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Reactions of Metal-to-Metal Multiple Bonds.[1] 6. Reversible Carbonylation of Hexakis(*tert*-butoxy)dimolybdenum $(M{\equiv}M)$. A Carbonyl-Bridged Metal-to-Metal Double Bond, $Mo_2(OBu\text{-}t)_6(CO)$ $(M{=}M)$

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Abstract: Hydrocarbon solutions of $Mo_2(OBu\text{-}t)_6$ $(M{\equiv}M)$ react with carbon monoxide at room temperature and 1 atm according to the stoichiometric equation $2Mo_2(OBu\text{-}t)_6 + 6CO = Mo(CO)_6 + 3Mo(OBu\text{-}t)_4$. The reaction proceeds via a slow and reversible formation of a monocarbonyl, $Mo_2(OBu\text{-}t)_6(\mu\text{-}CO)$, that has been isolated as a crystalline compound and characterized by a number of spectroscopic techniques. The compound shows a strong infrared absorption at 1670 cm^{-1} in the solid state and at 1690 cm^{-1} in hydrocarbon solutions assignable to $\nu(CO)$ of a carbonyl group bridging two molybdenum atoms. An X-ray study shows that in the crystalline state the molecule has virtual C_{2v} symmetry. The coordination polyhedron about each metal atom is a distorted square pyramid with the carbonyl carbon atom at the apex. The Mo-to-Mo distance is 2.489 (1) Å, which, together with the observed diamagnetism, is consistent with the existence of a metal-to-metal double bond. Crystal data for $Mo_2(OBu\text{-}t)_6(CO)$ follow: $a = 17.827$ (3) Å, $b = 9.335$ (2) Å, $c = 19.447$ (4) Å, $\alpha = \beta = \gamma = 90.00°$, $V = 3236$ (1) $Å^3$, $Z = 4$, space group $Cmc2_1$. In solution both IR and NMR data support the view that the carbonyl group remains bridging. Low-temperature ^{13}C NMR spectra indicate that the molecule is fluxional: only one type of OBu-*t* group is found on the NMR time scale. Carbon monoxide reacts readily under similar conditions with $Mo_2(OPr\text{-}i)_6$ $(M{\equiv}M)$ to give $Mo(CO)_6$ and as yet unidentified oxidized molybdenum alkoxides. A black, paramagnetic, crystalline compound of empirical formula $Mo(OPr\text{-}i)_3CO$ has been isolated from this reaction. Crystals of this compound repeatedly decomposed in the X-ray beam but based on limited X-ray data and mass spectral analysis this compound is formulated as a tetranuclear alkoxide $Mo_4(OPr\text{-}i)_{12}(CO)_4$. The difference in the course of the reactions between $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OPr\text{-}i)_6$ with CO is believed to be dominated by the different steric properties of the alkyl ligands. The reaction of CO with $Mo_2(OPr\text{-}i)_8$ $(M{=}M)$ produces a compound formulated as $(Pr\text{-}i\text{-}O)_4Mo(\mu\text{-}Pr\text{-}i)_2Mo(OPr\text{-}i)_2(CO)_2$ on the basis of analytical and spectroscopic data. These reactions of CO with dinuclear molybdenum alkoxides are compared with other carbonylation reactions involving compounds containing metal-to-metal triple bonds.

Introduction

Prior work has established that the triply bonded $(M{\equiv}M)$ compound $Cp_2Mo_2(CO)_4$ readily reacts with unsaturated molecules, un, to form 1:1 adducts in which the unsaturated molecules act as four-electron donors spanning metal-to-metal single bonds. The Mo-to-Mo distance increases from 2.448 (1) Å in $Cp_2Mo_2(CO)_4$[3] to 2.974 (1), 3.015 (1), and 3.117 (1) Å in the adducts $Cp_2Mo_2(CO)_4(un)$ when un = $HC{\equiv}CH$,[4] $Me_2NC{\equiv}N$,[5] and $CH_2{=}C{=}CH_2$,[6] respectively. These distances may be compared with the unbridged Mo-to-Mo single bond distance of 3.235 (1) Å in $Cp_2Mo_2(CO)_6$.[7] In each of these adducts the molybdenum atom attains an 18-electron valence shell and there is an Mo–Mo bond of order one. In the work reported here we have examined the reactivity of the $(M{\equiv}M)^{6+}$ moiety in Mo_2X_6 compounds ($X = NR_2$, OR, R) in which the metal atoms have less than the inert gas configuration even after forming the Mo-to-Mo triple bond.[8] The alkoxides, $Mo_2(OR)_6$, were our first choice in this series since we had previously established their ability to reversibly coordinate neutral donor ligands such as amines.[9,10] We report here our studies of the reaction between carbon monoxide and several dinuclear alkoxides, viz., $Mo_2(OBu\text{-}t)_6$, $Mo_2(OPr\text{-}i)_6$, and $Mo_2(OPr\text{-}i)_8$, and structural characterization of the first compound containing a carbonyl ligand bridging a metal-to-metal double bond[11] is also reported in detail.

Results and Discussion

Carbonylation of $Mo_2(OBu\text{-}t)_6$. Under 1 atm of carbon monoxide hydrocarbon solutions of $Mo_2(OBu\text{-}t)_6$ react smoothly, according to the equation

$$2Mo_2(OBu\text{-}t)_6 + 6CO = Mo(CO)_6 + 3Mo(OBu\text{-}t)_4 \quad (1)$$

The stoichiometry of (1) was determined by uptake of carbon monoxide using a gas buret. $Mo(CO)_6$ and $Mo(OBu\text{-}t)_4$[12] were identified by mass spectroscopy and IR spectroscopy and were separated by taking advantage of their respective low and high solubilities in alkane solvents.

