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Density Functional Study of N_2 Activation by Molybdenum(III) Complexes. Unusually Strong Relativistic Effects in 4d Metal Compounds

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All-electron generalized-gradient density functional (DF) calculations have been carried out on both the nonrelativistic and relativistic levels to address the mechanism of N_2 cleavage by L_3Mo(III) complexes. The reaction features computed for the model reactants with L = NH_2, NMe_2, and Me are compared to the recently published values for the $(H_2N)_3Mo$ derivative obtained with the help of the effective core potential (ECP) DF method and to the experimental data reported for the reaction of N_2 with $(RArN)_3Mo$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$). Despite a qualitative agreement between the reaction parameters of the present relativistic and the previous ECP DF calculations, some important quantitative differences are found, like a lower activation barrier by more than 10 kJ mol^{-1} and a higher overall reaction exothermicity by about 80 kJ mol^{-1}. The influence of the electronic and steric properties of the ligands L on the parameters of the cleavage reaction has been analyzed. The Mo(III) trialkyl complexes, at least those with small ligands, are predicted to scissor N_2 molecules less efficiently than the triamido derivatives. The relativistic effects, which are unusually large for 4d metal compounds, have been calculated and are attributed to the exceptionally strong Mo≡N bonds.

Introduction

Recently, a fascinating reaction has been discovered whereby under mild conditions dinitrogen is cleaved by the three-coordinate Mo(III) complex $(ArRN)_3Mo$, **1** (R = $C(CD_3)_2Me$, Ar = 3,5-$C_6H_3Me_2$, and Me = CH_3, methyl) leading to the $(ArRN)_3Mo{\equiv}N$ product, **1′**.[1] This discovery has benefited from the existence of stable alkyl,[2] amide,[3] and alkoxide[4] complexes of the type L_3MoN with a triply-bonded nitrogen atom. The formation of such a strong bond with nitrogen is an important prerequisite to thermodynamically allow the cleavage of one of the strongest known bonds, N≡N, which exhibits a dissociation energy as large as 942 kJ mol^{-1}.[5] This novel mode of nitrogen fixation[6−8] by means of a direct cleavage of N≡N at the expense of forming two Mo≡N bonds[1] raised a number of fundamental questions ranging from the detailed understanding of the reaction mechanism to the suggestion of other reactants which would induce the scission of dinitrogen perhaps more efficiently.

Some of these questions were addressed by a density functional (DF) investigation employing a relativistic effective core potential (ECP) approach.[9] In particular, the cleavage reaction mechanism was explored for the model reactants, L_3Mo, with L = H, Cl, and NH_2, where only the latter complex mimicked the electronic features of the experimentally studied systems with significantly bulkier amide ligands. The dinitrogen cleavage reaction path was calculated to be thermodynamically and kinetically favorable only for the reactant $(H_2N)_3Mo$, **2**, but not for the moieties H_3Mo or Cl_3Mo. This different behavior was assigned to the stronger π-donating ability of the NH_2 ligand, which “increases the electron density in the metal d_π orbitals and consequently makes the Mo−N bond stronger, the N−N bond weaker, and the reaction $L_3MoN_2MoL_3 \rightarrow 2NMoL_3$ more exothermic”.[9] An important prediction of those DF calculations was that the tungsten complex, $(H_2N)_3W$, should scissor N_2 molecules even more efficiently than the molybdenum analog.

Here, we report on the results of the DF calculations undertaken to further elucidate the details of the mechanism of dinitrogen cleavage by three-coordinate complexes of Mo(III). For this purpose, the computed reaction path of N_2 cleavage by $(H_2N)_3Mo$ was compared with those for (i) $(Me_2N)_3Mo$, **3**, better resembling both the electronic and steric features of the experimentally studied reactant $(ArRN)_3Mo$,[1] and (ii) the moiety $(H_3C)_3$-Mo, **4**, employed to mimic the reactivity of experimen-

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Table 1. Characteristic Energy Changes (kJ mol^{-1}, Negative Values Indicate an Exothermic Process) of the N_2 Cleavage Reaction $2L_3Mo + N_2 \rightarrow 2L_3Mo{\equiv}N$ Calculated by Nonrelativistic (nrel) and by Relativistic[a] (rel) DF Methods: Conversion of IM into the Products (P), ΔE(IM→P); Barrier toward the Corresponding Transition State[b] (TS), ΔE(IM→TS)[c]

