Inorganic Chemistry

· Communication

Theoretical Study of Catalytic Dinitrogen Reduction under Mild Conditions

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Density functional theory results on key steps of Schrock's catalytic cycle are presented. The quantum chemical modeling of the dinitrogen-reducing reaction steps is conducted without simplifying the bulky HIPT [HIPT = 3,5-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$] substituents at the triamidoamine ligand.

Chart 1

    In 2003, Yandulov and Schrock[1,2] synthesized the first dinitrogen-reducing transition-metal complex that works catalytically under ambient conditions. The active catalyst is a mononuclear molybdenum complex with a tetracoordinate triamidoamine [(TerN)$_3$N]$^{3-}$ chelate ligand (Chart 1). It represents a landmark in dinitrogen fixation research.[3] The substituent at the amide nitrogen atoms of the triamidoamine ligand is Ter = HIPT = 3,5-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$.[4,5] Other bulky substituents were investigated as well but showed reduced efficiency.[6] Many intermediates of Schrock's catalytic cycle were isolated, and a wealth of experimental data were provided. However, insight into the energetics of the molecular processes was still lacking, which was the starting point for this work.

    The main aim of this density functional theory (DFT) study is to uncover the thermodynamic boundary conditions for dinitrogen reduction under mild and ambient conditions (see the Supporting Information for information on the DFT methodology: BP86/RI/TZVP, SVP). We shall provide theoretical results for observables that are not directly accessible or not known experimentally such as reaction energetics of certain elementary steps and structures not yet isolated in an experiment. Schrock et al. note that the catalytic
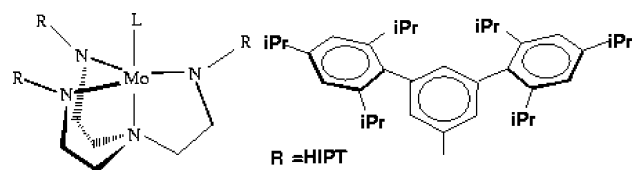
reaction is extremely finely balanced[7] and that relatively subtle steric and electronic variations of the [(TerN)$_3$N]$^{3-}$ ligand produce profound changes in the efficacy of the catalytic reduction of dinitrogen to ammonia.[6] For these reasons, we shall not simplify the triamidoamine chelate ligand of the complex but analyze the molybdenum complex with the full [(HIPT-N)$_3$N]$^{3-}$ chelate ligand.

    Cao et al.[8] presented some DFT results for a small model of Schrock's complex and Studt and Tuczek[9] for a very small model of the [(HIPT-N)$_3$N]Mo complex, where the bulky HIPT substituents were all substituted by hydrogen atoms. We carried out DFT calculations,[10] which showed that such models are oversimplified and do not reliably reproduce the energetics of all steps of the Schrock cycle (this is discussed in detail in the Supporting Information). Studt and Tuczek[8] presented energies relative to the proton source and to the reductant. We proceed in a different fashion and prefer to give the intrinsic reaction energies as obtained for the isolated complexes, although their absolute value may become very large.

    We concentrate on the most important steps: The first step comprises the ligand exchange at the end of the cycle, i.e., the dissociation of NH$_3$ and the addition of N$_2$. Figure 1 depicts all elementary reaction steps that may become relevant for the NH$_3$/N$_2$ exchange step. The experimental fact that [Mo]NH$_3^+$ is more difficult to reduce than [Mo]-N$_2^+$ is well reproduced by the calculation of the adiabatic electron affinity for [Mo]NH$_3^{+/0}$ and [Mo]N$_2^{+/0}$. Experimentally, the conversion of [Mo]NH$_3^+$ to [Mo]N$_2^+$ appears to