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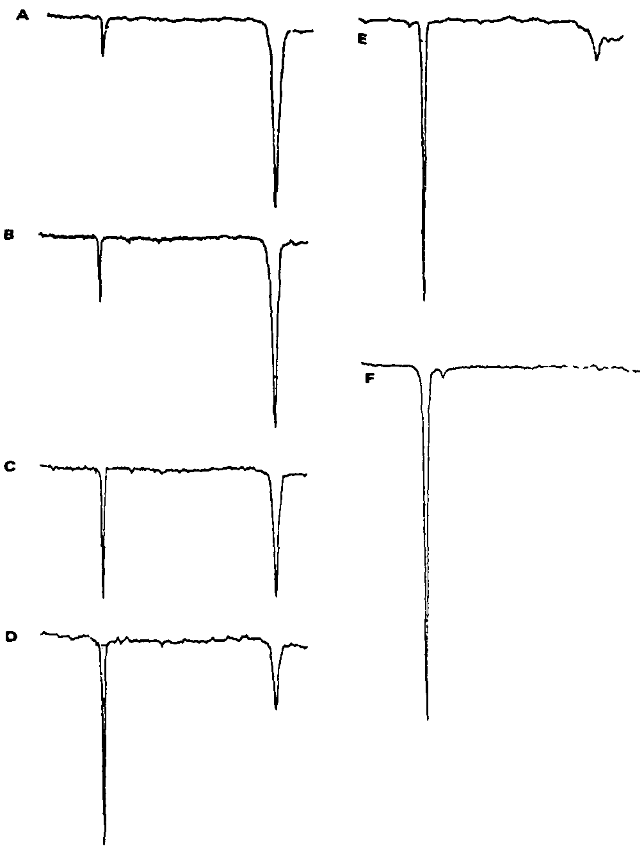

Figure 1. Infrared spectra of a hexane solution of $Mo_2(OBu\text{-}t)_6(CO)$ recorded as a function of time showing the disappearance of $Mo_2(OBu\text{-}t)_6(CO)$, $\nu(CO)$ 1690 cm^{-1} and the formation of $Mo(CO)_6$, $\nu(CO)$ 1985 cm^{-1}: A, t = 5 min; B, t = 10 min; C, t = 50 min; D, t = 140 min; E, t = 300 min; F, t = 1085 min.

At ca. 25 °C reaction 1 is complete within 4 days. When the progress of reaction 1 was monitored by IR spectroscopy, the slow growth of the band at 1985 cm^{-1} assignable to $Mo(CO)_6$ was seen. Significantly this was the *only* band which appeared in the carbonyl region of the IR spectrum (2100–1600 cm^{-1}). The reaction was also followed by ^{13}C NMR spectroscopy. When ^{13}CO was allowed to react with $Mo_2(OBu\text{-}t)_6$ in toluene-d_8, only the formation of $Mo(CO)_6$ was observed: the resonance that grew at δ 204.1 ppm (relative to Me_4Si) was the only ^{13}C resonance in the carbonyl region of the spectrum. However, when *near-saturated* alkane solutions of $Mo_2(OBu\text{-}t)_6$ are exposed to 2 equiv of carbon monoxide at room temperature and then cooled to ca. −15 °C in the refrigerator, dark purple crystals are formed. Crystalline samples prepared in this way are usually contaminated with traces of $Mo(CO)_6$ (readily detected by its intense absorption at 1985 cm^{-1}) but careful crystallizations yield the pure purple, crystalline compound $Mo_2(OBu\text{-}t)_6(CO)$.

$Mo_2(OBu\text{-}t)_6(CO)$ is thermally unstable, liberating CO and forming $Mo_2(OBu\text{-}t)_6$ when heated under vacuum. In the mass spectrometer the ion of highest mass corresponds to $Mo_2(OBu\text{-}t)_6^+$, which provides a further indication of the lability of the CO ligand in the 1:1 adduct $Mo_2(OBu\text{-}t)_6CO$. These observations establish the reversibility of the reaction

$$Mo_2(OBu\text{-}t)_6 + CO \rightleftharpoons Mo_2(OBu\text{-}t)_6(CO) \qquad (2)$$

which is reminiscent of the readily reversible reactions that occur between $Mo_2(OR)_6$ compounds and CO_2 to give $Mo_2(OR)_4(O_2COR)_2$ compounds.[13]

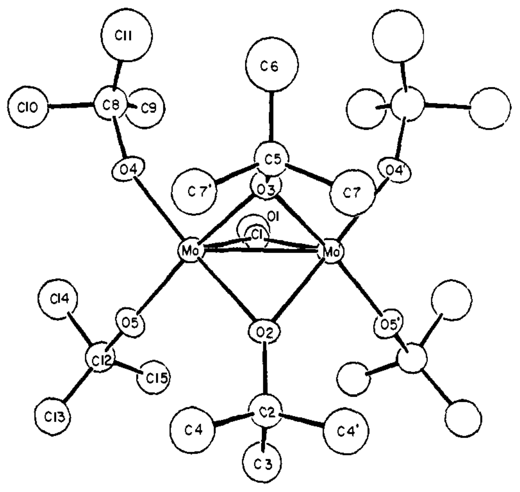

Figure 2. An ORTEP view of the $Mo_2(OBu\text{-}t)_6(CO)$ molecule showing the atomic numbering scheme used in Table II.

Hydrocarbon solutions of $Mo_2(OBu\text{-}t)_6(CO)$ have an intense purple color akin to that of the permanganate anion. However, when a solution of $Mo_2(OBu\text{-}t)_6(CO)$ is exposed to carbon monoxide (≤1 atm), this color is discharged rapidly. In one experiment the IR spectrum was recorded after a 15-min exposure to CO at 0.75 atm pressure. All the $Mo_2(OBu\text{-}t)_6$ had reacted to form $Mo(CO)_6$ along with traces of some additional compound(s) that have bands at ca. 1930 and 1830 cm^{-1}. These other bands may be due to intermediates in reaction 1.

We conclude that $Mo_2(OBu\text{-}t)_6(CO)$ is an intermediate in reaction 1 and furthermore its formation by attack of CO on $Mo_2(OBu\text{-}t)_6$ is probably the rate-determining step in the formation of $Mo(CO)_6$.

