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Reactions of Metal-to-Metal Multiple Bonds. 3.¹ Addition of Nitric Oxide to Hexakis(alkoxy)dimolybdenum Compounds. Preparation and Properties of Bis(nitrosyl)hexakis(alkoxy)dimolybdenum Compounds and Structural Characterization of the Isopropoxy Derivative

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Abstract: The reactions of Mo₂(OR)₆ compounds (R = Me₃C, Me₂CH, and Me₃CCH₂) with nitric oxide yield a heretofore unrecognized class of metal nitrosyl complexes of empirical formula Mo(OR)₃NO. The latter show NO stretching frequencies at ca. 1640 cm⁻¹ and are diamagnetic, dimeric, and fluxional in solution. The compound [Mo(OPr-*i*)₃NO]₂ crystallizes in space group *P* $\bar{1}$ with *Z* = 2 and unit cell dimensions *a* = 10.828 (1) Å, *b* = 15.848 (2) Å, *c* = 9.885 (2) Å, α = 90.21 (2)°, β = 115.93 (2)°, γ = 82.42 (1)°, and *V* = 1509.4 (5) Å³. There are two crystallographically independent molecules, one centered on the origin, the other at 1/2, 1/2, 1/2, which are essentially identical in structure. Each molybdenum atom is five coordinated in a trigonal bipyramidal manner and attains only a 14-valence shell electron configuration. The nitrosyl ligands occupy terminal axial positions and the two bridging OPr-*i* groups form short bonds in equatorial positions and long bonds in axial positions which are trans to the NO ligands. The Mo-N-O units are essentially linear (178°) and the bond lengths therein are 1.754 (7) Å for Mo-N and 1.19 (1) Å for N-O. The Mo-Mo separation of 3.335 (2) Å precludes metal-to-metal bonding. The M-M triple bonds that exist in Mo₂(OR)₆ compounds are thus shown to be cleaved by the addition of two NO ligands. The electronic structure in these new nitrosyl metal complexes can be formulated so that the highest filled MO is the ϵ level responsible for Mo to NO π bonding, made up of metal *d*_{xz}, *d*_{yz}, and NO π^* orbitals. It is likely that other, similar MX₃(NO)L molecules, where M is a group 6 transition metal, X is a univalent group, and L is a two-electron donor, should be obtainable.

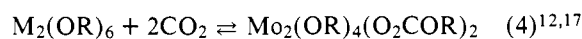
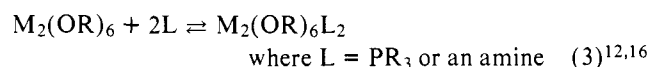
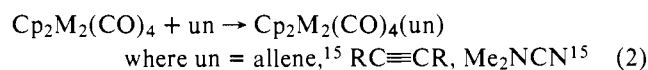
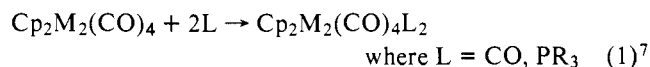
Introduction

The occurrence of compounds containing metal-to-metal multiple bonds is now a well-documented facet of transition metal chemistry.⁴ In this series we are studying the reactions of such compounds with regard to their ability (1) to undergo reactions of the type well documented in mononuclear chemistry⁵ and (2) to act as building blocks for the systematic synthesis of new cluster (polynuclear) compounds.⁶ Both have important catalytic implications.

In the compounds Cp₂M₂(CO)₄, where M = Mo or W, the formation of a metal-to-metal triple bond allows the metal atoms to achieve an 18-valence shell electron configuration.⁷ In compounds of the type M₂L₆, where M = Mo and W, L = R(alkyl),^{8,9} NR₂,^{10,11} and OR,^{12,13} which have metal-to-metal triple bonds and a central ethane-like M₂X₆ core (X = C, N, O), the metal atoms do not achieve an 18-valence shell electron configuration, even when ligand to metal π bonding is important as is the case where L = NR₂ and OR.¹⁴ The compounds Cp₂M₂(CO)₄ and M₂L₆ may be termed electronically saturated and unsaturated, respectively, and differences in their reactivity patterns may be expected. Some of these have already been observed.