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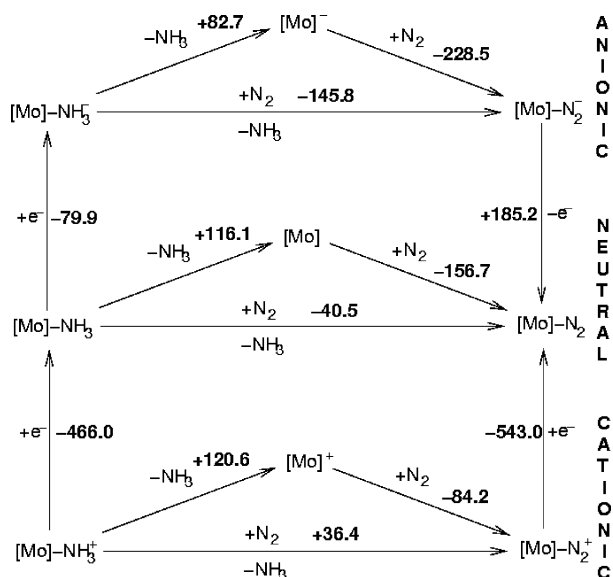(10) Le Guennic, B.; Kirchner, B.; Reiher, M. *Chem.—Eur. J.* **2005**, in press. (DOI: 10.1002/chem.200500935).

Figure 1. Calculated reaction energies (in kJ/mol) for all possible pathways of the initial NH_3/N_2 exchange.

Figure 2. Three possible paths of the first and most crucial proton and electron transfer onto coordinated N_2.

be slower by at least 1 order of magnitude than the conversion of $[Mo]NH_3$ to $[Mo]N_2$. The calculations corroborate these findings in view of the ligand dissociation and association energies given in Figure 1, though barrier heights were not calculated. While dissociation of the σ-donating NH_3 is more favorable for the neutral and most favorable for the anionic metal complex when compared to the cationic complex, the opposite trend is observed for the π-accepting dinitrogen ligand.

On the basis of the reaction energies in Figure 1, we find two routes of the mechanism especially favorable for the ligand-exchange step. In the presence of a strong reductant, the following elementary steps may become possible (path 1):

$$[Mo]NH_3^+ \rightarrow [Mo]NH_3 \rightarrow [Mo]NH_3^- \rightarrow [Mo]^- \rightarrow [Mo]N_2^-$$

If, however, reduction of the neutral ammine complex cannot be achieved, an alternative route will be the following path 2:

$$[Mo]NH_3^+ \rightarrow [Mo]NH_3 \rightarrow [Mo] \rightarrow [Mo]N_2$$

Both steps are consistent with experimental findings that different routes for the catalytic cycle are possible.[7] The question is whether a substitution of NH_3 by N_2 is favored over the alternative dissociation of NH_3 and subsequent addition of N_2 can be studied by investigation of the structure of the metal fragment [Mo]. In principle, four reaction channels are possible, but only three are viable because a third side-entrance channel appears to be always blocked for sterical reasons (see also the Supporting Information). The two remaining side-entrance channels are of similar size when compared to the top-entrance channel. However, any ligand approaching or leaving the metal center through the side-entrance channels needs to rearrange in the cavity for proper coordination. In the case of the top-entrance channel, an elimination–addition mechanism is the only reasonable
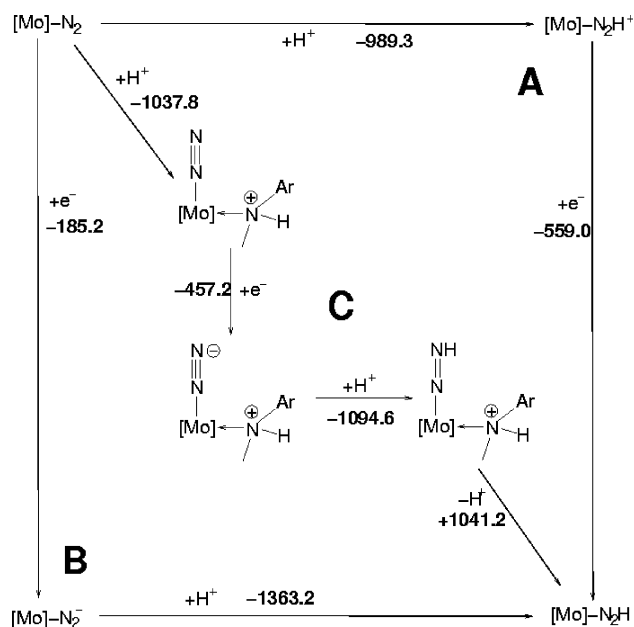
mechanism owing to the small size of the channel and the cavity. A substitution step appears to be only likely in the case of a side-entrance attack, though it involves a reorientation by rotation for proper coordination when the N_2 ligand approaches the metal center from the side.

