Inorg. Chem. **1981**, *20*, 871–876 **871**

The effects of anomalous dispersion for all nonhydrogen atoms were included in F by using the values of Cromer and Ibers[24] for $\Delta f'$ and $\Delta f''$.

The positions of the mercury and cobalt atoms in VIB were determined from three-dimensional Patterson functions calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier difference functions. A small amount of positional disorder was observed in the $(CH_3)_5C_5$ ring, but the disordered positions could not be adequately established and contributed little to the overall scattering. This disorder is also unimportant in terms of the interesting structural features of the molecule and was therefore not pursued further. The molecule was found to be dimerized about a crystallographic inversion center via a pair of Hg–Cl interactions. Anisotropic temperature factors were introduced for all nonhydrogen atoms. The position of the bridging hydrogen, H(56), was calculated and included in the refinement, except during the final three cycles. A final Fourier difference map was featureless. The esd of an observation of unit weight was 2.49.

For compound VIIA the positions of the cobalt and mercury atoms were determined from a three-dimensional Patterson function. The Hg atom was found to be at a center of inversion, thus requiring solution for only half of the molecule. The intensity data were phased sufficiently well by the coordinates of the Hg and Co atoms to permit location of the remaining nonhydrogen atoms from Fourier difference functions. After introducing anisotropic thermal parameters for all nonhydrogen atoms, some hydrogen atoms were found on Fourier difference maps, and those remaining were calculated and inserted. All hydrogen atoms were included in the refinement for three cycles and thereafter held fixed. A final Fourier difference map was featureless. The esd of an observation of unit weight was 4.62.

The models converged to $R = 0.044$ and $R_w = 0.055$ for VIB and $R = 0.081$ and $R_w = 0.094$ for VIIA, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material). The computing system and programs are described elsewhere.[25]

Acknowledgment. This work was supported by the Office of Naval Research and the National Science Foundation, Grant No. 79-09948. We are grateful to Professor Ekk Sinn for assistance in the X-ray crystallographic structure determinations.

Registry No. III, 65969-67-7; IV, 76095-34-6; VA, 76081-87-3; VB, 76081-88-4; VIA, 76081-89-5; VIB, 76081-90-8; VIIA, 76190-15-3; VIIB, 76190-16-4; $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$, 50932-66-6; $HgCl_2$, 7487-94-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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[23] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[24] Cromer, D. T.; Ibers, J. A. Reference 22.

[25] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

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Reactions of Metal–Metal Multiple Bonds. 7.[1] Addition of the Halogens Cl_2, Br_2, and I_2 and Diisopropyl Peroxide to Hexaisopropoxydimolybdenum (M≡M). Dinuclear Oxidative-Addition Reactions Accompanied by Metal–Metal Bond-Order Changes from 3 to 2 to 1

