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Steric Effects on Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: A Molecular Mechanics Study

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The universal force field approach is used to investigate the steric demand in nitrogen molecule cleavage by three-coordinate molybdenum complexes MoL_3 of different ligand types L (L = NH_2, NMe_2, N(mesityl)(*tert*-butyl), O(*tert*-butyl), Me, *tert*-butyl, neopentyl). Calculated geometries of the intermediates $L_3Mo-N_2-MoL_3$, of the products L_3MoN, and of the undersirable side product dimers L_3MoMoL_3 are presented. The primary role of ligand sterics appears to be the prevention of dimerization of MoL_3 monomers.

Introduction

The appealing problem of nitrogen fixation by transition metal complexes has been subject of numerous investigations.[1,2] Recently, Laplaza and Cummins reported an elegant way to cleave N_2 under mild conditions via reaction with the three-coordinate molybdenum(III) complex MoL_3 (L = NArR; Ar = 3,5-$C_6H_3Me_2$, R = CMe_3).[3,4] In the proposed first reaction step, N_2 rapidly reacts with MoL_3 species to form a relatively stable paramagnetic intermediate $L_3Mo-N_2-MoL_3$. Its structure has been proposed[3,4] to contain a linear Mo−N−N−Mo subunit similar to that of a structurally characterized complex $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$.[5] A subsequent transformation of this intermediate (rate-limiting step) is found to result in diamagnetic product complexes $L_3Mo{\equiv}N$.[3,4] A modified dinitrogen molecule splitting reaction involving simultaneously alkoxy and amido complexes of molybdenum, $NMo(OR)_3$ and $Mo(NArR)_3$, has also been reported,[6] where the intermediate was proposed to be a mixed-ligand moiety $L^1{}_3Mo-N_2-MoL^2{}_3$ (L^1 = OR; L^2 = NArR).

Density functional (DF) investigations on a series of model reactions $2ML_3 + N_2 \rightarrow 2NML_3$ with various small ligands (L = H, Cl, NH_2 and M = Mo, W;[7] L = NH_2, NMe_2, Me and M = Mo)[8] showed an overall exothermicity in each case, with the exception of the alkyl ligand complex $MoMe_3$. Furthermore, the reactivity of $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$, a complex which has not been shown to cleave dinitrogen, was analyzed by performing a calculation on the model compound $\{[N(HNCH_2CH_2)_3]Mo\}_2(\mu\text{-}N_2)$.[7] In the latter case, N−N bond breaking was found to be endothermic; this was attributed to the trans effect weakening the Mo−N bonds.[7] Moreover, unusually strong relativistic effects were identified to affect the bonding in the intermediate and in the products as well as the reactivity via the barrier height along the corresponding reaction path.[8]

Clearly, ligands play an important role for the activity of a metal complex with respect to dinitrogen cleavage. Because the N≡N triple bond is one of the strongest known, the creation of two Mo≡N bonds must be strongly exothermic for the cleavage reaction to proceed. Quantum chemical investigations on model complexes with small ligands have been employed to study the energetics of the bond breaking.[7,8] However, the ligand electronic effects are not the only influence on the reaction energetics. Ligand steric effects are crucial, particularly with respect to the prevention of reactant dimerization to yield L_3MoMoL_3, a byproduct undesirable in the context of dinitrogen cleavage. This aspect of the ligand design is difficult (at present, essentially impossible) to investigate by quantum chemical means for such large molecules. We have chosen force field calculations in order to quantify the steric consequences of the ligands.