All compounds containing metal-to-metal multiple bonds are inherently coordinatively unsaturated and Cp₂M₂(CO)₄

and M₂L₆ compounds react to expand the coordination number of the metal as shown:



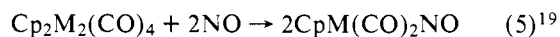
In reactions 1 and 2, the addition of four electrons to the electronically saturated M≡M moiety reduces the M-M bond order in Cp₂M₂(CO)₄L₂ and Cp₂M₂(CO)₄(un) compounds to a single M-M bond.¹⁸ Addition of 2L (four electrons) to Mo₂(OR)₆ compounds does not reduce the M-M bond order in the adducts. The structural characterization of the dimethylamine adduct of hexakis(trimethylsiloxy)dimolybdenum, Mo₂(OSiMe₃)₂(HNMe₂)₂,¹⁶ and Mo₂(OBU-*t*)₄(O₂COBU-*t*)₂¹⁷ reveals triple bonds between two four-coordinated molybdenum atoms with Mo-Mo distances of 2.242 (1) and 2.244 (1) Å, respectively; cf.¹² Mo-Mo = 2.222 (1) Å in Mo₂(OCH₂CMe₃)₆.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	-0.1085 (1)	0.05358 (8)	0.0592 (1)	0.0133 (1)	0.006 83 (6)	0.0181 (1)	-0.0010 (1)	0.0164 (2)	0.0008 (2)
Mo(2)	0.3931 (1)	0.55137 (8)	0.5638 (1)	0.0140 (1)	0.006 47 (6)	0.0197 (2)	-0.0028 (2)	0.0138 (2)	-0.0004 (2)
O(1)	0.0053 (7)	-0.0572 (5)	0.0883 (8)	0.0133 (8)	0.0058 (4)	0.018 (1)	-0.001 (1)	0.017 (1)	0.004 (1)
O(2)	-0.0235 (9)	0.1478 (6)	0.1392 (9)	0.0199 (11)	0.0075 (5)	0.020 (1)	-0.003 (1)	0.019 (2)	-0.004 (1)
O(3)	-0.2702 (8)	0.0760 (6)	-0.1203 (9)	0.0124 (9)	0.0088 (5)	0.022 (1)	-0.004 (1)	0.012 (2)	0.002 (1)
O(4)	-0.2279 (10)	0.0250 (8)	0.2695 (11)	0.0302 (13)	0.0154 (9)	0.036 (1)	-0.001 (2)	0.049 (2)	0.007(2)
O(5)	0.4039 (7)	0.5251 (5)	0.3764 (8)	0.0094 (9)	0.0085 (5)	0.015 (1)	-0.001 (1)	0.003 (2)	0.001 (1)
O(6)	0.4957 (10)	0.6310 (6)	0.6820 (11)	0.0242 (14)	0.0083 (6)	0.027 (2)	-0.006 (1)	0.020 (2)	-0.006 (2)
O(7)	0.3676 (8)	0.4652 (6)	0.6717 (9)	0.0164 (10)	0.0080 (5)	0.025 (1)	-0.005 (1)	0.020 (2)	0.000 (1)
O(8)	0.1159 (11)	0.6538 (7)	0.4427 (13)	0.0214 (14)	0.0106 (7)	0.040 (2)	0.009 (2)	0.024 (3)	0.008 (2)
N(1)	-0.181 (1)	0.0355 (8)	0.182 (1)	0.021 (1)	0.0113 (8)	0.024 (1)	0.004 (2)	0.030 (2)	0.004 (2)
N(2)	0.226 (1)	0.6108 (7)	0.489 (1)	0.017 (1)	0.0085 (7)	0.026 (2)	0.000 (2)	0.021 (2)	0.002 (2)
C(1)	0.034 (1)	-0.1349 (9)	0.182 (2)	7.7 (4)					
C(2)	0.100 (2)	-0.1130 (11)	0.357 (2)	9.6 (5)					
C(3)	-0.103 (2)	-0.1690 (11)	0.139 (2)	9.4 (5)					
C(4)	-0.011 (2)	0.1915 (11)	0.274 (2)	9.3 (5)					
C(5)	0.121 (2)	0.1494 (14)	0.416 (2)	13.4 (7)					
C(6)	-0.003 (2)	0.2814 (14)	0.250 (2)	13.9 (7)					
C(7)	-0.413 (2)	0.0696 (11)	-0.140 (2)	10.3 (5)					
C(8)	-0.495 (2)	0.1504 (16)	-0.212 (3)	16.2 (8)					
C(9)	-0.470 (3)	0.0096 (17)	-0.290 (3)	17.7 (10)					
C(10)	0.309 (2)	0.5507 (10)	0.215 (2)	8.8 (4)					
C(11)	0.175 (2)	0.5100 (13)	0.173 (2)	12.4 (6)					
C(12)	0.289 (2)	0.6457 (13)	0.196 (2)	12.0 (6)					
C(13)	0.454 (2)	0.7252 (14)	0.698 (2)	13.6 (7)					
C(14)	0.492 (3)	0.7677 (18)	0.596 (3)	18.9 (10)					
C(15)	0.494 (4)	0.7357 (22)	0.859 (4)	23.8 (13)					
C(16)	0.239 (2)	0.4529 (11)	0.686 (2)	10.4 (5)					
C(17)	0.237 (3)	0.3565 (17)	0.682 (3)	16.8 (9)					
C(18)	0.245 (2)	0.4828 (16)	0.825 (3)	15.6 (8)					