Hydrocarbon solutions of $Mo_2(OBu\text{-}t)_6(CO)$ react slowly in the absence of excess carbon monoxide to give $Mo(CO)_6$, $Mo_2(OBu\text{-}t)_6$, and $Mo(OBu\text{-}t)_4$. This reaction was followed in a solution IR study. The band at 1670 cm^{-1} arising from $Mo_2(OBu\text{-}t)_6(CO)$ slowly decreased in intensity as the band at 1985 cm^{-1} arising from $Mo(CO)_6$ grew as shown in Figure 1. Once again no other intermediates were detected. Since $Mo_2(OBu\text{-}t)_6(CO)$ reacts rapidly with free carbon monoxide and is itself labile to dissociation of CO it is quite possible that this reaction proceeds via an initial dissociation of CO, eq 2, but this has not been established.

Solid-State Structure of $Mo_2(OBu\text{-}t)_6(CO)$. Crystals of $Mo_2(OBu\text{-}t)_6(CO)$ consist of discrete dinuclear molecules with the structure shown in Figure 2, which also gives the atomic numbering scheme. Bond distances and bond angles are given in Table I. Each molecule possesses a crystallographically imposed mirror plane containing O(1), C(1), O(2), and O(3) which bisects the Mo–Mo bond. The virtual symmetry of the molecule is C_{2v} and the coordination polyhedron about each molybdenum atom is a distorted square pyramid with the carbonyl carbon atom at the apex. Figure 3 shows a view of the molecule omitting the *tert*-butyl groups. This view clearly reveals the geometry of the two MoO_4C polyhedra which are fused along a common triangular face defined by the atoms C(1), O(2), and O(3).

An interesting comparison can be made with the $Mo_2(OPr\text{-}i)_8$ molecule. Here, also, each molybdenum atom is coordinated by five ligand atoms, but the local geometry is that of a distorted trigonal bypyramid.[14] The Mo_2O_8 group may thus be viewed as two MoO_5 trigonal bypyramids joined on a common axial to equatorial edge. Figure 4 shows the Mo_2O_8 skeleton of the $Mo_2(OPr\text{-}i)_8$ molecule together with some important structure parameters. The comparison between the $Mo_2(OBu\text{-}t)_6(CO)$ and $Mo_2(OPr\text{-}i)_8$ molecules which is emphasized in Figures 3 and 4 shows that there is a close similarity in metal-metal and metal-oxygen bond dis-

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

atom	x	y	z	$B(1.1)$	$B(2.2)$	$B(3.3)$	$B(1.2)$	$B(1.3)$	$B(2.3)$
Mo	−0.070 06(5)	−0.268 38(8)	−0.2500(0)	0.002 36 (3)	0.006 49(8)	0.001 63(2)	−0.000 09(9)	−0.0002(1)	−0.0001(3)
O(1)	0.0000(0)	−0.557(1)	−0.2891(8)	0.0044(6)	0.007(1)	0.0034(4)	0.000(0)	0.0000(0)	0.0018(15)
O(2)	0.0000(0)	−0.187(1)	−0.1731(6)	0.0030(5)	0.010(2)	0.0014(3)	0.000(0)	0.0000(0)	−0.0012(12)
O(3)	0.0000(0)	−0.121(1)	−0.2971(7)	0.0028(4)	0.006(1)	0.0021(3)	0.000(0)	0.0000(0)	0.0011(12)
O(4)	−0.1357(6)	−0.279(1)	−0.3260(5)	0.0034(3)	0.010(1)	0.0017(2)	−0.002(1)	−0.0017(5)	0.0009(9)
O(5)	−0.1337(5)	−0.359(1)	−0.1867(5)	0.0027(3)	0.011(1)	0.0023(3)	−0.001(1)	0.0012(5)	−0.0003(10)

atom	x	y	z	$B(1.1)$
C(1)	0.0000(0)	−0.432(2)	−0.2730(9)	2.8(3)
C(2)	0.0000(0)	−0.149(2)	−0.1040(12)	4.1(4)
C(3)	0.0000(0)	−0.279(3)	−0.0586(16)	6.2(6)
C(4)	−0.0693(10)	−0.058(3)	−0.0875(12)	6.8(5)
C(5)	0.0000(0)	0.034(2)	−0.3047(11)	3.9(4)
C(6)	0.0000(0)	0.066(4)	−0.3785(20)	9.1(10)
C(7)	0.0684(11)	0.094(2)	−0.2720(10)	6.3(5)
C(8)	−0.1554(10)	−0.323(2)	−0.3940(9)	5.0(3)
C(9)	−0.1227(13)	−0.467(3)	−0.4065(12)	7.8(5)
C(10)	−0.2431(13)	−0.338(3)	−0.3919(13)	7.5(5)
C(11)	−0.1360(21)	−0.202(4)	−0.4422(19)	10.8(8)
C(12)	−0.1689(8)	−0.483(2)	−0.1577(8)	4.1(3)
C(13)	−0.2171(10)	−0.434(2)	−0.0991(11)	5.9(4)
C(14)	−0.2193(13)	−0.541(3)	−0.2175(12)	8.0(6)
C(15)	−0.1129(11)	−0.593(2)	−0.1396(9)	5.5(4)

[a] The form of the anisotropic thermal parameter is exp[−(*B*(1.1)**h***h* + *B*(2.2)**k***k* + *B*(3.3)**l***l* + *B*(1.2)**h***k* + *B*(1.3)**h***l* + *B*(2.3)**k***l*)].