For this purpose, a modern force field method, the universal force field,[9−12] in conjunction with the Valbond approach,[13,14] was used to study the steric influence of various ligands on all stable molecular species participating in the reaction. At the same time, comparison to the available quantum chemical and experimental results for educts, intermediates, and products[3,4,7,8] as well as for the dimers[15] provided an ideal testing ground for the chosen force field approach with respect to its capability to characterize structure and, in case of quantum chemical results, energetics of a variety of species involved in an important

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(1) Leigh, G. J. *Science* **1995**, *268,* 827 and references therein.
(2) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95,* 1115.
(3) Laplaza, C. E.; Cummins, C. *Science* **1995**, *268,* 861.
(4) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118,* 8623.
(5) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116,* 8804.
(6) Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118,* 709.
(7) Cui, Q.; Musaev, D. G.; Svensson, M.; Sieber, S.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117,* 12366.
(8) Neyman, K. M.; Nasluzov, V. A.; Hahn, J.; Landis, C. R.; Rösch, N. *Organometallics* **1997**, *16,* 995.
(9) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114,* 10024.
(10) Casewit, C. J.; Colwell, K. S.; Rappe, A. K. *J. Am. Chem. Soc.* **1992**, *114,* 10035.
(11) Casewit, C. J.; Colwell, K. S.; Rappe, A. K. *J. Am. Chem. Soc.* **1992**, *114,* 10046.
(12) Rappe, A. K.; Colwell, K. S.; Casewit, C. J. *Inorg. Chem.* **1993**, *32,* 3438.
(13) Root, D. M.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115,* 4201.
(14) Landis, C. R. To be submitted for publication.
(15) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms,* 2nd ed.; Clarendon Press: Oxford, U.K., 1993.

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reaction system. In this way, valuable experience is gained for the applicability of the UFF/Valbond force field approach to metal complex reactions of catalytic potential.

Methods

We have chosen the universal force field (UFF) approach because of its ability to treat all atoms of the periodic table including transition metals. In general, UFF and its parameters are employed as suggested by Rappe.[9−12] All adaptations and supplementary parameters of UFF necessary for the present case study are included in the Supporting Information. Novel and/or unique aspects of the UFF force field approach used in the present study will briefly be described in the following. The Valbond[13,14] approach was recently combined with UFF approach by C.R.L., replacing the original UFF Fourier methodology for treating valence angle bends. Beyond the algorithm for the assignment of the hybridization to individual bonds i for sp^m gross hybridization,[13] the bond-forming hybrids sp^{m_i}d^{n_i} are calculated by

$$m_i = \mathrm{pd}_i\,\mathrm{PD}_i/(1-\mathrm{pd}_i) \quad \text{and} \quad n_i = \mathrm{pd}_i(1-\mathrm{PD}_i)/(1-\mathrm{pd}_i)$$

with

$$\mathrm{pd}_i = n_{\mathrm{pd}}\,\mathrm{wt}_i/\sum_{j}^{\text{ligands}} \mathrm{wt}_j$$

representing the non-s orbital character of the hybrid in the molecule. n_{pd} is the number of p and d orbitals in gross hybridization and wt$_i$ is the weigthing parameter of the non-s part of the bond-forming hybrid. PD$_i$ measures the p/(d + p) character for a specific hybrid; it equals 0 or 1 depending on whether no p or no d orbital is included, respectively. For technical reasons, a cosine Fourier expansion is used for the linear Mo−N−N angle. The equilibrium angle is 180°, and the force constant is selected to be 500 kcal/(mol deg^2) throughout the calculations. Different force constants have been tested (ranging from 10 to 500 kcal/(mol deg^2)) without significant modifications of the overall conformation of the complexes under investigation.

Results and Discussion

The complexes of interest are the intermediates $L^1_3Mo-N_2-MoL^2_3$, the products L_3MoN, and the dimers $L^1_3MoMoL^2_3$. Unless otherwise stated, the ligands are chosen as L = L^1 = L^2. The following types of ligands are considered in the present study: L = NH_2, NMe_2, and NArR (Ar = 3,5-$C_6H_3Me_2$, mesityl; R = CMe_3, *tert*-butyl), for modeling amido complexes; L = Me, *tert*-butyl, and neopentyl, as characteristic ligands for alkyl complexes.