	NH_2		NMe_2		Me	
ligand L	nrel	rel	nrel	rel	nrel	rel
ΔE(R→IM)	−299	−295 (−226)	−316	−267	−320	−312
ΔE(IM→P)	−17	−95 (−86)	−32	−128	+91	+21
ΔE(IM→TS)	134	75 (87)	133	58	195	

[a] Computed for the structures optimized at the nonrelativistic level of theory. [b] The TS energy and geometry estimates are based on a stepwise variation of the N−N distance (see Figure 2). [c] For L = NH_2, the results of the relativistic effective core potential DF calculations[9] are also displayed in parentheses for comparison.

tally characterized alkyl complexes of Mo(III).[2] Another aspect of the present work is the delineation and analysis of the relativistic effects on the potential energy surface of the reaction under study. This issue was considered based on the advantage of the all-electron linear combination of Gaussian-type orbitals (LCGTO)-DF method to compute and compare the relativistic and nonrelativistic total energies of the reactants, intermediates, transition-states species, and products of the reaction. It will be shown that the relativistic effects, usually being of a subordinate importance for 4d metal compounds,[10−12] become crucial for a proper description of the exothermicity and the activation barrier of reactions involving the formation or breaking of such a strong bond as Mo≡N.

In the following, the reactant species L_3Mo will be labeled by bold arabic figures, ***n***, as has been already introduced. The corresponding product moieties L_3MoN will be referred to as ***n′***, and the notation ***n′***−***n′*** will be used to identify the reaction intermediates $L_3MoN_2MoL_3$.

Computational Details

A detailed description of the LCGTO-DF cluster method used here has been given elsewhere.[13,14] A gradient-corrected exchange-correlation functional suggested by Becke[15] and Perdew[16] (BP) was applied self-consistently, taking spin-polarization into account. The relativistic effects on the electronic structure and the total energy were calculated with a scalar-relativistic variant of the LCGTO-DF method,[11,17] using geometries optimized at the nonrelativistic level of theory. Test calculations showed that a geometry reoptimization at the relativistic level leads only to a small energy gain, 3 and 2 kJ mol^{-1} for **2** and **2′**, respectively. A relativistic geometry reoptimization of the intermediate (IM) and transition state (TS) complexes **2′**−**2′** resulted in the activation barrier differing by less than 1 kJ mol^{-1}, compared to the value in Table 1 obtained for the nonrelativistic geometries. A relativistic contraction of the Mo−NH_2 bond of the TS **2′**−**2′** and of the product **2′** by about 0.02 Å has been computed. Spin−orbit effects were neglected in all calculations. Although these interactions are likely to be involved in the spin changes that occur during the cleavage reaction, they are not expected to significantly affect the relative energies of 4d metal compounds if one takes the atomic spectra of the 4d elements as an indicator.[18]

Relatively large basis sets of triple-zeta quality or better have been employed. For Mo, a (17s11p8d) orbital basis set[19,20] was augmented by diffuse functions to (18s13p8d) and contracted in a generalized fashion to [8s6p4d]. Orbital basis sets of the type (9s5p1d) → [5s4p1d][21,22] and (6s2p) → [3s2p][21] were used for C, N, and H atoms, respectively. The two auxiliary basis sets employed in the LCGTO-DF method to represent the electron charge density and the exchange-correlation potential were constructed from the orbital exponents in a standard fashion.[13]

Geometries were optimized automatically using analytical energy gradients. Transition state geometries have been obtained in a stepwise fashion, considering the N−N distance as a reaction coordinate. This procedure implies that the located stationary point is characterized by only one imaginary frequency calculated under the given constraints. The following symmetry constraints were applied: C_{3v} or C_3 for the reactants $(R_2N)_3Mo$ and the products $(R_2N)_3MoN$; D_{3d} (linear Mo−N−N−Mo moiety) or C_{2h} (accounting for a possible bending of Mo−N−N−Mo) for intermediate and transition state complexes $(R_2N)_3MoNNMo(NR_2)_3$. Binding energies A−B were computed with respect to the calculated ground states of the fragments A and B. No correction has been applied to eliminate the small basis set superposition error. Harmonic vibrational frequencies were derived from the force constants computed numerically within a finite difference approach.

