CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201002010

Lewis Acid Assisted Stabilization of Side-On Bonded N_2 in [Ru(NCN)]-Pincer Complexes—Computational Catalyst Design Directed at NH_3 Synthesis from N_2 and H_2

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The direct reduction of N_2 with H_2 to give NH_3 is one of the most challenging chemical transformations, as the N−N triple bond of dinitrogen is very stable and unreactive. The heterogeneously catalyzed ammonia synthesis from N_2 and H_2 (Haber–Bosch process) was developed more than a century ago and has been investigated in detail ever since.[1] In contrast, there is currently no molecular catalyst that is able to transform N_2 to NH_3 using H_2 as the sole reductant. In living systems, the fixation of N_2 and its transformation to NH_3 occurs at the FeMoCo-cofactor of nitrogenases, where metal-bonded N_2 reacts stepwise with protons (H^+) and reduction equivalents such as ferredoxin.[2] This biological reaction was complemented by an organometallic counterpart by Schrock et al. recently[3] and the catalytic cycle[4] as well as the influences of a variety of ligand structures were investigated theoretically in detail.[5] Stimulated by these findings we became interested in investigating the direct reduction of N_2 with H_2 in the coordination sphere of transition metals computationally[6] and recently identified complexes bearing pincer ligands as promising lead structures for this fundamental challenge.[7]

Albeit the ruthenium–pincer fragments allowed the construction of complete reaction pathways leading to NH_3 from N_2 and H_2 several severe limitations were identified that need to be overcome before these transformations could lead to an active catalytic cycle. The two most important are: 1) catalytic cycles can be accessed from ruthenium–pincer complexes only when the N_2 molecule is coordinated side-on to the metal and 2) the coordination of N_2 must occur *trans* to the pincer backbone. Thermodynamically, ruthenium–pincer complexes with end-on coordinated N_2 are much more stable than the side-on coordinated counterparts. Consequently one arrives at the question how a side-on bonded N_2 molecule could be stabilized in late transition metal pincer complexes in such a way that side-on coordination is energetically competitive or even superior to end-on coordination. Here we report on a novel approach to resolve this issue, which is based on a bifunctional activation of the N_2 molecule by a metal and a nonmetal center within a well-defined coordination sphere.

The principle of stabilizing a metal-bonded N_2 molecule by introduction of a second metal atom is well established. Three possible modes of how N_2 can be placed between or near two metal atoms are possible: side-on, side-on; end-on, end-on; and side-on, end-on. N_2 complexes relevant to N_2 fixation and activation with all three binding modes are known and in the past decade the groups of Fryzuk[8] and Chirik[9] have contributed a wealth of work in this field. With side-on, side-on complexes such as $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu^2, \eta^2,\eta^2\text{-}N_2)$ it was possible to transform N_2 to NH_3, by a stochiometric reduction.[10] These dinuclear zirconium compounds were studied by theoretical methods by the groups of Morokuma and Hirao, and their mode of action was elucidated.[11] Starting with bis-end-on bonded N_2 complexes no transformation of N_2 to NH_3 has been reported to the best of our knowledge.

Instead of using two transition metal centers for the fixation/activation of N_2 we reasoned that a Lewis acidic group within the ligand could play a stabilizing role. This leads to a new approach in which the center, at which the reduction is supposed to take place (i.e. the reactive center) is the transition-metal center of an organometallic complex (i.e. ruthenium), while the second (i.e. assisting center) is a Lewis acidic group (e.g. boron), which is part of one of the substituents of the pincer ligand. With this concept, one arrives at the general metal hydride structure **A** (Scheme 1).