In the mixed-ligand complex $L^1_3Mo-N_2-MoL^2_3$ the ligands are L^1 = OR and L^2 = NArR. For the complexes with the smaller ligands L = NH_2, NMe_2, and Me, the UFF results were compared to available DF results.[8] Ligands of the dimers and intermediates that are placed more or less adjacent to the Mo···Mo axis will be referred to as "proximal", and the other ligand groups will be designated as "distal".[15] To distinguish nitrogen atoms of the MoNNMo moiety from those of the amide ligand, the latter will be referred to as N$_L$.

Structure of the Intermediates. Some geometrical characteristics of the intermediates $L_3Mo-N_2-MoL_3$ are listed in Table 1. Independent of the ligand type, all investigated intermediate state structures calculated by the UFF approach contain a linear Mo−N−N−Mo moiety (Figure 1). This structural feature has been proposed for the L = NArR derivative[3] and is supported by DF results for complexes with small ligands.[7,8] The Mo···Mo distance varies only within a small range, 5.00-5.07 Å (UFF) and 4.74−4.81 Å (DF).[8] In the intermediates with L = NH_2, NMe_2, and Me, essentially isoenergetic conformations (within 0.3 kcal/mol) arise when both $NMoL_3$ fragments are rotated against each other around the Mo···Mo axis; the free rotation is possible due to the large H···H distances $r_{\min}$ (Table 1). This is not the case for the larger ligands where staggered arrangements with a torsion angle Θ ≈ 60° are preferred. For example, in the case of L = NArR, the eclipsed conformation is about 8 kcal/mol higher in energy than the staggered one.

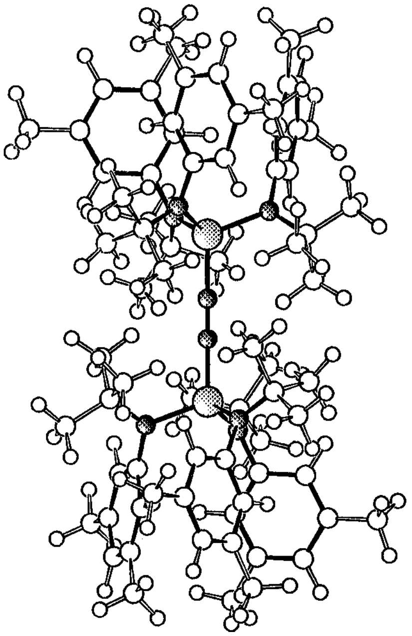

Figure 1. Lowest energy conformation of the intermediate $L_3Mo-N_2-MoL_3$ with L = NArR. The substituents Ar = mesityl and R = *tert*-butyl are arranged distal and proximal, respectively.[21]

Table 1. UFF Geometries of the Intermediates $L_3Mo-N_2-MoL_3$ with Various Ligands L (Bond Lengths in angstroms; Angles in Degrees)

ligand	Mo−N	Mo−X^a	N−N	$r_{\min}{}^b$	N−Mo−X^a	Θ^c
NH_2	1.90	2.00	1.20	4.98	109.4	*d*
NMe_2	1.90	2.00	1.20	3.24	109.1	*d*
NArR	1.92	2.02	1.21	2.20	110.4	57
OR, NArR	1.91	2.00	1.20	2.27	102.6−114.3	35
Me	1.90	2.09	1.20	5.60	109.4	*d*
tert-butyl	1.90	2.12	1.20	2.75	104.8	62
neopentyl	1.93	2.11	1.21	2.30	113.9	61

^{a} X = O, C, or N$_L$ (nitrogen atom of the ligand). ^{b} Minimum distance between hydrogen atoms of distinct monomeric units. ^{c} Torsion angle XMo···MoX (0°, eclipsed; 60°, staggered). ^{d} Several isoenergetic conformations exist within 0.3 kcal/mol.

