.61595500	-2.93030000
H	-4.73713400	0.48300400	-2.33817700
H	-3.92550900	1.55598900	-3.48032500
H	-3.76683600	-0.18076000	-3.67120800
C	-2.69449200	2.04093400	-1.27383300
H	-3.59372000	2.07494800	-0.65493900
H	-1.82109700	2.25744700	-0.66216900
H	-2.76929600	2.84412100	-2.01190000
C	-4.00946100	1.05920500	2.74097200
H	-4.09231500	2.11274300	3.02912100
H	-4.86400400	0.81345200	2.10639600
H	-4.07368600	0.46530000	3.65783600

C	-1.50440200	1.19523000	2.89454600
H	-1.55420800	2.25855800	3.14965000
H	-1.50131200	0.64380800	3.83959500
H	-0.55194000	1.00843300	2.39296300
H	0.02708600	-0.09220500	-1.77243400
Mg	1.22692900	0.23640400	-0.53134200
C	1.41784800	3.20342500	-0.29037000
C	0.62921300	3.86726100	0.65432600
C	1.46613700	3.69897400	-1.59668000
C	-0.07584400	5.01332800	0.30344000
H	0.56893000	3.47243800	1.66296900
C	0.75836600	4.84485700	-1.94392900
H	2.06893000	3.17877200	-2.33435100
C	-0.01249200	5.50887700	-0.99533200
H	-0.68250500	5.51781100	1.04863400
H	0.81051400	5.21882900	-2.96141000
H	-0.56515000	6.40171400	-1.26727500
C	2.75505100	-2.30351400	-0.21476300
C	2.36191900	-3.23239400	0.75304700
C	3.02358000	-2.75210400	-1.51129900
C	2.25727100	-4.58143100	0.43319500
H	2.13031300	-2.88665900	1.75509500
C	2.91749600	-4.10247100	-1.82732300
H	3.32034900	-2.03128800	-2.26662000
C	2.53630400	-5.02283600	-0.85661800
H	1.94816600	-5.28943900	1.19527800
H	3.13213400	-4.43458500	-2.83796600
H	2.45036300	-6.07528000	-1.10452900
C	-2.24289000	-1.70661300	-2.13495400
H	-1.87589600	-1.26409600	-3.06668200
C	-3.59497600	-2.38828900	-2.40777100
H	-3.58904700	-2.78465500	-3.42893900
H	-3.75012300	-3.22642300	-1.72655900
H	-4.45092300	-1.72726200	-2.30192200
C	-1.24773600	-2.79532700	-1.75610500
H	-1.31251600	-3.57619400	-2.52058100
H	-0.21874700	-2.44227100	-1.72642100
H	-1.50065100	-3.25511600	-0.79941300
C	-2.56030400	-1.59426500	2.40381200
H	-2.29207500	-1.11493700	3.35049200
C	-3.92403600	-2.26598600	2.63651600
H	-4.73201900	-1.53750100	2.71373500
H	-4.17391300	-2.95475500	1.82729500
H	-3.89401700	-2.83991700	3.56966400
C	-1.50481300	-2.66967300	2.16530000
H	-1.69989100	-3.21524000	1.23945400
H	-0.50130300	-2.24457400	2.10708500
H	-1.52425700	-3.39511100	2.98563900

II-Mg^{i}$_{Pr_2}$+ V-Mg^{i}$_{Pr_2}$: E(B3PW91) = 1603.8750055

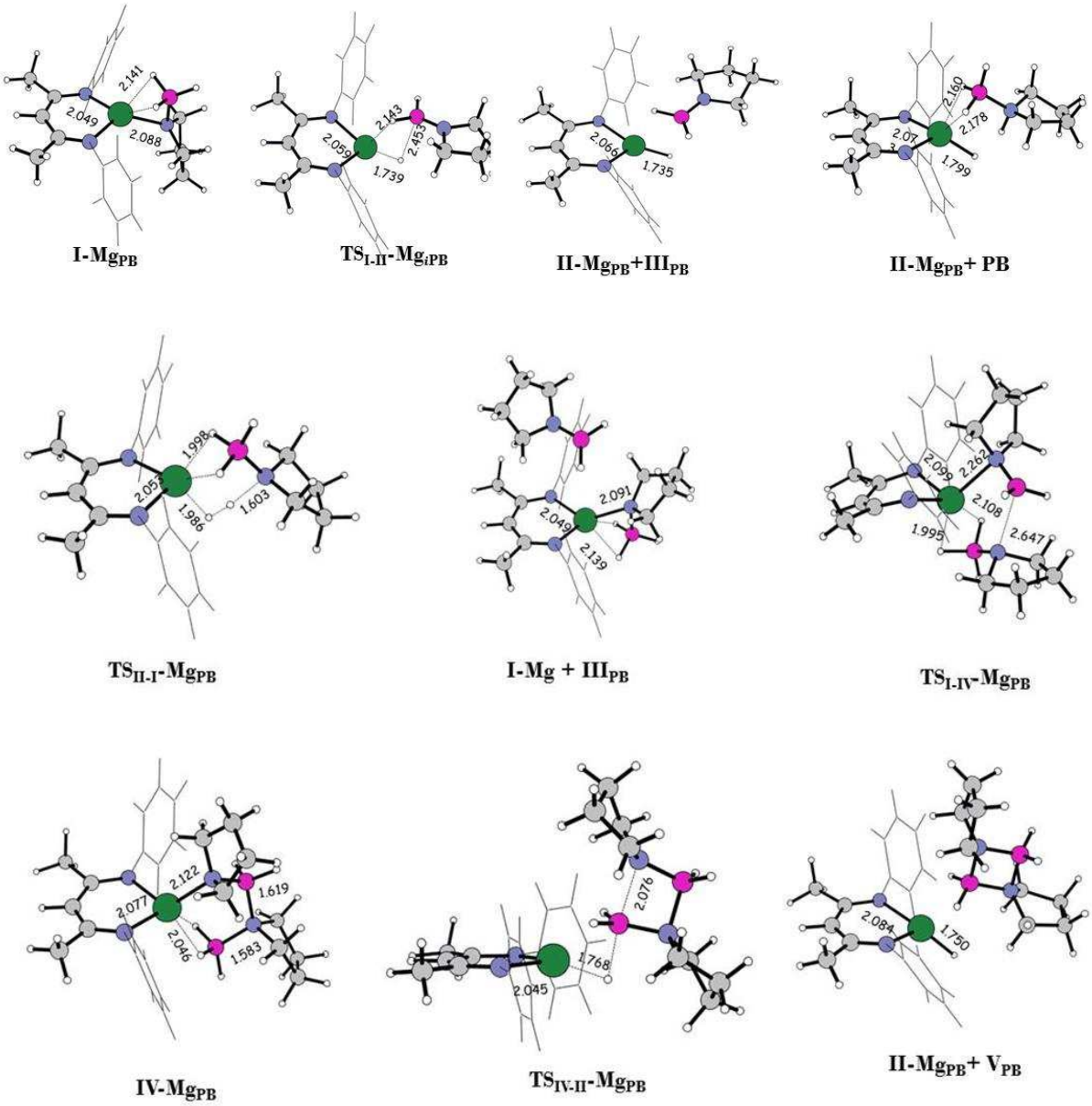
Gas-phase zero-point energy = - 1603.127798

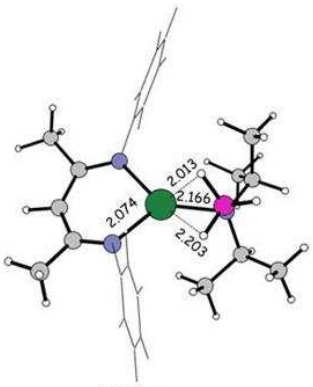
Gas-phase free energy = - 1603.200705

H	-0.31025900	0.46054400	-2.87254900
B	0.22066400	-1.30515700	0.00655100
H	1.11899200	-0.72913900	-0.56068400
N	-0.00367400	-2.79273100	-0.51550700
C	1.09521400	-3.28840800	-1.43987200
H	1.99309300	-3.11527000	-0.85025800
H	-0.80797200	-0.65707500	-0.01486300
N	0.59060300	-1.71637300	1.52230800
B	0.35292400	-3.22952900	1.01278500
H	1.35743300	-3.88495100	1.06500500
H	-0.56615300	-3.76980700	1.55840900
C	1.99173600	-1.35866000	1.97308300
H	2.00229000	-0.26728700	2.05327500
C	0.88509600	3.60202900	-0.02409800
C	-0.43024900	4.01913900	0.24457100
C	-1.65536400	3.33428100	0.14487600
C	1.94861100	4.65264200	0.22301500
H	2.77814400	4.55703500	-0.47934700
H	1.51489500	5.64844000	0.12562400
H	2.36378000	4.57277000	1.23203000
C	-2.87551000	4.11957000	0.57647400
H	-2.66442500	5.18894500	0.55645400
H	-3.72919900	3.91319200	-0.07233500
H	-3.17490500	3.85893800	1.59585100
N	-1.78263900	2.09750700	-0.32424100
H	-0.51423800	5.04187500	0.58949000
N	1.21011900	2.40089400	-0.49974700
C	1.28798100	-2.52337400	-2.75479000
H	0.98774700	-1.47560700	-2.68775900
H	2.35074400	-2.54948700	-3.01509000
H	0.74465200	-2.96988200	-3.58895900
C	1.01331900	-4.79348300	-1.67603300
H	0.91214900	-5.34565400	-0.73846800
H	0.18734500	-5.06630600	-2.33862600
H	1.93635400	-5.12303600	-2.16151700
C	2.34955600	-1.96267500	3.33192200
H	2.15926000	-3.03955200	3.33987200
H	3.41617000	-1.81288700	3.51788200
H	1.81100600	-1.50812000	4.16173900
C	3.09879900	-1.73049000	0.98922700
H	2.93976700	-1.32553200	-0.00842300
H	4.02976900	-1.29487000	1.36024100
H	3.23877500	-2.81197000	0.92988100

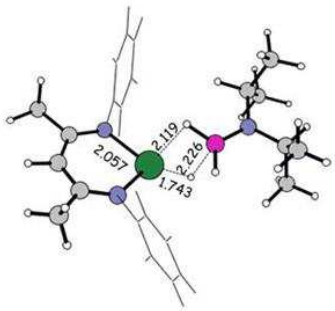
Mg	-0.21591900	1.06333700	-1.23957500
C	-3.04889300	1.46412500	-0.33956100
C	-3.72752300	1.13218200	0.84004100
C	-3.61111100	1.08221200	-1.56392500
C	-4.94900000	0.47022800	0.79345300
H	-3.28526900	1.39462300	1.79497600
C	-4.83226200	0.41786600	-1.60483100
H	-3.07909000	1.31618400	-2.48034500
C	-5.51065900	0.11322900	-0.42895100
H	-5.46215100	0.22730200	1.71875100
H	-5.25545800	0.13976800	-2.56477200
H	-6.46401900	-0.40308400	-0.46372300
C	2.56528200	2.03426200	-0.66915800
C	3.48083400	2.01852800	0.39202500
C	2.99816000	1.59207900	-1.92630600
C	4.79465500	1.61227400	0.19059400
H	3.15241300	2.32040900	1.38069600
C	4.31141600	1.17897800	-2.12045900
H	2.29259600	1.58448200	-2.75180500
C	5.21983900	1.19300900	-1.06651100
H	5.48919100	1.61725700	1.02511600
H	4.62599500	0.85058200	-3.10592400
H	6.24535500	0.87512000	-1.22089000
C	-1.39024800	-3.20236000	-0.97019200
H	-1.37510500	-4.29710200	-0.94650100
C	-2.51816600	-2.76003300	-0.04016700
H	-3.43258200	-3.26289800	-0.36657600
H	-2.34432000	-3.04437400	0.99625800
H	-2.70532100	-1.68589600	-0.09890400
C	-1.72968300	-2.73996900	-2.38768700
H	-1.18574400	-3.28844900	-3.15569800
H	-2.79565800	-2.90433600	-2.56572900
H	-1.52835000	-1.67277000	-2.52278900
C	-0.48352200	-1.22088100	2.47448100
H	-1.39330300	-1.31305700	1.88210800
C	-0.71776600	-2.05892200	3.73704900
H	-0.08426900	-1.76504200	4.57447900
H	-1.75478500	-1.91258500	4.05485900
H	-0.58098400	-3.12444300	3.55033400
C	-0.32846900	0.25705500	2.81948600
H	-1.23056500	0.59303500	3.33816700
H	0.51329400	0.44089200	3.49287100
H	-0.20730200	0.88080300	1.93016500

Optimized structures of minima and transition states for the dehydrocoupling reaction of pyrrolidine-borane and di-*iso*-propylamine-borane assisted by the I-Mg_{PB} and I-Mg^{i}_{Pr2} amidoborane complexes, respectively.