^a The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

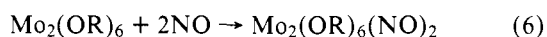
The addition of six electrons, in the form of two nitrosyl ligands, to the electronically saturated $M\equiv M$ moiety in $Cp_2M_2(CO)_4$ effects cleavage of the M-M triple bond with formation of 2 equiv of a mononuclear complex:



This latter observation prompted us to examine the reactivity of the electronically unsaturated $M\equiv M$ moiety in M_2L_6 compounds toward nitric oxide. We report here our studies of the reactions of $Mo_2(OR)_6$ compounds with NO.

Results and Discussion

Synthesis and Properties of $Mo_2(OR)_6(NO)_2$ Compounds. Hydrocarbon solutions of $Mo_2(OR)_6^{12}$ compounds, where R = Me_3C , Me_2CH , and Me_3CCH_2 , react with NO (2 equiv) at room temperature according to



The reaction is rapid, irreversible, and seemingly quantitative. The nitrosyl compounds may be purified by sublimation (70–110 °C, 10^{-4} cmHg). Analytical and other characterization data are recorded in the Experimental Section.

$Mo_2(OR)_6(NO)_2$ are yellow, crystalline, diamagnetic compounds, which, though thermally quite stable, are moisture and oxygen sensitive. They are soluble in hydrocarbon solvents, and a cryoscopic molecular weight determination in benzene confirmed the dinuclear nature of $Mo_2(OPr-i)_6(NO)_2$. The other compounds are assumed to be dinuclear in solution on the basis of their similar properties.

They show molecular ions $Mo_2(OR)_6(NO)_2^+$ followed by loss of NO in the mass spectrometer. Intense ions due to $Mo(OR)_3NO^+$ were also observed. The intensity of the latter is in sharp contrast with the mass spectra of $Mo_2(OR)_6$ compounds which show virtually only dinuclear ions (Mo_2 containing) in the mass spectrometer.

In the infrared spectra a single intense band at ca. 1640 cm^{-1} is attributed to $\nu_{str}(NO)$ of a terminally bonded NO ligand. IR data are recorded in the Experimental Section.

NMR Studies. Variable temperature 1H and ^{13}C NMR studies show that $Mo_2(OR)_6(NO)_2$ are fluxional molecules. The low-temperature limiting spectra indicate the freezing out on the NMR time scale of a structure having two types of alkoxy groups in 2:1 integral ratio: $Mo_2(OR)_2(OR')_4(NO)_2$. The rate of interconversion of alkoxy groups OR and OR' is dependent on the alkyl group: $T_c = 70, 40,$ and -20 °C for $OCMe_3$, $OCHMe_2$, and OCH_2CMe_3 , respectively. The low-temperature limiting ^{13}C NMR spectrum of the isopropoxide, corresponding to $Mo_2(OR)_2(OR')_4(NO)_2$, indicates that the R'-methyl carbon atoms are diastereotopic. 1H and ^{13}C NMR data are given in the Experimental Section.

