DOI: 10.1002/ejic.200600548

DFT Investigation of the Potential of [H-M{(NHCH$_2$CH$_2$)$_3$X}] Catalysts (M = Mo, Ru, Os; X = N, P) for the Reduction of N$_2$ to NH$_3$ by H$_2$

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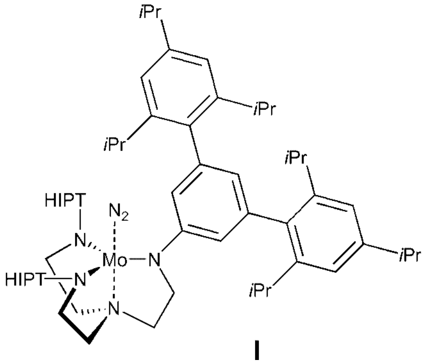
Keywords: DFT calculations / Nitrogen fixation / Nitrogen activation / Nitrogen reduction / Ammonia / Homogeneous catalysis

DFT calculations of model complexes [H-M{(NHCH$_2$CH$_2$)$_3$X}] (M = Mo, Ru, Os; X = N, P) were carried out to investigate the catalytic potential of these complexes towards the reduction of N$_2$ to NH$_3$ using only H$_2$ as the reducing agent. Closed catalytic cycles were calculated for all three metal hydrides. The calculations showed that [H-Mo{(NHCH$_2$CH$_2$)$_3$N}], **1**-Mo, is not an appropriate catalyst due to very high activation barriers for several steps of the reaction ($\Delta H^{\ddagger}_{\max}$ = 69.1 kcal/mol). Much lower activation barriers were found for the Ru and Os catalysts [H-Ru{(NHCH$_2$CH$_2$)$_3$N}], **1**-Ru, and [H-Os{(NHCH$_2$CH$_2$)$_3$P}], **1**-Os(P). With $\Delta H^{\ddagger}_{\max}/\Delta G^{\ddagger}_{\max}$ = 29.3/35.7 kcal/mol, **1**-Os(P) shows potential for future theoretical work. QM/MM calculations were used to investigate some properties of the Ru system empolying the hexaisopropylterphenyl ligand (HIPT). The results indicate that an HIPT substituent at the ligand core has a benefical influence on some reaction steps by lowering the activation barriers, while for other steps the activation energies increase.

Introduction

The reduction of dinitrogen (N$_2$) to ammonia (NH$_3$) has been of significant importance to chemical research for many years.[1] The conversion of the very inert N$_2$ molecule to NH$_3$ is currently put into practice by both natural and manmade processes, which have some important differences, such as the following: For the in vivo reaction of N$_2$ with the FeMoco-Cofactor of nitrogenase, protons and reducing agents are required. This process can be considered as a homogeneously catalyzed reaction. Conversely, the industrial reduction of N$_2$ to NH$_3$ (Haber–Bosch process) is a hetereogeneously catalyzed reaction in which N$_2$ is directly reduced by H$_2$. Any kind of synthetic, well-defined transition metal complex that catalyzes either of these reactions (H$^+$/reducing agent, or H$_2$ reduction) is of general interest, allowing for a greater understanding of the natural and technical processes, as they can provide important information about the individual reaction steps on the molecular level. Furthermore, routes to new processes might be identified in this way.

Especially important in this context is the seminal work published very recently by Schrock et al., who showed [N$_2$–Mo{(N(HIPT)CH$_2$CH$_2$)$_3$N}] (HIPT = hexaisopropylterphenyl) **I** to be an active catalyst for the reduction of N$_2$ to NH$_3$.[2] In the presence of **I**, protons, and a reducing agent, N$_2$ can be reduced in a stepwise protonation/reduction cycle to yield NH$_3$.



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These experimental results were recently rationalized by Tuczek and Studt using DFT calculations.[3] The reaction mechanism as postulated by Schrock et al. was supported by these calculations, and the energetic requirements for the reaction were related to the energetics of the reducing agent ATP which led to an experimentally, and theoretically, well-rounded picture of this synthetic N$_2$ reduction. Independently, Reiher et al. investigated, by means of DFT calculations, the geometries and electronic structures of complexes that participate in this type of nitrogen activation/transformation reaction and considered how the structures vary as a function of the ligand structure. The authors were able to prove the assumptions that were postulated by the Schrock

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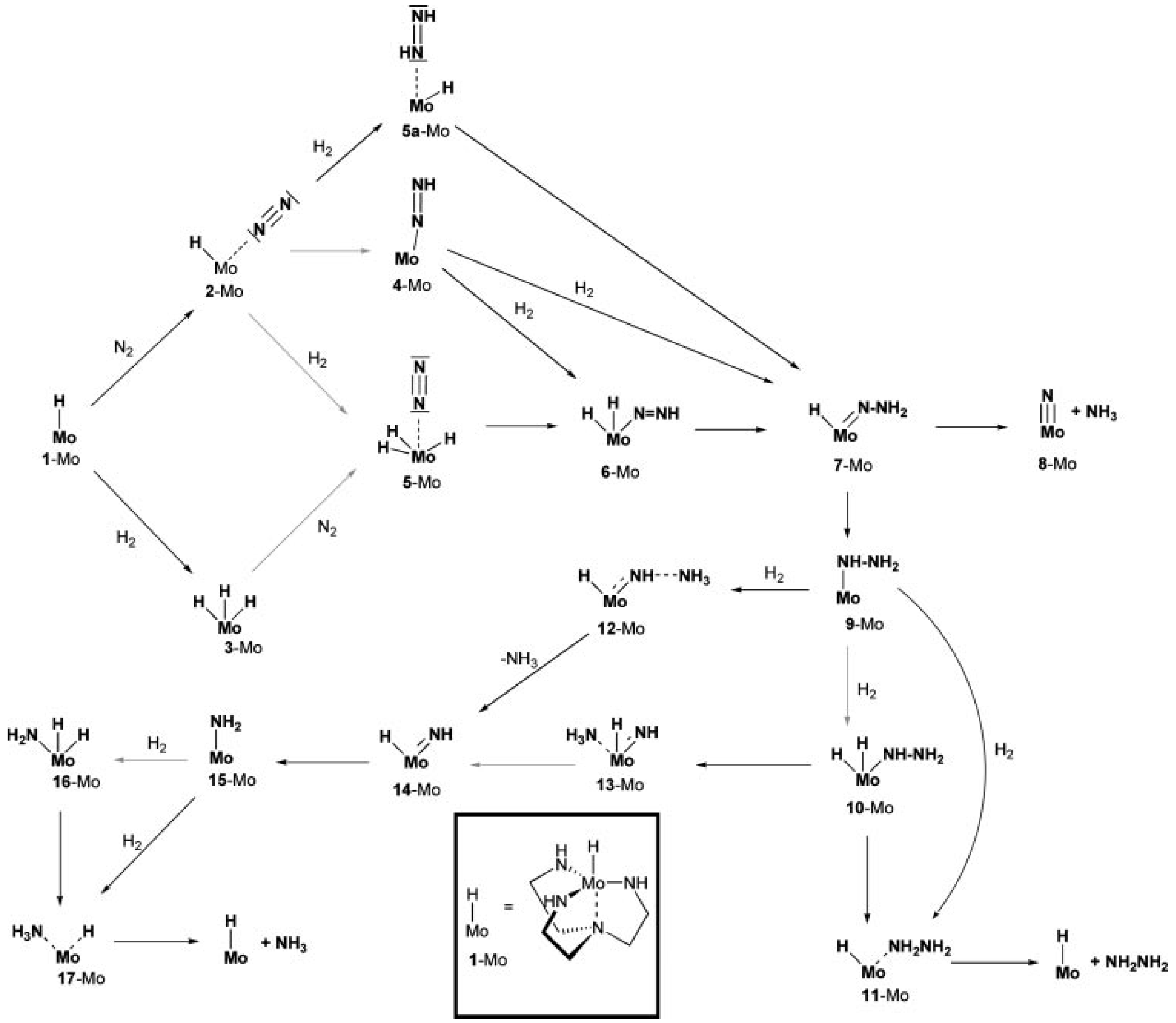
group with regards to some of the individual reaction steps.[4,5] Also, the work by Reiher et al. made it clear that the ligand structures (that is the HIPT substituent or other substituents at the trisamidoamine core of the ligand) can lead to significantly different energy profiles over multiple reaction steps. Furthermore, it was shown that the charge of the complex is crucial in enabling the catalyst to release NH_3 at the end of the reaction cycle, and for coordination to a new N_2 molecule. Cao et al. also reported DFT calculations using model complexes derived from **I**.[6] On the whole there is agreement between experimental and theoretical results that the reaction at the molybdenum center can take place because firstly, the HIPT substituent at the amido nitrogen centers of the ligand core efficiently shields the metal center and thus prevents the formation of nitrogen-bridged, unreactive complex dimers, and secondly, it leaves enough space to allow N_2 and H^+ to approach the metal center thus enabling the reaction to take place. For the release of NH_3 at the end of the catalytic cycle Reiher et al. suggested that a neutral or anionic pathway would be the most probable way for re-establishment of the original catalyst. Furthermore, experiments made it clear that the substituent at the trisamidoamine ligand core exerts a significant electronic influence, as Schrock et al. showed that changing the HIPT substituent to the HTBT substituent (HTBT = hexa-*tert*-butylterphenyl) results in a significant lowering of the catalytic activity, while the activities of catalysts with *para*-BrHIPT substituents are similar to the those catalysis carrying the HIPT substituent.[2e] Electronically, molybdenum seems to be a mandatory component of the catalyst as it was shown experimentally that the corresponding tungsten compound $[N_2\text{-W}\{(N(HIPT)CH_2CH_2)_3N\}]$ **II** does not catalyze NH_3 formation under identical reaction conditions.[7]