The orientation of the larger ligands relative to the Mo···Mo axis is also of interest. In the lowest energy structure of complexes with L = NArR, all *tert*-butyl groups are arranged proximal and all mesityl groups distal (see Figure 1), in agreement with experimental findings for similar molecules.[16] Because of dramatic repulsion effects, it is not possible to continuously change the orientations of Ar and R ligands relative to their proximal and distal arrangements by rotation around the Mo−N$_L$ bond. Yet, exchange of the fragments Ar and R of *one* amide ligand (by a 180° rotation around the Mo−N$_L$ bond) and subsequent minization result in a stable conformation, only about 5 kcal/mol higher in energy. The more amide ligands are rotated, the higher the energy. A similar behavior is seen also for complexes with neopentyl and with mixed alkoxide/amide ligands. In the latter case, with L^1 = OR and L^2 = NArR, the lowest energy conformation features two L^1 ligands in proximal and one L^1 ligand in distal orientation (Figure 2).

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(16) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042.

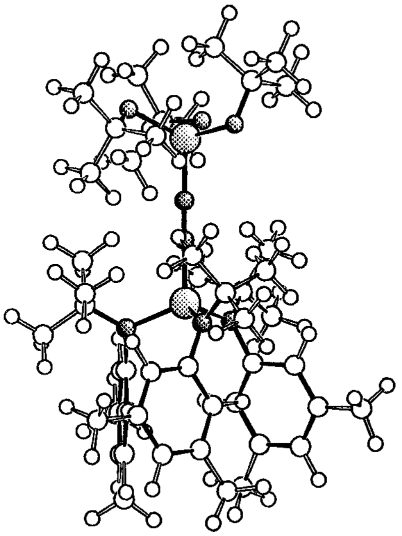

Figure 2. Lowest energy conformation of the intermediate $L^1_3Mo-N_2-MoL^2_3$ with L^1 = OR and L^2 = NArR. The fragments Ar and R of L^2 are arranged as in the case of $L_3Mo-N_2-MoL_3$ with L = NArR. For L^1 = OR, two ligands are directed proximal and one distal.[21]

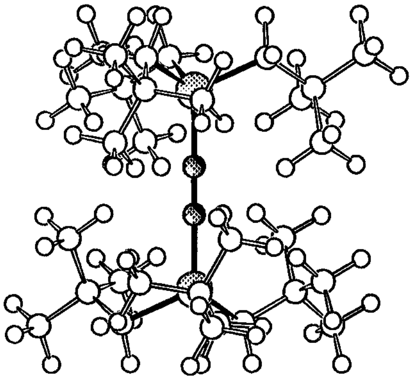

Figure 3. Lowest energy conformation of the intermediate $L_3Mo-N_2-MoL_3$ with L = neopentyl.[21]

The UFF angles N−Mo−X (X = N_L, C) for different small ligands (Table 1) are somewhat overestimated compared to the corresponding DF results (L = NH_2, 96.8°; L = NMe_2, 102.5°; L = Me, 103.5°).[8] Nevertheless, the results for the larger ligands where the steric interactions may significiantly influence these angles are quite reasonable, justifying the use of an sd^3 hybridization scheme for molybdenum in the Valbond approach. Increasing the size of the amide substituents from L = NH_2 to L = NMe_2 and to L = NArR decreases the minimum distance r_{min} between hydrogen atoms of distinct monomeric units (Table 1). Although, for example, r_{min} in the case of L = NArR, 2.2 Å, is substantially smaller than the H···H van der Waals distance, 3.2 Å, the angle N−Mo−N_L remains almost unchanged compared to those in complexes with smaller amide substituents. The bulky *tert*-butyl ligands try to avoid close contacts to neighboring ligands bonded at the same molybdenum center. Therefore, as some space is left in the proximal direction, the angle N−Mo−C is reduced to 104.8° as a consequence of the intraunit steric repulsion. Compared to the case of L = *tert*-butyl, the bulky part of neopentyl is located one bond away from the metal center; thus more space is available in the distal direction. In combination with the interunit repulsion of the proximal ligands, this results in an increase of the N−Mo−C angle to 113.9° (Figure 3). The tetravalent alkyl ligands under investigation are more space filling near molybdenum than the trivalent amide ligands. Therefore, as shown by the variation of the N−Mo−C angles, the problem of steric crowding is particularly important for the alkyl ligands.

