N_2 Activation

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Heterolytic Outer-Sphere Cleavage of H_2 for the Reduction of N_2 in the Coordination Sphere of Transition Metals—A DFT Study**

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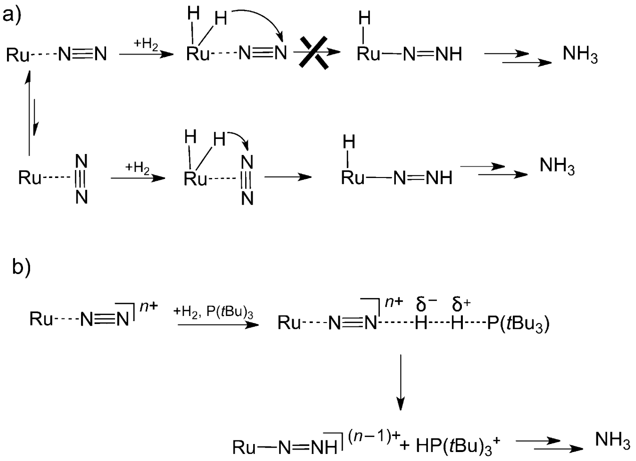
The catalytic reduction of dinitrogen to ammonia is of paramount importance for the value-creation chain in industry and also plays an important role in nature. Interestingly, in nitrogenases[1] a sequence of protonations and electron transfers[2] of N_2 coordinated at metal centers is used for the generation of NH_3, while in the established heterogeneously catalyzed Haber–Bosch process molecular hydrogen is used for the reduction of N_2.[3] The naturally occurring type of reduction (protons/reducing agent) could be replicated recently in seminal work from the Schrock[4] and Nishibayashi groups[5] using trisamidoamine molybdenum and molybdenum pincer complexes, respectively. Density functional theory (DFT)-based investigations conducted by the Tuczek[6] and Reiher groups[7] have generated a coherent picture of the reaction mechanism of the Schrock system. The catalytic hydrogenation of nitrogen with transition-metal complexes has the subject of intensive experimental[8] and theoretical[9] investigation. Very recently, the research groups led by Schneider and Holthausen succeeded in the stoichiometric reduction of a ruthenium(IV)nitrido pincer complex with molecular hydrogen to give the corresponding ruthenium tetrahydride and ammonia.[10a] Holland and co-workers very recently reported the hydrogenation of N_2 to NH_3 at an iron complex.[10b] However, the catalytic formation of azanes and azenes from N_2 and H_2 using homogenous transition-metal catalysts has not yet been realized despite all the progress made.

The transfer of a metal-bound hydrogen center onto a coordinated N_2 molecule is generally regarded as the key step for the homogeneously catalyzed hydrogenation of dinitrogen. This is exemplified in Scheme 1a with ruthenium as the central metal. The inner-sphere transfer onto an end-on-bound N_2 ligand, however, is not possible directly, according to earlier computational investigations by our group[11] and has not been realized experimentally to the best of our knowledge. Instead, the transfer of metal-bound hydrogen onto side-on-bound nitrogen can occur with activation barriers which in principle are low enough for practical application. However, mononuclear complexes with side-on-bonded N_2 are significantly less stable thermodynamically than the corresponding end-on-bound N_2 complexes and ruthenium complexes of this kind are not known.[11,12] Special bifunctional ligand systems have been proposed[12] to enforce side-on coordination and in this way pave the way for hydride transfer. These contradictory prerequisites for the effective binding of the N_2 molecule and a low activation barrier for hydrogen transfer currently represent a fundamental challenge.



Scheme 1. Key steps of the activation and transfer of hydrogen onto a coordinated N_2 molecule. a) Oxidative addition and inner-sphere transfer onto end-on- and side-on-bound N_2; b) heterolytic cleavage of the H_2 molecule in the presence of a bulky Lewis base and transfer onto end-on-coordinated N_2.

Herein we present a novel approach for the transfer of hydrogen onto the stable and ubiquitous intermediate having end-on-coordinated N_2. As is shown in Scheme 1b the dihydrogen molecule is activated remote from the coordination sphere of the metal by heterolytic cleavage.