The design of the architecture of structure **A** has to fulfil several criteria: First, the interaction between the coordinated nitrogen and the Lewis-acidic site must be strong enough

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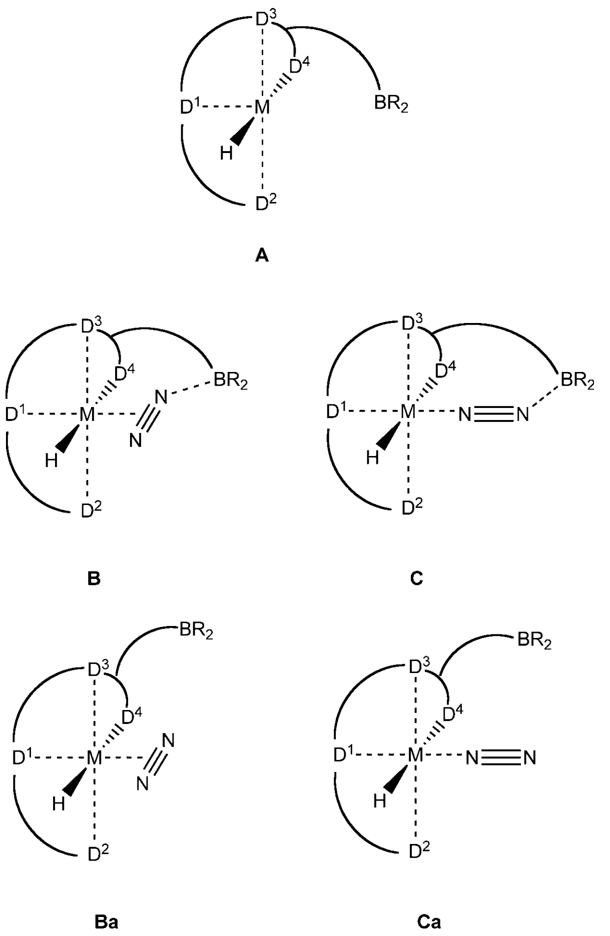
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002010.



Scheme 1. Generalized representation of catalyst **A** and associated N_2 complexes **B** and **C** showing the BR_2 rest as part of the pincer ligand. Depending on the choice of metal, the oxidation state and the choice of the group D^4, one or more of the donor atoms D^1–D^3 of the pincer ligand can be bonded covalently. Donor atoms D^1 to D^4 can but do not have to comprise the same element.