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$Mo_2(O\text{-}i\text{-}Pr)_6$ (M≡M) and i-PrOO-i-Pr react in hydrocarbon solvents, at room temperatures, and in the dark to give the previously characterized compound $Mo_2(O\text{-}i\text{-}Pr)_8$ (M=M). $Mo_2(O\text{-}t\text{-}Bu)_6$ (M≡M) fails to react with either i-PrOO-i-Pr or t-BuOO-t-Bu, and $Mo_2(O\text{-}i\text{-}Pr)_6$ and t-BuOO-t-Bu do not react under similar conditions. A reaction pathway involving an initial association reaction is proposed: $Mo_2(OR)_6 + ROOR \rightleftharpoons Mo_2(OR)_6(ROOR) \rightarrow Mo_2(OR)_8$. $Mo_2(O\text{-}i\text{-}Pr)_6$ reacts with each of the halogens Cl_2, Br_2, and I_2 to give $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ (M—M) compounds (X = Cl, Br, and I). These reactions proceed via intermediates, probably $Mo_2(O\text{-}i\text{-}Pr)_6X_2$ compounds, which are labile toward disproportionation to give $Mo_2(O\text{-}i\text{-}Pr)_6$ and $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds. The compounds $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ are thermally unstable and moisture sensitive. In vacuo or under a nitrogen atmosphere they decompose slowly at room temperature by the elimination of isopropyl halides. X-ray studies on the chloro and bromo compounds show that both compounds contain central $Mo_2O_6X_4$ units that have virtual D_{2h} symmetry. Each molybdenum atom is in a distorted octahedral environment formed by a pair of cis terminal halide ligands, a pair of trans terminal O-i-Pr ligands, and a pair of cis-bridging O-i-Pr ligands. There are planar $Mo_2(\mu\text{-}O)_2X_4$ units and the M–M distance in both is 2.73 Å, which, together with other characterization data, are indicative of Mo-to-Mo single bonds. These findings are compared with earlier work. Crystal data are as follows: for $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ $a = 20.722$ (6) Å, $b = 9.617$ (2) Å, $c = 14.747$ (4) Å, $\beta = 96.02$ (1)°, $V = 2922.6$ (1) Å^3, $Z = 4$, $d_{calcd} = 1.578$ g cm^{-3} with space group $P2_1/a$; for $Mo_2(O\text{-}i\text{-}Pr)_6Br_4\cdot{}^1/_2C_7H_8$ $a = 15.204$ (5) Å, $b = 12.849$ (5) Å, $c = 10.535$ (3) Å, $\beta = 120.76$ (1)°, $V = 1768.6$ (1) Å^3, $Z = 4$, $d_{calcd} = 1.638$ g cm^{-3} with space group $P2_1/a$.

Introduction

In mononuclear transition-metal chemistry, the term oxidative addition[2] is often used to describe reactions in which both the oxidation number and coordination number of the metal are increased by 2. The microscopic reverse reaction is called reductive elimination, and the two complementary reactions are incorporated into numerous catalytic cycles, involving especially the group 8 transition elements.[2] We have speculated[3] that dinuclear compounds of the transition elements containing metal-to-metal triple bonds[4] might also enter into these types of reactions and that M–M bond-order changes

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[1] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

[2] Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

[3] Chisholm, M. H. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 321; *Adv. Chem. Ser.* **1979**, *No. 173*, 396.

[4] For recent reviews see: Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27. Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 226. Chisholm, M. H.; Cotton, F. A. *Ibid.*, **1978**, *11*, 356.

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would occur. In this paper we describe some simple addition reactions involving $Mo_2(O\text{-}i\text{-}Pr)_6$ ($M{\equiv}M$)[5] in which the Mo-to-Mo bond order is changed in a stepwise manner from 3 to 2 to 1.

Results and Discussion

$Mo_2(O\text{-}i\text{-}Pr)_6$ + *i*-PrOO-*i*-Pr. Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ are pale yellow and upon addition of *i*-PrOO-*i*-Pr at room temperature quickly turn green-blue. In the presence of a fivefold excess of the diisopropyl peroxide, $Mo_2(O\text{-}i\text{-}Pr)_8$ is formed virtually quantitatively within 12 h at room temperature. The latter compound may be isolated by merely stripping the solvent and excess diisopropyl peroxide and can be purified by vacuum sublimation.[6] The reaction is accelerated by heat and light, though the latter is not required at room temperature. Below room temperature the reaction is slow and does not go to completion within a period of days. When the reaction was carried out in a sealed tube within the cavity of an ESR spectrometer, no signals were detected.

The addition of *t*-BuOO-*t*-Bu to hydrocarbon solutions of either $Mo_2(O\text{-}i\text{-}Pr)_6$ or $Mo_2(O\text{-}t\text{-}Bu)_6$ results in color changes, but little reaction evidently occurs at ambient temperatures since the $Mo_2(OR)_6$ compounds are recovered upon sublimation of the solids obtained by stripping the solvent and excess *t*-BuOO-*t*-Bu. In a similar experiment, *i*-PrOO-*i*-Pr was added to $Mo_2(O\text{-}t\text{-}Bu)_6$; again only $Mo_2(O\text{-}t\text{-}Bu)_6$ was recovered.