Stimulated by these fascinating experimental and theoretical results, we became interested in finding out if complexes of the general formula $[\text{H-M}\{(NHCH_2CH_2)_3X\}]$ (M = Mo, Ru, Os; X = N, P) could be suitable general catalysts for the reduction of N_2 to NH_3 using *only* H_2. If this is the case, the gap that presently exists in catalytic N_2 reduction chemistry could be closed, and one could arrive at the homogeneously catalyzed reduction of N_2 to NH_3 using a N_2/H_2 reactant gas mixture and well-defined transition metal complexes as catalysts, without the presence of any other reagents. As Schrock et al. have already reported the synthesis of, and analytical data for, $[\text{H-Mo}\{(N(HIPT)CH_2CH_2)_3N\}]$[2d] we considered model complexes $[\text{H-Mo}\{(NHCH_2CH_2)_3N\}]$ (**1**-Mo), $[\text{H-Ru}\{(NHCH_2CH_2)_3N\}]$ (**1**-Ru) and $[\text{H-Os}\{(NHCH_2CH_2)_3P\}]$ (**1**-Os(P)) to be potentially useful catalyst candidates for DFT investigations aimed at exploring the N_2 reduction reaction. Our aim was to check if closed catalytic cycles can be found in all cases, and if they exist, which energy profiles one would have to expect. To the best of our knowledge calculations of this kind have not yet been carried out.[8] We found for all three complexes, **1**-Mo, **1**-Ru and **1**-Os(P) that catalytic cycles do exist, but differ from one another, in some parts significantly so. With regards to a potential experimental application of catalysts of this kind, we postulate in accordance with our calculations and the experimental work by Schrock et al.[9] that **1**-Mo will not be a suitable catalyst for the generation of NH_3 using N_2/H_2. Whether or not complexes **1**-Ru and **1**-Os(P) will be suitable cannot be answered conclusively at this point; however, there is a higher probability that these compounds will be of potential use. Furthermore, they should be interesting starting points for theoretical and experimental investigations of modified ligands (vide infra). Our main aim in this first theoretical catalyst screening is to answer the following question: can an experimental search for potential catalysts be considered profitable in view of the high activation barriers that must be expected for this reaction?

DFT calculations using the B3LYP hybrid function were carried out successfully by Tuczek and Studer,[3] and by Reiher and co-workers,[4,5] using models of molybdenum complexes relevant to the N_2 reduction reaction, as reported by Schrock et al. Yates and co-workers compared the results of B3LYP and CCSD(T) calculations for nitrogen activation at model trigonal coordinated molybdenum complexes, and found both calculation methods yielded energies being well in accord with each other.[10] Thus, calculations using the B3LYP hybrid function can be considered a reasonable compromise between justifiable computer time for the calculations of model complexes, and the degree of accuracy with which the structures and energies are obtained from these calculations. Moreover, calculations of this kind are considered to predict reactivity trends correctly. A multitude of theoretical investigations of transition metal hydrides,[11] among them ruthenium[12] and osmium hydrides[13] also show the B3LYP hybrid function to be appropriate for obtaining plausible structures and energy trends. For this reason we used the B3LYP hybrid function in this work.[14] In a few selected cases we used QM/MM calculations to estimate the influence of the HIPT substituent on the calculated properties (see Computational Details). In the following discussion of energies and energy differences we refer to the reaction enthalpy, H,[15] as well as the Gibb's free energy, G (as well as to the activation enthalpies $H^{\ddagger}$ and Gibb's free activation energies $G^{\ddagger}$).

Results and Discussion

The catalytic cycle that was obtained using **1**-Mo is shown in Scheme 1 and an energy profile is depicted in Figure 1. Figures showing the structures and selected structural parameters are included in the supporting information. Complex **1**-Mo is more stable, by –14.2 kcal/mol, in the triplet state than in the singlet state, which is in accord with the experimentally observed paramagnetism of **1**-Mo.[2d,16] However, all other compounds of the Mo cycle are either significantly more stable in the singlet state, or they could not be located in the triplet state. To start the reaction cycle, N_2 or H_2 could be added to **1**-Mo, resulting in the formation of **2**-Mo and **3**-Mo, respectively. With regard to a closed catalytic cycle, only the addition of N_2 would be successful. A low lying transition state for the conversion of



Scheme 1. Catalytic cycle as calculated for **1**-Mo. Arrows in grey denote reactions for which a transition state could not be located.

1-Mo to **3**-Mo was located, but the addition of N_2 to **3**-Mo to give **5**-Mo is not feasible as a transition state leading to **5**-Mo could not be located. There is a transition state for the conversion of **1**-Mo to **2**-Mo ($\Delta H^{\ddagger}$ = 17.8 kcal/mol), but not for the oxidative addition of H_2 to **2**-Mo leading to **5**-Mo. As a result **5**-Mo cannot be formed in this way. Also the transfer of the metal bound hydride in **2**-Mo to a coordinated N_2 molecule does not seem to be possible. The corresponding product **4**-Mo, which has been characterized crystallographically,[2f] is a stable local minimum, however no transition state for the conversion of **2**-Mo to give **4**-Mo exists. However in an interesting, though energetically very unfavorable, σ-bond metathesis process H_2 can be added to **2**-Mo thus generating **5a**-Mo.

During this reaction the metal bound hydride is transferred to one of the nitrogen atoms of the N_2 molecule that is coordinated to the metal, while one of the hydrogen atoms of the H_2 molecule is transferred to the other nitrogen atom, and the second hydrogen atom is transferred to the metal center. However, the activation enthalpy $\Delta H^{\ddagger}$ for this step is extremely high (69.1 kcal/mol). A local minimum in which the incoming H_2 molecule initially coordinates in a non-classical manner to the metal center of **2**-Mo without being cleaved, was searched for, but not located. Complex **7**-Mo can be obtained from **5a**-Mo by hydrogen migration from the internal N atom of the Mo–NH=NH unit to the external N atom. Energetically speaking this reaction is slightly more unfavorable than the reaction of **4**-Mo with H_2 that also generates **7**-Mo, in both cases transition states were located. The activation enthalpies for both reactions are very high (52.3 and 43.4 kcal/mol, respectively). However, the reaction of H_2 and **4**-Mo to produce **6**-Mo is not possible. Complexes **6**-Mo and **5**-Mo can only be formed from **7**-Mo. With **7**-Mo as the staring material, two reactions can take place, either the metal bound hydrogen is transferred to the NH_2 unit generating one molecule of ammonia and the extremely stable molybdenum nitride complex **8**-Mo, or the H atom is transferred to the internal N atom of the $N=NH_2$ unit generating **9**-Mo. The latter reaction is kinetically preferred with respect to the formation of **8**-Mo due to its lower activation enthalpy ($\Delta H^{\ddagger}$ = 21.7 kcal/mol); the formation of **8**-Mo and NH_3 requires