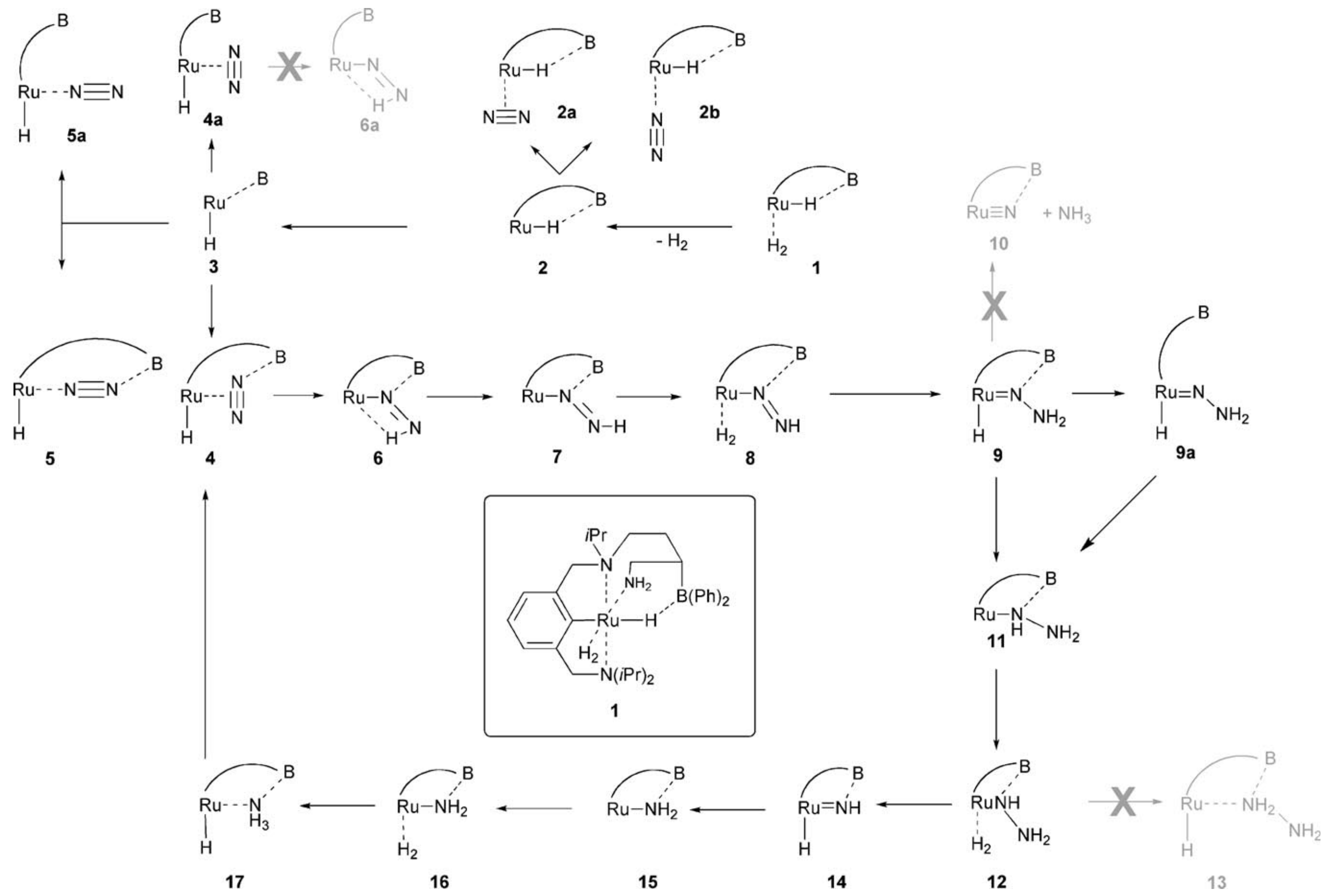
to make the bifunctional complexation (**B**, **C**) more stable than the open forms (**Ba**, **Ca**). Second, the side-on bonded nitrogen coordination in complex **B** has to be of similar or even higher stability than the end-on complex **C**. Finally, the coordination of N_2 must be directed *trans* to $\mathbf{D^1}$, if this is the anionic anchor group of the pincer ligand. To investigate this concept, we designed the hypothetical ligand depicted in the potential precursor **1** which served as a starting point for the computational study (Scheme 2).

As the catalyst is a metal hydride, the H center can be transferred during the reaction onto N_2 and be regenerated by uptake of H_2 via coordination at the metal center with concomitant splitting of the H_2 in a σ-bond metathesis in the following reaction(s).

As hydrides bonded at metal centers can in principle rearrange between available coordination sites it must also be taken into account that the hydride in **A** can move from the *cis* to the *trans* position. If it resides *trans* to the ligand backbone, the *cis* position is available for N_2 coordination. This is an important issue, as N_2 will most likely bind end-on at this site, and in this way stable, yet unreactive complexes would be generated (and were localized in this work, vide infra). This issue can only be resolved by introducing sterically demanding substituents at the apical donor centers D^2 and D^3 of the pincer ligand, which are occupying the area in the proximity of the *cis*-coordination site and in this way prevent N_2 coordination. These substituents in turn must leave enough space to enable classical hydrides and dihydrogen molecules to occupy the *cis* position, as the reaction otherwise could not proceed. This issue of shielding the *cis* position for N_2 but not for H_2 using appropriately designed substituents at the pincer nitrogen centers apart from simple isopropyl groups is not addressed here and is postponed for future work. Here we report on the computationally obtained results of the catalytic cycle of a system using **1** as the catalyst precursor as it is instructive for the initial evaluation of this concept (Scheme 2).