The calculated bond lengths do not change significantly among the various intermediates: the Mo−N distances vary in the range 1.90−1.93 Å, in reasonable agreement with experimental results for similar intermediates, 1.82−1.90 Å.[5,17] The N−N distance, calculated to 1.20−1.21 Å, agrees even more closely with the experimental data, 1.20−1.24 Å.[5,17] Similarly, the Mo−N_L distances, about 2.00−2.02 Å, are calculated close to the experimental values, 1.96 Å for L = NArR.[18] The same is true for the complexes with alkyl ligands; here, the Mo−C bond distances, 2.09−2.11 Å, are quite close to the corresponding DF result for L = Me, 2.11 Å.[8]

Structure of the Products. The low-energy conformations of the products are quite similar to those of the corresponding intermediate. For example, the *tert*-butyl fragments of L = NArR are arranged proximal while a rotation of about 180° around the Mo−N_L bond followed by a minimization results in a stable conformation of higher energy; again, the more ligands are rotated, the higher the energy. Also, as in the corresponding intermediate, the repulsive interaction between the alkoxide ligands penalizes the “all-proximal” conformation of the *tert*-butyl fragments by 1.3 kcal/mol (see Figure 2).

The angles N−Mo−X (X = N_L, O, C) differ by about ±4° from the values in the corresponding intermediate. Also, in the DF calculations, only a slight variation of these angles (103.7 and 105.6° for L = Me and L = NMe_2, respectively) is found compared to the case of the values of the corresponding intermediates (103.5 and 102.5°).[8] However, for L = NH_2 a significant increase occurs according to the DF results, from 96.8° in the intermediate to 105.9° in the product,[8] indicating a strong variation of the hybridization at the molybdenum center. While this change in the bond angle is detected by DF only for the small ligand system L = NH_2, the UFF calculations are in quite good agreement with the DF results for the somewhat larger complexes, L = Me and L = NMe_2.

As the Mo≡N bond is known to be strong,[7,8] no significant change in this bond length is expected in a comparison of the products $L_3Mo{\equiv}N$ having different ligands. The Mo≡N distances are calculated to be 1.69 Å in each case, in reasonable agreement with experimental values; for example, in $L_3Mo{\equiv}N$ (L = diphenylamide) this bond distance was determined to be 1.634(3) Å.[19] Furthermore, the vibrational frequency ν(Mo≡N) for the product molecule with L = NArR is calculated by UFF to be 1073 cm^{-1}; this value differs only slightly from the experimentally observed frequency of 1042 cm^{-1}.[18] Also, the Mo−N_L distances of the products, about 2.00−2.12 Å, are in accord with experimental values, which range from 1.960 to 1.977 Å.[18] In addition, Mo−C bond distances, calculated by UFF to be 2.09−2.12 Å, agree very well with the corresponding DF result, 2.11 Å.[8]

Structure of the Dimers. Force field calculations of the dimer L_3MoMoL_3 may provide some insight into the propensity of the L_3Mo molecules to form L_3MoMoL_3 dimers instead of $L_3Mo-N_2-MoL_3$ intermediates. The investigation of the L_3MoMoL_3 dimers was carried out in a model-type fashion by fixing the Mo···Mo distance at a typical value of 2.22 Å.[15]

The dimer structure may best be characterized and compared to the intermediate structure using the torsion angle Θ(X−Mo−Mo−X) around the Mo···Mo axis, the variation of the valence

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(17) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

(18) Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 4999.