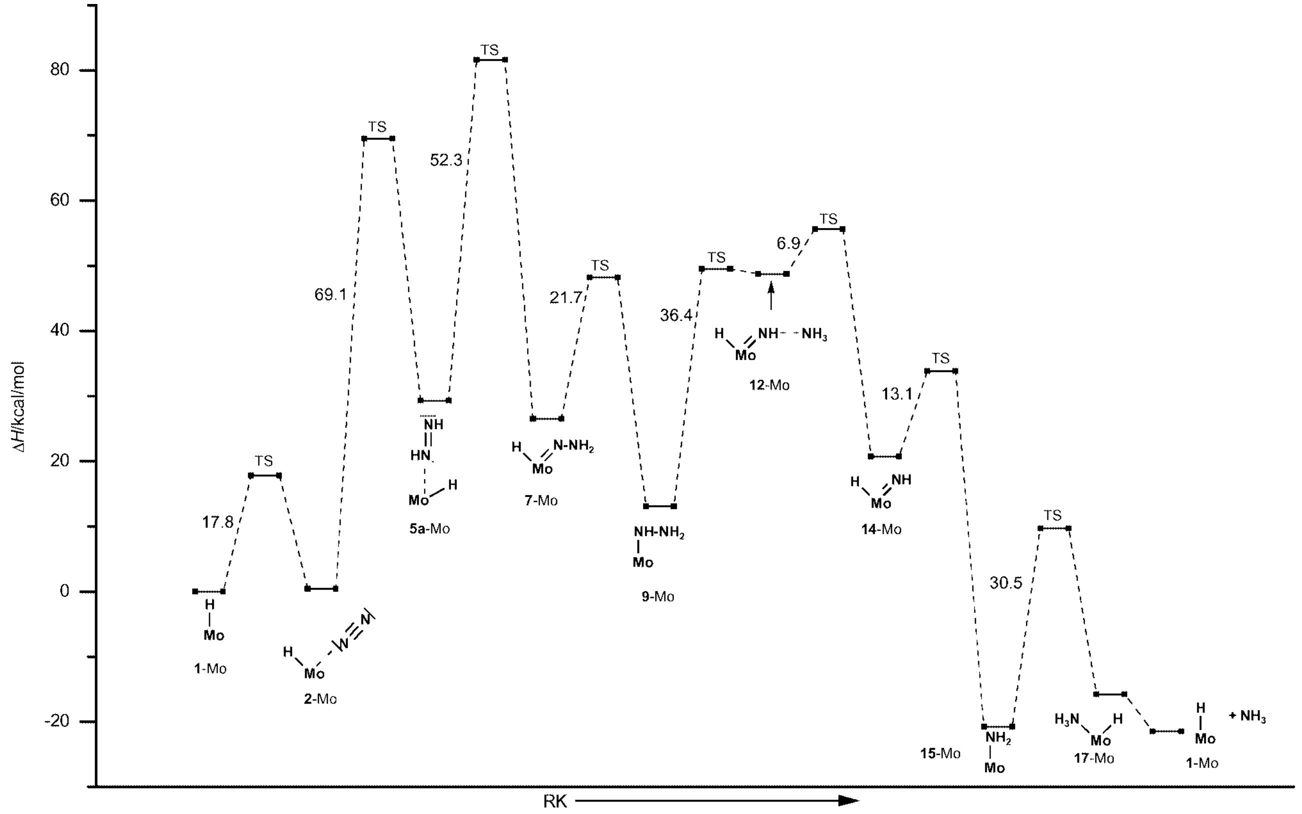


Figure 1. Energy profile (Δ*H*/kcal/mol) as calculated for the only completely closed cycle obtained with **1**-Mo. Relative activation energies ($\Delta H^{\ddagger}$/kcal/mol) are noted at the corresponding barriers.

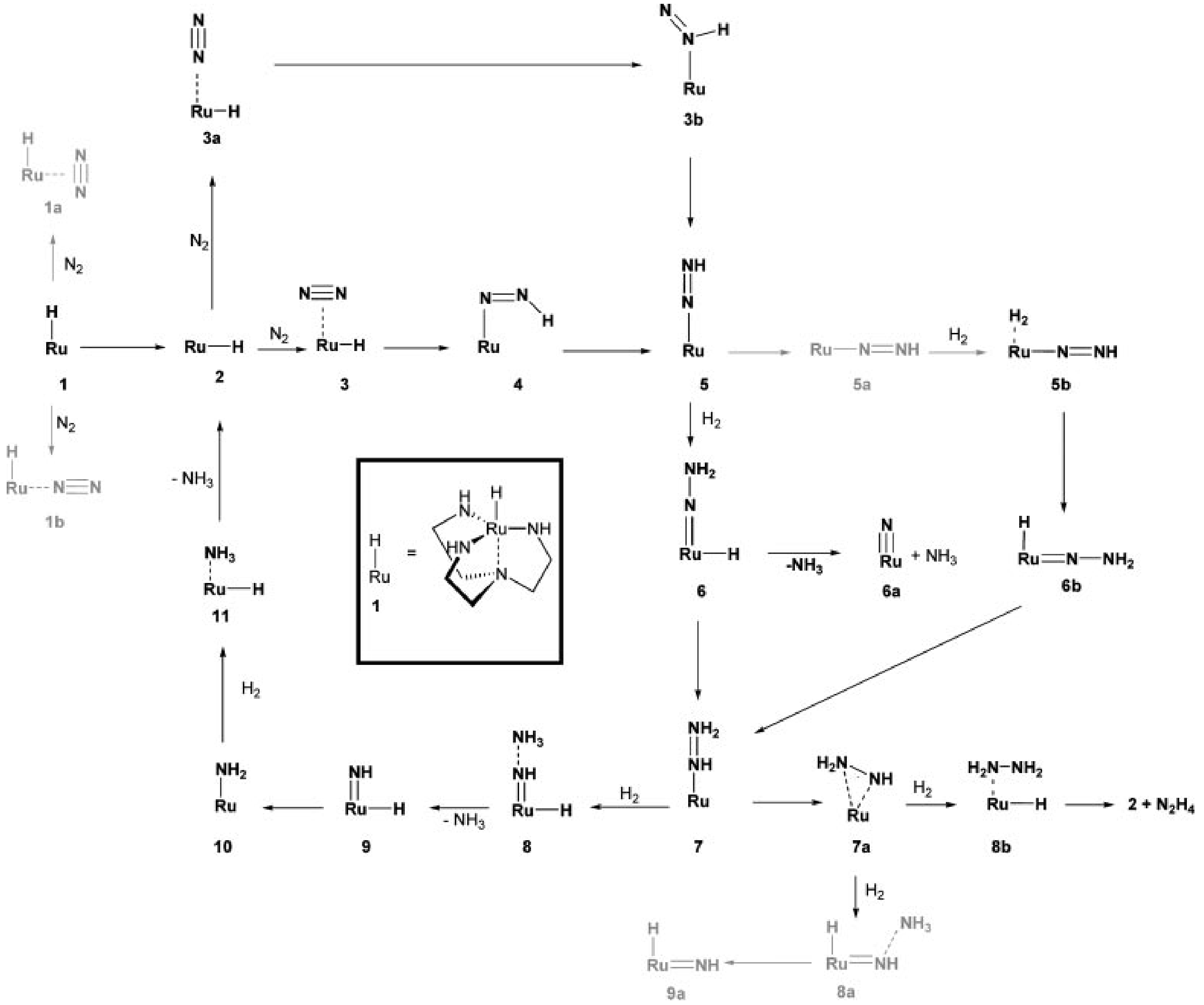
an activation enthalpy higher by ca. 20 kcal/mol ($\Delta H^{\ddagger}$ = 39.7 kcal/mol). However, thermodynamically speaking the formation of **8**-Mo and NH_3 is clearly preferred. The reintroduction of **8**-Mo into the catalytic cycle by the addition of H_2 is impossible.