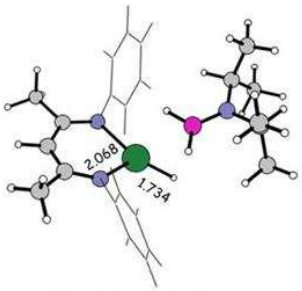




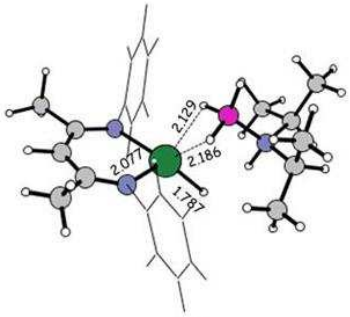
I-Mg $^{i}Pr_2$



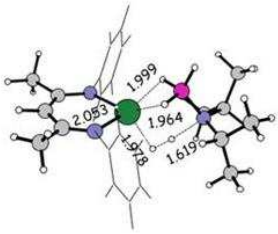
TS_{I-II}-Mg $^{i}Pr_2$



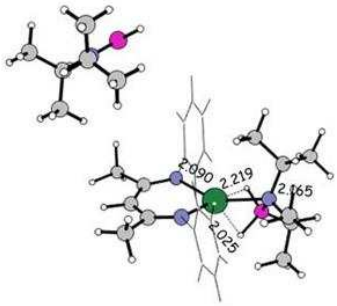
II-Mg $^{i}Pr_2$ +III $^{i}Pr_2$



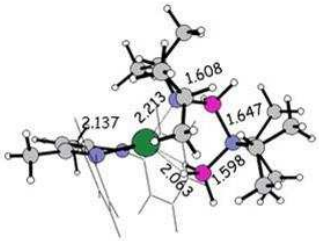
II-Mg $^{i}Pr_2$ + $^{i}Pr_2$



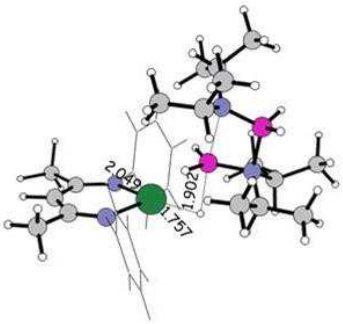
TS_{II-I}-Mg $^{i}Pr_2$



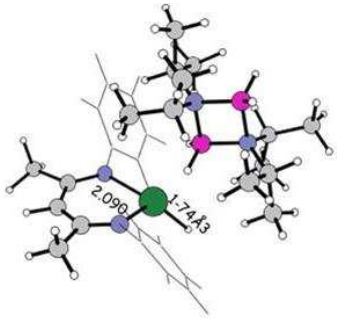
I-Mg + III $^{i}Pr_2$



IV-Mg$^{i}Pr_2$



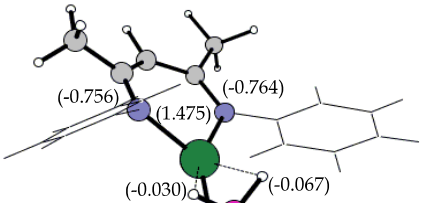
TS_{IV-II}-Mg$^{i}Pr_2$

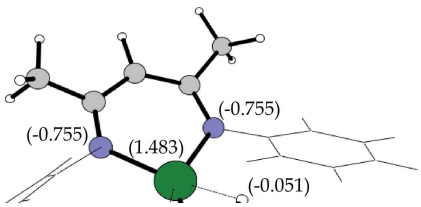


II-Mg$^{i}Pr_2$ + V$^{i}Pr_2$

S-5

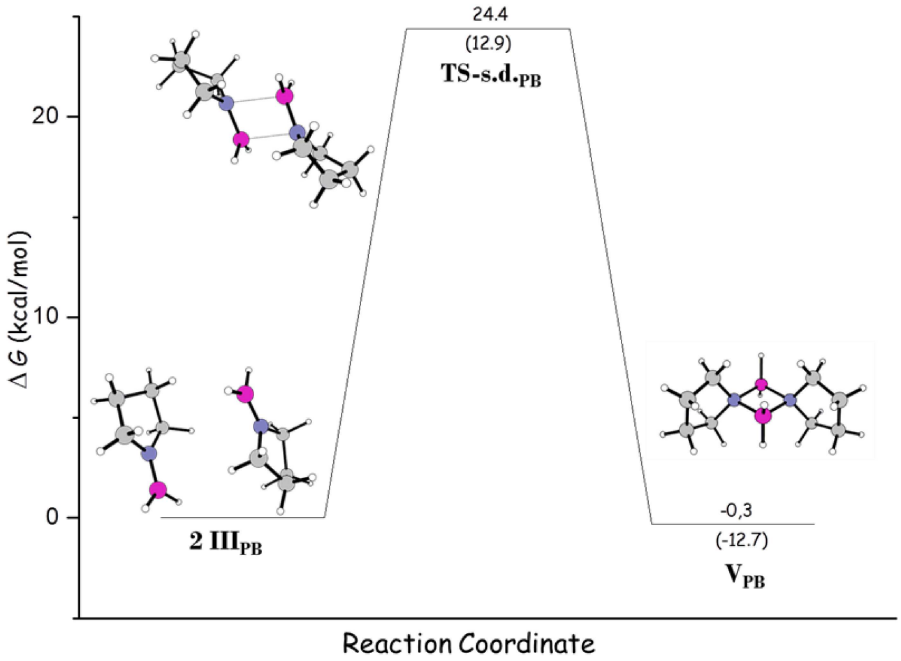
NBO population analysis of charge density distribution for I-Mg^{i}$_{Pr2}$ complex.





S-6

Calculated B3PW91 free energy profiles for the self-dimerization reaction of dehydrogenated PB and $^{i}Pr_2NH \bullet BH_3$ substrates.



TS-s.d.$_{PB}$: E(B3PW91) = -476.0717089
Gas-phase zero-point energy = -475.786929
Gas-phase free energy = - 475.826658

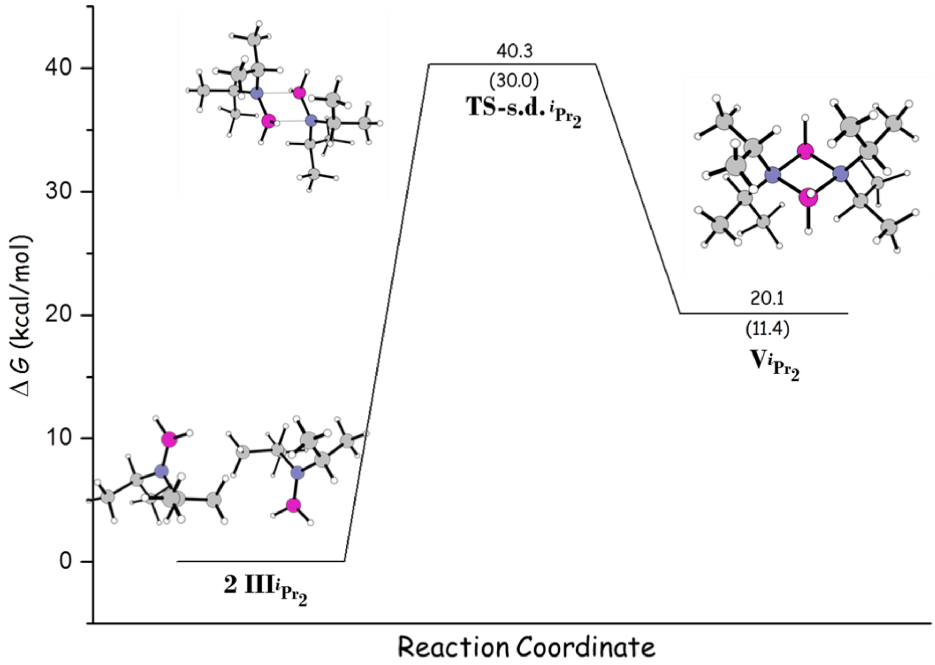
B	0.26261300	-0.26446400	-1.11988200
H	-0.11208500	0.68896500	-1.74255400
H	0.00753200	-1.37404900	-1.48788200
B	-0.26476600	-0.27194200	1.13005200

H	0.10972600	0.67779100	1.75855500
H	-0.00878100	-1.38350500	1.49135900
C	2.35317400	-1.17973800	0.07120500
C	2.10935900	1.20203600	-0.14854000
C	3.73078000	-0.57080300	-0.16613200
H	2.14498600	-2.06179400	-0.53705300
H	2.24497700	-1.46573700	1.12608600
C	3.52821000	0.86568100	0.32223700
H	1.58913400	1.85695900	0.55715000
H	2.11780000	1.70062900	-1.12382400
H	4.52556300	-1.10007800	0.36516000
H	3.96959500	-0.58104800	-1.23522800
H	3.58115400	0.89497800	1.41559600
H	4.27128400	1.56676900	-0.06430700
C	-2.10995500	1.20007400	0.16544300
C	-2.35578700	-1.18188900	-0.06578400
C	-3.51687100	0.86935500	-0.34106000
H	-1.57447500	1.86652200	-0.51750000
H	-2.14210100	1.68318200	1.14825400
C	-3.73507000	-0.56587500	0.14338900
H	-2.16259200	-2.05951100	0.55383900
H	-2.23115700	-1.47819600	-1.11586800
H	-4.26704800	1.57309500	0.02648500
H	-3.54155600	0.89819400	-1.43547200
H	-3.99626800	-0.57403800	1.20728700
H	-4.52100800	-1.09238300	-0.40353700
N	-1.42045300	-0.10078900	0.28174400
N	1.41802900	-0.09746200	-0.27059300

V_{PB}: E(B3PW91) = -476.115963
Gas-phase zero-point energy = -475.827736
Gas-phase free energy = -475.864226

B	0.00006900	0.00203800	1.47010300
H	-0.00005100	1.01942800	2.12046500
H	-0.00001700	-1.01357000	2.12325100
B	0.00000600	-0.00080500	-0.73064800
H	0.00001900	1.01402800	-1.38571400
H	-0.00000300	-1.01730800	-1.38313300
C	-2.08737300	-1.15519200	0.35027000
C	-2.08744000	1.15621400	0.34738600
C	-3.15885200	-0.77525500	-0.67706700
H	-2.52017200	-1.27247300	1.35050500
H	-1.54015200	-2.06513300	0.10555200
C	-3.15886200	0.77367300	-0.67903100
H	-1.54027300	2.06558800	0.10044200
H	-2.52027000	1.27594500	1.34731700
H	-2.89181700	-1.15885000	-1.66442200
H	-4.13142400	-1.19748000	-0.41439200
H	-2.89176900	1.15477100	-1.66733700
H	-4.13145300	1.19655300	-0.41748400
C	2.08759400	1.15613900	0.34759200
C	2.08723400	-1.15531500	0.35010500