(19) Gebeyehu, Z.; Weller, F.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *593*, 99.

angle Mo−Mo−X (X = N_L, C, O), and the minimum distance r_{min} for hydrogen atoms located at distinct monomers. Experimentally, the dimer L_3MoMoL_3 with the ligands L = NMe_2 features a staggered arrangement ($\Theta = 60°$).[15] The UFF calculations confirm this finding for dimers with small ligands (and for the corresponding intermediates). The valence angles Mo−Mo−X for dimers with ligands NH_2, NMe_2, and Me are almost the same as those of the corresponding intermediates and products, although r_{min} is becoming smaller; e.g., in the case of the Me ligand, r_{min} values for the intermediate and the dimer are 5.60 and 3.22 Å, respectively. Dimers with bulkier ligands exhibit a conformational change when compared with the corresponding intermediates. For L = *tert*-butyl, the N−Mo−C angle increases from 104.8 and 105.7° in the intermediate and product, respectively, to 114.5° in the metal−metal-bonded dimer. This reflects a strong ligand−ligand repulsion, especially in proximal positions, which may also be deduced from the small value of r_{min}, 1.88 Å. In this context, it is worth recalling the small N−Mo−C angles calculated for the intermediate (Table 1) and for the corresponding products with the *tert*-butyl ligands because of the strong ligand−ligand interaction between two ligands bonded to the same molybdenum atom. The larger the ligands are, the closer they approach each other in proximal positions and the larger the resulting interunit ligand−ligand repulsion becomes. For example, the complexes with L = NArR and L = neopentyl exhibit r_{min} distances of 2.07 and 2.00 Å, respectively. Consequently, the steric interactions of the bulky ligands result in a significant rearrangement of the dimer conformations. For L = neopentyl, the Mo−Mo−C angle increases to 128.6° and the torsion angle changes to $\Theta \approx 30°$. A more dramatic effect on the conformation is seen for L = NArR, where a reasonable Mo−Mo distance may only be achieved at the expense of nesting proximal ligands of different Mo fragments within each other. To rationalize the occurrence of dimer formation or the lack of it, we quantify the van der Waals interactions between the ligand spheres of different Mo subunits in the following section.

Energetics. To estimate the nonbonded intermonomer interaction in the dimer, we resorted to the approximation of using the difference of total energies $\Delta E_D = E(r_2) - E(r_1)$ for two different values of the Mo···Mo distances, $r_1 = 30.0$ Å and $r_2 = 2.22$ Å. We chose to exclude from the force field any term representing the Mo···Mo interaction. As expected, the interunit van der Waals interaction varies significantly with the size of the ligands. Comparing ΔE_D to the dissociation energy D_E for a Mo≡Mo triple bond, about 75 kcal/mol,[15] one deduces exothermic formation of dimers for small ligands like NH_2, NMe_2, and Me because the steric interaction is small, even attractive ($\Delta E_D \approx -4$ kcal/mol). For all other complexes, the dimerization is sterically penalized; i.e., ΔE_D is positive. For complexes with L = OR, one expects dimerization, in accord with experiments,[20] as ΔE_D is calculated to be only 8 kcal/mol. Even for L = *tert*-butyl with $\Delta E_D = 51$ kcal/mol, dimerization cannot be excluded. On the other hand, for L = NArR and neopentyl, the force field estimate for the interaction energy ΔE_D substantially exceeds the Mo≡Mo dissociation energy D_E (113 and 102 kcal/mol, respectively). These findings are in good agreement with experiment, where no dimerization was observed for $(RArN)_3Mo$.[3] In addition, complexes with mixed ligands are also predicted by UFF calculations not to dimerize ($\Delta E_D \approx 98$ kcal/mol).

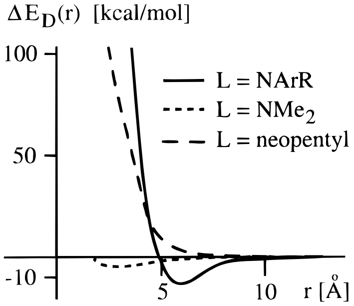

Figure 4. Energy difference ΔE_D between two L_3Mo moieties as a function of the Mo−Mo separation *r* during the dimerization process, $2L_3Mo \rightarrow L_3MoMoL_3$, for the ligands L = NArR, neopentyl, and NMe_2.