Solid State Structure. There are two crystallographically independent molecules per unit cell, each possessing crystallographically imposed C_i symmetry. Table I lists the atomic positional and thermal parameters. Bond distances and angles are given in Tables II and III, respectively. An ORTEP view and a stereoview of molecule I, showing the atom labeling scheme, are shown in Figures 1 and 2. No views of molecule II are shown, since, as Tables II and III show, it is virtually identical with molecule I, including the shapes of thermal vibration ellipsoids. The labeling scheme used for molecule II parallels that of molecule I as can be deduced from Tables II and III; for example, O(5), . . . , O(8) in molecule II correspond, in order, to O(1), . . . , O(4) in molecule I. Figure 3 depicts the coordination about the metal atoms and lists some pertinent bond distances averaged for both molecules and rounded off to 0.01 Å.

The $[Mo(OPr-i)_3NO]_2$ molecule consists of two equivalent (inversion-related) distorted trigonal bipyramidal $Mo(OR)_4NO$ units fused along a common axial-to-equatorial edge through the agency of bridging OPr-*i* groups. With a Mo-Mo

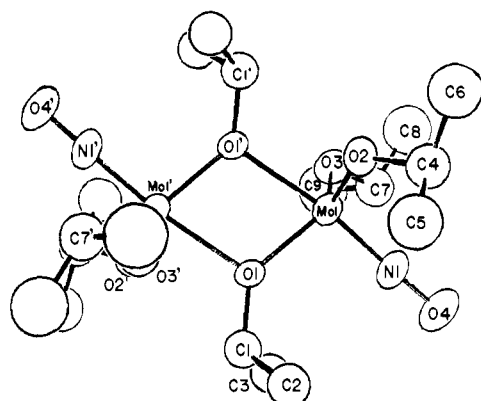


Figure 1. An ORTEP view of molecule I using 40% probability ellipsoids and showing the atom labeling scheme.

distance of 3.335 (2) Å it may be assumed that no significant direct Mo–Mo interaction exists. It will be shown later that the electronic structure can be understood quite satisfactorily without recourse to any such metal-to-metal interaction.

The distortions of the trigonal bipyramid are all understandable in terms of the nature and function of the ligands. The principal axis is slightly bent (171.9°), presumably because of stress imposed by the bridging system. The Mo(1)–O(1) and Mo(2)–O(5) bonds, 1.95 Å, are longer than the other equatorial Mo–O bonds, 1.85 Å, since O(1) and O(5) are bridging atoms. The Mo(1)–O(1') and Mo(2)–O(5') bonds, 2.194 Å, are much longer than any of the Mo–O equatorial bonds, which is indicative of the high trans influence of the NO ligand.^{20,21} Finally, the three equatorial Mo–O bonds are slightly bent away from the NO ligand and toward the long Mo–O axial bond, the N–Mo–O angles being 99 ± 1°, which is an expected steric consequence of closeness of the N and remoteness of the axial O atoms.

Table II. Bond Distances (Å)

Molecule I		Molecule II	
Atoms	Distance	Atoms	Distance
Mo(1)–Mo(1)'	3.334 (2)	Mo(2)–Mo(2)'	3.337 (2)
–O(1)	1.951 (6)	–O(5)	1.946 (6)
–O(1)'	2.195 (6)	–O(5)'	2.194 (6)
–O(2)	1.850 (7)	–O(6)	1.849 (8)
–O(3)	1.861 (6)	–O(7)	1.857 (7)
–N(1)	1.747 (9)	–N(2)	1.761 (10)
N(1)–O(4)	1.205 (11)	N(2)–O(8)	1.184 (11)
C(1)–O(1)	1.46 (1)	C(10)–O(5)	1.50 (1)
–C(2)	1.61 (2)	–C(11)	1.55 (2)
–C(3)	1.53 (2)	–C(12)	1.49 (2)
C(4)–O(2)	1.46 (2)	C(13)–O(6)	1.53 (2)
–C(5)	1.56 (2)	–C(14)	1.44 (2)
–C(6)	1.47 (2)	–C(15)	1.47 (3)
C(7)–O(3)	1.49 (2)	C(16)–O(7)	1.49 (2)
–C(8)	1.44 (2)	–C(17)	1.53 (2)
–C(9)	1.68 (2)	–C(18)	1.42 (2)