C	3.16029900	0.77324100	-0.67761800
H	2.51937500	1.27633900	1.34788600
H	1.54065000	2.06534000	0.09960500
C	3.15736300	-0.77568000	-0.67854200
H	1.53976700	-2.06538000	0.10644200
H	2.52111000	-1.27190500	1.34996200
H	2.89641700	1.15680100	-1.66581700
H	4.13314100	1.19360300	-0.41295200
H	2.88705900	-1.15674600	-1.66599900
H	4.12965000	-1.20047300	-0.41901400
N	1.16455400	0.00054300	0.37493900
N	-1.16454700	0.00057300	0.37491800



TS-s.d. ^{i}Pr2**:** E(B3PW91) = =-635.7044177
Gas-phase zero-point energy = -635.266378
Gas-phase free energy = -635.312224

B	-0.38294400	-0.12062300	1.09802100
H	-0.20108700	0.85826800	1.75806300
N	-1.43610600	-0.06850500	0.08183100
C	-2.11716800	1.24564400	-0.10221200
H	-1.29838600	1.96511500	-0.16378100
H	-0.09748500	-1.17517800	1.57143500
N	1.43613400	0.06845700	-0.08166700
B	0.38295900	0.12036100	-1.09786600
H	0.09745800	1.17479800	-1.57152400
H	0.20112100	-0.85870200	-1.75766700

C	2.20856500	1.27176500	0.32729400
H	2.46440200	1.13340500	1.38452600
C	-2.97716800	1.68742800	1.08815900
H	-2.42693900	1.57044000	2.02475800
H	-3.22722000	2.74794700	0.97862700
H	-3.91533900	1.13654600	1.17024100
C	-2.87389200	1.35910900	-1.42375800
H	-2.23911000	1.08063000	-2.26818800
H	-3.77733900	0.74378800	-1.45151300
H	-3.18642400	2.39715400	-1.56766700
C	3.51436400	1.44633600	-0.46016900
H	3.31210400	1.48394700	-1.53505000
H	3.99106200	2.38872400	-0.17395400
H	4.23531000	0.64996100	-0.27498900
C	1.42878900	2.58143600	0.23376000
H	0.47841800	2.53674300	0.76427100
H	2.02837200	3.37048700	0.69669400
H	1.24187800	2.87061100	-0.80255900
C	-2.20852700	-1.27171800	-0.32745400
H	-2.46394600	-1.13333900	-1.38478700
C	-1.42895100	-2.58147900	-0.23351600
H	-2.02828300	-3.37042400	-0.69695600
H	-0.47818500	-2.53685800	-0.76330800
H	-1.24282600	-2.87074800	0.80292600
C	-3.51467000	-1.44614800	0.45949200
H	-4.23557100	-0.64983600	0.27383400
H	-3.99120900	-2.38861000	0.17325800
H	-3.31288600	-1.48354700	1.53446700
C	2.11730600	-1.24562700	0.10236500
H	1.29855500	-1.96512700	0.16401400
C	2.97722300	-1.68748000	-1.08804300
H	3.91561900	-1.13695900	-1.16998500
H	3.22686700	-2.74811400	-0.97868600
H	2.42707400	-1.57012700	-2.02464600
C	2.87413300	-1.35897900	1.42385200
H	3.18681600	-2.39697900	1.56775900
H	3.77750600	-0.74353700	1.45153000
H	2.23937400	-1.08056200	2.26832000

V^{i}_{Pr2}: E(B3PW91) = =- 635.7373653
Gas-phase zero-point energy = - -635.295993
Gas-phase free energy = - -635.341715

B	0.11500800	0.11166300	1.08355900
H	0.25280200	-0.78609500	1.86664100
N	1.18273900	0.07358200	-0.11672800
C	2.00658000	-1.19728800	-0.15152100
H	1.24223300	-1.97148500	-0.18969700

H	0.09478500	1.17853400	1.63830000
N	-1.18293900	-0.07380900	0.11700100
B	-0.11514800	-0.11232300	-1.08322300
H	-0.09496200	-1.17953100	-1.63744000
H	-0.25300000	0.78516000	-1.86669000
C	-2.00697400	-1.32052400	0.34312700
H	-2.52150700	-1.16326000	1.29665900
C	2.85524100	-1.50846100	1.08620900
H	2.35858400	-1.19806800	2.00645900
H	2.99606800	-2.59273700	1.13890300
H	3.84971300	-1.06166000	1.05478300
C	2.82430400	-1.32654400	-1.43335400
H	2.21209000	-1.12741600	-2.31645600
H	3.69091500	-0.65908900	-1.44759500
H	3.20562900	-2.34865600	-1.51291900
C	-3.05069700	-1.55579300	-0.75168400
H	-2.58923400	-1.50423700	-1.74185400
H	-3.47419300	-2.55688500	-0.63453500
H	-3.87943000	-0.85121500	-0.71706900
C	-1.19604400	-2.60754200	0.49525100
H	-0.42225500	-2.53148600	1.25649700
H	-1.88433100	-3.40098200	0.80073000
H	-0.74488600	-2.91125300	-0.45206600
C	2.00645600	1.32040800	-0.34354600
H	2.52006600	1.16305700	-1.29756100
C	1.19542000	2.60745700	-0.49486100
H	1.88336000	3.40086000	-0.80120500
H	0.42080400	2.53144100	-1.25526100
H	0.74527400	2.91114500	0.45293800
C	3.05133800	1.55570400	0.75020200
H	3.88076500	0.85198500	0.71388400
H	3.47376300	2.55730300	0.63347700
H	2.59118300	1.50290100	1.74090300
C	-2.00641300	1.19733700	0.15180100
H	-1.24176800	1.97124400	0.18986100
C	-2.85512000	1.50886200	-1.08581400
H	-3.85016100	1.06333600	-1.05369100
H	-2.99465500	2.59328000	-1.13901100
H	-2.35930200	1.19729300	-2.00611500
C	-2.82391800	1.32709100	1.43374600
H	-3.20459800	2.34943900	1.51341600
H	-3.69096400	0.66020400	1.44803800
H	-2.21171900	1.12752000	2.31675600

Cartesian coordinates (Å) and absolute energies (Hartrees) of optimized structures for the dehydrocoupling reaction of DMAB assisted by the amidoborane I-Ca$_{DMAB}$, I-Ca$_{PB}$ and I-Ca^{i}$_{Pr2}$ complexs respectively complex.

I-Ca$_{DMAB}$+ DMAB: E(B3PW91) = =-1768.1622236

Gas-phase zero-point energy = - 1767.622370
Gas-phase free energy = - 1767.690266

Ca	-0.00061600	0.31639400	0.15751100
N	1.51691600	-1.41332300	-0.38336400
N	-1.51807300	-1.41276200	-0.38409000
C	2.44349400	-3.59435200	-1.02424400
C	1.27887000	-2.66947600	-0.74035200
C	-0.00084600	-3.23176400	-0.89848200
C	-1.28038200	-2.66907200	-0.74078600
C	-2.44534700	-3.59337200	-1.02516200
H	3.03056100	-3.77205900	-0.11862300
H	2.10127400	-4.55534600	-1.40688200
H	3.12353200	-3.14584100	-1.75406100
H	-0.00095300	-4.26878200	-1.20810300
H	-3.12444600	-3.14462300	-1.75573100
H	-2.10343300	-4.55470800	-1.40720700
H	-3.03333000	-3.77037800	-0.12001300
N	0.00033000	0.93175900	2.51510000
B	0.00054100	2.33622300	1.85176600
C	-2.85417400	-0.96415400	-0.24923700
C	-3.58112600	-1.18799500	0.92832400
C	-3.44616800	-0.19561100	-1.26056900
C	-4.86268000	-0.67151100	1.08097100
H	-3.12477000	-1.76936800	1.72311200
C	-4.72873600	0.31980900	-1.10287500
H	-2.88763800	-0.01464100	-2.17322600
C	-5.44399300	0.08423000	0.06676800
H	-5.40914900	-0.85808700	2.00022700
H	-5.17102600	0.90685500	-1.90180300
H	-6.44352000	0.48757800	0.18910500
C	2.85327800	-0.96526200	-0.24879900
C	3.58003900	-1.18857200	0.92894500
C	3.44575200	-0.19791900	-1.26075900
C	4.86193300	-0.67277300	1.08119700
H	3.12333600	-1.76904500	1.72418500
C	4.72864800	0.31678400	-1.10348500
H	2.88730600	-0.01727100	-2.17352900
C	5.44374900	0.08171200	0.06636800
H	5.40826000	-0.85894100	2.00061900
H	5.17132500	0.90288700	-1.90289300
H	6.44353900	0.48451700	0.18836400
H	0.00052300	3.28325000	2.61533900
H	1.00573500	2.39081300	1.11880700
H	-1.00469800	2.39092100	1.11880700
H	1.01575800	1.76787400	-1.53570400
H	0.00133800	3.53741900	-0.12824800
N	0.00164000	3.76758500	-1.12932000

B	0.00136600	2.35266600	-1.88585400
H	-1.01412800	1.76890700	-1.53722900
H	0.00237300	2.54625800	-3.07655100
C	1.19399400	0.69774400	3.32025300
H	2.09319600	0.85323700	2.71852700
H	1.24712000	1.38408200	4.18160900
H	1.21017500	-0.32953800	3.70517400
C	-1.19293300	0.69872000	3.32112600
H	-2.09243900	0.85515200	2.72008700
H	-1.20983300	-0.32861900	3.70589500
H	-1.24477800	1.38497100	4.18262800
C	-1.22145700	4.54722800	-1.41098800
H	-1.27390700	4.74250300	-2.48283800
H	-2.08798700	3.95909000	-1.11168300
H	-1.20838800	5.49103300	-0.86055200
C	1.22536900	4.54644900	-1.41036200
H	1.21316000	5.48971400	-0.85899400
H	2.09142700	3.95725800	-1.11175700
H	1.27787300	4.74272200	-2.48202500

TSI-Ca$_{DMAB}$: E(B3PW91) = =- 1768.1073346
Gas-phase zero-point energy = - 1767.576057
Gas-phase free energy = - 1767.644344

Ca	-0.00607500	0.47218800	-0.03344200
N	1.65988900	-1.15805300	-0.49608600
N	-1.33987900	-1.46891700	-0.10887100
C	2.71841500	-3.29020200	-1.16061100
C	1.52214100	-2.45857400	-0.74150200
C	0.30566300	-3.15749700	-0.67757900
C	-1.00257500	-2.71986400	-0.39675400
C	-2.07641300	-3.78494200	-0.45366600
H	3.30162800	-3.61981000	-0.29568100
H	2.39099300	-4.18137500	-1.69639200
H	3.39082600	-2.71824600	-1.80359000
H	0.38244100	-4.21074700	-0.91569600
H	-2.76788300	-3.59356900	-1.27944900
H	-1.64399400	-4.77581000	-0.58853000
H	-2.67549400	-3.78170700	0.46103100
N	0.77840100	1.13144900	2.52405300
B	-0.41912200	1.85693700	2.78403500
C	-2.71179100	-1.14847700	0.06326100
C	-3.27196700	-1.05210200	1.34186000
C	-3.51244200	-0.83610500	-1.04288200
C	-4.59891000	-0.67006300	1.50761300
H	-2.65741200	-1.28586200	2.20510600
C	-4.83903400	-0.45601200	-0.87308400
H	-3.07882800	-0.89505700	-2.03646800