Complex **1** comprises a ruthenium center in the formal oxidation state +2, a modified NCN pincer ligand (NCN = 2,5-bis(dimethylaminomethyl)benzene),[12] a hydride center covalently bonded *trans* to the pincer backbone, and a nonclassical hydride molecule bonded coordinatively *cis* to it (Scheme 2). The parent NCN pincer ligand was modified and thus carries two isopropyl groups at the amino-nitrogen atom in the D^2 position, with the N atom in the D^3 position being substituted with one isopropyl group and one $(CH_2)_3$ chain linked to a a CH_2-NH_2 group and a $B(Ph)_2$ group. The amino group coordinates at the ruthenium center in the D^4 position and blocks the coordination site.[13]

The isomer of **1**, in which the hydride center is located *cis* to the pincer backbone with the H_2 unit being *trans* to it, does not exist on the hypersurface as repeated attempts to optimize such a local minimum failed and in all cases led to structure **1**. To generate the catalytically active species the H_2 molecule is cleaved from the complex in an endergonic reaction (5.2 kcal mol^{-1}) and yields **2** (we refer to ΔG and $\Delta G^{\neq}$ values throughout the text). As was mentioned before, N_2 can add to **2**, yielding complexes **2a** and **2b**. While the formation of the side-on bonded **2a** is uncritical due to its endergonic formation (6.6 kcal mol^{-1}), complex **2b** is a strongly exergonic compound (−19.2 kcal mol^{-1}) and upon generation would prevent any further reactions making appropriate shielding components at the ligand inevitable (vide supra). To enable the desired reaction the hydride center in **2** needs to rearrange from the *trans* to the *cis* position by passing over transition state **TS(2–3)** with an activation barrier of 24.5 kcal mol^{-1}. N_2 can add to the resulting complex **3**, which is 9.8 kcal mol^{-1} less stable than **2**, yielding **4, 4a**, **5**, and **5a**. All four compounds were located. Although the calculations show structure **5a** to be the most stable of these four competing complexes, structure **4** is only less stable than **5a** by 3.8 kcal mol^{-1} (Figure 1). The stabilization by the B–N interaction is significant and amounts to 6.1 kcal mol^{-1}, as can be deduced from the energy differences of **4** and **4a**. The comparison of **4** and **5** shows **5** to be 2.4 kcal mol^{-1} less stable than **4**, indicating that the B–N interaction in **5** is different and weaker than that in **4.** This is



Scheme 2. Valence bond structure of **1** and simplified representations of compounds calculated for the associated catalytic cycle. For complexes shown in gray, the corresponding transition states could not be localized.

most likely the result of the carbon chain of the side arm being slightly too short for an optimum interaction, which compensates in part for the gain in energy. In an experimental system one would expect **4** to be present along with **5** and **5a**, which for the first time creates a situation in which a side-on bonded N_2 molecule is stabilized well enough to be able to react with the metal-bonded hydrogen center. Although **4a** might not play a role in an experimental system, a detailed analysis was made for a transition state leading from **4a** to **6a** to exclude the possibility of a reaction pathway in which the boron substituent does not bond to the coordinated N_2 molecule. Despite several attempts such a transition state could not be localized, indicating pathways of this kind not to exit. A transfer of the hydride in **5a** to the terminal N atom of the N_2 molecule is highly unlikely as was shown before.[7]

The N−N distance of the coordinated N_2 in **4** is 1.169 Å, indicating a significant amount of activation. When the boron center is not interacting with the N_2 molecule (**4a**) the N−N distance is notably shorter (1.142 Å), indicating that the B−N interaction in **4** is of significant strength (Figure 1). In **5** the N−N bond is 1.157 Å long, reflecting a significant amount of activation as well, however, to a lesser extent than in **4**. The least activation is found in **5a**, as the N−N bond is only 1.135 Å long. The B−N distance in **4** and **5** amount to 1.609 and 1.690 Å, respectively, reflecting also the lower degree of attractive interaction for the end-on complex **5**.