Complex **9**-Mo can also react in two ways. The addition/cleavage of H_2 generates **11**-Mo, which can be considered as the adduct of **1**-Mo and hydrazine. Hydrazine can leave the complex while the catalytic cycle is endothermically closed (ΔH = 57.8 kcal/mol). The oxidative addition of H_2 to **9**-Mo does not seem to be possible, as the reaction product **10**-Mo exists on the hyper surface, but this is not case for the corresponding transition state that leads to **10**-Mo. However, the transfer of one metal bound hydride of **10**-Mo to the NH–NH_2 unit to form **11**-Mo is possible, and the corresponding activation enthalpy is comparatively low ($\Delta H^{\ddagger}$ = 16.2 kcal/mol).

Alternatively, **9**-Mo can react with one H_2 molecule to produce **12**-Mo. By cleavage of H_2 one molecule of NH_3 is generated, which participates in attractive interactions with a neighboring N atom. The NH_3 molecule can be cleaved off easily ($\Delta H^{\ddagger}$ = 6.9 kcal/mol) thus forming **14**-Mo. The rearrangement of **14**-Mo to give **15**-Mo requires only a comparatively small amount of energy ($\Delta H^{\ddagger}$ = 13.1 kcal/mol), and the product **15**-Mo is significantly more stable than **14**-Mo (ΔH = –37.8 kcal/mol).

Complex **15**-Mo cannot participate in an oxidative addition reaction with H_2 to produce **16**-Mo, as the corresponding transition state does not exist. Instead, the H_2 molecule is cleaved directly upon reaction with **15**-Mo generating **17**-Mo, which is an adduct of NH_3 and **1**-Mo. The activation enthalpy for this reaction that generate **17**-Mo amounts to 30.5 kcal/mol. In the last step NH_3 is cleaved off from the complex, and **1**-Mo is regenerated.[17]

Due to the high activation enthalpies, which amount to very high values at the beginning of the reaction cycles (i.e. **2**-Mo → **5a**-Mo, **5a**-Mo → **7**-Mo), it cannot be expected that **1**-Mo would be a useful catalyst for the reduction of N_2 to NH_3 using only H_2, this is in accordance with experimental results.[9] As an alternative to molybdenum, we considered ruthenium to be interesting, as a variety of molecular ruthenium hydrides have been synthesized[18] and have been employed as catalysts by us[19] and others.[20] Furthermore, novel heterogeneous ruthenium catalysts[21] have been developed recently, and Haber–Bosch ruthenium-containing catalysts are also known. Additionally, by keeping the formal oxidation state of the metal center the same, by exchanging molybdenum with ruthenium (and also osmium, vide infra) one obtains a catalyst system possessing an additional two electrons. This should enable direct information to be generated as to whether or not, for the given ligand core, an electron-rich metal center is most useful for promoting the N_2 reduction reaction. Interestingly, a closed catalytic cycle for the N_2 reduction reaction could also be calculated using **1**-Ru as the catalyst. However, this cycle is different from the molybdenum cycle in some ways.



Scheme 2. Catalytic cycle as calculated for **1**-Ru. Compounds and arrows in grey denote structures and reactions which were not located, respectively.

The catalytic cycle obtained with **1**-Ru is shown in Scheme 2 and Figure 2 contains the corresponding energy profile (the supporting information contains graphical representations of the calculated structures). The cycle for the Ru catalyst was calculated with all compounds being in the singlet spin state (this was also the case for the cycle incorporating Os compounds, vide infra). Both the side-on and end-on addition of N_2 to **1**-Ru forming **1a**-Ru and **1b**-Ru, respectively, are not possible (H_2 could not be coordinated side-on, or end-on, to **1**-Ru either).

However, in contrast to **1**-Mo, the hydride in **1**-Ru can flip from the axial to the equatorial position generating **2**-Ru. This flipping requires a significant amount of energy ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 43.5/43.2 kcal/mol) and product **2**-Ru is significantly richer in energy (ΔH = 42.9) than the reactant. Dinitrogen can coordinate to **2**-Ru at the axial position in either end-on (**3a**-Ru) or side-on (**3**-Ru) fashion, with end-on-addition clearly being exergonic relative to **2**-Ru ($\Delta H/\Delta G$ = –24.1/–13.3 kcal/mol), while side-on addition yields only a small energy gain (ΔH = –5.0 kcal/mol), which is compensated for by the unfavorable entropic contribution (ΔG = 4.7 kcal/mol). Transfer of the Ru bound hydride in **3**-Ru to the coordinated N_2 molecule leads to **4**-Ru, and the activation enthalpy for this reaction amounts to $\Delta H^{\ddagger}$ = 19.4 kcal/mol ($\Delta G^{\ddagger}$ = 20.9 kcal/mol). This is clearly different to the molybdenum system in which hydride transfer is not possible in this way. Complex **4**-Ru can rearrange to give the slightly more stable complex **5**-Ru, which is also obtainable via **3a**-Ru. The transfer of the hydride of **3a**-Ru to form **3b**-Ru is possible, however, energetically it is much more unfavorable than the reaction sequence already described, namely the transformation of **3**-Ru to **5**-Ru via **4**-Ru. Indeed, the activation barrier for the formation of **3b**-Ru from **3a**-Ru is higher by ca. 20 kcal/mol ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 42.0/41.9 kcal/mol), and the barrier for the reaction of **3b**-Ru to give **5**-Ru is very high with $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values of 47.2 and 46.8 kcal/mol, respectively. The sequence **3**-Ru → **4**-Ru → **5**-Ru requires much less energy.

It can be envisaged that the reaction continues from **5**-Ru via the equatorial conformer **5a**-Ru. For the subsequent steps (reaction of **5b**-Ru to **6b**-Ru and **7**-Ru) the corresponding minima and transition states were located, and

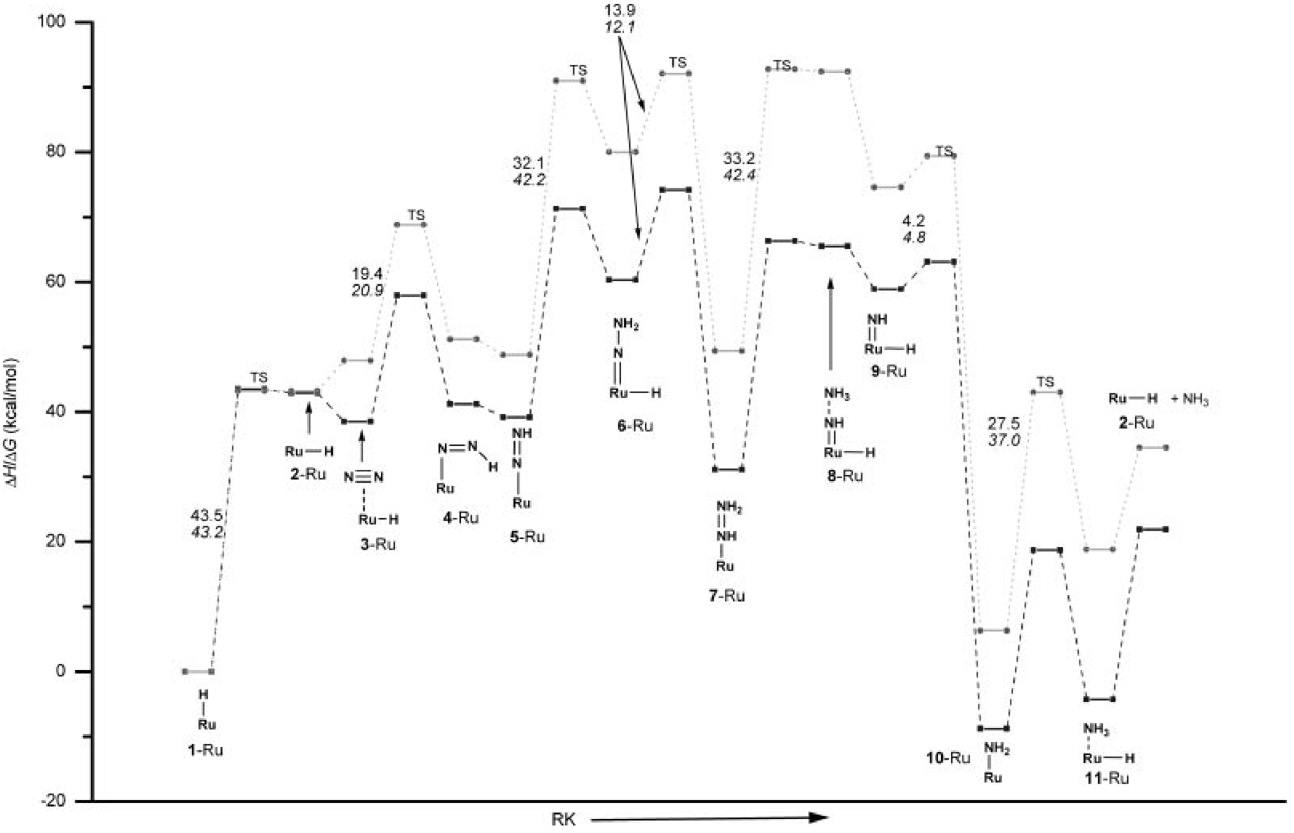


Figure 2. Energy profile (ΔH [squares; broken lines] and ΔG [circles; dotted lines], all in kcal/mol) as calculated for the main cycle obtained for **1**-Ru. Relative activation energies ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ plain/italics) are noted at the corresponding barriers.