C	-5.38917000	-0.37225800	0.40236900
H	-5.01545900	-0.60268100	2.50756300
H	-5.44434400	-0.22077600	-1.74283300
H	-6.42303700	-0.07171300	0.53389400
C	2.93797500	-0.55982400	-0.50122400
C	3.93880800	-0.91288000	0.41956500
C	3.19216100	0.50885400	-1.37370300
C	5.14923600	-0.23197800	0.45202800
H	3.75348400	-1.72202100	1.11830000
C	4.40344200	1.19233200	-1.33153400
H	2.43611200	0.79021900	-2.10029400
C	5.38918600	0.82598700	-0.42161500
H	5.90825000	-0.52537900	1.17068300
H	4.57437100	2.01314400	-2.02035700
H	6.33352900	1.35857300	-0.39094800
H	-1.36150100	1.26250900	3.21468500
H	-0.39527100	3.04730400	2.72178200
H	-1.47557800	1.94217800	0.94023600
H	0.73764100	2.44327200	-0.99909900
H	-1.51207900	2.41599500	0.19172400
N	-1.39105700	3.20025800	-1.11743700
B	-0.20342300	2.48971400	-1.81499600
H	-0.55092900	1.32767600	-2.09335800
H	0.19141000	3.03134000	-2.82713400
C	0.95694300	-0.23944300	3.00729600
H	-0.01666900	-0.70160200	3.17081700
H	1.52013500	-0.84592000	2.28979200
H	1.50662400	-0.24562700	3.95686800
C	2.04714000	1.83507800	2.31675300
H	2.59753700	1.92658000	3.26158000
H	2.69155300	1.30088400	1.61109700
H	1.85103300	2.83540500	1.93165800
C	-2.64077500	3.13838900	-1.86074300
H	-2.89233200	2.09721300	-2.07403300
H	-3.45911300	3.57804500	-1.27834700
H	-2.57240500	3.67506600	-2.81947400
C	-1.07945100	4.56619100	-0.72163100
H	-1.90610700	5.00290100	-0.14882300
H	-0.18362900	4.57249900	-0.09523600
H	-0.88424300	5.20725200	-1.59434200

I-Ca$_{DMAB}$+II$_{DMAB}$+H$_2$: E(B3PW91) = =- 1768.1310904
Gas-phase zero-point energy = - 1767.603783
Gas-phase free energy = - 1767.681903

Ca	0.01854000	0.58149400	-0.72757300
N	1.53148200	-1.23345000	-0.54104600
N	-1.52405800	-1.18537400	-0.46311300

C	2.37570400	-3.47099500	-1.16784800
C	1.25472800	-2.48339300	-0.90700300
C	-0.04084800	-2.98999500	-1.10887300
C	-1.30854700	-2.44518100	-0.81990200
C	-2.47282400	-3.40440400	-0.95934000
H	2.63809700	-4.02711100	-0.26277000
H	2.06335300	-4.19893300	-1.91787500
H	3.27900200	-2.96766200	-1.51736800
H	-0.06752600	-4.00882300	-1.47571100
H	-3.35972800	-2.89739900	-1.34542300
H	-2.21300600	-4.22602500	-1.62749000
H	-2.74334300	-3.83770300	0.00830100
N	0.58454300	1.36033400	2.33611300
B	-0.32505800	2.31248000	1.88156500
C	-2.80057900	-0.77466600	-0.02239200
C	-3.33838700	-1.22262500	1.19348000
C	-3.51610200	0.18462400	-0.75196700
C	-4.55361100	-0.73318900	1.65547100
H	-2.78675000	-1.95451100	1.77516600
C	-4.73192100	0.67299700	-0.28321900
H	-3.11951800	0.52487600	-1.70433600
C	-5.25724700	0.21798800	0.92119900
H	-4.95184800	-1.09322300	2.59903800
H	-5.27223100	1.40973600	-0.86896100
H	-6.20428500	0.60061300	1.28585500
C	2.82883800	-0.87243100	-0.13581200
C	3.46756000	-1.47582500	0.96094500
C	3.47909500	0.20052300	-0.76538400
C	4.70798200	-1.02899900	1.39878500
H	2.97421600	-2.29484500	1.47421800
C	4.71765000	0.64898800	-0.31766700
H	3.01761200	0.65703500	-1.63697300
C	5.34061100	0.03851600	0.76598200
H	5.18158900	-1.51495100	2.24632900
H	5.20221500	1.47386700	-0.83028200
H	6.30802600	0.38631600	1.11141000
H	-1.43521200	1.94862000	1.60909100
H	0.02446800	3.44519600	1.75902000
H	-11.38951800	0.50452800	1.81036600
H	1.03345900	1.37568800	-2.69595500
H	-11.19252100	-0.00763100	1.30578900
N	0.00114800	2.92249400	-1.39811200
B	0.02693000	2.10643200	-2.73369100
H	-0.95978900	1.34826600	-2.71672800
H	0.02857200	2.76990200	-3.74653300
C	1.18057300	3.77075500	-1.25917800
H	1.17351300	4.29890800	-0.29834300
H	2.09075500	3.16670300	-1.31310900

H	1.23680500	4.52303900	-2.06266500
C	-1.20232300	3.74237300	-1.29006000
H	-1.24034000	4.26017700	-0.32474200
H	-1.24888700	4.49946300	-2.08948100
H	-2.09490300	3.11720300	-1.37752700
C	1.95328200	1.69887500	2.71642700
H	2.08342800	1.58998800	3.79973100
H	2.66970200	1.03713500	2.22054600
H	2.16597800	2.72978600	2.43757200
C	0.20766000	-0.00015900	2.70992600
H	0.85562100	-0.73525900	2.22269600
H	0.30094600	-0.12979600	3.79458300
H	-0.82770400	-0.18830000	2.42633100

I-Ca$_{PB}$ + PB: E(B3PW91) = =- =-1922.9856055

Gas-phase zero-point energy = 1922.372442

Gas-phase free energy = - 1922.446728

Ca	-0.05118500	-0.06944000	-0.13500500
N	0.91424000	-2.18193200	-0.57879100
N	-1.97146300	-1.27345600	-0.80930500
C	1.24792600	-4.44450000	-1.46583500
C	0.37722200	-3.24251800	-1.16798100
C	-0.97313300	-3.35402100	-1.54812200
C	-2.05863400	-2.48171500	-1.35267100
C	-3.40477400	-2.99640100	-1.81892500
H	1.67301600	-4.85139400	-0.54367700
H	0.68210500	-5.23099700	-1.96416400
H	2.09304000	-4.16384400	-2.10107400
H	-1.22697800	-4.28502100	-2.03833200
H	-3.93942400	-2.22943900	-2.38556200
H	-3.28940100	-3.88247000	-2.44304300
H	-4.03970400	-3.26080800	-0.96820300
B	0.48677700	1.91443600	1.52018000
C	-3.14596600	-0.53020200	-0.55262500
C	-3.97339600	-0.83312700	0.53863500
C	-3.45393800	0.59729400	-1.32604500
C	-5.07813100	-0.04479100	0.83405200
H	-3.72946600	-1.69075300	1.15753400
C	-4.56045500	1.38579400	-1.02425700
H	-2.82243700	0.83713400	-2.17579900
C	-5.37890500	1.06929500	0.05452400
H	-5.70519100	-0.29799800	1.68331300
H	-4.78447000	2.25056100	-1.64112100
H	-6.24026500	1.68561000	0.28876400
C	2.27896400	-2.20878300	-0.20234100
C	2.65844100	-2.63679900	1.07678200

C	3.27123700	-1.72030700	-1.06291200
C	3.98930000	-2.58962000	1.47656300
H	1.89321200	-3.00725800	1.75139400
C	4.60146700	-1.67573900	-0.65876800
H	2.98370900	-1.37804800	-2.05184900
C	4.96818000	-2.11039600	0.61113600
H	4.26192500	-2.92860200	2.47116100
H	5.35585200	-1.29914400	-1.34273800
H	6.00595800	-2.07317000	0.92481700
H	0.75623600	2.85135600	2.24579200
H	1.51168100	1.56979300	0.90170600
H	-0.35359500	2.27860500	0.67717100
H	1.51270300	0.83341500	-1.76632200
B	0.81161100	1.72966400	-2.21352100
H	-0.37066700	1.56178100	-1.94677600
H	0.97420800	1.85443400	-3.40260500
C	-1.33936400	0.84685200	2.92385400
C	0.79523200	0.05322400	3.21744400
C	-0.93261500	1.37489100	4.31491000
H	-1.87099600	-0.10858900	3.03218900
H	-1.99323900	1.52882200	2.37604500
C	0.49977000	0.83106000	4.51809700
H	1.84050300	0.11222200	2.90615700
H	0.54687900	-1.00814600	3.35893300
H	-0.93414500	2.46692500	4.32411600
H	-1.62509400	1.03872100	5.09136300
H	1.20963600	1.65131500	4.64345700
H	0.58412700	0.18735400	5.39790200
C	2.69215600	3.44578800	-1.65155500
C	0.51115800	4.29546200	-1.87674700
H	1.10308900	2.91562000	-0.47907700
C	2.77242900	4.87756300	-1.12802100
H	2.91443200	3.38200200	-2.71990300
H	3.31862600	2.72880100	-1.12075100
C	1.38874800	5.48787200	-1.45549100
H	-0.47201900	4.27083800	-1.40692700
H	0.37712200	4.24787800	-2.95924300
H	2.94083900	4.87020300	-0.04802200
H	3.59656800	5.42967900	-1.58321000
H	0.97279200	6.00071700	-0.58643900
H	1.44931000	6.21908200	-2.26405500
N	-0.08496900	0.62707700	2.18894400
N	1.26415900	3.07317500	-1.48203700

TSI-Ca$_{PB}$: E(B3PW91) = =- =- 1922.9325349

Gas-phase zero-point energy = 1922.327371

Gas-phase free energy = - 1922.400473

Ca	-0.07919700	0.17382200	-0.24295000
N	1.84595100	-0.97323600	-1.03027900
N	-0.91521400	-2.02543500	-0.34945900
C	3.20592400	-2.65937900	-2.21072400
C	1.93209700	-2.20469800	-1.52706300
C	0.89916100	-3.15565000	-1.49090300
C	-0.38875800	-3.09858900	-0.92557800
C	-1.20182300	-4.37219500	-1.00582600
H	3.96318600	-2.96403500	-1.48241100
H	3.00717100	-3.51213700	-2.85994900
H	3.64074800	-1.85389400	-2.80702400
H	1.14183300	-4.10060500	-1.95982300
H	-2.13832000	-4.20221200	-1.54450700
H	-0.64885500	-5.16542100	-1.50766500
H	-1.47700500	-4.71721700	-0.00497900
B	-0.53014700	1.32266800	2.66693900
C	-2.22593300	-2.09978500	0.18788000
C	-2.43045600	-2.43021300	1.53273800
C	-3.33698700	-1.75662800	-0.59245300
C	-3.70984900	-2.42777200	2.07714700
H	-1.57320000	-2.69361600	2.14412300
C	-4.61513700	-1.75618400	-0.04433100
H	-3.18383200	-1.49335400	-1.63452100
C	-4.80815800	-2.09187500	1.29202900
H	-3.84823600	-2.68781900	3.12184000
H	-5.46408300	-1.48975100	-0.66594200
H	-5.80520100	-2.08720500	1.71908300
C	2.98524500	-0.13997500	-1.00555900
C	4.09341300	-0.42183900	-0.19018500
C	2.98114300	1.06494600	-1.72304800
C	5.16007900	0.46438100	-0.10676500
H	4.10406200	-1.34301700	0.38364100
C	4.04910800	1.95258700	-1.62980500
H	2.13807900	1.29470000	-2.36703900
C	5.14357800	1.65874200	-0.82366400
H	6.00857000	0.22283500	0.52613400
H	4.02286400	2.87669800	-2.19808800
H	5.97588300	2.35084100	-0.75459700
H	-1.29916100	0.52078700	3.10549400
H	-0.74943400	2.49472000	2.68725000
H	-1.77682600	1.28033500	0.87127400
H	0.14562000	2.27946100	-1.14598000
B	-0.84314900	2.16815900	-1.89853200
H	-0.98352600	0.96650900	-2.19397800
H	-0.61990300	2.79669300	-2.91419900
C	1.33132500	-0.41813600	2.67065400
C	1.90294300	1.78337100	2.10100700
C	2.49047900	-0.04275900	3.61420500