We then investigated the catalytic cycle for NH_3 formation and found that a representative amount of stationary points could be localized, yielding a closed cycle (Figure 2). The transfer of the hydride center of **4** onto the N_2 molecule is possible as the corresponding transition state **TS(4–6)** could be located and the activation barrier for this reaction is 35.2 kcal mol^{-1}. Complex **6** is less stable than **4** by 28.6 kcal mol^{-1}. To exclude the possibility that the reaction from **4** to **6** takes place with the boron center not interacting with the nitrogen atom of the N_2 molecule, the BR_2 side arm was rotated away (like in **4a**) and the corresponding transition state was searched for. Interestingly this transition state could not be localized, which is in contrast to the behavior of the [Ru(POP)] pincer complexes investigated earlier.[7] The rearrangement of the hydrogen position in **6** to **7** requires an activation barrier of 19.8 kcal mol^{-1}. The addition of H_2 to **7** to give **8** is slightly endergonic (2.6 kcal mol^{-1}). The activation barrier for the transformation of **8** to **9** is 12.8 kcal mol^{-1}, and **9** is more stable than **7** by 8.4 kcal mol^{-1}. If the hydride center in **9** is transferred to the NH_2 group of the N-NH_2 moiety, one molecule of NH_3 would be generated together with ruthenium nitride **10**. It

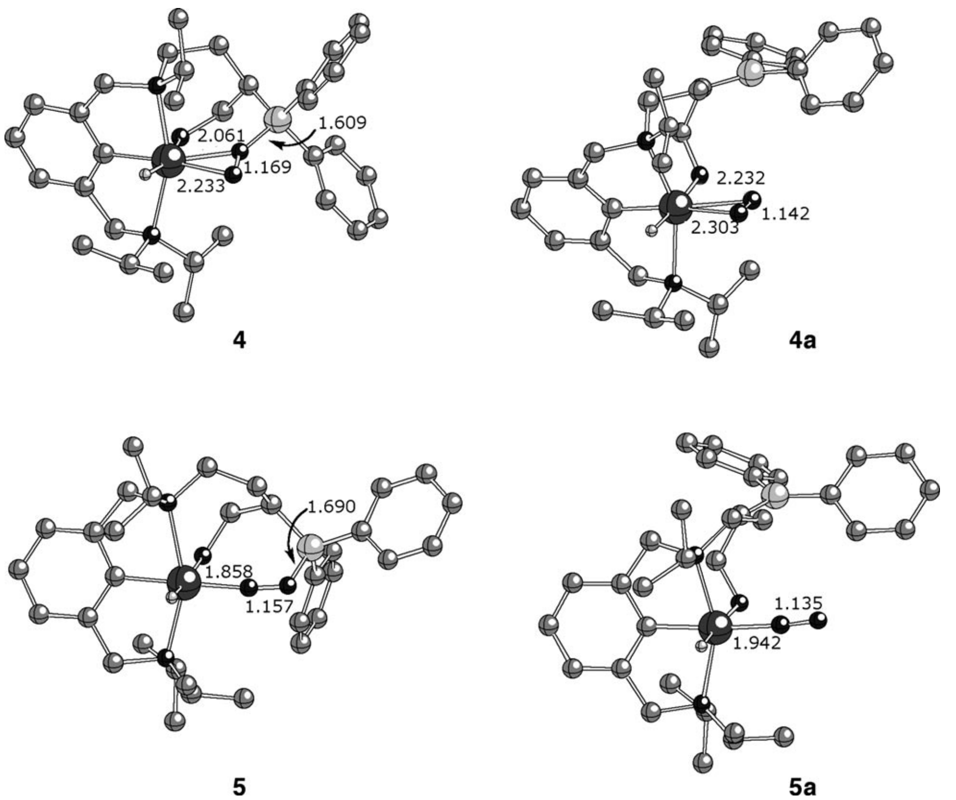


Figure 1. Calculated structures **4**, **4a**, **5**, and **5a** with selected interatomic distances [Å] (except for the metal-bound hydride, all other hydrogen centers were omitted for clarity). Balls in decreasing size represent elements Rh, B, C, N, and H, respectively.

was not possible to locate a transition state for this reaction. However, **10** was localized and **10**/NH_3 is more stable than **9** by 0.6 kcal mol^{-1}.