As an example for the computational-based evaluation of this type of reaction, we chose a ruthenium complex with bulky substituents on the ligand. The first two steps of hydrogen transfer are summarized in Scheme 2. The starting point is the dicationic ruthenium pincer complex $[Ru(PNP)(CO)_2(N_2)]^{2+}$ (PNP = 2,6-bis(di-*tert*-butylphosphanylmethyl)pyridine)[13] with a N_2 molecule coordinated end-on to the metal center. As a sterically demanding Lewis base, tri-*tert*-butylphosphane ($PtBu_3$) was chosen. The computations showed that $PtBu_3$ cannot coordinate to the complex fragment and thus cannot replace the N_2 ligand because of its steric bulk. The electron-poor N_2 complex and the phosphane therefore can be considered to be a "frustrated Lewis pair"[14] in combination **1**.

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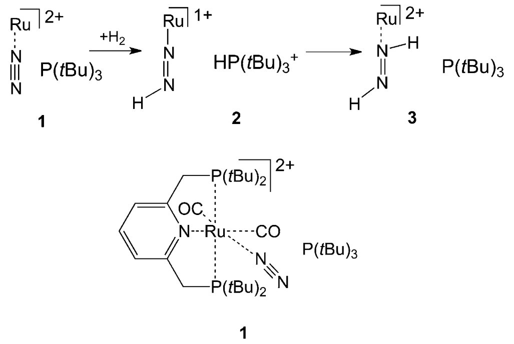


Scheme 2. Transfer of hydrogen onto the end-on-coordinated nitrogen by means of the heterolytic cleavage of H_2 by Lewis acid/base-induced outer-sphere mechanism.

Geometry optimizations on **1** and all other structures were carried out in all cases for the combination of the complex and phosphane in order to describe correctly the dispersion-induced interactions[15] in addition to the binding energies and electrostatic interactions of these sterically demanding systems. The computations therefore were carried out with the M06-L density functional,[16] which is especially useful for such systems, and the def2-TZVP basis set (including ECP for ruthenium),[17] and the results are summarized in Table 1. The energies of the gas-phase structures obtained in this way were recalculated using the B2PLYP-D[18] double-hybrid functional and were augmented with the zero-point energy corrections as well as with the thermochemical corrections from the M06-L computations, so that the enthalpies and Gibb's free energies can be compared with the original M06-L results (Table 1). In addition to the gas-phase calculations single-point energies were calculated by applying the IEF-PCM solvent model[19] for the moderately polar solvent tetrahydrofuran, and the entropic contributions of the solvent were considered by introducing correction factors that stem from gas-phase frequency calculations at elevated pressures[20] and corrections for the standard state[21] (the details of the computations are fully described in the Supporting Information). If not noted otherwise, the Gibb's free energies ΔG of the M06-L gas-phase computations are used for the following discussion.

Table 1: Calculated relative enthalpies (ΔH) and Gibb's free energies (ΔG) of the compounds shown in Scheme 3 (all in kcal mol^{-1}).[a]

Compd.	$\Delta H/\Delta G$ (B2PLYP-D, gas)	$\Delta H/\Delta G$ (M06-L, gas)	ΔG (M06-L, THF)[b]
1	0.0/0.0	0.0/0.0	0.0
2	6.1/13.6	1.3/8.8	8.5
2a	8.7/16.2	5.7/13.1	11.6
3	13.1/21.0	12.6/20.6	18.3
3a	21.9/31.4	20.4/29.9	25.5
4	21.1/28.6	19.0/26.5	23.9
TS1–2	25.9/32.0	19.7/25.8	28.1
TS2–3	23.0/33.1	22.1/32.2	32.2
TS2a-3a	25.7/36.3	24.6/35.3	33.9
TS2–4	21.1/29.0	20.1/28.0	27.5

[a] All calculations were carried out with the def2-TZVP(ECP) basis set.[17] [b] IEF-PCM, corrected for standard state. For details see the Supporting Information.