H	1.71966600	-0.95892600	1.79775700
H	0.56416200	-1.03435000	3.13963900
C	2.81790500	1.43406600	3.28297200
H	1.56060400	2.81794400	2.09464800
H	2.42213800	1.58543300	1.15556900
H	2.18220100	-0.14541600	4.65709400
H	3.34873100	-0.70035400	3.46182100
H	2.58491500	2.07614400	4.13610300
H	3.86966600	1.58426000	3.03292600
C	-2.05305200	4.02181700	-0.63711100
C	-3.39165800	2.41809400	-1.73498400
H	-1.96229100	1.76228800	0.16333700
C	-3.52277200	4.48734000	-0.54740500
H	-1.47900500	4.65372600	-1.32760700
H	-1.54172300	4.05747600	0.33313400
C	-4.34398600	3.22764400	-0.86097100
H	-3.62656700	1.34941400	-1.76187000
H	-3.40305200	2.78633800	-2.77419000
H	-3.76783800	4.91355500	0.42824100
H	-3.71730500	5.26065900	-1.29616500
H	-4.56166100	2.67182600	0.05647500
H	-5.29444500	3.44932500	-1.35287100
N	0.75409600	0.87395100	2.25646900
N	-2.08643300	2.63085200	-1.11369700

I-Ca$_{PB}$ + *II*$_{PB}$+H2: E(B3PW91) = =- 1922.9597363
Gas-phase zero-point energy = 1922.359051
Gas-phase free energy = - 1922.443356

Ca	0.08765700	-0.65263200	1.00189100
N	-1.41547200	-2.12741100	-0.06723100
N	1.59582400	-1.84992000	-0.36561500
C	-2.22389300	-4.28233300	-0.95243900
C	-1.11840500	-3.30728600	-0.59950300
C	0.18857300	-3.75760500	-0.86421100
C	1.41887200	-3.07376400	-0.85018500
C	2.59258200	-3.83920700	-1.42777400
H	-2.62182200	-4.08400000	-1.95225800
H	-1.84410900	-5.30470200	-0.94685300
H	-3.05758200	-4.20839900	-0.25097400
H	0.24671000	-4.77731900	-1.22480200
H	3.51644800	-3.61240200	-0.89131600
H	2.40733500	-4.91286300	-1.37888300
H	2.75535400	-3.57963600	-2.47819100
B	-0.32463100	1.63954400	-0.80122300
C	2.80720000	-1.16116600	-0.57550900
C	3.21578600	-0.75803700	-1.85654200
C	3.57989400	-0.75778200	0.52314900

C	4.36393800	0.00348200	-2.02954100
H	2.60985200	-1.03744200	-2.71242200
C	4.72718600	0.00963100	0.34408500
H	3.28330600	-1.07332000	1.51935200
C	5.12753500	0.39283400	-0.93119000
H	4.66238600	0.30144500	-3.03011800
H	5.31328100	0.30150000	1.20978300
H	6.02284800	0.98938400	-1.06939800
C	-2.74725500	-1.66927200	-0.02896300
C	-3.46005300	-1.37096400	-1.20096600
C	-3.35304500	-1.38729500	1.20398100
C	-4.73674200	-0.82834700	-1.13757700
H	-2.99082200	-1.55596800	-2.16186800
C	-4.63103200	-0.83874100	1.26130900
H	-2.81907400	-1.62625900	2.11922800
C	-5.33126400	-0.55844100	0.09324100
H	-5.27107000	-0.60920800	-2.05712700
H	-5.08199100	-0.63872500	2.22811800
H	-6.32840600	-0.13402500	0.13926200
H	0.79490800	1.26493300	-0.57599100
H	-1.28311600	1.07613600	-0.34547200
H	9.95463100	-0.82897700	3.55601300
H	-0.65168300	-1.12549300	3.19322000
H	10.39426100	-0.32838100	3.89042600
B	0.31539600	-0.40872900	3.50780000
H	1.32006500	-0.93429200	2.99582400
H	0.43173900	-0.36450100	4.71321900
C	1.20023700	1.93084200	3.03351000
C	-1.07511100	1.70876200	3.26027900
C	0.64326100	3.28144100	2.56085900
H	2.10751200	1.62584900	2.50309400
H	1.45203800	1.97786100	4.10658000
C	-0.88994200	3.13306500	2.71687500
H	-1.11764700	1.72491100	4.36251000
H	-1.99298000	1.22680600	2.90988400
H	1.04680800	4.11085000	3.14715600
H	0.90873400	3.46588200	1.51617000
H	-1.31718800	3.87936900	3.39141900
H	-1.38975800	3.24770900	1.75099600
C	-1.82421500	3.30928000	-1.97281800
C	0.56539700	3.49445300	-2.27668800
C	-1.52816100	4.23841700	-3.14724600
H	-2.21707300	3.88035300	-1.12375100
H	-2.54024000	2.52000300	-2.20708900
C	-0.12206000	4.74535300	-2.81990600
H	0.98805800	2.90059100	-3.09452100
H	1.36886600	3.71214700	-1.57095000
H	-1.51658000	3.67305100	-4.08516400

H	-2.26660700	5.03666200	-3.24509200
H	0.40033800	5.16781700	-3.68051100
H	-0.17248000	5.51764000	-2.04513800
N	0.11211200	0.97353700	2.81480400
N	-0.51359500	2.73088800	-1.61802300

I-Ca$^{i}{}_{Pr_2}$ + i_{Pr_2}: E(B3PW91) = =- 2082.6233625

Gas-phase zero-point energy = 2081.857628
Gas-phase free energy = - 2081.937253

Ca	-0.26184300	-0.18779800	-0.04142700
N	0.46917600	-2.25733200	-0.97418500
N	-2.15432200	-0.74319900	-1.35898100
C	0.50877400	-4.34598200	-2.26229300
C	-0.17837800	-3.08265900	-1.78716900
C	-1.48458800	-2.88398700	-2.27463200
C	-2.38785300	-1.82212700	-2.09812400
C	-3.69580100	-1.94709200	-2.85263600
H	0.85313800	-4.94385300	-1.41380200
H	-0.15788200	-4.95435700	-2.87255100
H	1.39694800	-4.10437600	-2.85342300
H	-1.84240000	-3.67221900	-2.92434800
H	-3.93682700	-1.01293700	-3.36708600
H	-3.64694800	-2.75099500	-3.58663100
H	-4.52713500	-2.15755700	-2.17366500
N	-0.55951600	-0.06726500	2.42546300
C	-0.11897100	-1.31768500	3.11407100
H	0.88028300	-1.50119500	2.70558700
B	0.68981800	0.84144600	2.14907000
C	-0.93973800	-2.56586700	2.76112800
H	-1.06640000	-2.66638500	1.67853900
H	-0.41186400	-3.45868100	3.11465200
H	-1.93156800	-2.57936500	3.21365700
C	0.07456600	-1.18237500	4.62853700
H	0.59552800	-2.06439300	5.01369500
H	0.68079500	-0.30447900	4.86451500
H	-0.87250100	-1.10333000	5.17005300
C	-3.15132000	0.24895200	-1.22699900
C	-4.29846200	0.04579100	-0.44532400
C	-2.95702300	1.51310700	-1.80164200
C	-5.22277400	1.06596800	-0.25935900
H	-4.44914800	-0.92149600	0.02280700
C	-3.88406100	2.53326000	-1.60890000
H	-2.07626900	1.67843300	-2.41412500
C	-5.02183400	2.31589400	-0.83940600
H	-6.10294000	0.88563800	0.34990100
H	-3.71615000	3.50172700	-2.06975900
H	-5.74315800	3.11194700	-0.68924900

C	1.81255500	-2.55428100	-0.63061600
C	2.11977700	-3.24208400	0.54947400
C	2.87004600	-2.09894000	-1.42954800
C	3.44179500	-3.47255900	0.91545100
H	1.30773300	-3.60165500	1.17217200
C	4.19030700	-2.33557600	-1.06257500
H	2.63946100	-1.55691300	-2.34077300
C	4.48420000	-3.02230100	0.11202800
H	3.65668800	-4.01006400	1.83378300
H	4.99442200	-1.98174700	-1.70077700
H	5.51467500	-3.20430600	0.39822600
H	1.17625200	1.40375000	3.11397200
H	1.54358700	0.14006000	1.59171700
H	0.36576100	1.70055600	1.31573700
H	1.61708700	0.59833700	-1.19944600
H	1.81360400	2.36697200	0.45184700
N	2.22696600	2.63671600	-0.44847800
B	1.36154500	1.75779100	-1.48504900
H	0.18158900	2.01666100	-1.29198700
C	3.66352700	2.17216500	-0.34946400
H	3.57852100	1.08304900	-0.37525300
C	4.50780800	2.61287300	-1.53505700
H	5.48325100	2.12382400	-1.47293200
H	4.04669100	2.32723600	-2.48198300
H	4.68428700	3.69240300	-1.53651500
C	4.27801900	2.56480700	0.98983700
H	3.66158400	2.21887800	1.82441900
H	5.25927400	2.09332400	1.08666600
H	4.42586300	3.64481400	1.08536600
H	1.67527600	1.96671400	-2.62663200
C	-1.65041100	0.66861500	3.11661200
H	-1.27985500	0.99117900	4.10354900
C	-2.04517600	1.94073600	2.36430200
H	-2.40802600	1.71560200	1.35397300
H	-2.86613300	2.43291700	2.89356100
H	-1.22142000	2.64911600	2.28998600
C	-2.91767500	-0.15965300	3.34714900
H	-3.70443100	0.48473200	3.75075200
H	-3.28250900	-0.58657900	2.40846700
H	-2.77107100	-0.97035900	4.06076400
C	2.05380600	4.14060400	-0.53514900
H	2.97565600	4.57490200	-0.13672700
C	1.85865300	4.64510000	-1.95878600
H	1.85065900	5.73884200	-1.94027600
H	2.65413300	4.32420400	-2.63106100
H	0.90894500	4.30185400	-2.37271700
C	0.90192800	4.57252500	0.36506300
H	1.06472600	4.27339500	1.40391800

H	0.80487600	5.66076800	0.33768100
H	-0.04290400	4.13936700	0.02763900

TSI-Ca ^{i}$_{Pr2}$: E(B3PW91) = =- 2082.5800391
Gas-phase zero-point energy = 2081.823654
Gas-phase free energy = - 2081.907209