Results and Discussion

The cleavage of N_2 by the complex $(ArRN)_3Mo$, **1**, to produce $(ArRN)_3Mo{\equiv}N$, **1′**, has been proposed to proceed via the purple paramagnetic intermediate **1′**−**1′** with a linear MoNNMo unit.[1] Indeed, a subsequent characterization of the intermediate by EXAFS[23] confirmed this prediction. The conversion of the species **1′**−**1′** to **1′** has been found to take place in an inert solvent via a slow first-order reaction, with a half-life of 35 min at 30 °C, forming the rate-limiting step of the scissor reaction.[1] Below, we shall present both the structural and energetic parameters calculated with the help of the LCGTO-DF method for the reactants, intermediates, transition state complexes, and products of the dinitrogen cleavage reaction mediated by three different model complexes L_3Mo, which are exemplified in Figure 1 by the $(Me_2N)_3Mo$ species.

$2(H_2N)_3Mo + N_2 \rightarrow 2(H_2N)_3MoN$ Reaction. This system represents the simplest model of the prototype reaction.[1] The calculated energetics of the elementary

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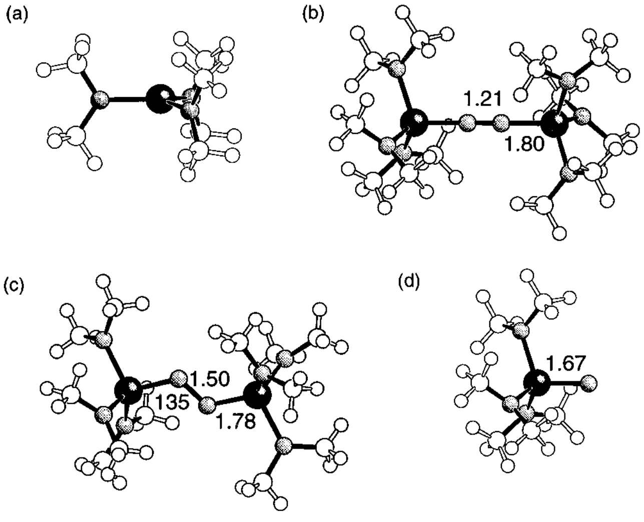

Figure 1. SCHAKAL[24] representation of the calculated structures of the following complexes, characterizing the dinitrogen cleavage reaction: (a) the reactant $(Me_2N)_3MO$, **3**, (b) the intermediate **3′**−**3′**, (c) the transition state, (d) and the product **3′**. Calculated Mo−N and N−N distances are in Å; the Mo−N−N angle is the degrees.

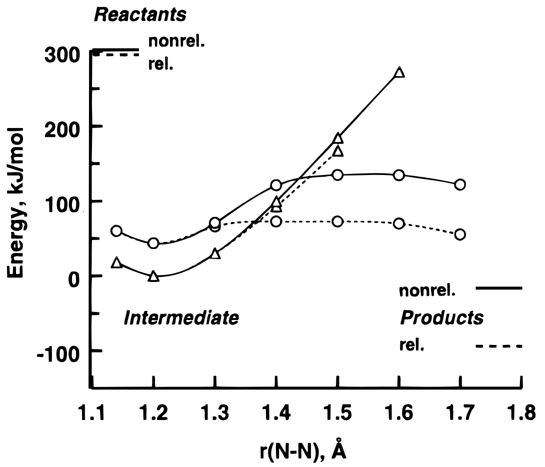

Figure 2. Potential energy curves of the reaction $2(H_2N)_3Mo + N_2 \rightarrow 2(H_2N)_3Mo{\equiv}N$ calculated for the lowest lying paramagnetic ${}^3A_{2g}$ (e_u^2, D_{3d} symmetry constraints, triangles) and the lowest lying diamagnetic ${}^1A_g$ states (b_u^2, C_{2h}, circles) of the intermediate complexes **2′**−**2′**. Dashed lines indicate the potential energy curves when relativistic effects are taken into account. Energies of the reactants and the products (corresponding to an infinite N−N distance) are also displayed relative to the ground state energy of the intermediate.

steps of the process under investigation are displayed in Figure 2. However, to estimate the accuracy of the present theoretical approach and to validate the choice of the models, it is instructive to begin with the computed parameters for the reactant **2** and product **2′**, which can be more directly compared to the experimental data.