The geometry optimizations of structures **1**–**3** and the corresponding transition states **TS1–2** and **TS2–3** of the reaction sequence shown in Scheme 2 led to stable stationary points (Figure 1). In the starting structure **1** the phosphane is at a distance of 3.282 Å from the outer N atom of the coordinated N_2 molecule, indicating the existence of attractive interactions despite the repulsive forces present between the lone pairs of the phosphane and the N_2 molecule (sum of the van der Waals-radii: 3.350 Å).[22]

The distance between the two N atoms is 1.107 Å and therefore elongated only negligibly relative to unbound N_2 (1.090 Å). The structural similarity of **1** with frustrated Lewis pairs also is reflected in its reactivity towards hydrogen.[14,20] The H_2 molecule is activated in transition state **TS1–2** between the N and the P atom and its bond is elongated from 0.743 Å in unbound H_2 to 0.985 Å. The hydrogen atom that becomes negatively polarized in the course of the heterolytic cleavage is 1.433 Å away from the outer N atom of the N_2 molecule and the length of the N–N bond increases to 1.157 Å. After complete cleavage of the H_2 molecule in structure **2** the resulting Ru-N=NH unit adopts the typical *trans* conformation. The Gibb's free energy of **2** is 8.8 kcal mol^{-1} higher than that of the reference point **1**. The overall charge of the metal complex is reduced from +2 to +1, and there are no noticeable directed interactions to the phosponium ion $HPtBu_3^+$. Comparisons of IRC computations and independent optimizations of **2** show that there is no further minimum prior to the cleavage of the hydrogen molecule, which is consistent with computations of similar systems.[23]

The Ru-N=N-H unit in **2** is protonated in the next reaction step via transition state **TS2–3** (Scheme 3, Figure 1). The N–N distance remains largely unchanged, while the Ru–N distance is decreased to 2.161 Å in structure **3**. The two N–H bonds have similar lengths of 1.057 Å and 1.053 Å, and the short contacts to the phosphane of roughly 2.4 and 2.7 Å indicate weak interactions with the phosphorus atom.

The stepwise transfer of a hydride and a proton onto the end-on-coordinated N_2 ligand initiated by the Lewis base occurs with remarkably low activation barriers. For the reduction step of **1** to **2** the enthalpy of activation amounts to $\Delta H^{\neq} = 19.7$ kcal mol^{-1}. If one includes the losses in entropy upon activation of the H_2 molecule, the Gibb's free energy of activation $\Delta G^{\neq}$ amounts to 25.8 kcal mol^{-1} (Figure 2, Table 1). The corresponding values for the protonation step leading from **2** to **3** are $\Delta H^{\neq} = 20.8$ kcal mol^{-1} and $\Delta G^{\neq} = 23.4$ kcal mol^{-1}. The comparison of the M06-L and the B2PLYP-D energies shows a difference of a few kilocalories per mole, with the M06-L energies being lower in all cases. A remarkable exception is the cleavage of the H_2 molecule in **TS1–2**, with the Gibbs free energy of activation rising from 25.8 kcal mol^{-1} (M06-L) to 32.0 kcal mol^{-1} (B2PLYP-D). As B2PLYP-D computations have repeatedly yielded very precise energies,[24] this is a hint that M06-L underestimates the barrier for H–H cleavage significantly.

The rotation of the N=NH unit of **2** about the Ru–N bond leads to the insignificantly less stable rotamer **2a** which also can be protonated resulting in the formation of **3a** by passing a barrier of $\Delta G^{\neq} = 22.2$ kcal mol^{-1}. Also the barrier for the transfer of the proton to the outer N atom of the N=NH unit