Table II. Bond Distances (Å) and Angles (deg) in $Mo_2(OBu\text{-}t)_6(CO)$

atoms	distance	atoms	angle
Mo-Mo′	2.498(1)	C(1)-Mo-O(4)	99.7(4)
C(1)	2.022(10)	-O(5)	100.3(4)
O(2)	2.093(8)	O(2)-Mo-O(3)	73.4(4)
O(3)	2.074(8)	O(4)	161.7(4)
O(4)	1.888(7)	O(5)	93.2(4)
O(5)	1.876(8)	O(3)-Mo-O(4)	93.6(3)
O(1)-C(1)	1.21(2)	O(5)	162.6(4)
C(2)-O(2)	1.39(2)	O(4)-Mo-O(5)	96.6(3)
C(3)	1.50(3)	Mo-C(1)-O(1)	141.8(2)
C(4)	1.53(2)	Mo-O(2)-C(2)	141.6(3)
C(5)-O(3)	1.45(2)	Mo-O(3)-C(5)	135.0(6)
C(6)	1.47(3)	Mo-O(4)-C(8)	153.3(8)
C(7)	1.49(2)	Mo-O(5)-C(12)	152.6(7)
C(8)-O(4)	1.43(2)	O(2)-C(2)-C(3)	111(2)
C(9)	1.49(2)	C(4)	110(1)
C(10)	1.57(2)	C(3)-C(2)-C(4)	109(1)
C(11)	1.51(3)	C(4)-C(2)-C(4′)	107(2)
C(12)-O(5)	1.43(1)	O(3)-C(5)-C(6)	108(2)
C(13)	1.50(2)	C(7)	109(1)
C(14)	1.56(2)	C(6)-C(5)-C(7)	110(1)
C(15)	1.48(2)	C(7)-C(5)-C(7′)	110(2)
		O(4)-C(8)-C(9)	108 (1)
		C(10)	104(1)
		C(11)	108(1)
		C(9)-C(8)-C(10)	108(1)
		C(11)	119(2)
		C(10)-C(8)-C(11)	108(2)
		O(5)-C(12)-C(13)	108(1)
		C(14)	104(1)
		C(15)	111(1)
		C(13)-C(12)-C(14)	110(1)
		C(15)	115(1)
		C(14)-C(12)-C(15)	109(1)

atoms	angle
Mo′-Mo-C(1)	51.9(2)
O(2)	53.4(2)
O(3)	53.0(2)
O(4)	128.3(3)
O(5)	127.3(3)
Mo′-C(1)-Mo	76.3(5)
Mo′-O(2)-Mo	73.3(3)
Mo′-O(3)-Mo	74.0(3)
C(1)-Mo-O(2)	93.7(4)
O(3)	91.9(4)

[a] Atoms are labeled in Figure 2.

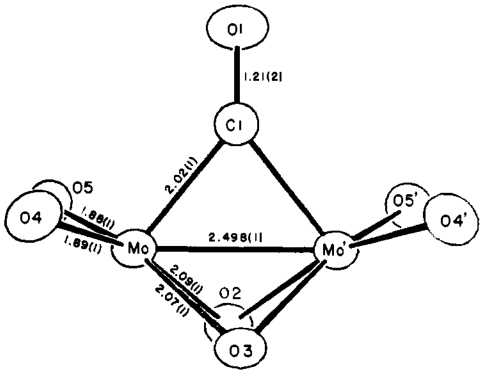

Figure 3. A view of the $Mo_2O_6(CO)$ skeleton of the $Mo_2(OBu\text{-}t)_6(CO)$ molecule together with pertinent internuclear distances. The molecule possesses a rigorous plane of symmetry containing atoms O2, O3, C1, and O1 and has virtual C_{2v} symmetry.

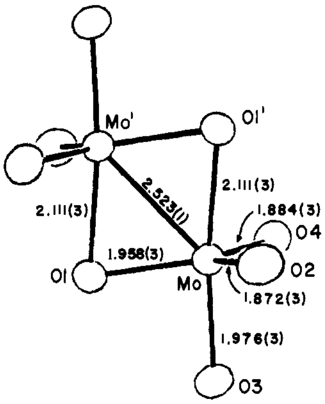

Figure 4. The Mo_2O_8 skeleton of the $Mo_2(OPr\text{-}i)_8$ molecule together with pertinent internuclear distances. The molecule possesses rigorous C_i and virtual C_{2h} symmetry.

tances despite the very different geometries of the molybdenum polyhedra.

Bonding in $Mo_2(OBu\text{-}t)_6(CO)$. At this time M-M bonds of order two are relatively rare. Indeed no transition-metal compounds are known to have M-M double bonds unbridged by ligand atoms and whenever bridging atoms are present it is not possible to distinguish unequivocally between the direct coupling of electron spins (M-M bonding) and indirect coupling through bridges. Nevertheless, we believe that in both $Mo_2(OPr\text{-}i)_8$ and $Mo_2(OBu\text{-}t)(CO)$ there are molybdenum to molybdenum double bonds. The bonding in $Mo_2(OPr\text{-}i)_8$ has recently been compared with that in the structurally related molecule $Mo_2(NO)_2(OPr\text{-}i)_6$ which has no Mo-to-Mo bond[15] (Mo-Mo distance 3.335 (2) Å.

The $Mo_2(OBu\text{-}t)_6(CO)$ molecule is diamagnetic and the electron counting for each molybdenum atom may be conducted as follows. The neutral molybdenum atom has six electrons, each terminal OR ligand contributes one as does the bridging CO group, and the pair of bridging OR ligands contribute three electrons to each metal atom. Thus, before metal-metal bond formation is considered, each metal atom has ten electrons involved in the formation of metal to ligand

σ bonds and two that are not. Three possibilities for the allocation of these electrons merit consideration. (1) The two electrons remain localized with paired spins and there is no Mo–Mo bond. (2) There is a direct single bond between the metal atoms, while the remaining two electrons have their spins coupled through the bridging ligands. (3) There is a direct double bond between the metal atoms. The Mo–Mo distance of 2.489 (1) Å indicates that there is a direct Mo–Mo bond and renders (1) or any other scheme that does not include an Mo–Mo bond unacceptable.