The transfer of the first proton and electron onto the coordinated N_2 ligand is the crucial step in any dinitrogen activation scheme. Schrock et al. proposed three possible activation paths, A–C, which we also considered (cf. Figure 2).

For the assessment of the energetics of these paths, the calculated protonation and reduction energies are given in Figure 2. Experimentally, path B was considered more likely than path A, while path C was considered tentative owing to the absence of additional characterization. In the calculations, path B starts with a reduction of the dinitrogen complex $[Mo]N_2$, which is exothermic by -185.2 kJ/mol. Oxidizing the (isolated) reductant decamethylchromocene present in the experiment would, however, require 467.3 kJ/mol (BP86/RI/TZVP), so path B does not appear to be likely at first sight (see also the electron affinities given in Figure 1 for comparison). For simple electrostatic reasons, the addition of a proton prior to reduction is very favorable. If differential solvation of all species could be reliably calculated, path B could still turn out to be likely. Interestingly, the protonation of the amide nitrogen atom of the chelate ligand in path C is about 40 kJ/mol more favorable than direct protonation of the terminal nitrogen atom of the N_2 ligand (path A). Also, the following reduction step of path C is thermoneutral by $467.3 - 457.2 = 10.1$ kJ/mol if we compare it to that of isolated decamethylchromocene. After the complex was prepared by transformation of one amide of the chelate ligand into an amine, the protonation of the terminal N of dinitrogen is now favorable by more than 105 kJ/mol when compared to path A. Thus, path C appears to be a viable route for

dinitrogen activation, provided that the protons can be transferred onto the amide nitrogen atoms.

With respect to the important N−N bond-breaking step, which one would consider to be a crucial step in dinitrogen activation, we found that NH_3 immediately dissociates from the nitride complex once the cationic complex $[Mo]NNH_3^+$ is reduced. Schrock et al. note that, although the nitride [Mo]N is a plausible and catalytically competent intermediate accessible under catalytic conditions, the actual mechanism and the precise nature of $[Mo]NNH_3^+$ remain to be elucidated. The cationic complex is stable (see the Supporting Information) and exhibits a N−N bond length of 147 pm. It liberates the terminal ammonia moiety when an electron is added to the complex. The energy gain may be estimated by direct comparison with the reductants used in the experiment: The ionization energies of (isolated) cobaltocene, decamethylchromocene, and decamethylcobaltocene are calculated to be 504.2, 467.3, and 439.5 kJ/mol, respectively. (For a better understanding of these intrinsic ionization energies, we stress that decamethylcobaltocene is a strong reductant.) With an electron affinity of −676.9 kJ/mol for $[Mo]NNH_3^+$, we obtain reaction energies for the reduction of $[Mo]NNH_3^+$, which leads to N−N bond rupture, of −172.7, −209.6, and −273.4 kJ/mol, respectively. However, the main portion of these energies stems from the electron affinity of the cation. For the sake of completeness, we estimate that the dissociation of NH_3 from the cationic complex $[Mo]NNH_3^+$ would require only 80.6 kJ/mol.

The subsequent protonation−reduction steps in the Schrock cycle are calculated to be more energetically favorable when they occur later in Schrock's cycle: It is easier to transfer a proton and an electron onto [Mo]NH than onto [Mo]N or even onto [Mo]NNH (see the Supporting Information for protonation energies). However, note that each proton-transfer step path C of Figure 2, which utilizes protonation of an amide nitrogen, might also represent a viable route, especially for facilitating activation of [Mo]NNH.

In conclusion, we have presented quantum chemical results for the electronic energies of important intermediates in Schrock's catalytic dinitrogen reduction cycle without using simplified models for the chelate ligand. Our results complement the wealth of experimental data, which was lacking appropriate thermodynamic information, and rule out certain reaction paths.

Supporting Information Available: A detailed description of the DFT methodology as well as additional energetical data and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0517568