Ca	-0.09561900	0.62043300	-0.60317200
N	-1.14562300	2.54577300	0.23926400
N	1.63581100	2.19537600	-0.89779200
C	-1.70270200	4.90304100	0.63336800
C	-0.76634000	3.81534500	0.15341300
C	0.46671800	4.24944300	-0.36487700
C	1.58486800	3.51935000	-0.80658600
C	2.78832000	4.34625800	-1.20905400
H	-1.85950000	4.83160100	1.71364000
H	-1.30757200	5.89303600	0.40780800
H	-2.68671000	4.80052000	0.16708100
H	0.59054700	5.32435600	-0.39312700
H	3.22525600	3.97191000	-2.13832200
H	2.51359800	5.39254000	-1.34245500
H	3.57203000	4.29734100	-0.44742500
N	1.40710000	-1.84774500	2.49295900
C	2.47666000	-2.81064800	2.16625900
H	2.84231300	-2.50215400	1.18320700
B	1.04926600	-0.85356200	1.59899900
C	1.94478700	-4.23836500	2.03597200
H	1.13281600	-4.28274600	1.30663500
H	2.74351800	-4.90558100	1.69976000
H	1.57366300	-4.62759500	2.98908700
C	3.65028200	-2.72355600	3.14262200
H	4.45481600	-3.38975800	2.81853700
H	4.04669500	-1.70610300	3.18333800
H	3.36665100	-3.02356500	4.15616800
C	2.85092000	1.55764300	-1.23888600
C	3.91406200	1.47244600	-0.32768000
C	2.97597100	0.89875600	-2.46915600
C	5.06787900	0.76817400	-0.64642100
H	3.81603500	1.95681000	0.63873300
C	4.13240700	0.18987000	-2.78165400
H	2.16047000	0.95808800	-3.18305600
C	5.18457900	0.12250400	-1.87534300
H	5.88004900	0.71786200	0.07235500
H	4.20892600	-0.30810200	-3.74298100
H	6.08570900	-0.42913400	-2.12106800
C	-2.38367200	2.22295300	0.84531700
C	-2.49041800	2.08016400	2.23570900
C	-3.50856700	1.94397200	0.05818700
C	-3.68962600	1.68755000	2.81905500
H	-1.61881500	2.28329100	2.85004900
C	-4.70623300	1.54996500	0.64675200
H	-3.43233700	2.04963400	-1.01938500

C	-4.80390300	1.42091400	2.02824500
H	-3.75306100	1.58731700	3.89815800
H	-5.56790100	1.34484300	0.01939700
H	-5.73816000	1.11230800	2.48487800
H	0.20331300	-0.04785800	1.88339600
H	1.66985500	-0.74233600	0.57426500
H	-1.11520200	-1.74034800	-0.90786000
H	-1.68327600	0.34193000	-2.27151300
H	-0.73864800	-1.48843300	-0.07533200
N	-1.64354100	-1.93144100	-2.22400200
B	-1.10349700	-0.59282800	-2.84610900
H	0.10588900	-0.47894300	-2.60827900
C	-3.13507000	-1.88948600	-2.12672700
H	-3.35249800	-0.82714200	-1.98749400
C	-3.85290200	-2.30792500	-3.41056100
H	-4.91860200	-2.07360900	-3.32755800
H	-3.45476600	-1.76939300	-4.27380400
H	-3.77005900	-3.38160300	-3.60368900
C	-3.71416000	-2.58905400	-0.88998700
H	-3.15077200	-2.32718000	0.00829100
H	-4.74601300	-2.25419700	-0.74351100
H	-3.73526900	-3.67646900	-0.97438000
H	-1.26825300	-0.48178600	-4.04252200
C	-1.07211300	-3.15165100	-2.85170100
H	-1.45036000	-3.21292400	-3.88335100
C	0.72788700	-2.02027500	3.79720900
H	1.19042400	-2.88860500	4.27610500
C	-0.75778600	-2.32858100	3.62312900
H	-1.21925000	-2.53187000	4.59424800
H	-1.28259800	-1.48493500	3.16779700
H	-0.90453500	-3.20088400	2.98239700
C	0.95654300	-0.81659900	4.71001300
H	2.02337800	-0.62373600	4.84633100
H	0.49950500	0.08238100	4.28785000
H	0.51048000	-0.99275300	5.69351600
C	-1.45305600	-4.44776500	-2.13011200
H	-1.18788200	-4.39993800	-1.06975500
H	-2.51539500	-4.67938000	-2.20679000
H	-0.90802000	-5.28446400	-2.57682200
C	0.45346600	-3.07279200	-2.94074600
H	0.78596900	-2.25547200	-3.57931000
H	0.90242900	-2.93902000	-1.95185400
H	0.83563300	-4.00810200	-3.35994600

I-Ca$^{i}{}_{Pr_2}$ + $^{i}Pr_2$ +H_2: E(B3PW91) = =- 2082.6233625

Gas-phase zero-point energy = 2080.684576
Gas-phase free energy = - 2080.774277

Ca	-2.47465100	0.48310500	0.23724100
N	-2.13541400	-1.28108600	1.74806700
N	-1.05671800	1.54993700	1.79822300
C	-1.72316500	-2.46644300	3.86228200

C	-1.65794600	-1.23206400	2.98826700
C	-1.08457900	-0.09339900	3.57967000
C	-0.74853900	1.15824600	3.02871400
C	0.01779900	2.09152400	3.94192500
H	-0.97896400	-3.20574600	3.55168900
H	-1.53420800	-2.21595300	4.90597000
H	-2.70046700	-2.94970500	3.78320600
H	-0.79584800	-0.22086700	4.61510000
H	-0.37412000	3.10984400	3.87940600
H	-0.03290700	1.75356400	4.97688600
H	1.07204100	2.14005000	3.65307600
N	6.95723200	-0.55329400	-0.91087000
C	7.96084800	-1.58730600	-1.23169300
H	7.54971300	-2.53516000	-0.85686500
B	6.61271600	0.50796100	-1.73911200
C	9.27473100	-1.31596600	-0.49445800
H	9.12184500	-1.21607100	0.58354200
H	9.98621900	-2.13108900	-0.65695800
H	9.72390100	-0.38815800	-0.86087700
C	8.20199400	-1.76611600	-2.72439000
H	8.83709800	-2.64274300	-2.88122800
H	7.26383600	-1.91932800	-3.26304300
H	8.70780400	-0.90278300	-3.16163700
C	-0.55439900	2.77834500	1.30469200
C	0.77692500	2.90002100	0.88259300
C	-1.41399600	3.86922300	1.12269400
C	1.23464600	4.08099700	0.31138800
H	1.44345700	2.05114500	0.99853000
C	-0.95143500	5.04924000	0.54806100
H	-2.44804600	3.78511300	1.44223100
C	0.37355200	5.16211600	0.14143300
H	2.26878100	4.15471400	-0.01012500
H	-1.63393300	5.88296700	0.41842600
H	0.73184000	6.08139100	-0.30907900
C	-2.56300800	-2.51572500	1.20590300
C	-1.63890000	-3.48065400	0.77848600
C	-3.92587800	-2.75708800	0.98811000
C	-2.06778000	-4.65503800	0.17272900
H	-0.57963800	-3.29235000	0.92382900
C	-4.35012300	-3.93366000	0.37763600
H	-4.65099000	-2.01889600	1.31749600
C	-3.42550900	-4.88883800	-0.03002900
H	-1.33652100	-5.38996000	-0.14897200
H	-5.41108700	-4.10295900	0.22418700
H	-3.75811300	-5.80496700	-0.50587700
H	5.77827100	1.28422800	-1.37565000
H	7.13249800	0.65217100	-2.80278400
H	-4.73317900	0.59708700	-0.17565700
N	-3.40880100	0.49608800	-2.00221000
B	-4.39651400	1.34035100	-1.12459100
H	-3.75069100	2.26984800	-0.60932800
C	-4.02002200	-0.74523300	-2.52927600

H	-4.63471500	-1.12336500	-1.70356300
C	-4.96341200	-0.53597600	-3.71884300
H	-5.48728300	-1.46776700	-3.95418800
H	-5.71064700	0.22614800	-3.48858200
H	-4.42035400	-0.23137200	-4.61968200
C	-2.97907700	-1.82312900	-2.84189600
H	-2.37424900	-2.06359600	-1.96170600
H	-3.47126500	-2.74714500	-3.15861700
H	-2.30345000	-1.52327600	-3.64975100
H	-5.39487400	1.78050200	-1.64331800
C	6.30966100	-0.75463300	0.40717400
H	6.87536800	-1.54910400	0.90733800
C	6.38506800	0.48151500	1.29925500
H	5.99181700	0.25121200	2.29413500
H	7.41809000	0.82143100	1.40814500
H	5.79890900	1.30505800	0.88574300
C	4.87356200	-1.24720800	0.23438900
H	4.84081900	-2.14970000	-0.38241900
H	4.42142900	-1.47883400	1.20373400
H	4.26618500	-0.48012900	-0.25428300
C	-2.60673500	1.24766900	-2.99942000
H	-2.35586800	0.54989900	-3.80621600
C	-3.31829100	2.44414200	-3.63814100
H	-3.53257200	3.21658500	-2.89559300
H	-2.68483100	2.88412000	-4.41576900
H	-4.26473100	2.15191700	-4.09488400
C	-1.27873100	1.69552900	-2.38225400
H	-0.69519900	0.83546400	-2.02708400
H	-0.65210700	2.21848000	-3.11051900
H	-1.43474100	2.40237100	-1.55720100

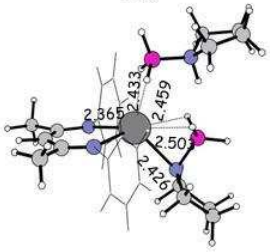
H_2: E(B3PW91) = -1.1785766
Gas-phase zero-point energy = 1.168519
Gas-phase free energy = 1.180013

H	0.00000000	0.00000000	0.49000000
H	0.00000000	0.00000000	-0.49000000

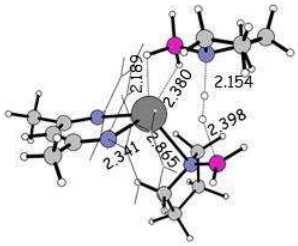
S-8

Optimized structures of minima and transition states for the dehydrocoupling reaction of pyrrolidine-borane and di-*iso*-propylamine-borane assisted by the I-Ca$_{PB}$ and I-Ca$^{i}_{Pr2}$ amidoborane complexes, respectively.

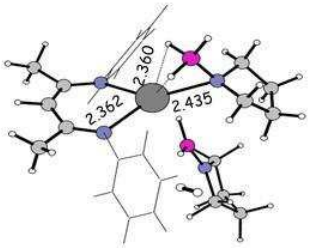
I-Ca$_{PB}$+PB



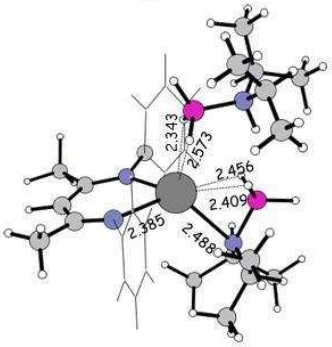
TSI-Ca$_{PB}$



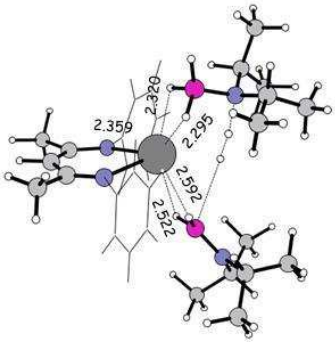
I-Ca$_{PB}$+II$_{PB}$+H$_2$



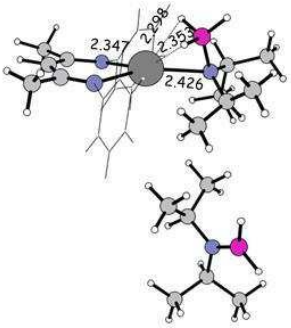
I-Ca ^{i}Pr$_2$+ ^{i}Pr$_2$



TSI-Ca ^{i}Pr$_2$



I-Ca ^{i}Pr$_2$ +II ^{i}Pr$_2$+H$_2$



Chapter 4

High temperature PEMFCs:
a preliminary investigation on P4VI systems

Thanks to the talent of Christian Friederich Schönbein and Sir William Robert Grove, a technology with significant potential for solving the energy needs of today and tomorrow, such as FCs, is now available. Basing on the same working principles, in the early 1960s Willard Thomas Grubb and Leonard Niedrach invented the first PEM fuel cell. Since then, a wide variety of materials has been studied for application in PEM fuel cells, all with some advantages and disadvantages. Among theme, a potential candidate is P4VI.

Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attention, particularly as promising candidates for a variety of power generation applications[1]. This is largely attributed to several advantageous features, such as high energy density (especially compared to that of battery systems) and high conversion efficiencies, up to 60%. In addition, PEMFCs are more environmentally friendly than alternatives, operating with hydrogen as a clean fuel, with essentially no discharge of pollutants. These benefits have created many opportunities for further development, aiming to improve the overall efficiency of PEMFCs.

4.1. Toward the development of advanced PEMFCs.

Development of PEMs for fuel cells has undergone a number of technological transformations since their inception. The currently well-developed PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion)[2,3] as electrolyte with pure hydrogen as fuel. In this system proton transport occurs through H_3O^+ ions that are formed by the dissociation of sulfonic acidic groups when solvated with water. Therefore, the transport properties in these materials largely depend on the water content. Thus, in order to be practical, such systems must operat at temperatures below the dew point of water[4-8]. However, working at higher temperatures has several advantages such as decreasing CO poisoning of the electrode catalysts[9-11] and increasing the kinetics of the electrode reaction catalytic activity[12]. In fact, Savinelli et al.[13] demonstrated that fuel cell operation at elevated temperatures can improve the tolerance of anode catalysts with respect to fuel impurities. A principal approaches for enabling operation of PEMs at higher temperature is the replacement of water with alternative proton solvents possessing higher boiling points. Most heterocyclic groups, such as imidazole and imidazole derivatives[14,15], have high boiling points which make them attractive for the development of more temperature-tolerant proton conductive membranes. In addition, unlike water, they can be incorporated into the polymer structure to further reduce their volatility during operation[16,17]. In these particular heterocycles their protonated and unprotonated nitrogen functions may act as donors and acceptors in proton transfer reactions while the ring itself is non-polar and avoids strong solvent effects[18-20]. Furthermore, pure heterocycles in the liquid state show higher conductivity. As mentioned above, Imidazole (Im) is one of the most simple and widely used heterocycles. Im is a solid material at standard condition with a boiling point of ~257 ◦C. Its proton conductivity at its melting point (90 ◦C) is approximately 10^{-3} S/cm. The pK_a for Im is reported to be approximately 14.9 while the pK_a for imidazolium is about 7[21]. The proposed mechanism for the proton conduction in Im-based systems involves proton transfer between the neighboring protonated and unprotonated guest molecules (the Grotthuss mechanism, figure 4.1.)[22,23].

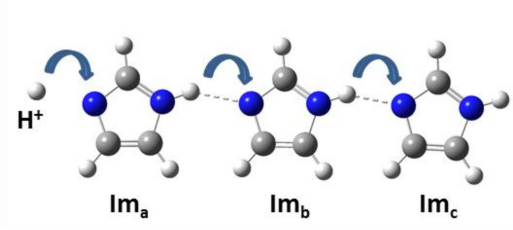


Figure 4.1. Grotthuss-type mechanism in liquid imidazoles.

This occurs as a result of aggregation of Im moieties in hydrogen-bonded chains. However, the potential use of liquid imidazole in fuel cells has a big limitation due to its leakage into the electrode areas, which leads to a permanent damage to the membrane and an increasing of poisoning risk of the Pt-electrode.[24] This leakage problem can be avoided by the immobilization of the imidazole groups to the membrane materials[16,17] using flexible spacers preventing the heterocycles from being dragged out of the membrane while a high local mobility is retained. Following this strategy, several N-heterocyclic polymers have been produced and, among these, poly(4-vinyl-imidazole), P4VI, is one of the first anhydrous studied proton conductors[25]. Moreover, as emerged from some experimental evidences, the adding of a strong acid, generally phosphoric or sulfuric acid,[26] can improve the proton conductivity of this membrane [27,28]. Notably, strong acids plasticize the material shifting the T_g to lower temperatures[29]. Reaching lower T_{gs} enhances the local mobility of the heterocycles and makes possible a major flexibility of the system, hence leading to higher conductivity.

Although pure P4V1 systems does not present conductivity level needed for fuel cells applications, a complete comprehension of the proton conduction mechanism can be useful in the development of a series of modified polymers showing better performance. Moreover, the understanding of the effective role that strong phosphoric acid molecules have in the conductivity mechanism represents the goal in order to improve the conductivity of P4VI to the levels requested by a PEMFCs applications.

4.2. Objectives

The understanding of the mechanistic aspects involved in the charge transport could be the key of the development of other membranes that show better performance. In this context, computational chemistry can play an important role in obtaining a better understanding of the structural and energetic aspects of the proton transfer reactions.

Following this line of reasoning, a detailed DFT analysis of the processes related to the proton conductivity in azole-based polymeric systems has been performed. In particular, density functional theory and classical molecular dynamics have been used first to investigate how the charge transport occurs considering a pure trimer P4VI system in which, for the first time, is explicitly considered the polymeric backbone.

The second part of our investigation has been focused on a H_3PO_4-doped P4VI model in order to shed light on the role that phosphoric acid has in the proton conductivity.

4.2.1. Pure P4VI: properties and proton transfer mechanism

The synthesis, thermal and conduction properties of blends of P4VI with phosphoric acid have recently been studied by Bozkurt and Meyer[25]. These studies stated also the existence of H-bridges between aryl N-H and aryl-N in the pure P4VI. Later Pu and co-workers[30] reported that pure polymer and blends are thermally stable up to about 150°C and their proton conductivity depends on the operative conditions such as temperature and pressure. However, an exact knowledge of the proton conduction mechanism is necessary to shed light on how the structure of the proton wire and of the polymer are related to the membrane performance.

4.2.3. H3PO4-doped P4VI: a DFT investigation of proton transfer mechanism.

As mentioned above, heterocycles such as imidazole has already been shown to exhibit proton conductivity that improves significantly when the system is doped with a strong acid, generally phosphoric or sulfuric acid[26-28]. Bozkurt and Meyer[25] have proposed that after the addition of H_3PO_4 to P4VI the protonation of the free nitrogen atoms of the imidazole rings occurs with the consequent formation of a polysalt as shown in figure 4.2.

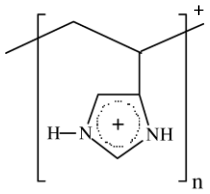


Figure 4.2. Schematic rapresentation of the 'polysalt formation'

What is emerged from experimental findings is that proton conduction mechanism deeply depends on the strong acid concentration[25] (see figure 4.3.). In particular, when a small amounts of acid (up to 15 mol % with respect to the imidazole units) is added, mobile excess protons are introduced into the system so that it serves as a proton source ("extrinsic charge carriers") rather than a proton solvent. At the same time, it acts as plasticizer shifting the T_g to lower temperatures.[29] This means a major flexibility of the system and an increased local mobility of the heterocycles with a consequent higher conductivity. On the contrary, when the polymer is swelled with a huge molar excess of strong acid, proton conductivity is related to the properties of bulk phosphoric acid. In this case, the conductivity of the blends is mainly based on proton transfer between acid moieties[31-33] as well as on their self diffusion (vehicular mechanism). However, although the conductivity increases over proportionally when the protonation of P4VI (formally) reaches saturation, it is worthy to note that a high quantity of phosphoric acid has also some disadvantages. It can be leached from the membrane so poisoning the electrodes and accelerating their corrosion.[34] From a technical point of view, therefore, the usage of a few amount of acid, which is supposed to be not able to alter the mechanism of conduction, is preferred[35].

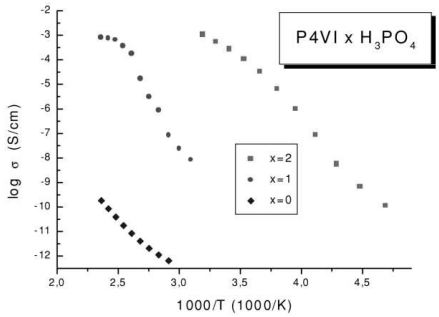


Figure 4.3. Temperature dependence of DC conductivities of P-4VI and the P-4VI–*x*H PO blends.

Although several studies have been performed in the last years, they are still far from giving insights into the mechanism of conduction of the H_3PO4-doped materials.

Based on these evidences, we have performed a DFT based study with the aim to investigate the role that phosphoric acid has in the proton conductivity mechanism. Such investigation has been performed taking into account the same azole-based polymer recently investigated, namely P4VI, for which an alternative to Grotthuss mechanism has been hypothesized for the pure form.

4.2.3.1. Computational Details

Following the same computational protocol that we have used in our previous work[36], geometry optimizations as well as frequency calculations for all the structures of minima and transitions states have been performed at the Density Functional level of theory by using the B3LYP functional[34] as implemented by GAUSSIAN09[35] code. Single point energy refinements with the BMK functional were also performed.[36] The standard 6-311G* basis sets of Pople and co-workers were employed for the atoms of the backbone. A bigger basis set is used to describe the atoms belonging to imidazoles. In particular diffuse functions on carbons and nitrogen and polarization functions also on hydrogen (leading to the 6-311+G(d,p) basis) were added. Relative energies are reported in kcal/mol.

4.2.3.2. Model selection

In order to investigate proton conductivity mechanism in acid-doped P4VI, a molecular model consisting of a trimer of P4VI with two molecules of phosphoric acid was used, as shown in figure 4.4.

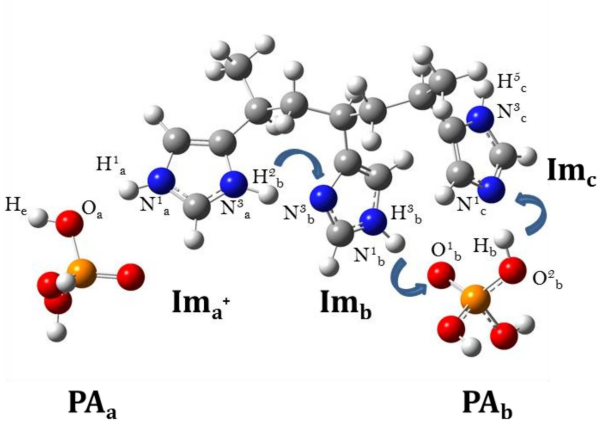


Figure 4.4. Optimized structure for the H_3PO_4-doped trimer P4VI model.

As the arrows in figure 4.4. indicate, a proton conduction mechanism from the left to the right side is hypothesized. As mentioned above, within trimer P4VI model selected, different proton transfers have to be taken into account. In particular, a N_3^a- N_3^b PT occurs from the Im_a to Im_b and a N_1^b- N_1^c from the Im_b to Im_c. In the following paragraphs a detailed description of all the PTs will be described focusing the attention on the role of phosphoric acid molecules.