The choice between (2) and (3) is more difficult since the Mo–Mo distance might be considered consistent with either a single or a double bond between the metal atoms. If there is a double bond, which we consider likely, it is perhaps best formulated in the following way. Each molybdenum atom may be assumed to use atomic s, p_x, p_y, $d_{x^2-y^2}$, and d_{z^2} atomic orbitals to form five σ bonds to the four oxygen atoms and the carbonyl carbon atom which are disposed in a square pyramidal manner. (The z axis is taken to be coincident with the Mo–C bond.) In the C_{4v} symmetry of a regular square pyramid the d orbitals not used in M–L σ bonding fall into two sets: the d_{xy} orbital (b_2) and the degenerate d_{xy}, d_{yz} pair (e). In the actual dinuclear molecule the latter degeneracy is, of course, lifted. One of these orbitals has good overlap with the corresponding one on the other metal atom, while the other one overlaps very little with its twin on the other metal atom. In this way we may envision the formation of one σ bond with maximum electron density approximately along the Mo–Mo line. The two d_{xy} orbitals also can overlap to form a bent, somewhat weaker bond with maximum overlap density inside the flattened tetrahedron formed by the two Mo atoms and the two μ-O atoms.

The form of double bond just described can be contrasted with that in $Mo_2(OPr\text{-}i)_8$, where, by defining the z axis to be coincident with the axial oxygen atoms, the d_{xy} and d_{yz} orbitals are available for M–M bonding. Then by defining the central planar Mo_2O_2 moiety as the xz plane one can easily form a σ bond by a d_{xz}–d_{xz} interaction of atomic orbitals. The d_{yz}–d_{yz} interaction could then allow the formation of a rather unusual π type of M–M bond.[17]

A few key points concerning the work described so far deserve emphasis. The $Mo_2(OBu\text{-}t)_6CO$ molecule provides what is probably the first example of a bridging carbonyl group across a double M=M bond. The low value of ν(CO), 1690 cm^{-1} in hexane solution, may be indicative of some interaction with the Mo–Mo double bond, but it could also be the result of some electron density from the C–O π system moving into the empty d orbitals on each metal atom; according to the above selection of orbitals to form the double bond, those that remain are very well oriented for this type of interaction. This compound is also one of the very few compounds so far reported that contain both alkoxy ligands and CO, and all those previously reported were prepared in a manner opposite to that used here, namely, by introducing OR$^-$ into a metal carbonyl compound.[18]

Finally, of all known routes to $Mo(CO)_6$, reaction 1 is the most economical in carbon monoxide and offers the most advantageous route to heavily (or fully) labeled $Mo(CO)_6$. Reaction 1 does not, of course, make efficient use of molybdenum, but for some purposes, such as that just mentioned, this will be unimportant. The reaction may be carried out in pentane and the labeled CO recovered in the form of crystalline labeled $Mo(CO)_6$ in greater than 90% yield. This method of preparation may be compared to the more conventional preparations which use $MoCl_5$ + CO in which phosgene is formed,[19] the high-pressure (300 °C, 2000 atm) carbonylation of MoO_3 which yields CO_2 as the oxidation product,[20] or photochemical exchange of $Mo(^{12}CO)_6$ with ^{13}CO which requires much excess ^{13}CO for high enrichment.

Carbonylation of $Mo_2(OPr\text{-}i)_6$. Hydrocarbon solutions of $Mo_2(OPr\text{-}i)_6$ (M≡M) react readily with carbon monoxide at pressures of ≥1 atm to form $Mo(CO)_6$ and an as yet uncharacterized oxidized molybdenum-containing product. The reaction does not proceed according to the stoichiometry of reaction 1 since the molybdenum(4+) isopropoxide is dinuclear $Mo_2(OPr\text{-}i)_8$ (Mo=Mo)[17] and itself reacts further with CO (vide infra). Hydrocarbon solutions of $Mo_2(OPr\text{-}i)_6$ react with CO (1 or 2 equiv) to give a black, crystalline substance of empirical formula $Mo(OPr\text{-}i)_3CO$. The compound shows four bands in the infrared spectrum assignable to ν(CO): 1957 (s), 1882 (s), 1837 (s), and 1819 (s) cm^{-1}. The compound does not give an NMR spectrum (either ^{1}H or ^{13}C) and is believed to be paramagnetic. It is unstable in solution, slowly reacting to form $Mo(CO)_6$. In the presence of added CO this reaction is fast. An attempted X-ray structural determination was thwarted by the fact that the crystals repeatedly and quite rapidly decomposed in the X-ray beam. It was possible, however, to measure enough reflections to locate the molybdenum atoms with some degree of certainty.[21] A tetrameric structure is indicated, with an Mo_4 chain that is nonplanar and zigzag with the following distances and angles: Mo(1)–Mo(2) = 2.93, Mo(2)–Mo(3) = 2.59, Mo(3)–Mo(4) = 3.05 Å; Mo(1)–Mo(2)–Mo(3) angle = 157°; Mo(2)–Mo(3)–Mo(4) angle = 156°. The dihedral angle between the Mo(1)–Mo(2)–Mo(3) and Mo(2)–Mo(3)–Mo(4) planes is 105°. Other crystals having the same empirical formula, $Mo(OPr\text{-}i)_3(CO)$, have been examined at the Molecular Structure Center, Indiana University. A similar MO_4-containing pattern emerges but the detailed refinement of the structure is hindered here because of the large size of the unit cell of these crystals.[22] For the present, at least, efforts to obtain a satisfactory crystal structure on this compound have been discontinued.

Since the compound is unstable in solution with respect to disproportionation a cryoscopic molecular weight determination was not undertaken. However, further support for the tetrameric nature of these compounds was found by mass spectrometry. The compound is not thermally stable and may not be sublimed, but it did yield in the mass spectrometer at 173 °C (4 × 10^{-8} cmHg) a detectable (weak) molecular ion, $Mo_4(OPr\text{-}i)_{12}(CO)_4^+$. Other ions of much greater intensity were attributable to $Mo_3(OPr\text{-}i)_9(CO)_3^+$ and $Mo_2(OPr\text{-}i)_6(CO)_2^+$. Based on the present limited data for $[Mo(OPr\text{-}i)_3(CO)]_4$ one can do little but speculate upon its structure. It is, however, an intermediate in the reaction between $Mo_2(OPr\text{-}i)_6$ and CO that leads ultimately to $Mo(CO)_6$ and the Mo–Mo distances found in the Mo_4 skeleton suggest that a redox reaction is occurring such that the terminal molybdenum atoms are in the +2 oxidation state, while the central Mo–Mo distance (ca. 2.5 Å) is like that found in $Mo_2(OPr\text{-}i)_8$, which contains the $(Mo{=}Mo)^{8+}$ moiety. Further work on the structural characterization of $Mo_4(OPr\text{-}i)_{12}(CO)_4$ is in progress.