The reaction from **9** to **11** deserves special consideration, as the activation barrier amounts to 58.3 kcal mol^{-1}, clearly indicating that this reaction is not possible in practice. As this is the largest barrier calculated for this cycle, it was investigated whether an alternative reaction would open a path lower in energy. Therefore the boron-containing side arm was rotated away from its position in the vincinity of the NH_2 group of **9**, generating **9a**, in which there is no interaction between the NH_2 group and the boron center. Interestingly **9a** is a highly endergonic compound (59.6 kcal mol^{-1}) and will not form in an experimental system. However, the activation barrier for the reaction from **9a** to **11** is much lower (12.1 kcal mol^{-1}) than the one for the reaction from **9** to **11** (vide supra). The addition of H_2 to **11** yields **12** in an exergonic reaction, in which **12** is 6.2 kcal mol^{-1} lower in energy than **11**/H_2. The transformation of **12** to **13**, in which one molecule of hydrazine is obtained, is not possible as the corresponding transition state could not be localized. The

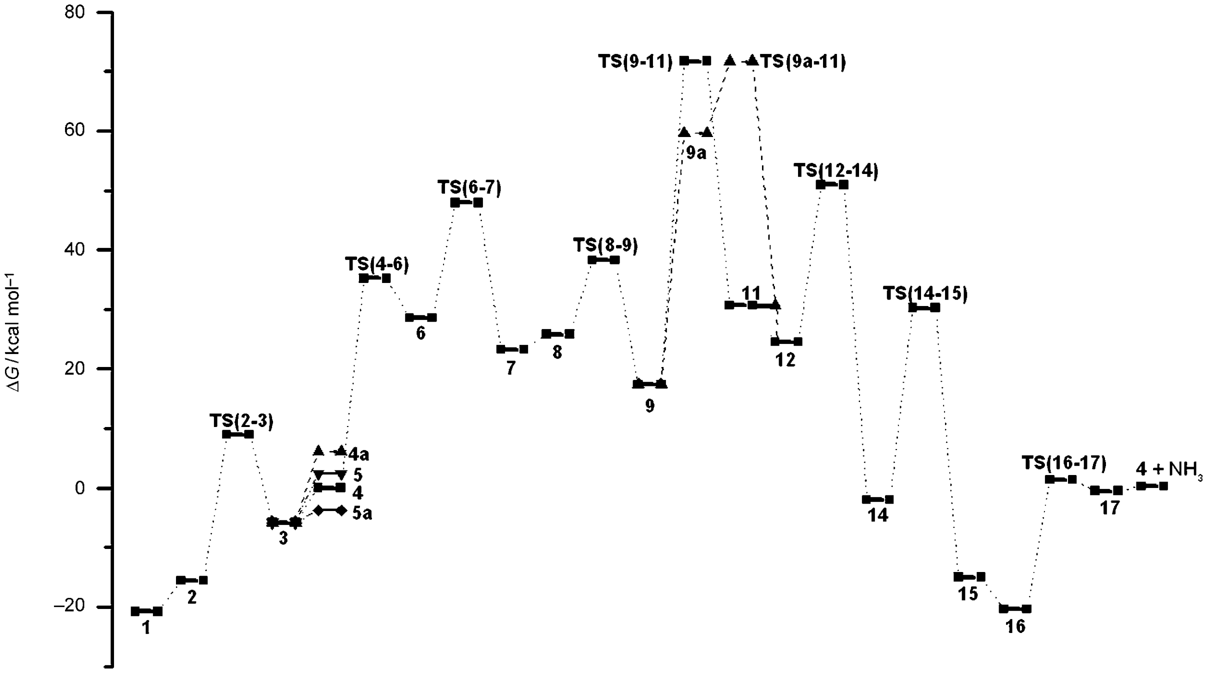


Figure 2. Energy profile for most of the compounds calculated in this work.

hydrazine complex **13** is less stable than **12** by 13.2 kcal mol^{-1}.