the energies of these were low. For example, the activation energies for the conversion of **5b**-Ru to **6b**-Ru are $\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 9.5/10.5 kcal/mol. Complex **6b**-Ru can then be transformed to **7**-Ru, a process that also has a low activation barrier ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 9.4/9.5 kcal/mol). However, it was not possible to locate compound **5a**-Ru, making the reaction sequence **5**-Ru → **5a**-Ru → **5b**-Ru → **6b**-Ru → **7**-Ru questionable.

Conversely, if an H_2 molecule approaches **5**-Ru, the H–H bond is cleaved and **6**-Ru is formed. One hydrogen atom is transferred to the terminal NH group, and the other hydrogen atom migrates to the metal. Transfer of the Ru bound hydride of **6**-Ru to the terminal NH_2 group of the NNH_2 unit generates the first NH_3 molecule of this cycle. In an analogous manner to the molybdenum system, the corresponding ruthenium nitride complex **6a**-Ru is formed. In a similar way to the molybdenum system, this reaction step has a large activation energy ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 43.6/43.3 kcal/mol), however, the reaction products are strongly endothermic ($\Delta H/\Delta G$ = 51.7/58.2 kcal/mol) relative to the sum of the energies for **1**-Ru, N_2 and H_2, and this is in clear contrast to the molybdenum system. According to these results ruthenium nitride, **6a**-Ru, is significantly less stable than the analogous molybdenum nitride complex, **8**-Mo.

Alternatively, the hydride in **6**-Ru can be transferred from the metal center to the internal N atom of the NNH_2 unit generating complex **7**-Ru ($\Delta H/\Delta G$ = 31.1/49.4 kcal/mol) that is significantly lower in energy. The Gibb's free energy required for the formation of **7**-Ru from **6**-Ru is relatively small ($\Delta G^{\ddagger}$ = 12.1 kcal/mol), and clearly differs from the Gibb's free energies for the steps described so far. The even less energy consuming complex **7**-Ru is obtained following the alternative route (which is not completely closed) **5b**-Ru to **6b**-Ru, and then from **6b**-Ru complex **7**-Ru can be obtained, with a Gibb's free energy of only 9.5 kcal/mol.

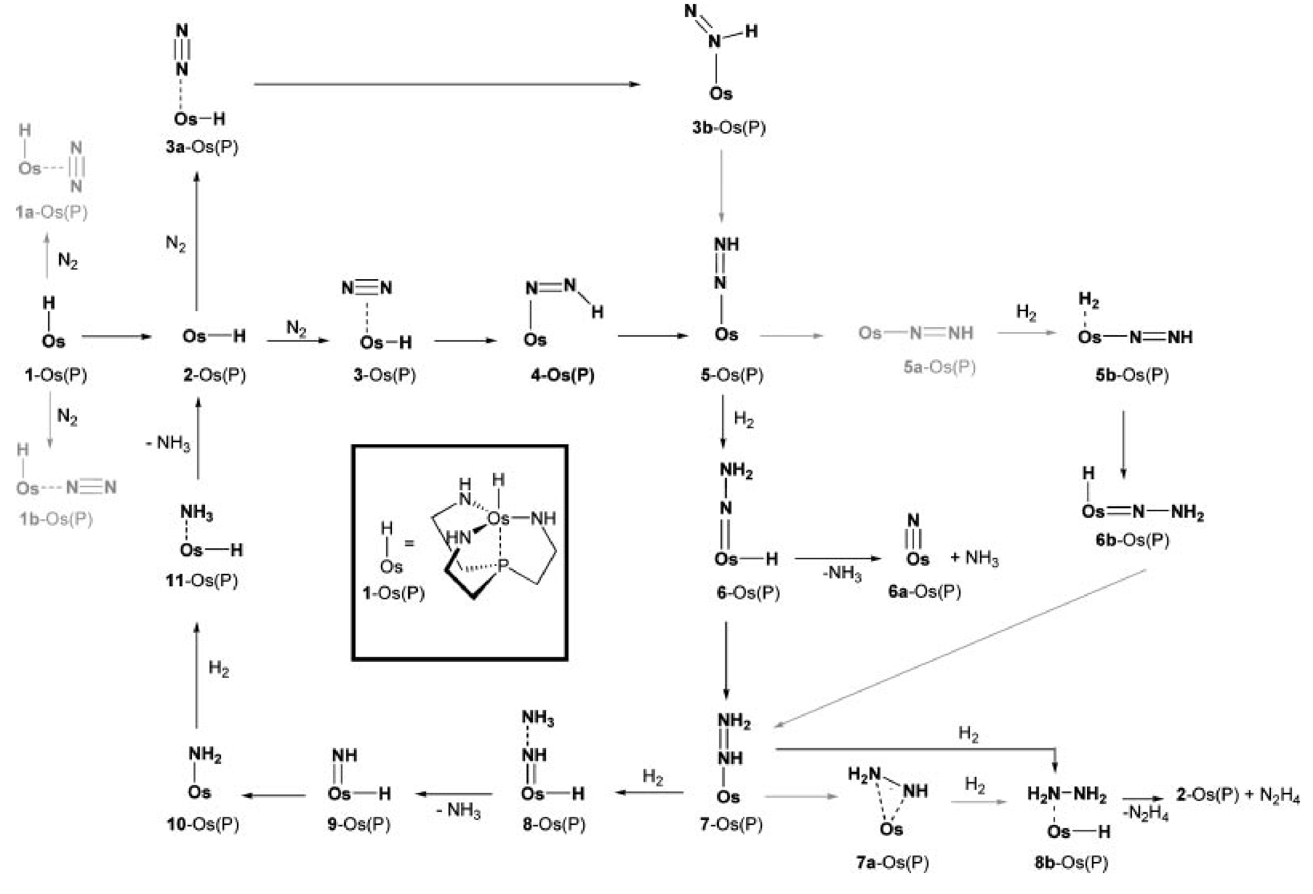
By rotating the $NHNH_2$ unit that is bound to the metal center in **7**-Ru to a side-on coordination mode, complex **7a**-Ru is formed in which both N atoms of the $NHNH_2$ unit have bonding interactions with the ruthenium center, as can be deduced from the N–Ru distances of 2.081 (NH_2–Ru) and 2.186 Å (NH–Ru). With **7a**-Ru as a starting material one can arrive at **8b**-Ru (the adduct of **2**-Ru and hydrazine), and the imidoruthenium complex **8a**-Ru can also be formed, from which the second ammonia molecule of the cycle is generated, which shows bonding interactions with the imido unit.[22] However, the resultant product **9a**-Ru could not be located, and as a result the cycle cannot be continued in this way. Due to the formation of hydrazine and **2**-Ru the catalytic cycle ends endothermically as expected.

If H_2 is added to **7**-Ru the H–H bond is cleaved, and the axial imidoruthenium complex **8**-Ru is formed. The newly formed NH_3 molecule that is incorporated in this complex has bonding interactions with the imido group. The activation barrier for this reaction ($\Delta H^‡/\Delta G^‡$ = 33.2/42.4 kcal/mol) is significantly higher than the barrier for the conversion of **7a**-Ru to **8a**-Ru ($\Delta H^‡/\Delta G^‡$ = 28.2/28.6 kcal/mol).