We believe that steric factors are important in determining the rates of these addition reactions and that the reactivity order $Mo_2(O\text{-}i\text{-}Pr)_6 > Mo_2(O\text{-}t\text{-}Bu)_6$, which parallels that observed toward Lewis bases,[5] aryl azides,[7] and molecular oxygen,[8] may be rationalized by the requirement that the dialkyl peroxide must coordinate to the dimetal center before O–O bond cleavage and oxidative addition is achieved.

$$Mo_2(O\text{-}i\text{-}Pr)_6 + i\text{-}PrOO\text{-}i\text{-}Pr \rightleftharpoons Mo_2(O\text{-}i\text{-}Pr)_6(i\text{-}PrOO\text{-}i\text{-}Pr) \quad (1)$$

$$Mo_2(O\text{-}i\text{-}Pr)_6(i\text{-}PrOO\text{-}i\text{-}Pr) \rightarrow Mo_2(O\text{-}i\text{-}Pr)_8 \quad (2)$$

$Mo_2(O\text{-}i\text{-}Pr)_6 + X_2$ (X = Cl, Br, and I). $Mo_2(O\text{-}i\text{-}Pr)_6$ in CCl_4 reacts rapidly with Cl_2 and Br_2 to give orange crystalline solids $Mo_2(O\text{-}i\text{-}Pr)_6X_4$, where X = Cl and Br, respectively. In hexane $Mo_2(O\text{-}i\text{-}Pr)_6$ and I_2 react to give $Mo_2(O\text{-}i\text{-}Pr)_6I_4$ as a brown solid. The rate of addition follows the order $Cl_2 > Br_2 > I_2$. When only 1 equiv of Br_2 is added slowly, the solution is initially green, but with time it turns orange as $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ crystallizes from solution. The solution contains $Mo_2(O\text{-}i\text{-}Pr)_6$. Addition of I_2 (1 equiv) to $Mo_2(O\text{-}i\text{-}Pr)_6$ in hexane gives an intense green solution from which hexane-soluble green crystals can be isolated. This compound, believed to be $Mo_2(O\text{-}i\text{-}Pr)_6I_2$, is currently the subject of further studies.

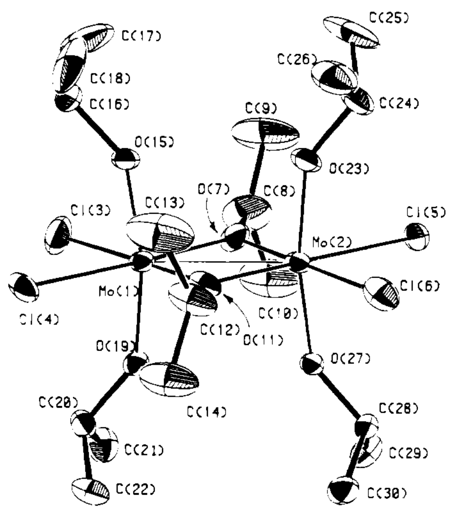

Figure 1. ORTEP view of the $Mo_2Cl_4(O\text{-}i\text{-}Pr)_6$ molecule showing the atom numbering scheme used in the tables. Hydrogen atoms have been omitted for clarity; atoms are drawn at the 40% probability level.

Physicochemical Properties of $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ Compounds (X = Cl, Br, I). All the compounds are moisture sensitive and thermally unstable. They slowly decompose in vacuo and under nitrogen at room temperature by the elimination of isopropyl halides. The resultant black molybdenum-containing residues are insoluble in all common organic solvents and have not been characterized. The $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds are insoluble in hexane and other aliphatic hydrocarbons, but they are appreciably soluble and can be recrystallized from toluene and benzene solutions. In the mass spectrometer there were no molybdenum-containing ions: the spectra showed intense PrX^+ ions. When samples were heated in vacuo to 60 °C, isopropyl halides were evolved and were identified by ^1H NMR spectroscopy. Cryoscopic molecular weight determinations were carried out on both the chloro and bromo compounds: in both instances low molecular weights were obtained. We attribute this to the instability of the compounds and to their ready decomposition by the elimination of *i*-PrX. The ^1H NMR spectra of all three compounds were similar, indicative of two types of O-*i*-Pr ligands in the ratio 2:1. The spectra are consistent with the maintenance of the solid-state structure in solution, and the two types of O-*i*-Pr ligands can be assigned to terminal and bridging O-*i*-Pr ligands, both of which lie in planes of molecular symmetry. One point of initial concern to us was the anomalous deshielding associated with one of the methyne protons which increased in the order I > Br > Cl. As is shown later this can be rationalized by structural considerations.