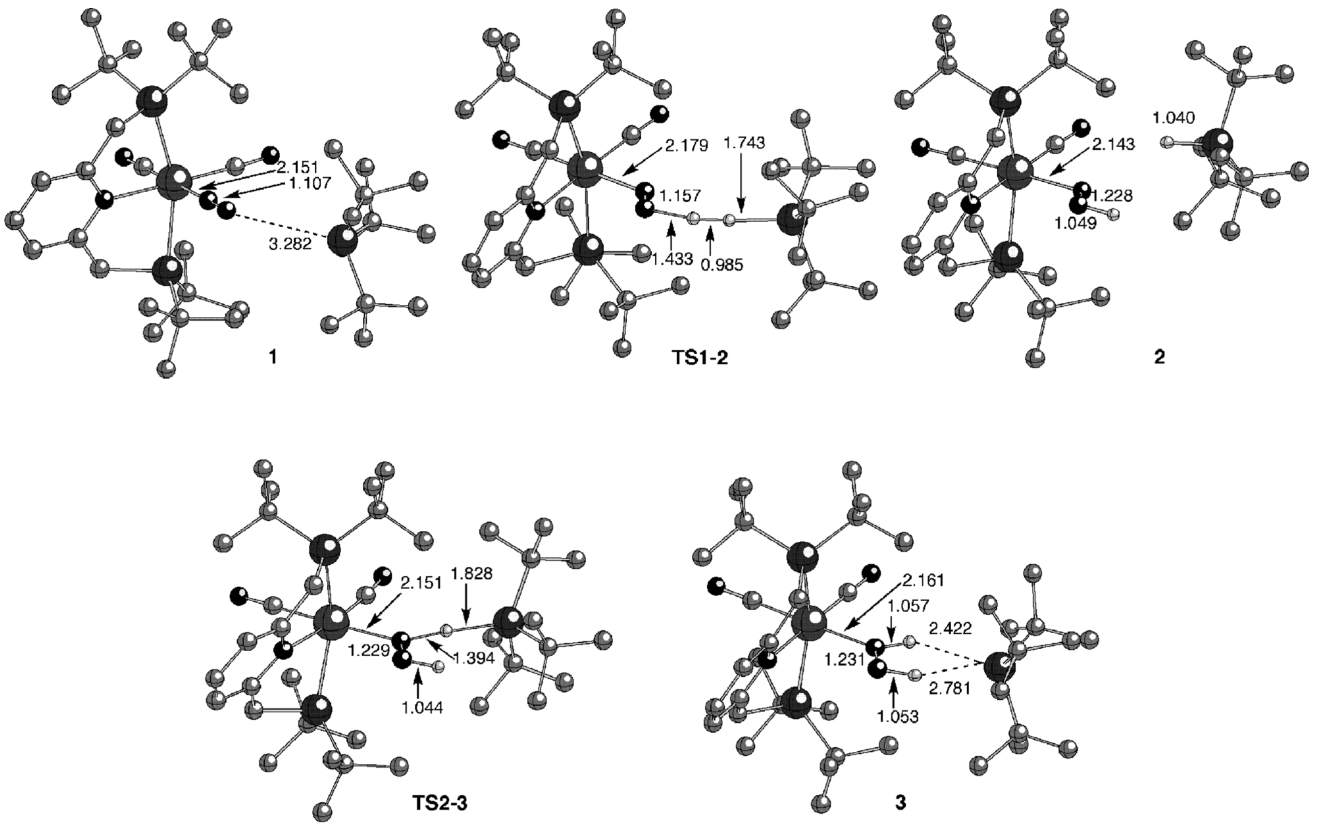
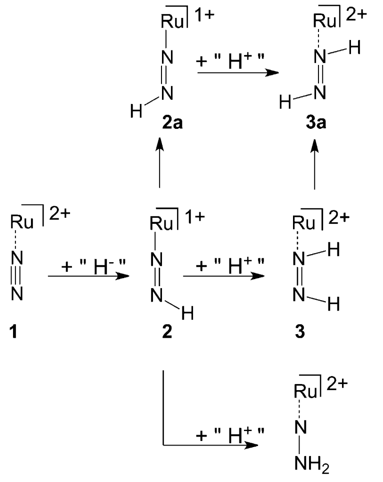


Figure 1. Calculated structures **1**–**3** with associated transition states and selected atom distances [Å]. Hydrogen atoms were omitted for clarity except for at the reactive centers.



Scheme 3. Complete scheme showing the transfer of both hydrogen atoms of the H_2 molecule. The base has been omitted for clarity.