Alternatively, the NH_3 molecule can be cleaved from **8**-Ru and the resultant imido complex **9**-Ru can then react to give the amido complex **10**-Ru, which requires only a small amount of activation energy ($\Delta H^‡/\Delta G^‡$ = 4.2/4.8 kcal/mol). The reaction of **10**-Ru with H_2 cleaves the H–H bond and generates complex **11**-Ru that can be considered as an adduct of **2**-Ru and NH_3. This reaction requires an activation energy of $\Delta H^‡/\Delta G^‡$ = 27.5/36.7 kcal/mol. Cleaving NH_3 off **11**-Ru generates a second ammonia molecule, and regenerates the catalyst **2**-Ru.[16]

In summary, a closed catalytic cycle could be calculated using **1**-Ru with local minima and transition states that enable a plausible reaction scheme to be suggested. It is interesting to note that the highest activation barriers of this cycle are much lower than those for the molybdenum system. However, some activation enthalpies and Gibb's free energies (i.e. reactions **5**-Ru → **6**-Ru and **7**-Ru → **8**-Ru) have values of ca. 30 and 40 kcal/mol, respectively and thus are probably too high to enable the reaction to occur in practice. Also we note that the usage of the real HIPT ligand seems to influence the reaction trend. Some steps of the cycle (**1**-Ru → **2**-Ru; **3**-Ru → **4**-Ru; **10**-Ru → **11**-Ru, **5b**-Ru → **6b**-Ru) were re-optimized, using the HIPT ligand, by applying QM/MM-methods (see Computational Details). Interestingly, the presence of the real ligand reduces the activation barrier, in comparison to the model ligand, by ca. 10 kcal/mol for the reaction **1**-Ru → **2**-Ru ($\Delta H^‡/\Delta G^‡$ = 30.8/31.4 kcal/mol). Conversely, the activation barriers for the reactions **3**-Ru → **4**-Ru and **5b**-Ru → **6b**-Ru are slightly higher relative to the model ligand. An even clearer increase in the activation barrier was found for the **10**-Ru → **11**-Ru reaction. For this reaction the activation enthalpy $\Delta H^‡$ is raised by 3.3 kcal/mol, and the Gibb's free activation energy, $\Delta G^‡$, rises by 4.1 kcal/mol relative to the model ligand system. These results indicate that fine tuning of the ligand may be crucial in future experimental work.

In the third part of this evaluation of the potential of transition metal complexes with TREN- and TREN-type ligands, we investigated the behavior of **1**-Os(P). In this complex the ligand core is not tris(2-aminoethyl)amine, but tris(2-aminoethyl)phosphane. Phosphanes of this kind can be obtained synthetically and have been structurally characterized.[23] Similar phosphanes were used for the syntheses of zirconium complexes.[24] In test calculations of a few steps of the cycles involving **1**-Os and **1**-Os(P) it turned out that the usage of the triamidophosphane ligand seems to be slightly more favorable, with regards to activation barriers, than the other ligands discussed thus far. Accordingly, we



Scheme 3. Catalytic cycle as calculated for **1**-Os(P). Compounds and arrows in grey denote structures and reactions which were not located, respectively.

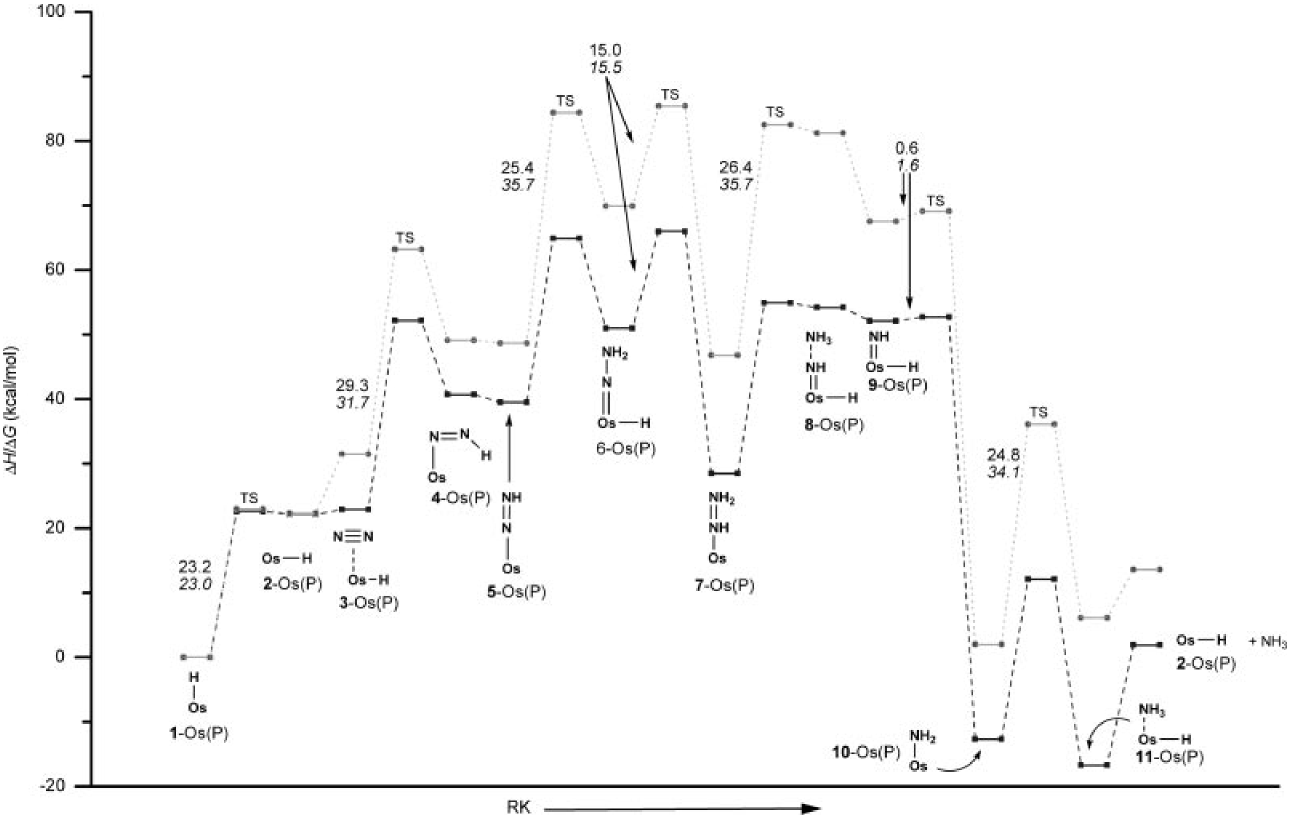


Figure 3. Energy profile (ΔH [squares; broken lines] andΔG [circles; dotted lines], all kcal/mol) as calculated for the main cycle obtained for **1**-Os(P). Relative activation barriers ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ plain/italics) are noted at the corresponding barriers.

used this ligand for the calculation of the following cycle. All of our investigations hint that the cycle proposed for **1**-Ru would be applicable to **1**-Os(P) with a few small differences.[25] Accordingly the cycle is discussed only briefly. Scheme 3 and Figure 3 show the corresponding catalytic cycle and the energy profile for **1**-Os(P), respectively.