Discussion

The work reported here is important because it implies the existence of a new and heretofore unrecognized, and potentially large, class of metal nitrosyl compounds. To appreciate the relationship of this compound to the known types of metal nitrosyls let us compare it with previously known trigonal bipyramidal complexes having the NO ligand in an axial position. According to the tabulation of Eisenberg and Meyer²¹ there are only two of these, viz., RuH(NO)(PPh₃)₃²² and [IrH(NO)(PPh₃)₃]ClO₄,²³ in each of which there is a formal 18-electron configuration for the metal atoms. As is generally recognized, these 18 electrons can be assigned as shown in Figure 4a.

It is then straightforward to assign the 14 electrons in the present case as shown in Figure 4b. In this way the strong π

Table III. Bond Angles (deg)

Molecule I				Molecule II			
Atoms			Angle	Atoms			Angle
Mo(1)'	Mo(1)	O(1)	39.1 (2)	Mo(2)'	Mo(2)	O(5)	38.9 (2)
Mo(1)'	Mo(1)	O(1)	34.1 (2)	Mo(2)'	Mo(2)	O(5)	33.8 (2)
Mo(1)'	Mo(1)	O(2)	102.8 (2)	Mo(2)'	Mo(2)	O(6)	102.8 (3)
Mo(1)'	Mo(1)	O(3)	101.4 (2)	Mo(2)'	Mo(2)	O(7)	102.6 (2)
Mo(1)'	Mo(1)	N(1)	137.9 (3)	Mo(2)'	Mo(2)	N(2)	138.9 (3)
O(1)	Mo(1)	O(1)'	73.1 (3)	O(5)	Mo(2)	O(5)'	72.7 (3)
O(1)	Mo(1)	O(2)	119.3 (3)	O(5)	Mo(2)	O(6)	119.1 (3)
O(1)	Mo(1)	O(3)	117.3 (3)	O(5)	Mo(2)	O(7)	118.6 (3)
O(1)	Mo(1)	N(1)	98.8 (4)	O(5)	Mo(2)	N(2)	99.1 (4)
O(1)'	Mo(1)	O(2)	84.4 (3)	O(5)'	Mo(2)	O(6)	84.6 (3)
O(1)'	Mo(1)	O(3)	83.8 (3)	O(5)'	Mo(2)	O(7)	84.6 (3)
O(1)'	Mo(1)	N(1)	171.9 (4)	O(5)'	Mo(2)	N(2)	171.9 (4)
O(2)	Mo(1)	O(3)	115.1 (3)	O(6)	Mo(2)	O(7)	114.2 (3)
O(2)	Mo(1)	N(1)	100.8 (4)	O(6)	Mo(2)	N(2)	100.0 (4)
O(3)	Mo(1)	N(1)	99.5 (4)	O(7)	Mo(2)	N(2)	99.4 (4)
Mo(1)'	O(1)	Mo(1)	106.9 (3)	Mo(2)'	O(5)	Mo(2)	107.3 (3)
Mo(1)	O(1)	C(1)	134.8 (6)	Mo(2)	O(5)	C(10)	132.8 (6)
Mo(1)'	O(1)	C(1)	118.3 (6)	Mo(2)'	O(5)	C(10)	119.8 (6)
Mo(1)	O(2)	C(4)	129.9 (7)	Mo(2)	O(6)	C(13)	131.1 (9)
Mo(1)	O(3)	C(7)	125.7 (7)	Mo(2)	O(7)	C(16)	128.5 (8)
Mo(1)	N(1)	O(4)	178 (1)	Mo(2)	N(2)	O(8)	177 (1)
O(1)	C(1)	C(2)	109.3 (9)	O(5)	C(10)	C(11)	108 (1)
O(1)	C(1)	C(3)	108.1 (9)	O(5)	C(10)	C(12)	108 (1)
C(2)	C(1)	C(3)	110 (1)	C(11)	C(10)	C(12)	116 (1)
O(2)	C(4)	C(5)	111 (1)	O(6)	C(13)	C(14)	103 (2)
O(2)	C(4)	C(6)	108 (1)	O(6)	C(13)	C(15)	107 (2)
C(5)	C(4)	C(6)	111 (1)	C(14)	C(13)	C(15)	130 (2)
O(3)	C(7)	C(8)	105 (1)	O(7)	C(16)	C(17)	105 (1)
O(3)	C(7)	C(9)	101 (1)	O(7)	C(16)	C(18)	111 (1)
C(8)	C(7)	C(9)	99 (2)	C(17)	C(16)	C(18)	111 (2)