If instead the H_2 unit in **12** is split in such a way that one hydrogen center is transformed to the NH_2 group of the NH–NH_2 unit, the first molecule of ammonia is formed by passing transition state **TS(12–14)** with an activation barrier of 26.5 kcal mol^{-1}. The imide **14** is significantly more stable than **11** by 13.4 kcal mol^{-1}. The reaction of **14** to **15** is possible with an activation energy of 32.3 kcal mol^{-1} and the amide **15** is formed in an exergonic reaction. A H_2 molecule adds to **15**, liberating 5.4 kcal mol^{-1} of energy and resulting in **16**, which reacts to **17** by passing transition state **TS(16–17)** with an activation barrier of 21.8 kcal mol^{-1}. During this reaction the second molecule of NH_3 is formed, and complex **17** is less stable than **15** by 19.9 kcal mol^{-1}. Releasing NH_3 from **17** and replacing it with N_2 to yield **4** and NH_3 is a process, which is endergonic by 0.8 kcal mol^{-1}.

Clearly, some activation barriers in the cycle are too high to make the [Ru(NCN)] catalyst system investigated here a potential candidate for practical realization of NH_3 synthesis. However, the interaction of the Lewis acid and the side-on coordinated N_2 yields a significant stabilization relative to the open end-on form, which makes it plausible to assume that this approach is worth investigating for a variety of other pincer ligands/complexes. As was pointed out, it would be necessary though to shield the *cis* position of the pincer complex from N_2 coordination by introducing sterically demanding, yet not too demanding substituents, as the site needs to be available for the addition of H_2. We have already shown earlier that the pincer ligand has a drastic influence on the activation barriers of hydrogen-transfer reactions onto coordinated N_2. Therefore it is reasonable to assume, that the investigation of other pincer ligands and the inclusion of solvent effects could lead to a catalyst that allows the reaction to proceed with much lower activation barriers.

We showed here for the first time that appropriately modified pincer ligands in ruthenium hydride complexes enable the stabilization of side-on coordinated N_2 molecules by attractive interaction with a Lewis acidic boron substituent. Such complexes were used as the starting point for the calculation of a catalytic cycle, which satisfyingly could be computed. This demonstrates that the reaction is possible in general using such catalysts. However, at certain stages of the reaction, single activation barriers rise to unreasonable high values preventing practical realization. Further computational studies to elucidate potentially active catalysts are underway.

Computational Details

All calculations were carried out with the Gaussian09 program.[14] All local minima and transition states were optimized by using the B97-D functional[15] together with the def2-TZVP basis set and associated ECP for the ruthenium center[16] and the density fitting approximation switched on (set to auto). The nature of all stationary points was verified by frequency calculations proving the existence of zero and one imaginary frequency for minima and transition states, respectively. To evaluate the energies by an alternative functional corrected for dispersion interactions single-point energy calculations were carried out using the same def2-TZVP basis set and ECP with the M06[17] functional. The B97-D- and M06-energies are compared in Table S1 in the Supporting Information. While some differences can be noted between the M06 and the B97-D-energies the general conclusions do not change. Free enthalpies and Gibb's free energies obtained with the B97-D functional include zero-point energy corrections as well as thermal corrections for $T = 298.15$ K and $p = 1$ atm. Tables listing the energies obtained are included in the Supporting Information (see Table S2) as well as Cartesian coordinates of all compounds. In the main text we refer to B97-D obtained ΔG values unless noted otherwise.

Acknowledgements

Generous allocation of computer time by the Rechenzentrum of RWTH Aachen University is gratefully acknowledged. This work was supported in part by the Cluster of Excellence "Tailor-Made Fuels from Biomass" (TMFB), which is funded by the Excellence Initiative of the German federal and state governments to promote science and research at German universities.

Keywords: computational chemistry · density functional calculations · homogeneous catalysis · ammonia synthesis · pincer complexes

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Received: July 16, 2010