With regards to the main cycle it is striking that some activation barriers and Gibb's free activation energies are lower – in some cases significantly lower – compared to the ruthenium system. For example the Gibb's free activation energy, $\Delta G^{\ddagger}$, for the flipping of the hydride from the axial position in **1**-Ru to the equatorial position in **2**-Ru amounts to 43.2 kcal/mol, while for the conversion of **1**-Os(P) to **2**-Os(P) it is only 23.0 kcal/mol. Also for the conversion of **5**-Os(P) to **6**-Os(P) the Gibb's free activation barrier ($\Delta G^{\ddagger}$ = 35.7 kcal/mol) is lower by 6.5 kcal/mol than the barrier for the conversion of **5**-Ru to **6**-Ru ($\Delta G^{\ddagger}$ = 42.2 kcal/mol). Less pronounced is the reduction in the Gibb's free activation barrier in the osmium system for the conversion of **10**-Os(P) to **11**-Os(P) when compared to the analogous reaction within the ruthenium system. The barrier is $\Delta G^{\ddagger}$ = 34.1 kcal/mol for the conversion of **10**-Os(P) to **11**-Os(P), while for the conversion of **10**-Ru to **11**-Ru 36.7 kcal/mol of energy are required. In an analogous manner to the Ru system, complexes **1a**-Os(P), **1b**-Os(P) and **5a**-Os(P) could not be located. Additionally, relative to the Ru system there is a drastic increase in the activation energy for the conversion of **3**-Os(P) to **4**-Os(P) ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 29.3/31.7 kcal/mol with respect to $\Delta H^{\ddagger}/\Delta G^{\ddagger}$ = 19.4/20.9 kcal/mol for the Ru system).

In summary, for **1**-Os(P) a closed catalytic cycle can be calculated for the N_2 reduction reaction. In this cycle the highest Gibb's free activation barriers, $\Delta G^{\ddagger}$, using the model ligand, only amounts to 35.7 kcal/mol [**5**-Os(P) → **6**-Os(P) and **7**-Os(P) → **8**-Os(P)],[26] while the activation enthalpy $\Delta H^{\ddagger}$ has a maximum value of 29.3 kcal/mol [**3**-Os(P) → **4**-Os(P)]. Compared to the molybdenum system ($\Delta H^{\ddagger}_{max}$ = 69.1 kcal/mol) the activation energies are generally much lower for this system. These results are encouraging as it can be expected that, as in the case of the ruthenium system, the osmium system with the use of HIPT or other real ligands might prove useful by actively reducing the activation barriers further.

Summary

We have showed that all three metal hydrides investigated in the calculations reported herein yield closed catalytic cycles for the reduction of N_2 to NH_3 by H_2. The extremely high activation barriers of the molybdenum system, in accordance with experimental work by Schrock et al., hint at the fact that **1**-Mo is not a suitable catalyst for such a N_2 reduction reaction. The activation barriers are much lower in catalytic cycles incorporating **1**-Ru and **1**-Os(P), however the Gibb's free activation barriers, $\Delta G^{\ddagger}$, have values that are significantly higher than 30 kcal/mol for some reaction steps. As a result, predictions as to the experimental behavior of catalysts of this type cannot be made accurately at this point, and further clarification is need, especially with regards to the influence of real substituents at the ligand core, and the effects of solvent. According to QM/MM calculations for some of the reaction steps for the Ru system, the presence of the HIPT ligand seems to be beneficial with regards to lowering the activation barriers. However, for other steps it seems to generate slightly higher activation barriers. In general it is important to note that by varying the metal center (Mo, Ru, Os), as well as varying the type of ligand, it has been shown clearly that it may be possible to create catalyst systems that lead to reactions with comparatively low activation barriers. We believe that these results are promising, and proved a starting point for further theoretical work.

Computational Details

The geometry optimizations reported herein were carried out using the Gaussian 03 and the Turbomole 5.7 suite of programs.[27] Table 1 lists relative energies for all compounds. Tables S1 (Mo), S2 (Ru) and S3 (Os) in the supporting information list energies, enthalpies and free enthalpies in atomic units obtained from the different computational studies. Cartesian coordinates for all calculated compounds are contained in the supporting information. Ball-and-Stick representations of the calculated structures are shown in Figures S4 (Mo), S5 (Ru) and S6 (Os) in the supporting information.

Mo: The structures were first optimized using Gaussian 03 (B3LYP[28] hybrid function) with the 6-31G(d) basis set[29] for elements C, N and H. For Mo, a quasirelativistic small-core ECP[30] was used with a (441/2111/31) valence basis set. This basis set shall be called basis set BII.[31] The relaxed structures were inputted into frequency calculations to successfully characterize the nature of the stationary points (i = 0 for local minima, and 1 for saddle points of order 1; frequency calculations were carried out throughout this

Table 1. Relative enthalpies ΔH [kcal/mol] and Gibb's free enthalpies ΔG [kcal/mol] and the number of imaginary frequences i [cm^{-1}] for the compounds calculated in this work.[a]

Compd.[b]	ΔH	i	Compd.[c]	ΔH	ΔG	i	Compd.[c]	ΔH	ΔG	i
1-Mo($^{3\Sigma}$)	0.0	0	**1**-Ru	0.0	0.0	0	**1**-Os(P)	0.0	0.0	0
1-Mo($^{1\Sigma}$)	14.8	0	**2**-Ru	42.9	43.0	0	**2**-Os(P)	22.6	22.3	0
2-Mo	0.4	0	**3**-Ru	38.5	47.9	0	**3**-Os(P)	22.9	31.5	0
3-Mo	1.7	0	**3a**-Ru	19.4	29.9	0	**3a**-Os(P)	7.6	17.7	0
4-Mo	2.9	0	**3b**-Ru	51.0	60.6	0	**3b**-Os(P)	50.2	60.0	0
5-Mo	36.7	0	**4**-Ru	41.2	51.2	0	**4**-Os(P)	40.7	49.1	0
5a-Mo	29.3	0	**5**-Ru	39.2	48.8	0	**5**-Os(P)	39.5	48.7	0
6-Mo	47.3	0	**5b**-Ru	67.4	86.0	0	**5b**-Os(P)	56.8	75.4	0
7-Mo	26.5	0	**6**-Ru	60.3	80.0	0	**6**-Os(P)	51.0	69.9	0
8-Mo	–17.5	0	**6a**-Ru	51.7	58.2	0	**6a**-Os(P)	49.1	56.2	0
9-Mo	13.1	0	**6b**-Ru	64.8	83.8	0	**6b**-Os(P)	55.3	74.4	0
10-Mo	35.9	0	**7**-Ru	31.1	49.4	0	**7**-Os(P)	28.5	46.8	0
11-Mo	21.8	0	**7a**-Ru	45.9	65.6	0	**7a**-Os(P)	36.8	56.6	0
12-Mo	48.7	0	**8**-Ru	65.5	92.4	0	**8**-Os(P)	54.2	81.2	0
13-Mo	23.1	0	**8b**-Ru	36.7	63.3	0	**9**-Os(P)	52.1	67.5	0
14-Mo	20.7	0	**9**-Ru	58.9	74.6	0	**10**-Os(P)	–12.7	2.0	0
15-Mo	–20.8	0	**10**-Ru	–8.8	6.3	0	**11**-Os(P)	–16.7	6.1	0
16-Mo	8.3	0	**11**-Ru	–4.3	18.8	0	TS(**1**,**2**-Os(P))	23.2	23.0	1(–128.3)
17-Mo	–15.8	0	TS(**1**,**2**-Ru)	43.5	43.2	1(–267.2)	TS(**3**,**4**-Os(P))	52.2	63.2	1(–754.8)
TS(**1**,**2**-Mo)	17.8	1(–115.6)	TS(**3**,**4**-Ru)	57.9	68.8	1(–929.5)	TS(**3a**,**3b**-Os(P))	58.2	68.3	1(–810.0)
TS(**1**,**3**-Mo)	18.9	1(–255.0)	TS(**3a**,**3b**-Ru)	61.4	71.8	1(–808.3)	TS(**5**,**6**-Os(P))	64.9	84.4	1(–1300.9)
TS(**2**,**5a**-Mo)	69.5	1(–501.6)	TS(**3b**,**5**-Ru)	98.2	107.4	1(–2185.0)	TS(**6**,**7**-Os(P))	66.0	85.4	1(–902.4)
TS(**5**,**6**-Mo)	53.1	1(–802.3)	TS(**5**,**6**-Ru)	71.3	91.0	1(–1488.3)	TS(**6**,**6a**-Os(P))	103.2	122.8	1(–1509.6)
TS(**4**,**7**-Mo)	46.3	1(–1449.3)	TS(**5b**,**6b**-Ru)	76.9	96.5	1(–1190.4)	TS(**7**,**8**-Os(P))	54.9	82.5	1(–1089.5)
TS(**5a**,**7**-Mo)	81.6	1(–2059.0)	TS(**6**,**6a**-Ru)	103.9	123.3	1(–1453.5)	TS(**7**,**8b**-Os(P))	55.0	82.2	1(–512.5)
TS(**6**,**7**-Mo)	72.9	1(–1572.7)	TS(**6**,**7**-Ru)	74.2	92.1	1(–951.8)	TS(**9**,**10**-Os,P))	52.7	69.1	1(–630.1)
TS(**7**,**8**-Mo)	66.2	1(–1524.2)	TS(**7**,**7a**-Ru)	59.3	78.0	1(–336.0)	TS(**10**,**11**-Os(P))	12.1	36.1	1(–393.0)
TS(**7**,**9**-Mo)	48.2	1(–1054.9)	TS(**7**,**8**-Ru)	64.3	91.8	1(–1109.8)				
TS(**9**,**11**-Mo)	42.3	1(–1127.6)	TS(**7a**,**8a**-Ru)[d]	65.3	93.2	1(–979.1)				
TS(**10**,**11**-Mo)	52.1	1(–1075.0)	TS(**7a**,**8b**-Ru)	61.4	88.8	1(–541.6)				
TS(**9**,**12**-Mo)	49.5	1(–1124.4)	TS(**9**,**10**-Ru)	63.1	79.4	1(–763.3)				
TS(**10**,**13**-Mo)	58.1	1(–1326.4)	TS(**10**,**11**-Ru)	18.7	43.0	1(–412.6)				
TS(**12**,**14**-Mo)	55.6	1(–499.4)								
TS(**14**,**15**-Mo)	33.8	1(–1327.4)								
TS(**15**,**17**-Mo)	9.7	1(–1047.3)								
TS(**16**,**17**-Mo)	18.8	1(–1083.8)								