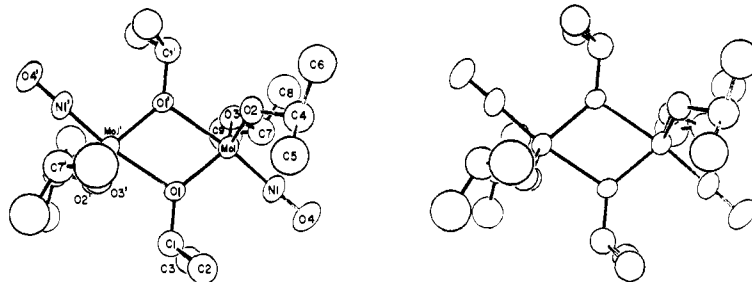


Figure 2. A stereoview of molecule 1 using 40% probability ellipsoids.

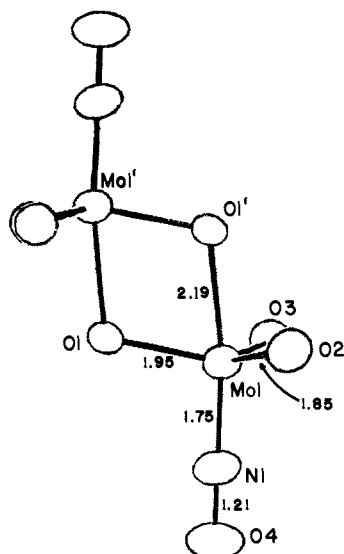
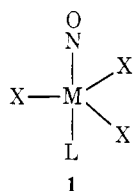


Figure 3. An ORTEP view showing the coordination geometry and average bond distances in the two essentially identical molecules.

interaction via the overlap between metal d_{xz} and d_{yz} orbitals with NO π^* orbitals is maintained and accounts for the short Mo–N distance and the low value of ν_{NO} . All that is lost in going from the configuration of Figure 4a to that of Figure 4b are the 2e electrons which are essentially nonbonding.

It may also be emphasized that the essential features of Figure 4 are not dependent upon the precise fulfillment of trigonal bipyramidal geometry. In particular, the bending down of the equatorial bonds (i.e., away from NO), and the lengthening of the bond to the donor, L, trans to NO, even to the limit of eliminating L and having a four-coordinate structure of C_{3v} symmetry, do not invalidate the analysis. The monomeric diamagnetic compounds $\text{Cr}(\text{NPr}_2\text{-}i)_3\text{NO}$ and $\text{Cr}(\text{NSi}_2\text{Me}_6)_3\text{NO}$ provide examples of this limiting situation.^{24,25}

There would not seem to be any reason why discrete mononuclear complexes of the type **1**, where X represents a univalent ligand, L a σ donor, and M any atom or ion isoelectronic with Mo(II), should not exist as a general class. In the particular context of the present case, the possibility of converting the dinuclear molecule to two molecules of type **1** in which X



= OPr-*i* by a bridge-splitting reaction with some neutral ligand, L, can be envisioned.

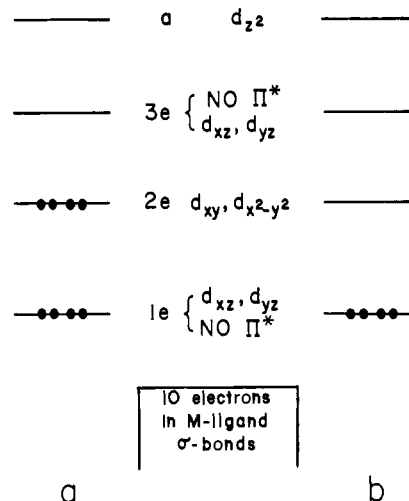


Figure 4. MO diagrams, showing only the highest filled and lowest unfilled orbitals, for trigonal bipyramidal molecules of the type $\text{MX}_3\text{L}(\text{NO})_1$ where L and NO are axial, for (a) the 18-electron case and (b) the 14-electron case.

