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N_2 Cleavage by Three-Coordinate Group 6 Complexes. W(III) Complexes Would Be Better Than Mo(III) Complexes

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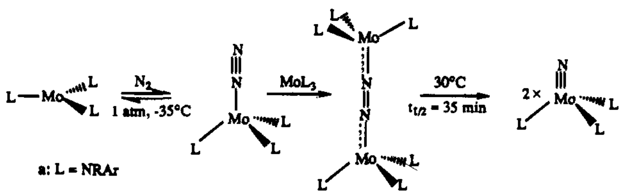
It has been reported recently[1−4] that the strong N−N bond of N_2 and N_2O molecules, as well as the N−O bond of NO^+, can be cleaved by a three-coordinate Mo(III) complex, $Mo(NRAr)_3$, **1a**, where R = $C(CD_3)_2CH_3$ and Ar = 3,5-$C_6H_3Me_2$. The purification of red-orange **1a** under an atmosphere of N_2 at −35 °C led to an intensely purple colored solution (ethyl ether, 0.1 M), which gradually became gold on warming to 30 °C and lost its paramagnetism. The ^1H NMR spectroscopy study confirmed that the final product is a terminal nitrido Mo(VI) complex, $NMo(NRAr)_3$, **5a**. The proposed mechanism[1] in Scheme 1 involves two different intermediates, **2a** and **3a**. However, the validity of the proposed mechanism has not been tested, and there remain important unanswered questions: (i) Is this proposed mechanism reasonable from an electronic structural point of view? (ii) What are the geometrical and electronic structures as well as the relative energies of the reactants, assumed intermediates, transition states, and products? (iii) How does the ease of the reaction depend on the nature of coligand L and metal M?

In order to answer the above mentioned questions and predict the factors controlling this fascinating reaction, we have carried out quantum chemical calculations of the model reaction

$$\underset{\mathbf{1}}{2ML_3} + N_2 \rightarrow \underset{\mathbf{5}}{2NML_3} \qquad (1)$$

where L = H, Cl, and NH_2 and M = Mo and W. Geometries and energetics of the stationary points on the potential energy surface of reaction 1 have been calculated with the density functional theory (DFT) B3LYP method[5] in conjunction with the doubl-ζ quality basis set lanl2dz.[6] For transition metal atoms and Cl we used the Hay and Wadt relativistic effective core potential (ECP).[7] All the stationary points have been positively identified for equilibrium structure (the number of imaginary frequencies (NIMAG) = 0) and transition state (NIMAG = 1). All calculations were performed by using the GAUSSIAN92/DFT package[6] supplemented with the ECP analytical second derivative capability.[8] The gradient-corrected DFT method like B3LYP has been shown to be quite reliable both in geometry and in energies for semiquantitative discussions.[9]

Scheme 1. Proposed Sequence of Reactions[1] for the Conversion of MoL_3 to $NMoL_3$ in the Presence of N_2



The ground state of the Mo or W atom is $s^1d^5(^7S)$, with $s^2d^4(^5D)$ lying 34 or 4.3 kcal/mol, respectively, higher.[10] Therefore, the lower lying electronic states of the complex ML_3, **1**, are expected to be a quartet and a doublet with unpaired electrons in the $d_{xy}(e'')$, $d_{xz}(e'')$, and $s(a')$ orbitals. As seen in Figure 1 the quartet is always the ground state for all ML_3 complexes considered. However, the calculated energy gap of 5 kcal/mol between the ground quartet $^4A''$ and the first excited doublet $^2A'$ state for M = W (and L = NH_2) is substantially smaller than those (14−28 kcal/mol) for M = Mo.

Coordination of the N_2 molecule to the ML_3 complex takes place without barrier. As seen in Figure 2, N_2 coordinates end-on by one of the N atoms to give the complex $(N_2)ML_3$, **2**. The side-on complex is not energetically favorable and rearranges spontaneously to structure **2**. The N−N distance in **2** is not much longer than that in free N_2, indicating that the N≡N triple bond is not yet broken. The doublet ML_3 interacts with N_2 more strongly than the quartet, crosses with the quartet, and gives the doublet ground state for **2**.