It is instructive to inspect the energy difference $\Delta E_D(r) = E(r) - E(r_1)$ as a function of the Mo···Mo distance *r*. For L = NH_2, NMe_2 (Figure 4), Me, and OR, the energy decreases with decreasing Mo···Mo distance (from $r = r_1 = 30.0$ Å down to the equilibrium distance of $r = 2.22$ Å). On the other hand, for L = *tert*-butyl and neopentyl (Figure 4), this interaction is repulsive, increasing continuously when the two units approach each other. Interestingly, the curve $\Delta E_D(r)$ for the Mo complexes with the ligands L = NArR, which have experimentally been shown to carry out dinitrogen cleavage, exhibits a local energy minimum of $\Delta E_D(r) \approx -13$ kcal/mol at a Mo···Mo distance of about 6 Å (Figure 4). At the Mo···Mo distance of 5 Å, calculated for the reaction intermediate, the nonbonded energy difference reduces to about −3 kcal/mol. A similar minimum of the nonbonded interaction at $r \approx 6$ Å is also calculated between Mo complexes with mixed ligands (L^1 = OR, L^2 = NArR).

Summary and Conclusions

The structures of the various intermediate and product compounds resulting from the Valbond-augmented UFF approach are very satisfactory when compared to experiment and to results from DF calculations. The present study underlines the possibilities offered by the UFF method for treating problems that were for a long time inaccessible to force field methods. In particular, a combined strategy seems very promising for describing metal complex reactions. Thereby, the change in the electronic structure is treated by a high-level quantum chemistry method using a model system with simplified ligands whereas the system with realistic ligands, in particular with regard to the change of their nonbonded interactions, is studied with a force field method. Of course, an adequate force field representation of steric interactions as well as of the bond deformations is necessary to make such a strategy successful.

The present UFF/Valbond study was devoted to various Mo(III) complexes that are of interest in the context of dinitrogen cleavage. It was shown that the reaction intermediates $L_3Mo-N_2-MoL_3$ with various amide, alkyl, and alkoxide ligands L as well as the corresponding products $L_3Mo{\equiv}N$ feature very similar conformations for a specific ligand system. Therefore, it is anticipated that the ligand conformations of the transition states do not vary significantly when compared to those of the intermediates and the products. In the case of bulky ligands, steric effects were shown to prevent Mo···Mo distances from being shorter than about 4.5 Å. This separation just fits the structural requirements for the formation of the dinitrogen-bridged intermediates but disfavors the formation of direct Mo−Mo dimers. Complexes with sterically less demanding ligands are predicted to form Mo−Mo dimers because the interunit ligand−ligand repulsion is missing.

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[20] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

[21] Graphic representation by the program SCHAKAL92 (E. Keller, Kristallographisches Institut der Universität Freiburg, 1992).

Combining the results of the present force field study with those of previous DF calculations[7,8] one may picture the following scenario for the dinitrogen cleavage by triamidomolybdenum(III) complexes with bulky ligands. The reaction begins with dinitrogen addition to L_3Mo to form L_3MoN_2. Then, a second monomer MoL_3 approaches the L_3MoN_2 species because of the attractive nonbonded interunit interaction; the Mo···Mo distance is reduced to about 6 Å. In order to further decrease the Mo···Mo distance to about 5 Å to form the intermediate $L_3Mo-N_2-MoL_3$, a strongly attractive electronic interaction is necessary, as the interunit ligand−ligand interaction becomes repulsive in this distance range. The cleavage reaction proceeds via a rearrangement of the electronic structure, as described by the DF calculations,[7,8] strengthening the Mo−N bonds and weakening the N−N bond. As the N−N distance increases and the Mo−N distance decreases toward the transition state, the Mo···Mo distance and closest interunit van der Waals contacts remain approximately unchanged.[8] After reaching the transition state, the product molecules separate.

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Supporting Information Available: Text giving simulation details, UFF terms, UFF/Valbond parameters, and minimization details (2 pages). Ordering information is given on any current masthead page.

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