In order to check whether elimination of *i*-PrBr was reversible, we prepared $(CD_3)_2CHBr$. Addition of $(CD_3)_2CHBr$ to a solution of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ in toluene-d_8 gave no evidence (from ^1H NMR studies) for the reversible reaction

$$Mo_2(O\text{-}i\text{-}Pr)_6Br_4 \rightleftharpoons Mo_2O_2(O\text{-}i\text{-}Pr)_4Br_2 + 2i\text{-}PrBr \quad (3)$$

We conclude that when $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds eliminate *i*-PrX, they do so irreversibly. In this and all other respects, the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds appear to be analogous to the tungsten compounds $W_2(OR)_6Cl_4$ (R = Me, Et, and *n*-Pr) studied by Brubaker and his co-workers[8] and originally prepared by Klejnot.[9] On the basis of IR studies these authors favored the existence of chloride bridges. We show, however, that for molybdenum there are alkoxy bridges and only terminal halide groups.

Solid-State Structures. $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$. In the crystalline state the compound is composed of discrete molecules of $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$. An ORTEP view of the molecule indicating the coordination geometry and atom numbering scheme is shown in Figure 1. Final atomic coordinates and thermal parameters are given in Table I. Complete listings of bond distances and angles to nonhydrogen atoms are given in Tables II and III, respectively. Bond distances and angles to hydrogen atoms and nonbonding distances to 3.0 Å are given in the supplementary material.

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

(6) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

(7) (a) Chisholm, M. H.; Ratermann, A., to be submitted for publication. (b) Chisholm, M. H.; Kirkpatrick, C. C., to be submitted for publication.

(8) Rillema, D. P.; Reagan, W. J.; Brubaker, C. H., Jr. *Inorg. Chem.* **1969**, *8*, 587. Rillema, D. P.; Brubaker, C. H., Jr. *Ibid.* **1969**, *8*, 1645. Reagan, W. J.; Brubaker, C. H., Jr. *Ibid.* **1970**, *9*, 927.

(9) Klejnot, O. *Inorg. Chem.* **1965**, *4*, 1668. In this paper a chloride-bridged bioctahedral structure was proposed for $W_2Cl_4(OEt)_6$.

Table I. Fractional Coordinates for the $Mo_2Cl_4(O\text{-}i\text{-}Pr)_6$ Molecule[a, b]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	−1133.8 (2)	3073.1 (4)	3252.3 (3)	20
Mo(2)	−1238.5 (2)	1382.7 (4)	1756.3 (3)	17
Cl(3)	−642 (1)	2934 (1)	4813 (1)	37
Cl(4)	−1458 (1)	5385 (1)	3660 (1)	31
Cl(5)	−905 (1)	−929 (1)	1356 (1)	24
Cl(6)	−1690 (1)	1578 (1)	181 (1)	30
O(7)	−821 (2)	1122 (3)	3041 (2)	24
C(8)	−451 (3)	52 (6)	3596 (5)	44
C(9)	−842 (4)	−1021 (8)	3878 (6)	64
C(10)	205 (3)	−8 (7)	3413 (6)	55
O(11)	−1568 (1)	3314 (3)	1976 (2)	21
C(12)	−1991 (3)	4322 (6)	1450 (5)	37
C(13)	−2616 (3)	4414 (8)	1778 (7)	65
C(14)	−1628 (3)	5506 (7)	1182 (6)	49
O(15)	−1871 (2)	2502 (4)	3703 (3)	36
C(16)	−2263 (3)	2631 (7)	4451 (5)	49
C(17)	−2194 (7)	1303 (9)	4999 (9)	121
C(18)	−2934 (3)	2983 (12)	4063 (6)	94
O(19)	−386 (1)	3898 (3)	3013 (2)	17
C(20)	91 (2)	4930 (5)	3336 (3)	20
C(21)	725 (2)	4187 (6)	3626 (4)	26
C(22)	141 (2)	5970 (5)	2583 (4)	27
O(23)	−2001 (2)	564 (3)	1963 (3)	27
C(24)	−2488 (3)	−447 (6)	1649 (5)	36
C(25)	−2529 (3)	−1512 (7)	2391 (6)	58
C(26)	−3113 (3)	308 (7)	1405 (5)	44
O(27)	−486 (1)	1958 (3)	1351 (2)	16
C(28)	−54 (2)	1823 (5)	650 (3)	18
C(29)	599 (2)	1356 (6)	1095 (4)	26
C(30)	−35 (3)	3197 (5)	173 (4)	26