The Mo−N distance of 2.00 Å calculated for the reactant **2** is close to the mean value of 1.97 Å measured for the complex **1** with more bulky ligands.[25] The reactant complexes L_3Mo under study may be considered isolobal to a nitrogen atom. Their calculated electronic configuration a^1e^2 exhibits three unpaired electrons (${}^4A_2$, C_{3v}), in line with the experimental findings for **1**. The strong molybdenum−nitrogen triple bond in the diamagnetic complexes $L_3Mo{\equiv}N$ is manifested by a short bond distance (measured, 1.63 Å for L = diphenylamide;[26] calculated, 1.67 Å for the NH_2 derivative **2′**) as well as by a rather high vibrational frequency ν(Mo≡N) (measured,[1,25] 1042 cm^{-1}; calculated, 1081 cm^{-1}). The corresponding bond energy E_b(Mo≡N) is 678 kJ mol^{-1}. Overall, the formation of two Mo≡N bonds provides sufficient energy to induce the cleavage of N_2: $2E_b(L_3Mo{\equiv}N) \approx 1360$ kJ mol^{-1} (calculated) > $E_b(N{\equiv}N) = 950$ kJ mol^{-1} (calculated) and 942 kJ mol^{-1} (experimental).[5]

The calculations confirmed the suggestion[1] that N_2 cleavage proceeds via a stable paramagnetic intermediate of a linear Mo−N−N−Mo arrangement (see Figure 1b). This intermediate exhibits D_{3d} symmetry and has an electron configuration, e^2, with two unpaired electrons (${}^3A_{2g}$). It is stabilized by about 300 kJ mol^{-1} compared to the reactant system $2L_3Mo + N_2$ (Table 1, Figure 2). The structure of the intermediate **2′**−**2′** is similar to those of known analogous complexes L_nMo−N−N−MoL_n.[27,28] The corresponding Mo−N bond length is calculated to be 1.77 Å for **2′**−**2′**, whereas the experimental distances range from 1.82 to 1.91 Å.[27,28] Better agreement is achieved for the N−N distance, which is calculated to be 1.20 Å; the measured values fall into the range 1.20−1.24 Å.[27,28] This finding shows that even a reaction of moiety **2** with a N_2 molecule leads to the intermediate **2′**−**2′**, which exhibits a structure very close to that formed in the case of more bulky ligands with similar electronic properties. The main function of bulky ligands coordinated to Mo(III) in **1′**−**1′** is to exert a steric screening of the coordination site needed for the dinitrogen cleavage by penalizing the dimerization of the reactant species, which would otherwise result in rather stable $L_3Mo{\equiv}MoL_3$ complexes.[29] Indeed, the DF Mo≡Mo bond energy for the dimer **2**−**2**, ~390 kJ mol^{-1}, and the corresponding value estimated experimentally,[29] ~300 kJ mol^{-1}, are both lower than the energy of the intrafragment ligand repulsion, ~470 kJ mol^{-1}, estimated with the help of a force field method[30−32] for **1′**−**1′** with a fixed Mo−Mo distance of 2.22 Å,[33] typical for $L_3Mo{\equiv}MoL_3$ compounds.[29]

A quite unusual zigzag structure of the Mo−N−N−Mo unit, with Mo−N−N angles of 137° for **2′**−**2′**, has been found by DF calculations (see also ref 9) to be in the vicinity of the transition state (${}^1A_g$, r(N−N) = ~1.5 Å). This structure suggests a bonding scheme of the type Mo=N−N=Mo, with sp^2 hybridization and one lone pair at each nitrogen. Interestingly, the calculated Mo−

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Mo distance remains almost unchanged, 4.74−4.81 Å, when the N−N bond stretches from the equilibrium of the intermediate to the transition state. Along the reaction path, the N−N moiety simultaneously stretches and turns around its center by an angle of up to ∼30° with respect to the line Mo−Mo. The implied breaking of the effective D_{3d} symmetry entails a lowering of the activation barrier by 57 kJ mol^{-1}. This effect, together with the relativistic stabilization of the product species, brings the calculated height of the reaction barrier, 75 kJ mol^{-1} (Table 1), in reasonable agreement with the measured kinetic parameters.[34]

The zigzag structure of the transition state may be considered intermediate between the structures of complexes with end-on bonded N_2[6−8] and those determined for the complex $\{[(R_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, which features a N_2 species coordinated side-on between two Zr atoms.[35] In the latter structure, probably the most elongated N−N fragment reported so far, $r(\text{N−N}) = 1.55$ Å, has been found, even longer than that in N_2H_4, 1.47 Å. The relationship between end-on and side-on complexes has been studied previously with the help of ab initio calculations of naked M_2N_2 species (M = Zr, Ti, Y, Nb).[36] There, ligated complexes were predicted to be paramagnetic for N_2 bonded end-on but diamagnetic for the more strongly perturbed N_2 moiety coordinated side-on. The results presented here for the paramagnetic intermediate and the closed shell transition state (with N_2 elongated and rotated) are in agreement with these predictions.