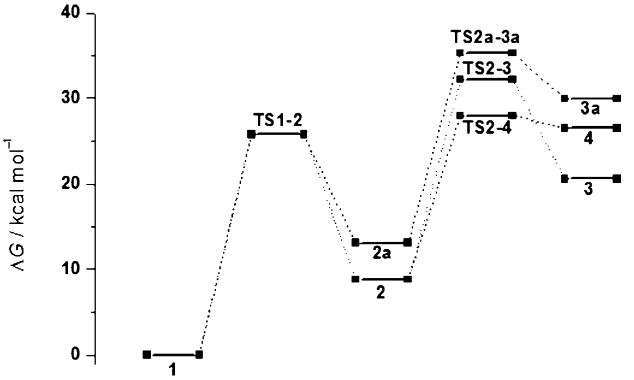


Figure 2. Energy profile (M06-L/def2-TZVP(ECP) of the reduction of **1** to **2** and to **3**, **3a**, and **4**.

of **2** yielding **4** is gratifyingly low ($\Delta G^{\neq} = 19.2\ \text{kcal mol}^{-1}$). These results prove that this novel mode of transferring molecular hydrogen onto metal-bound nitrogen can occur with low energy barriers. As compounds **3**, **3a**, and **4** are clearly endergonic, the back reaction to **2** and **2a** is, however, inevitable. With regard to the question whether **2** and **2a** can actually be synthesized, it should be pointed out that both the B2PLYP-D gas-phase barrier and the barrier obtained in THF solution are somewhat elevated ($\Delta G^{\neq}_{\text{Gas,B2PLYP-D}} = 32.0$, $\Delta G^{\neq}_{\text{THF,M06-L}} = 28.1\ \text{kcal mol}^{-1}$) relative to that obtained with M06-L in the gas phase, but suggest that **2** and **2a** will form and be present in the reaction mixture at temperatures between 100 °C and 200 °C. The replacement of N_2 in **1** by H_2 is possible as the geometry optimization of the corresponding H_2 compound yields the expected nonclassical hydride complex $[Ru(PNP)(CO)_2(H_2)]^{2+}$ (**5**). The reaction of **1** with H_2 to give **5** and N_2 has a Gibbs free energy of −1.8 and −4.6 kcal mol⁻¹ in the gas phase and in the solution phase, respectively, indicating both **1** and **5** to be present in an experimental system under reaction conditions (elevated reaction temperatures and pressures). The nonclassical H_2 molecule in **5** is not cleaved by the Lewis base.[25]

The activation and transfer of H_2 by heterolytic cleavage with the participation of a metal center has been evoked frequently in recent years to rationalize efficient organometallic hydrogenations.[26] We have shown here that this also is possible for the hydrogen transfer onto metal-bound nitrogen, without the necessity to coordinate the H_2 molecule at the metal center prior to reaction. This novel reaction type opens hithertho unknown low-energy pathways for nitrogen reduction.

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[25] Following the argument of a referee the results presented in this work also have been compared with results calculated for the very similar catalyst complexes $[Ru(PNP\mathit{i}pr)(CO)_2(N_2)]^{2+}$ and $[Ru(PONOP)(CO)_2(N_2)]^{2+}$ (PNP*i*pr = 2,6-bis(diisopropylphosphanylmethyl)pyridine; PONOP = 2,6-Bis(diisopropylphosphanyloxy)pyridine. The comparison shows that the activation barriers for the transfer of hydrogen onto the complex-bound N_2 molecule and the relative energies of the corresponding local minima are very similar in all cases. However, there is one important difference with regard to the replacement of N_2 in **1** by H_2: While the catalyst with the *t*Bu substituents allows for the

localization of complex $[Ru(PNP)(CO)_2(H_2)]^{2+}$ **5**, in the case of the catalysts with *i*pr substituents at the ligand the hydrogen molecule is directly cleaved by the Lewis base P*t*Bu$_3$, forming the ion pair $[Ru(PNP\textit{i}pr)(CO)_2(H)]^+$ $[HP(\textit{t}Bu)_3]^+$ **6**-*i*pr. The Gibbs free energy ΔG of the reaction of **1**-*i*pr with H_2 to give **6**-*i*pr and N_2 amounts to $-42.3\,\text{kcal}\,\text{mol}^{-1}$. This indicates that the desired transfer of hydrogen onto coordinated nitrogen is only possible when the catalyst complex bears *t*Bu substituents, which are bulky enough prevent the Lewis base from coming too close to the coordinated H_2 molecule, thus preventing the formation of **6**.

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