Since it seemed that $Mo_2(OPr\text{-}i)_8$ might be formed in the above reaction, in view of the formation of $Mo(OBu\text{-}t)_4$ in reaction 1, we studied the reaction between $Mo_2(OPr\text{-}i)_8$ and CO. Again $Mo(CO)_6$ is formed along with an as yet uncharacterized, oxidized, molybdenum-containing compound. When hydrocarbon solutions of $Mo_2(OPr\text{-}i)_8$ were exposed to 2 equiv of CO at room temperature and the solution was then cooled to −15 °C in a refrigerator, black crystals of empirical formula $Mo(OPr\text{-}i)_4(CO)$ were formed. The compound showed two bands in the infrared spectrum (Nujol mull) at 1940 and 1818 cm^{-1} which we assign to cis terminal carbonyl groups.[23] The compound failed to give an NMR spectrum, which leads us to believe that it is paramagnetic. It is also unstable in solution, slowly yielding $Mo(CO)_6$ and the same uncharacterized molybdenum-containing compound. The compound is thermally unstable, liberating CO and generating $Mo_2(OPr\text{-}i)_8$. A mass spectrum, however, was obtained at 6 °C (7×10^{-8} cmHg) which showed an intense molecular ion at *m/e* 724 corresponding to $Mo_2(OPr\text{-}i)_8(CO)_2^+$. In addition there was a weaker ion at *m/e* 665 corresponding to $Mo_2(OPr\text{-}i)_7(CO)_2^+$. The only other ions of major intensity were mononuclear: $Mo(OPr\text{-}i)_4^+$ and $Mo(O)(OPr\text{-}i)_3^+$. Though the data are limited, we believe that this compound may be formulated as $(Pr\text{-}iO)_4Mo^V(\mu\text{-}OPr\text{-}i)_2Mo^{III}(OPr\text{-}i)_2(CO)_2$ in which each molybdenum atom has approximately octahedral coordination. Efforts to obtain crystals suitable for X-ray work are continuing.

Carbonylation of Related Compounds with M–M Triple Bonds. $Mo_2(CH_2SiMe_3)_6$. This molecule[24] reacts readily with CO at 1 atm pressure to give $Mo(CO)_6$. The accompanying product, which presumably contains oxidized molybdenum, is a thermally unstable substance that is very sensitive to oxygen and moisture. It has IR absorptions at 1943 and 1859 cm^{-1}, indicative of the presence of MCO groups rather than insertion to give $MC(O)CH_2SiMe_3$.

$Mo_2(NMe_2)_6$, which was the second member of the class of $(Mo{\equiv}Mo)^{6+}$ compounds to be characterized,[26] rather interestingly does not react with CO at 1 atm pressure.

$Cp_2Mo_2(CO)_4$, which is assumed to contain a Mo-to-Mo triple bond (despite its long Mo–Mo distance, 2.448 (1) Å[3], relative to $(Mo{\equiv}Mo)^{6+}$-containing compounds[27]) readily reacts with CO. The only product ever detected[28] results from the addition of two CO molecules to give $Cp_2Mo_2(CO)_6$, which has an Mo-to-Mo single bond (Mo–Mo distance 3.235 (1) Å[7]). Presumably this addition of CO proceeds in a sequential manner with the second addition being much more rapid than the first.

$Re_2X_4(PR_3)_4$ compounds (X = Cl, Br, R = Et, Pr-*n*) containing triple bonds based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration have been shown by Walton and co-workers[29] to react with CO under slightly more forcing conditions than those employed in our work. The Re–Re bonds are cleaved to give the mononuclear products $ReX_2(PR_3)_2(CO)_2$ and $ReX(PR_3)_4(CO)$.

Conclusions

(1) Carbon monoxide reacts readily with most compounds that contain metal-to-metal triple bonds. (2) The carbonylation study reported here provides the first example of a structurally characterized compound in which one CO molecule has been added to an M–M triple bond in a carbene-like manner. The molecule $Mo_2(OBu\text{-}t)_6(CO)$ is in fact the first structurally characterized molecule having a CO ligand bridging a metal-to-metal double bond. (3) This work indicates a vast new area of polynuclear chemistry involving alkoxy and carbonyl ligands which hitherto was not recognized.

Further studies of the carbonylation of dimolybdenum and ditungsten alkoxides are being undertaken at Indiana University.

Experimental Section

General procedures, including the preparation of $Mo_2(OBu\text{-}t)_6$, $Mo_2(OPr\text{-}i)_6$, and $Mo_2(OPr\text{-}i)_8$, have been reported.[9,30]

Preparation of $Mo_2(OBu\text{-}t)_6(CO)$. $Mo_2(OBu\text{-}t)_6$ (0.3011 g, 0.4775 mmol) was dissolved in hexane (5 mL) to give a deep red solution. The solution was frozen at −196 °C (liquid N_2) and the nitrogen atmosphere of the flask was removed by evacuation. Carbon monoxide (0.96 mmol) was then added and the reaction mixture was allowed to warm to room temperature. The flask was then placed in the cold compartment of a refrigerator at ca. −15 °C. After several days deep purple crystals of $Mo_2(OBu\text{-}t)_6(CO)$ had formed and were collected by filtration and dried in vacuo at room temperature, yield 0.045 g, 16% based on $Mo_2(OBu\text{-}t)_6$. ^{13}C NMR data obtained at −20 °C, on $Mo_2(OBu\text{-}t)_6(^*CO)$ in toluene-d_8 (*CO represents 92% ^{13}C enrichment): δ (C=O) 272.51, δ (OC–) 83.64, δ (CH_3) 32.31 ppm (δ relative to Me_4Si). The spectrum was unchanged at −60 °C. The ^1H NMR spectrum of the above sample at 100 MHz at −60 °C showed just one single resonance at δ 1.44 ppm assignable to the *tert*-butyl protons. The sample was warmed to room temperature whereupon a new resonance at δ 1.52 ppm assignable to $Mo_2(OBu\text{-}t)_6$ grew in at the expense of the methyl signal of $Mo_2(OBu\text{-}t)_6(CO)$. Note that $Mo(OBu\text{-}t)_4$ is paramagnetic and does not give a sharp *tert*-butyl methyl resonance in the ^1H NMR spectrum.[12] IR data obtained from a Nujol mull between CsI plates: 1670 vs, 1410 vs, 1232 m, 1167 vs(br), 1027 m, 960 vs(br), 926 vs, 895 vs, 782 s, 720 w, 578 m, 560 s, 528 m, 500 vw, 476 m, 457 m, 392 vw, 363 m, 350 w, 295 m, 284 m cm^{-1}.