The overall scenario of the N_2 cleavage by the reactant **2** can be summarized as follows (Table 1). A stable intermediate **2′**−**2′** is formed without a barrier; the enthalpy gain is as large as 300 kJ mol^{-1}. The transformation of the species **2′**−**2′** into two product molecules **2′** is the rate-limiting step, with an exothermicity of 95 kJ mol^{-1}, once the barrier of 75 kJ mol^{-1} has been overcome. This step can be pictured as a N_2 fragment bracketed between two Mo atoms, but kept apart at a constant distance. The N_2 moiety starts to rotate around an axis perpendicular to the Mo−Mo direction; in order to, first, significantly elongate and, finally, completely break the N−N bond. Figure 3 illustrates the evolution of the electronic states along the reaction path of the N≡N bond breaking, due to the formation of two Mo≡N bonds, from the educts with six unpaired electrons via the paramagnetic intermediate and the diamagnetic transition state to the closed shell products.

Comparison of the Present and Previous ECP DF Data for the Reaction with $(H_2N)_3Mo$. A comparison of the present results with those of a previous ECP DF study[9] is in order because of the following significant differences of the two DF computational techniques employed: (i) an all-electron method is used here instead of the ECP approach; (ii) basis sets of different quality; (iii) an accurate scalar-relativistic description of the reaction energetics on the one hand and implicit account of relativistic effects for the core electrons only in the ECP methodology; (iv) different gradient-corrected exchange-correlation functionals.

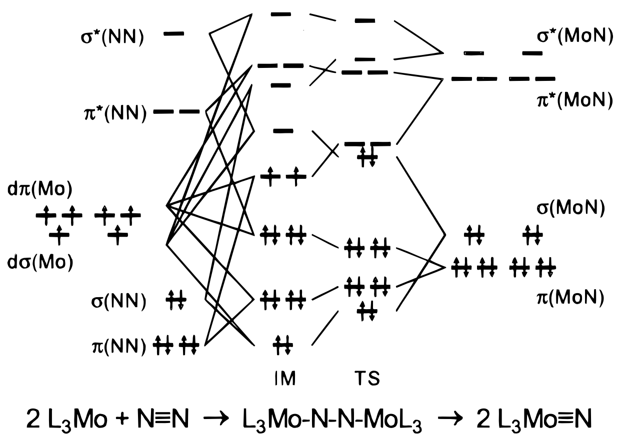

Figure 3. Schematic interaction diagram based on the Kohn−Sham orbitals of the educts $2L_3Mo + N_2$ along the reaction path of N_2 cleavage via the intermediate (IM) and the transition state (TS) complexes $L_3Mo{-}N{-}N{-}MoL_3$ to the products $2L_3Mo{\equiv}N$. For clarity, only orbitals crucial either to the N≡N bond cleavage or to the Mo≡N bond formation are shown.

From a qualitative point of view, the two descriptions of the reaction mechanism agree very nicely with each other, including the extraordinary calculated zigzag structure of the transition state moiety. However, quantitatively some of the calculated observables differ significantly in these two studies. For example, the Mo−N and N−N bond lengths in the intermediate **2′**−**2′** are 1.77 and 1.20 Å, respectively, in the present work compared to the values of 1.86 and 1.22 Å found in ref 9. This leads to the alteration of the Mo−Mo distance by as much as 0.2 Å. Interestingly, going from the intermediate to the transition state complex, we found a slight elongation of the Mo−Mo distance by 0.07 Å, in contrast with the previously computed contraction by 0.15 Å.[9] The geometric features of the reactant **2** and product **2′** calculated in the both studies are in perfect agreement. The latter finding implies that the overall reaction exothermicity obtained in the present and the previous[9] calculations should be similar enough. Surprisingly, these values amounting to 390 and 311 kJ mol^{-1}, respectively, are quite different. A smaller increase of the barrier height, which nevertheless is crucial for estimation of the reaction rate, from 75 kJ mol^{-1} (present work) to 87 kJ mol^{-1} (ref 9) is also noted.