In a formal sense, the reaction of the $(\text{RO})_3\text{Mo}\equiv\text{Mo}(\text{OR})_3$ molecule with 2NO to give two $(\text{RO})_3\text{MoNO}$ units (which then associate via bridging RO groups) corresponds to the replacement of the Mo \equiv Mo triple bond (a σ bond plus two π bonds) by two Mo \equiv N–O bonds. Of course this is only one of the three resonance forms (the other two being Mo $=$ N=O and Mo–N \equiv O) which may be used, in proportions appropriate to each case, to represent any given linear M–N–O group. Again, there is a σ electron pair and two π electron pairs shared by the Mo atom and its partner, which is now the nitrogen atom instead of another molybdenum atom. Cleavage of the M–M triple bond in reaction 5 may be viewed in a similar manner. However, the detailed mechanism of the reaction which leads to cleavage of the M–M triple bond remains to be established.

Future work will be directed toward (1) the synthesis of monomeric compounds of the general formula $\text{Mo}(\text{OR})_3(\text{NO})\text{L}$, where L = a neutral donor ligand, and (2) an elucidation of the fluxional properties of $\text{Mo}_2(\text{OR})_6(\text{NO})_2$ compounds.

Experimental Section

General procedures have been described previously.¹⁰ All reactions were carried out under a dried and purified nitrogen atmosphere using standard Schlenk or vacuum-line procedures.

Preparation of $\text{Mo}_2(\text{OR})_6(\text{NO})_2$ Compounds (R = Me_3C , Me_2CH , and Me_3CCH_2). All reactions were carried out in a similar manner, which is exemplified by the reaction described below.

$\text{Mo}_2(\text{OPr-}i)_6(\text{NO})_2$. $\text{Mo}_2(\text{OPr-}i)_6$ (0.38 g, 0.7 mmol) was dissolved in hexane (10 mL) in a 25-mL round-bottomed flask to give a pale yellow solution. The flask was cooled in liquid nitrogen and evacuated, and, by use of a calibrated vacuum manifold, nitric oxide (1.4 mmol) was added. Upon warming to room temperature the solution darkened.

After 12 h the solvent was stripped yielding a light brown solid from which upon heating under vacuum (75 °C, 10⁻³ cmHg) gave the yellow compound [Mo(OPr-*i*)₃NO]₂ (0.15 g, 36% yield) by sublimation. In an NMR tube experiment the reaction between Mo₂(OPr-*i*)₆ and NO (2 equiv) to give Mo₂(OPr-*i*)₆(NO)₂ was seen to be rapid and apparently quantitative.

Analytical Data. Anal. Calcd for Mo₂(OPr-*i*)₆(NO)₂: C, 35.65; H, 6.98; N, 4.62. Found: C, 35.36; H, 6.75; N, 4.56. Calcd for Mo₂(OBu-*t*)₆(NO)₂: C, 41.74; H, 7.88; N, 4.06. Found: C, 41.49; H, 8.02; N, 4.22. Calcd for Mo₂(OCH₂CMe₃)₆(NO)₂: C, 46.51; H, 8.59; N, 3.62. Found: C, 46.34; H, 8.29; N, 3.65.

Infrared data in the range 2000–400 cm⁻¹ obtained from Nujol mulls between KBr plates Mo₂(OPr-*i*)₆(NO)₂: 1640 vs, 1330 w, 1771 w, 1132 w, 1110 s, 1022 vw, 961 s (br), 940 s, 851 m, 835 m, 666 m, 650 m, 629 w, 598 m, 485 w cm⁻¹. Mo₂(OBu-*t*)₆(NO)₂: 1632 vs, 1310 w, 1245 m, 1163 s (br), 976 w, 950 s, 938 vs, 910 m, 847 s, 788 s, 769 s, 738 m, 725 m, 645 s, 631 s, 622 m, 595 m, 400 w cm⁻¹. Mo₂(OCH₂CMe₃)₆(NO)₂: 1643 vs, 1300 w, 1264 w, 1218 w, 1182 w, 1168 w, 1050 s, 1040 vs, 1016 vs, 998 s, 937 m, 920 w, 905 w, 850 w, 805 w, 760 w, 723 w, 708 w, 670 m, 633 w, 623 m, 571 m, 540 m, 489 w, 469 w, 436 w, 415 w cm⁻¹.