In hexane solution the IR band assignable to $\nu(\mu\text{-}CO)$ is shifted (relative to mull spectrum) to 1690 cm^{-1}.

X-ray Crystallography. A crystal of $Mo_2(OBu\text{-}t)_6(CO)$ measuring ca. $0.4 \times 0.4 \times 0.6$ mm was mounted embedded in epoxy cement in a thin-walled glass capillary. ω scans of several intense reflections had peak widths at half-height of ca. 0.2°. Cell constants and axial photographs indicated that the crystal belonged to the orthorhombic system with a = 17.827 (3) Å, b = 9.335 (2) Å, c = 19.447 (4) Å, V = 3236 (1) Å^3. The volume is consistent with that expected for Z = 4.

Data were collected at 23 °C on a Syntex P_1 autodiffractometer using graphite-crystal monochromatized Mo Kα radiation (λ = 0.710 730 Å). The θ-2θ scan technique was used with scans ranging from 1.0° above to 1.0° below the calculated Kα_1, Kα_2 doublet, with variable scan speeds ranging from 6.0 to 24.0°/min and a background to scan time ratio of 0.5. The intensities of three standard reflections were monitored frequently and decreased by 10% over the course of data collection. The integrated intensities of 1637 unique reflections having $0° < 2\theta(\text{Mo K}\alpha) \leq 50°$ were collected.

The data were reduced to a set of relative $|F_o|^2$ and corrected for crystal decay. An absorption correction was not deemed necessary (μ = 8.0 cm^{-1}). The 1239 unique data having $|F_o|^2 > 3\sigma(|F_o|^2)$ were used in subsequent structure solution and refinement.

The observed systematic absences, hkl ($h + k = 2n + 1$) and $h0l$ ($h = 2n + 1$, $l = 2n + 1$), were consistent with the space groups $Cmc2_1$, $Ama2$, and $Cmcm$ (no. 36, 40, and 63, respectively). Statistical tests and an inspection of the Patterson map suggested that the acentric space group $Cmc2_1$ was correct. This was verified by successful solution and refinement of the structure.

The structure was solved by conventional heavy-atom methods and refined to convergence using anisotropic thermal parameters for the Mo and O atoms and isotropic thermal parameters for the carbon atoms. The hydrogen atoms were not located. Final unweighted and weighted residuals were 0.067 and 0.0853, respectively, and the esd of an observation of unit weight was 1.96. A value of 0.07 was used for p in the calculation of the weights. Refinement of the other enantiomorph yielded R_w = 0.0855, which is not significantly different from the former. A final difference Fourier map revealed numerous unexpected peaks, none of which was chemically significant.

Axial photographs taken along the a and c axes showed some streaking at low 2θ, indicative perhaps of a small amount of twinning or disorder. However, since the observed peaks in the difference Fourier map were relatively small and chemically insignificant, no further attempt was made to explain the crystal defect.

Preparation of $Mo_4(OPr\text{-}i)_{12}(CO)_4$. To $Mo_2(OPr\text{-}i)_6$ (0.928 g, 1.7 mmol) dissolved in hexane (10 mL) was added carbon monoxide (3.4 mmol) via a vacuum manifold. The closed flask containing the solution of $Mo_2(OPr\text{-}i)_6$ and the carbon monoxide was left at room temperature for 24 h, after which time the solution had turned dark. The solution was then placed in the refrigerator of a Vacuum Atmospheres drybox at ca. −40 °C. After 1 week a mass of black crystals had formed and were separated from the mother liquor by filtration within the drybox. The crystals were collected and dried in vacuo, yield 0.62 g, 60% based on $Mo_2(OPr\text{-}i)_6$. Anal. Calcd: C, 39.88, H, 7.03. Found: C, 39.88; H, 7.06.

IR data (Nujol mull between CsI plates): 1957 (s), 1882 (s), 1837 (s), 1819 (s), 1819 (s), 1320 (m), 1154 (m), 1120 (s), 1105 (s, br), 988 (m), 950 (s, br) 842 (m), 831 (m), 722 (m), 621 (m), 595 (s), 500 (w), 450 (m, br), 382 (m), 215 (w) cm^{-1}.

Mass spectral data were obtained from an AEI MS9 spectrometer by the method of direct insertion. The molecular ion *m/e* 1212 corresponding to $Mo_4(OPr\text{-}i)_{12}(CO)_4^+$ was detected on the oscilloscope. Other ions of greater intensity are given in the text.

Preparation of $Mo_2(OPr\text{-}i)_8(CO)_2$. $Mo_2(OPr\text{-}i)_8$ (0.2256 g) was dissolved in hexane (5 mL) to give an intense blue solution. An excess of CO was added and the solution immediately turned dark. The solution was placed in a refrigerator at −15 °C under 1 atm of carbon monoxide. The solvent was subsequently stripped and the black residue was examined by IR spectroscopy. IR bands assignable to ν(CO) were found at 1940 and 1820 cm^{-1}. These are attributed to $Mo_2(OPr\text{-}i)_8(CO)_2$; in addition there was a band at 1985 cm^{-1} arising from $Mo(CO)_6$. The solid was dissolved in hexane and the solution cooled slowly to yield black crystals (ca. 100 mg) of $Mo_2(OPr\text{-}i)_8(CO)_2$. Anal. Calcd: C, 43.3, H, 7.8. Found: C, 43.2; H, 7.4. Mass spectral data obtained by the method of direct insertion at 6 °C on an AEI MS9 show M$^+$ at *m/e* 724, $(M - OPr\text{-}i)^+$ at *m/e* 665, and $(M - 2OPr\text{-}i)^+$ at *m/e* 606 as the major Mo_2-containing ions.