More Realistic Model: $2(Me_2N)_3Mo + N_2 \rightarrow 2(Me_2N)_3MoN$. One does not expect that the mechanism of the cleavage reaction changes significantly when the hydrogen atoms in the amide ligand are substituted by the methyl groups. However, by switching to the reactant **3**, one should be able to account for most of the electronic effects and at least for some of the steric effects on the reaction parameters inherent in the system with the reactant **1**, which really works as N_2 scissor agent.[1]

Indeed, the electronic properties of the complexes with H_2N and Me_2N ligands are quite similar, as is reflected in the calculated geometric parameters. For instance, the computed Mo≡N bond length equals 1.67 Å in both

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[34] On the basis of the measured rate constant for the conversion of the intermediate **1′**−**1′** into the product moieties **1′**, $k = 3.3 \times 10^{-4}$ s^{-1}, and assuming a pre-exponential factor in the Arrhenius equation of 10^{12}−10^{14} s^{-1} (Benson S. W., *The Foundation of Chemical Kinetics*; McGraw-Hill: New York, 1960), one may estimate the height of the reaction barrier to be 90−100 kJ mol^{-1}.

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species **2′** and **3′**. The corresponding metal–ligand distances are only slightly different, 1.99 and 2.01 Å, respectively. Almost equal overall calculated reaction exothermicities, 390 kJ mol^{-1} for $2(H_2N)_3Mo + N_2 \rightarrow 2(H_2N)_3MoN$ and 395 kJ mol^{-1} for $2(Me_2N)_3Mo + N_2 \rightarrow 2(Me_2N)_3MoN$ (Table 1), provide additional evidence for the similar electronic properties of **2** and **3** as well as of the complexes **2′** and **3′**. On the other hand, the energy gain which accompanies the formation of the intermediates is by about 30 kJ mol^{-1} larger for the conversion of **2** than for that of **3**. This relative destabilization of the intermediate **3′**–**3′** compared to that of the **2′**–**2′** moiety is probably the main reason why the computed activation barrier for the decay of **3′**–**3′** is lower by 17 kJ mol^{-1} than that of **2′**–**2′**. As in the transition state of **2′**–**2′**, the transition state corresponding to the cleavage of **3′**–**3′** is also stabilized, although to a lesser extent (by 26 kJ mol^{-1} only), by the zigzag distortion of the Mo–N–N–Mo fragment, which is linear in the intermediate. It is not the aim of this study to precisely differentiate between the electronic and steric conditions of the ligand substitution $H_2N \rightarrow Me_2N$ leading to the barrier lowering. Nevertheless, it is important to note that the more realistic model $2(Me_2N)_3Mo + N_2 \rightarrow 2(Me_2N)_3MoN$ furnishes reaction parameters which are more favorable for a rate acceleration of the dinitrogen cleavage.

On the Reactivity of Alkyl Mo(III) and Similar Complexes. To further characterize the role of the amido ligands and to evaluate the potential of other Mo complexes[2–4] for the scission of dinitrogen, we have also carried out DF calculations for analogous alkyl Mo(III) complexes modeled by Me_3Mo, **4** (Table 1). Trialkyl complexes are calculated to be unfavorable for N_2 cleavage; the activation barrier is found to be about 60 kJ mol^{-1} higher at the nonrelativistic level than that for $(Me_2N)_3Mo$ (Table 1). Also, the transformation of the intermediate **4′**–**4′** into two product species **4′** is endothermic by ~20 kJ mol^{-1}. On the basis of this value, one might conclude that the thermodynamic equilibrium is shifted in the direction of the reverse reaction, the dimerization of **4′**. However, the positive enthalpy contribution to the free energy of the reaction may be overcompensated by a negative entropy term. Indeed, at the semiempirical AM1/d level, the value of $T\Delta S$ for the splitting of the intermediate **2′**–**2′** is calculated to be as large as 56 kJ mol^{-1}.[37] Because the entropy contribution is of a similar size for the reaction of other complexes under study, the cleavage process should still be thermodynamically preferred for an endothermicity of up to ~50 kJ mol^{-1}. According to the AM1/d estimations, the entropy factor increases the activation barrier by about 6 kJ mol^{-1}.