¹H NMR data were obtained in toluene-*d*₈, relative to Me₄Si, *J* in hertz. Mo₂(OPr-*i*)₆(NO)₂, *T* = 80 °C, δ(CH₃) 1.27, δ(CH) 5.25, *J* = 6.5; *T* = 20 °C, δ(CH₃) 1.23, 1.40, δ(CH) 4.98, 5.40, *J* = 6.5. Mo₂(OBu-*t*)₆(NO)₂: *T* = 80 °C, δ(CH₃) 1.47; *T* = 20 °C, δ(CH₃) 1.40, 1.60. Mo₂(OCH₂CMe₃)₆(NO)₂: *T* = 20 °C, δ(CH₂) 4.75, δ(CH₃) 0.92; *T* = -40 °C, δ(CH₂) 4.61, 4.82, (CH₃) 0.86, 1.01.

Low-temperature limiting ¹³C NMR data corresponding to Mo₂(OR)₂(OR')₄(NO)₂ were obtained in toluene-*d*₈, relative to Me₄Si. Mo₂(OBu-*t*)₆(NO)₂: δ(R-methyl) 32.69, δ(R-C tertiary) 88.29, δ(R'-methyl) 33.10, δ(R'-C tertiary) 83.78. Mo₂(OPr-*i*)₆(NO)₂: δ(R-methyl) 25.69, δ(R-CH) 79.04, δ(R'-methyl) 26.75, δ(R'-CH) 81.01. Mo₂(OCH₂CMe₃)₆(NO)₂: δ(R-methyl) 26.96, δ(R-C tertiary) 34.09, δ(R-CH₂) 91.61, δ(R'-methyl) 26.60, δ(R'-C tertiary) 34.62, δ(R'-CH₂) 91.50.

X-Ray Crystallography. A crystal of Mo₂(OPr-*i*)₆(NO)₂ measuring ca. 0.2 × 0.3 × 0.5 mm was wedged in a mineral oil filled capillary and mounted with the longest crystal dimension nearly coincident with φ. The ω scans of several intense low-angle reflections had peak widths at half-height of ca. 0.2°. Cell constants indicated that the crystal belonged to the triclinic system with *a* = 10.828 (1), *b* = 15.848 (2), *c* = 9.885 (2) Å; α = 90.21 (2)°, β = 115.93 (2)°, γ = 82.42 (1)°, *V* = 1509.4 (4) Å³. The observed volume was consistent with that expected for *Z* = 2. The space group was presumed to be *P* $\bar{1}$ (no. 2) and this was confirmed by the subsequent structure solution and refinement.

Data were collected at 24 °C on a Syntex P $\bar{1}$ autodiffractometer using Mo Kα (λ = 0.710 730) radiation with a graphite crystal monochromator. The θ–2θ scan technique was used with scans ranging from 1.0° above to 1.0° below the calculated Kα₁, Kα₂ doublet, variable scan speeds from 4.0 to 24.0°/min, and a scan to background time ratio of 0.5. The intensities of three standard reflections were monitored frequently throughout data collection and showed a maximum decrease of 27%. A total of 4121 reflections having 0° < 2θ (Mo Kα) < 45.0° were collected. The intensities were reduced to a set of relative |*F*_o|² values and corrected for crystal decay.²⁵ The 2052 reflections having |*F*_o|² > 3σ(|*F*_o|²) were used in subsequent structure solution and refinement. In general, reflections of the type *hkl*, *h* + *k* + *l* = 2*n* + 1, were weak. The data were not corrected for absorption (μ = 8.5 cm⁻¹). The structure was solved using conventional heavy atom methods,²⁵ and refined to convergence utilizing anisotropic thermal parameters for the Mo, O, and N atoms and isotropic thermal

parameters for the remaining nonhydrogen atoms. The final residuals are

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.061$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.093$$

A value of 0.07 was used for *P* in the calculation of the weights, *w*. The end of an observation of unit weight was 2.01. A final difference Fourier map showed no peaks of structural significance.

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Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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