Then the second ML_3 coordinates to **2** without barrier, leading to the complex L_3MNNML_3, **3**. The structure of **3** in Figure 2 indicates that this is a double end-on complex, with the N−N distance stretched by 0.08−0.13 Å from free N_2, suggesting that the N=N bond is now like a double bond. The triplet complex **3** for M = Mo, being much more stable (6−23 kcal/mol) than the singlet, is considered as the resting stage of the reaction, and this paramagnetic intermediate should be experimentally detectable.[4] For M = W (and L = NH_2), however, the singlet lies only a few kilocalories/mole higher than the triplet, and both states are likely to be populated.

The N−N cleavage of complex **3** in the singlet state takes place through transition state **4**, which has an N−N bond distance of 1.46−1.60 Å, corresponding qualitatively to an N−N single bond; the N=N π bond has been broken before the transition state. The N−N cleavage of **3** in the triplet leads to an excited state of the product and is energetically unfavorable. Thus the N−N cleavage from the resting state, triplet intermediate **3**, for M = Mo requires spin flip to the singlet before or during the cleavage process. In addition, the barrier for this rate-determining step is substantial (21−41 kcal/mol). On the other hand, the barrier for N−N cleavage in the singlet complex **3** for M = W is small (5 kcal/mol). Furthermore, since a substantial population is expected in the singlet for **3** for M = W, no spin flip is required for this reaction step. In addition, a large spin−orbit interaction would mix triplet and singlet strongly and make the reaction easier. The overall reaction for every case is highly exothermic, which provides the thermodynamic driving force for the N_2 cleavage reaction studied here.

The entire reaction scheme presented here is smooth and reasonably consistent with the experimental findings for M =

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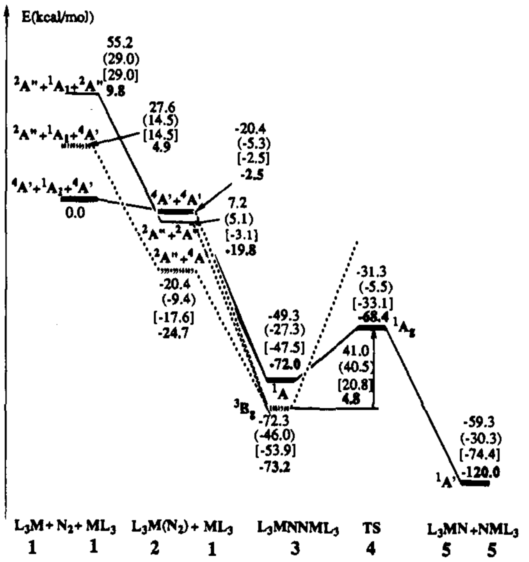

Figure 1. Calculated relative energies (kcal/mol) of the stationary points on the potential energy surface of the reaction $N_2 + 2ML_3 \rightarrow 2(NML_3)$, where L = H, Cl (in parentheses) and NH_2 (in brackets) for M = Mo, and L = NH_2, M = W (bold). The energy scale depicted is for $Mo(NH_2)_3$.

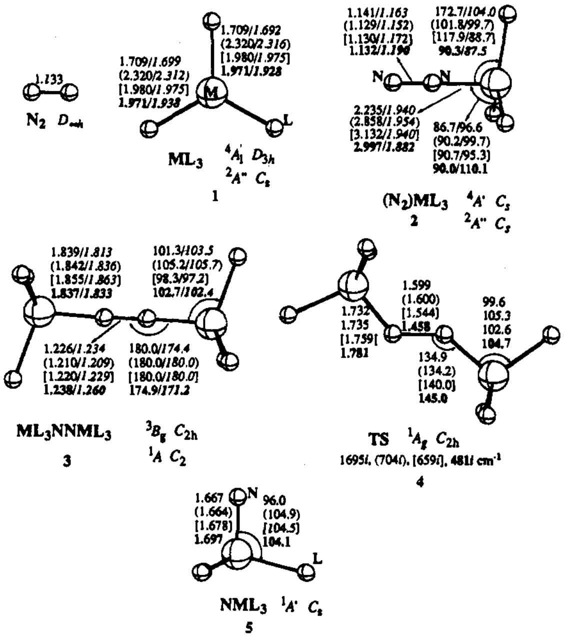

Figure 2. Selected geometrical parameters (distances, Å; angles, deg) of stationary points on the potential energy surface of the reaction $2ML_3 + N_2 \rightarrow 2NML_3$, where L = H, Cl (in parentheses) and NH_2 (in brackets) for M = Mo, and L = NH_2, M = W (bold). Numbers before and after slash are parameters for the high- and low-spin states, respectively. Symmetry labels are for L = NH_2.