4.2.3.3. Proton transfer mechanism

As already mentioned, in order to trigger the conduction an excess positive charge has to be added to the considered model. When an excess proton is added to the PA_a molecule, H^1_a is transferred to N^1_a with the consequent protonation of the P4VI trimer through the overcoming of a very low energy barrier of about 1.0 kcal/mol. This could be considered the first step of the proton transfer mechanism. After that, an energetically favored N^3_a-N^3_b PT occurs from the first Im_a to the second imidazole, Im_b. This second proton transfer requires 2.5 kcal/mol. Such a value is comparable to that calculated considering the protonated dimer in absence of phosphoric acid. As a consequence, the presence of phosphoric acid doesn't influence such a proton transfer. Finally, the transfer from the second imidazole to the third one, Im_c, occurs mediated by the presence of the phosphoric acid molecule (third and fourth transfer). In this case, a direct PT between the imidazole moieties, Im_b and Im_c, involves a N^1_b- N^1_c PT. As reported in our previous work, this type of PT is energetically disadvantaged (23.5 kcal/mol) because of long distance (3.733 Å) between the acceptor N^1_c respect to the H^3_b that has to be transferred, which prevents the retention of the hydrogen bond network. In this acid-doped model, the second dopant molecule PA_b establishes two hydrogen bond interactions with Im_b and Im_c and, at the same time, it behaves as donor and acceptor of a proton. In particular, in a concerted mechanism O^1_b accepts H^3_b while H_b is donating to N^1_c. A relaxed scan calculation confirms this behavior and the computed energy barrier for the considered concerted PT is of about 5 kcal/mol. Such a value is much lower than that obtained considering a N^1_b- N^1_c PT in absence of phosphoric acid molecule reported above.

Table 4.1. shows the distances between the considered hydrogen atoms and the corresponding acceptors (N_A) and the relative energy barrier computed.

Table 4.1. hydrogen-bond distance values (Å) between H and acceptor nitrogen atoms before each PT considered and relative energy barriers (kcal/mol) .

	$H...N_A$ (Å)	ΔE (kcal/mol)
$H^1{}_a...N^1{}_a$	1.531	1.0
$H^2{}_b...N^3$	2.032	2.5
$H^3{}_b...O^1{}_b$	1.831	
$H_b...N^3{}_c$	1.561	5

Therefore, the establishment of a hydrogen bond network between Im_b and Im_c through the intermediacy of PA_b molecule occurs. This means that in acid-doped systems a Grotthuss-type mechanism of conduction is possible and energetically favored.

4.2.3.4. Rate determining step

Once that the proton has reached the cathode following a Grotthuss-type mechanism, a cooperative rotation of all the imidazoles in the system is necessary in order to reestablishes the original conformation of the system, so that a new proton can be accepted and conducted in the same way it was just described. It is worthy noting that because of the presence of non-equivalent nitrogen atoms in the system (as a consequence of the casting in position 4 of the heterocycles), a cooperative rotation involving only the imidazole moieties would not be able to give a suitable conformation for a new proton shuttling along the chain. Indeed, since the involved nitrogen atoms would be those in position 1, an H-bond between Im_a and Im_b would not be possible in absence of an acid molecule between these heterocycles. In the considered molecular model, therefore, the flipping process must also involve one doping molecule, namely PA_b which, at the end of the process, must be located between Im_a and Im_b.

In order to calculate the energy barrier a relaxed scan has been performed varying the dihedral angle 1-2-3-4 of the second imidazole, see Fig 4.5., fixing the $H^3{}_b$-$O^1{}_b$ distance corrisponding to the interaction between Im_b and PA_b. During the relaxed scan performed, the phosphoric acid establishes hydrogen bond interactions with H that contribute to reduce the energy barrier that is of only 6.5 kcal/mol.[25]

When the rotation is completed, the trimer return to its original conformation and a new incoming proton can be accepted in order to assure transport in the right direction.

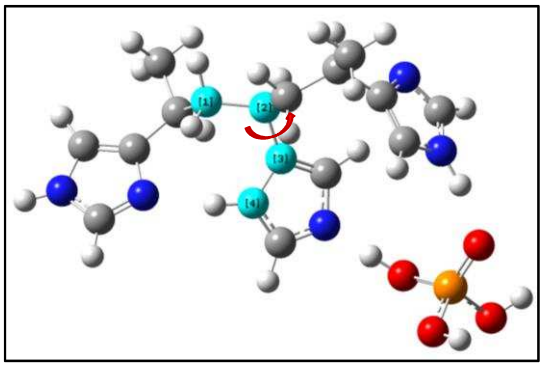


Figure 4.5. Dihedral angle corresponding to the rotation of the central imidazole around the C-C bond between Imb and the backbone keeping fix the interaction between Im_b and PA_b.

4.2.3.5. Conclusion

Although experimental findings concerning P4VI systems have shown proton conductivity values that are some order of magnitude lower with respect to fluorosulfonic acid membranes, it is worthy to note that in order to develop new materials with better performance a complete understanding of the mechanistic aspects involved in the proton conductivity mechanism of these azole-based membranes could be essential.

Following this line of reasoning, a theoretical DFT investigation has been performed considering, for the first time, a more realistic pure imidazole-based system in which polymeric matrix is included. Our investigation has shown that including polymeric matrix implies the distinction between nitrogen position of the heterocycles, properly N^1 and N^3, and because of polymeric constraints no H-bond is formed between the N^1—N^1. The loss of a hydrogen bond network means that Grotthuss-type mechanism couldn't occur and a new proton mechanism is hypothesized. In this alternative mechanism a frustrated rotation of the protonated imidazole before the proton transfer to the subsequent imidazole occurs, requiring the overcoming of about 10.5 kcal/mol. Therefore, through *n* frustrated rotations along the polymeric chain the proton can reach the cathode.

However, as experimental evidences shown, when P4VI is doped with a strong acid, such as phosphoric acid, proton conductivity improves. Density Functional Theory can be used to explain the role that phosphoric acid molecule has in the proton conduction mechanism. What our investigations have underlined is that when the phosphoric acid is added it participates actively to the proton transfer accepting and releasing protons. This leads to re-establishment of the network of hydrogen bonds making possible proton conductivity according to the known Grotthuss mechanism with an energy barrier value lower than that found in absence of acid.

Although a deeper investigation considering a bigger more realistic system is necessary in order to shed light on all the mechanistic aspects involved in the proton conductivity mechanism of pure and acid-doped P4VI, this preliminary study can be considered the starting point of a more detailed investigation, underlining that:

- polymeric matrix has to be included in the selected model
- phosphoric acid molecules actively participate in the proton conduction mechanism making possible a Grotthuss-type proton conduction mechanism.

Referents

1) M.F.H. Schuster, W.H. Meyer, *Annu. Rev. Mater. Res.*, **2003**, 33, 233.

2) G. W. Crabtree, M. S. Dresselhaus, *MRS Bull.*, **2008**, 33, 421.

3) F. Barbir, Fuel cells: Theory and Practice; Elsevier Academic Press: New York, **2005**.

4) A. J. Appleby, F. R. Foulkes, Fuel Cell Handbook, Van Nostrand Reinhold, New York, **1989**.

5) P. E G&G Services, Inc. and Science Applications International Corporation for the U.S. Department of Energy, Fuel Cell Handbook, 5th edn, **2000**.

6) J. S. Wainright, M. H. Litt, R. F. Savinell, High-Temperature Membranes, in Handbook of Fuel Cell, Fundamentals, Technology, and Applications, ed. W. Vielstich, A. Lamm and H. A. Gasteiger, John Wiley & Sons, vol. 3, **2003**, p. 436.

7) S.Ü. Celik et al., *Progress in Polymer Science,* **2012**, 37,1265.

8) Y. Zhai et al., *Journal of Power Sources*, **2007**, 169, 259.

9) Q. Li, R. He, J. O. Jensen, N. J. Bjerrum, *Fuel Cells*, **2004**, 4, 147.

10) C. Pan, R. He, Q. Li, J. O. Jensen, N. J. Bjerrum, H. A. Hjulmand, A. B. Jensen, *J. Power Sources*, **2005**, 145, 392.

11) Q. Li, R. He, J.-A. Gao, J. O. Jensen, N. J. Bjerrum, *J. Electrochem. Soc.*, **2003**, 150, A1608.

12) J. S.Wainright, M. H. Litt, R. F. Savinell, in Handbook of Fuel Cells: Fundamentals Technology and Applications, ed. W. Vielstich, A. Lamm and H. A. Gasteiger, Wiley, West Sussex, **2003**, vol. 3, pp. 436.

13) R. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt, C. Rogers, *J. Electrochem Soc*,**1994**,141, L46.

14) A. Kawada, A. R. McGhie, M. M. Labes, *J. Chem. Phys.*, **1970**, 52(6), 3121.

15) K. D. Kreuer, *Solid State Ionics*, **1997**, 97, 1.

16) a) M. F. H. Schuster, W. H. Meyer, M. Schuster, K. D. Kreuer, *Chem. Mater.* **2004**, 16, 329; b) A. Noda, M. Susan, H. A. Bin, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B,* **2003**, 107, 4024.

17) J. C. Persson, P. Jannasch, *Macromolecules,* **2005,** *38,* 3283.

18) P. Jannasch, Curr. Opin. Coll. Int. Sci., **2003**, 8, 96.

19) K. D. Kreuer, Proton conduction in fuel cells. editors. Hydrogen-transfer reactions. Weinheim: Wiley-VCH Verlag GmbH & Co.; **2007**. p. 709.

20) H. Steininger, M. Schuster, K. D. Kreuer, A. Kaltbeitzel, B. Bingöl, W. H. Meyer, S. Schauff, G. Brunklaus, J. Maier, H. W. Spiess, *Phys Chem Chem Phys*, **2007**, 9,1764.

21) W. Münch, K. D. Kreuer, W. Silvestri, J. Maier, G. Seifert, *Solid State Ionics*, **2001**,145, 437.

22) M. Casciola, S. Chieli, U. Costantino, A. Peraio, *Solid State Ionics*, **1991**, 46, 53.

23) K. D. Kreuer, *Solid State Ionics*, **1997**, 97, 1.

24) W.Q. Deng, V. Molinero, W. A. Goddard, J. *Am. Chem. Soc.*, *2004*, 126, 15644.

25) A. Bozkurt, W.H. Meyer , *Solid State Ionics,* **2001**, 138, 259.

26) H. Pu, W. H. Meyer, G. Wegner, *Macromolecular Chemistry and Physics* **2001,** *202,* 1478.

27) A. Bozkurt, W.H. Meyer, *Journal of Polymer Science: Part B: Polymer. Physics.*, **2001,** 39, 1987.

28) H. Steininger, M. Schuster, K.D. Kreuer, J. Maier, *Solid State Ionics*, **2006,** 177, 2457.

29) A. Bozkurt, Thesis, University of Mainz, Mainz, Germany, 1998.

30) H. Pu et al., *Journal of Membrane Science,* **2008,** *322, 392.*

31) M. E. Tuckerman, K. Laasonen, M. Sprike, M. Parrinello, *J. Chem. Phys.* **1995**, 103, 150.

32) N. Agmon, *Chem. Phys. Lett.,* **1995**, 244, 256.

33) K. D. Kreuer, *Solid State Ionics,* **2000**, 136, 149.

34) *Macromol. Chem. Phys.* **2001**, 202, 1478.

35) M. F. H. Schuster, W. H. Meyer, M. Schuster, K. D. Kreuer, *Chem. Mater.*, **2004,**16.

36) G. F. Mangiatordi, V. Butera, N. Russo, D. Laage, C. Adamo, *Physical Chemistry Chemical Physics,* **2012**, 14, 10910.

37) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

38) M. J. Frisch et al. *Gaussian G09, Revision A.01* Gaussian, Inc., Wallingford CT, **2009**.

39) A. D. Boese, J. M. L. Martin, *J. Chem. Phys.* **2004**, 121, 3405.