[a] Structures and energies for compounds located in the triplet state (Mo system only) are included in the supporting information. [b] Calculated on B3LYP/BII. [c] Calculated on B3LYP/BIII. [d] The transition state TS(**7a**,**8a**-Ru) was unequivocally established. However, no energy value for **8a**-Ru is reported here, as no true minimum could be located for this compound. Frequency calculations showed four imaginary frequencies related to skeletal vibrations and NH_3 rotations.[22]

work with T = 298.15 K and p = 1 atm). Furthermore, optimized transition state geometries were inputted into IRC calculations to check if the transition states correspond to the correct reactants and products. The zero-point vibrational energies (*ZPE*) were used without scaling. To gain an insight into the relative energy differences for the different spin states, the optimized structures were then geometry optimized for the triplet state (B3LYP/BII), and for the cases were local minima or transition state structures could be found, their energies, relative to the energy of the singlet state, are reported in Table S1 in the supporting information. To obtain more accurate structures and energies, the B3LYP/BII geometries were inputted into geometry optimization calculations at the B3LYP level of theory employing the TZVP basis set designed by Ahlrichs[32] et al. for elements C, H and N. For Mo, the Stuttgart/Köln relativistic effective core potential was used in combination with a (311111/22111/411) valence basis.[33] This basis set is denoted as basis set BIII. For the calculations of the Mo system the Turbomole 5.7 program was used. In the Discussion section of the text the enthalpies H obtained from the B3LYP/BII calculations are quoted. Comparison of these values with the B3LYP/BIII-derived energies showed that the deviations between these values were small, and consequently do not to require extra discussion (see Table S1, supporting information).

Ru and Os: Geometry optimizations were carried out using Gaussian03 (B3LYP) with the TZVP basis set for elements C, H, N, P.[32] For Ru and for Os the Stuttgart/Köln relativistic effective core potential was used in combination with a (311111/22111/411) valence basis.[33] This is denoted as basis set BIII. The stationary points obtained from these calculations were characterized as local minima or transition states according to frequency calculations (i = 0 for local minima, and 1 for saddle points of order 1), and in some cases IRC calculations were carried out. Zero point energies were used without scaling. Relative enthalpies, H, and Gibbs free energies, G, are listed in Table 1 and are quoted in the Discussion section of the text. Tables S2 and S3 in the supporting information show energies, enthalpies, and free enthalpies in atomic units.

QM/MM Calculations: For some ruthenium compounds the HIPT ligand, as developed by Schrock et al., was used. For these large molecules QM/MM calculations were employed using the ONIOM method:[34] The ruthenium center, all atoms of the reacting substrates, the TREN part of the ligand, and the phenyl rings attached to the amido nitrogen centers were treated at the DFT level (BLYP[35] function) using the 6-31G(d) basis set for elements C, H, N. For Ru, a quasirelativistic small-core ECP[29,30] was used with a (441/2111/31) valence basis set. The DFT part of the calculations was run using the density fitting approximation[36] employing the density fitting set developed by Godbout et al.[37] and Sosa et al.[38] The atoms of the phenyl rings bearing the isopropyl groups, as well as the isopropyl groups themselves, were treated at the molecular mechanics level using the UFF force field.[39] The boundary atoms were treated as H atoms at the highest calculation level. Figure 4 gives a graphical example of the two layers. The optimized local minima and transition states were successfully characterized by frequency calculations (i = 0 and i = 1 for minima and saddle points of order 1, respectively).

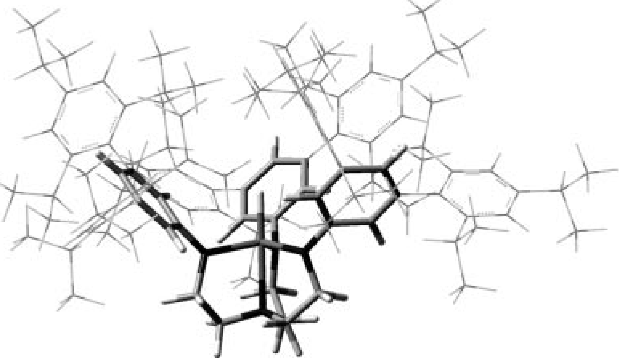


Figure 4. Assignment of atoms to layers in QM/MM calculations with **1**-Ru(HIPT) as an example. The atoms in the high layer are shown with a stick representation, whereas the atoms in the low layer appear as a wireframe representation.

Supporting Information: Energies and figures for most of the compounds calculated in this work, as well as the Cartesian coordinates employed.

Acknowledgments

The generous allocation of computer time by the Calculation and Communication Centre of the RWTH Aachen is gratefully acknowledged.

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substituents are compared in detail, and these errors must be considered.

[15] For the Mo system only enthalpies H and $H^{\ddagger}$ are included in the energy profile, as these values clearly show the activation barriers to be very high. Gibb's free energies are expected to be, and were shown by us, to be significantly higher for a few steps (as can be seen in the energy profiles of the Ru and the Os systems), but as no new relevant information can be deduced from the ΔG curve, it is not included in the energy profile. In the case of the Ru and Os catalysts some of the $H^{\ddagger}$ values are fairly low, which calls for the inclusion of G and $G^{\ddagger}$ in these systems to obtain an impression of how large the differences between the enthalpies $H/H^{\ddagger}$ and Gibb's free energies $G^{\ddagger}/G^{\ddagger}$ really are.

[16] The calculated structures of compounds **4**-Mo and **8**-Mo are in good agreement with the structures carrying the HIPT substituent that have been determined crystallographically by Schrock et al..

[17] Attempts to locate transition states for the cleavage of NH_3 from **17**-Mo, as well as N_2H_4 from **11**-Mo, were not successful. Instead only local minima were found, in which the N centers of the NH_3 and N_2H_4 molecules are bridged by the protons at the amido N centers of the complex. For this reason we have not attempted to locate these transition states in the ruthenium and osmium systems. If the real HIPT ligand was employed this would not occur, as in the real system C atoms are attached to the amido N centers.

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[25] a) Complex **8a**-Os(P), as well as the transition states TS(**7**,**7a**-Os(P)) and TS(**7a**,**10**-Os(P)), could not be located.

[26] For reactions like the conversion of **5**-Os(P) to **6**-Os(P), in which the H–H bond of a H_2 molecule is broken, it can be seen that this process is energetically more favorable than in the Ru system (and also the Mo system). However, we agree with the opinion of one referee that these barriers are high. Therefore this issue needs to be addressed in further analyses of the electronic structure of the catalysts, with the aim of developing modified catalyst structures.

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Received: June 14, 2006