The data discussed so far demonstrate a significant electronic effect of the ligands on the reactivity of the Mo(III) complexes. The existence of a strong electronic influence is reflected also by the fact that a trisamidoamine complex $L_nMo–N–N–MoL_n$,[28] where the axial position at the Mo center trans to the N_2 moiety is occupied by an amine ligand, is stable with respect to the scission of the N–N bond, although other structural characteristics are very similar to those computed here for the intermediates **2′**–**2′** and **3′**–**3′**.

As for the Mo(III) complexes with other ligand types, our preliminary results indicate that reactants with three phosphido ligands are also able to induce the bond cleavage of N_2, albeit with a small exothermicity of only 12–14 kJ mol^{-1}. On the basis of this finding, one expects a higher activation barrier for Mo(III) phosphides than for amides.

Crucial Role of Relativistic Effects. As mentioned in the Introduction, relativistic effects on the electronic structure and properties of 4d metal complexes are frequently considered to be of only minor importance. In the present study, we exploited the advantage of our all-electron computational method to calculate the electronic structures and other features of the reaction species involved in the N_2 cleavage by various Mo(III) complexes at both scalar-relativistic[11,17] and nonrelativistic levels.

Let us first look at the bond energy $E_b(Mo{\equiv}N)$ of the product species: the nonrelativistic values are 643 kJ mol^{-1} for **2′** and 657 kJ mol^{-1} for **3′**. Relativistic effects increase these energies to 678 and 681 kJ mol^{-1}, respectively. This relative bond strengthening by 4–6% is smaller than that calculated for other 4d metal compounds;[38] however, the absolute effect is significant in the present case, particularly for the reaction barrier (see below), because of the unusually strong Mo≡N bond.

Other calculated relativistic and nonrelativistic results are compared in Table 1 and in Figure 2. It is seen from Figure 2 that for N–N distances from about 1.1 Å (corresponding to free N_2) to about 1.3 Å, relativistic effects on the potential energy curves of the dimers are of subordinate importance only. A further stretching of the N–N bond leads to the transition state complex $L_3Mo–N–N–MoL_3$, where relativistic effects become crucial because N_2 cleavage is accompanied by formation of two new very strong Mo≡N bonds. Only these bonds are notably affected by relativistic effects. Figure 2 shows that the size of the relativistic stabilization depends critically on the electronic state of the reaction species and is significant only for the singlet state ^1A_g (b_u^2) corresponding to forming the Mo≡N bond. Relativistic effects also seem to facilitate an earlier crossover from the open shell to the closed shell electronic structure (Figure 3), around $r(N–N) = 1.4$ Å, and they increase the exothermicity for the conversion of the intermediate into products by 80–100 kJ mol^{-1} (Table 1). The most dramatic consequence is, of course, the relativistic lowering of the reaction barrier by as much as about 60 kJ mol^{-1}. The nonrelativistic values, above 130 kJ mol^{-1}, would correspond to a kinetically forbidden reaction. For a proper description of the barrier height of the reaction under study, it is mandatory to take relativistic effects into account. This statement may also hold for other reactions of second-row (or heavier) transition metal compounds, which proceed via elementary steps of building or breaking very strong bonds with heavy metal atoms.

The present discussion of the reaction parameters of N_2 cleavage by various L_3Mo complexes showed that relativistic DF calculations can furnish valuable structural and energetic information on the series of elementary steps, including data not easily accessible experi-

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(37) Voityuk, A. A.; Rösch, N. Unpublished results.

(38) See e.g.: Li, J.; Schreckenbach, G.; Ziegler, T. *Inorg. Chem.* **1995**, *34*, 3245, where a relativistic increase by 16–32 kJ mol^{-1} (or by 20–30%) has been computed for various Pd–ligand bonds which ehxibit energies of 65–130 kJ mol^{-1}.

mentally, like geometry and energy of transition state complexes. Such large-scale calculations of the reaction mechanisms of transition metal complexes became possible only very recently, due to the development of computational facilities and of new DF software improvements, like gradient-corrected exchange-correlation potentials, analytic total energy gradients for automatic geometry optimization, and scalar-relativistic methods. Clearly, high-level quantum chemical studies are now a powerful tool to efficiently help in a thorough understanding of even quite delicate and complicated reactions of transition metal chemistry.

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