Reaction of $Mo_2(CH_2SiMe_3)_6$ with Carbon Monoxide. $Mo_2(CH_2SiMe_3)_6$ (0.166 g) in hexane (5 mL) gave an orange solution. An excess of CO was added and the solution changed color from orange to deep purple within 12 h. The solution was cooled in the refrigerator at −15 °C, which led to the formation of white crystals identified as $Mo(CO)_6$ by IR spectroscopy. A dark purple, sticky solid remained which failed to crystallize from hydrocarbon solvents. It was both oxygen and moisture sensitive and could not be purified by sublimation (decomposed >50 °C, 10^{-6} cmHg). The IR spectrum of this crude purple solid showed strong bands at 1942 and 1860 cm^{-1} assignable to ν(CO). There was also a weak band at 1895 cm^{-1}.

Reaction of $Mo_2(NMe_2)_6$ with CO. $Mo_2(NMe_2)_6$ (0.2 g) in hexane (20 mL) gave a yellow solution. An excess of CO was added and the solution was stirred for 24 h under 1 atm of carbon monoxide. No apparent reaction occurred. The solvent was stripped to yield a finely divided, yellow, crystalline substance which was identified as $Mo_2(NMe_2)_6$ by ^{1}H NMR and IR spectroscopy.

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Supplementary Material Available: A table of observed and final calculated structure factors (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 5: M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, **18**, 116 (1979).

(2) (a) Indiana University; (b) Texas A&M University.

(3) R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975); **100**, 5034 (1978).

(4) W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 5764 (1978).

(5) M. H. Chisholm, F. A. Cotton, M. W. Extine, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 807 (1978).

(6) W. I. Bailey, M. H. Chisholm, F. A. Cotton, C. A. Murillo, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 802 (1978).

(7) R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, **13**, 1086 (1974).

(8) For a recent review of the chemistry of these compounds, see M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, **11**, 356 (1978).

(9) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, **16**, 1801 (1977).

(10) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978).

(11) A preliminary account has appeared: M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, **100**, 2256 (1978).

(12) M. H. Chisholm, P. Thornton, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 2744 (1978).

(13) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 1727 (1978).

(14) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, **17**, 2744 (1978).

(15) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, **100**, 2556 (1978).

(16) F. A. Cotton, *J. Less-Common Met.*, **54**, 3 (1977).

(17) Our earlier suggestions concerning this double bond in ref 14 and 12 are supplanted by the present discussion.

(18) E. W. Abel, G. Farrow, and I. D. H. Towle, *J. Chem. Soc., Dalton Trans.*, 71 (1979), and references cited therein.

(19) For a previous preparation of $Mo(^{13}CO)_6$ see L. H. Jones, R. S. McDowell, and M. Goldslatt, *Inorg. Chem.*, **8**, 2349 (1969).

(20) A. P. Hagen, T. S. Miller, D. L. Terrell, B. Hutchinson, and R. L. Hance, *Inorg. Chem.*, **17**, 1369 (1978).

(21) Cell constants: $a = 35.936\ (1)$ Å, $b = 15.184\ (4)$ Å, $c = 21.616\ (5)$ Å, $\beta = 108.66\ (2)^\circ$; $V = 11\,174$ Å^3, space group *C*2/*c*. A full data set was collected to $2\theta = 25^\circ$, a partial set from 25 to 40°, by which time more than 50% decomposition had occurred. Of the 4800 reflections which were collected only 1400 had $I > 3\sigma$. Solution of the structure by location of the Mo atoms was attempted and gave $R_1 = 0.30$ and $R_2 = 0.37$.

(22) Cell constants: $a = 64.03\ (2)$ Å, $b = 14.994\ (4)$ Å, $c = 17.613\ (4)$ Å, $\beta = 73.45\ (1)^\circ$, $V = 16\,209.4$ Å^3, $d_{calcd} = 1.48$ g cm^{-3}. Data were collected at −165 °C. A total of 12 914 reflections were scanned in the range $4^\circ \leq 2\theta \leq 45$ using a scan speed of 3.5°/min, a scan width of 1.25° (+ dispersion), and stationary background counts of 5 s at either end of the scan range. After averaging of equivalent reflections 10 899 unique reflections remained. Of these, 9272 had $F_o > 2.33\sigma(F_o)$. At the present time a three-dimensional Patterson function has been computed and direct methods have been used to obtain tentative Mo-atom positions. I. C. Huffman and K. Straub, personal communication.

(23) This assignment of *cis*-CO ligands follow from the intensity relationship outlined in F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed., Wiley, New York, 1972, p 696.

(24) F. Huk, W. Mowat, A. Shortland, A. C. Skapki, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

(25) E. C. Guzman, G. Wilkinson, J. L. Atwood, R. D. Rogers, W. E. Hunter, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 465 (1978).

(26) M. H. Chisholm, F. A. Cotton, B. Frenz, W. W. Reichert, and L. Shive, *J. Am. Chem. Soc.*, **98**, 4469 (1976).

(27) For a comparison of Mo–Mo distances in compounds containing a central $(Mo\equiv Mo)^{6+}$ core see either ref 8 or M. H. Chisholm, *Transition Met. Chem.*, **3**, 321 (1978).

(28) M. S. Ginley, C. R. Block, and M. S. Wrighton, *Inorg. Chim. Acta*, **23**, 85 (1977).

(29) C. A. Hertzer, R. E. Myers, P. Brant, and R. A. Walton, *Inorg. Chem.*, **17**, 2383 (1978).

(30) M. H. Chisholm, P. Thornton, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 2744 (1978).