Mo and L = NRAr, **1a**. The reaction from the quartet ground state of this ML_3 complex is likely to proceed by easy formation of the quartet intermediate **2**, which, upon coupling with another reactant, **1**, gives a stable intermediate, **3**, in the triplet ground state. Since this state is not adiabatically connected to the quartet intermediate **2**, some nonadiabatic process would be required and may slow down the reaction. From the triplet intermediate **3**, the reaction has to flip spin and go over a substantial barrier at **4** to reach the product **5**.

The present results show that the strongly π donating ligand NH_2 decreases the energy gap between the triplet ground state and the singlet excited state of the intermediate binuclear complex **3**. The decreased energy gap leads to a decrease in the barrier at the rate-determining transition state **4** relative to the triplet resting state of **3**. The NH_2 ligand also gives the largest exothermicity for this reaction step, **3** → **4** → **5**, as well as the overall reaction. Obviously an excellent choice has been made in the recent experiment concerning ligand L.[1-4]

The present results for $W(NH_2)_3$ also indicate that the use of the W(III) complex, as compared with the Mo(III) complex used in the experiments, brings about very similar, even more profound effects. The smaller energy gap between the ground s^1d^5 and excited s^2d^4 states for the atomic W, compared to that for atomic Mo, puts the singlet state of **3** only slightly above the triplet ground state. Thus the rate-determining barrier at **4** is the smallest. Furthermore, since the reaction of this step will take place from the substantially populated singlet state of **3**, no spin flip is required, which would make the reaction more efficient. The exothermicity of this step and the entire reaction is the largest. Therefore, we expect that W(III) complexes WL_3 with a strong π-donor ligand L would be more efficient in N_2 activation than the reported Mo(III) complex. We encourage experimental tests of the proposal. The present prediction is consistent with the fact that C≡C bond are cleaved more easily by the W≡W compounds than by the Mo≡Mo compounds.[11]

The MO correlation diagram for $N_2{-}MoL_3$ indicates that both σ and π interactions are involved. The σ component is donation of the N_2 σ electrons to an empty σ (s and d) orbital of the metal center, while the π component is back-donation from the occupied d_π orbitals of MoL_3 to the empty π^* antibonding orbitals of N_2. Increase in the π-donating capability of the L ligand 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. The results presented in Figures 1 and 2 are, in general, consistent with this qualitative picture.

Experimentally a related paramagnetic complex $(\mu\text{-}N_2)\{Mo[N(t\text{-}BuMe_2SiNCH_2CH_2)_3]\}_2$, **6**, has been isolated, and its structure has been determined.[4b] Very interestingly, in this complex with an amine ligand trans to the N_2 ligand, the N−N cleavage reaction does not take place. The optimized structure of the ground triplet state of its model complex, $(\mu\text{-}N_2)\{Mo[N(HNCH_2CH_2)_3]\}_2$, **7**, agrees very well with the experimental structure, confirming the reliability of the present method: N−N distance of 1.22 Å (calculated) vs 1.20 Å (X-ray), Mo−N(trans to N_2) distance of 2.30 Å (calculated) vs 2.29 Å (X-ray), and the other Mo−N distances of 1.97 Å (calculated) vs 2.01 Å (average, X-ray). The N−N cleavage reaction from the intermediate complex **7** to give the product 2 $N{-}Mo[N(HNCH_2CH_2)_3]$, **8**, is calculated to be *endothermic* by 10 kcal/mol, compared to *exothermic* by 20 kcal/mol for $(NH_2)_3MoN_2Mo(NH_2)_3$ in Figure 1, which has no trans ligand. A σ ligand trans to N_2 donates an electron to the metal center, competes against σ donative interaction from N_2, and leads to weakening of both $Mo{-}N_2$ and $Mo{-}L_{trans}$ interactions, the so-called trans effect. This undesirable trans effect persists throughout the N−N cleavage reaction, making it thermodynamically and kinetically unfavorable.

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