[a] The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalents: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609. [b] Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

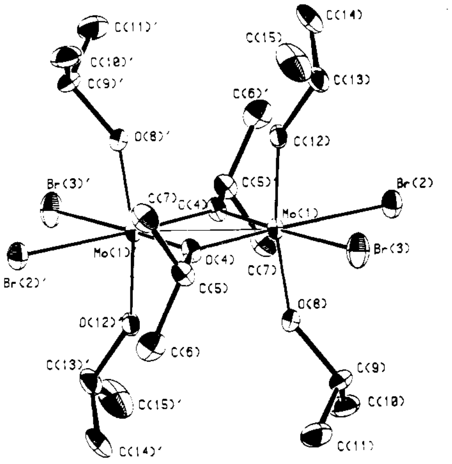

Figure 2. ORTEP view of the $Mo_2Br_4(O\text{-}i\text{-}Pr)_6$ molecule showing the atom numbering scheme used in the tables. Atoms are drawn at the 40% probability level; hydrogen atoms have been omitted for clarity.

The central $Mo_2O_6Cl_4$ unit has virtual D_{2h} symmetry. Each molybdenum atom is in a distorted octahedral geometry. There are a pair of cis Mo–Cl groups, a pair of trans-terminal O-*i*-Pr ligands, and a pair of cis-bridging O-*i*-Pr ligands.

$Mo_2(O\text{-}i\text{-}Pr)_6Br_4$. This compound crystallized with a molecule of solvent (toluene) in the unit cell. The toluene molecule was disordered and was refined isotropically. All hydrogen atoms (other than those of the solvent molecule) were located and refined. An ORTEP view of the $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ molecule showing the coordination geometry and the atom numbering scheme is shown in Figure 2. Final atomic coordinates and thermal parameters are given in Table IV.

Table II. Bond Distances (Å) for the $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ Molecule

Mo(1)–Mo(2)	2.731 (1)	O(19)–C(20)	1.446 (5)
Mo(1)–Cl(3)	2.421 (2)	O(23)–C(24)	1.442 (6)
Mo(1)–Cl(4)	2.416 (1)	O(27)–C(28)	1.442 (5)
Mo(1)–O(7)	2.020 (3)	C(8)–C(9)	1.402 (9)
Mo(1)–O(11)	2.013 (4)	C(8)–C(10)	1.414 (9)
Mo(1)–O(15)	1.815 (3)	C(12)–C(13)	1.432 (9)
Mo(1)–O(19)	1.808 (3)	C(12)–C(14)	1.443 (8)
Mo(2)–Cl(5)	2.419 (1)	C(16)–C(17)	1.510 (13)
Mo(2)–Cl(6)	2.419 (2)	C(16)–C(18)	1.486 (12)
Mo(2)–O(7)	2.014 (4)	C(20)–C(21)	1.517 (7)
Mo(2)–O(11)	2.016 (3)	C(20)–C(22)	1.506 (7)
Mo(2)–O(23)	1.819 (3)	C(24)–C(25)	1.508 (10)
Mo(2)–O(27)	1.814 (3)	C(24)–C(26)	1.496 (8)
O(7)–C(8)	1.478 (7)	C(28)–C(29)	1.509 (7)
O(11)–C(12)	1.472 (6)	C(28)–C(30)	1.500 (7)
O(15)–C(16)	1.442 (6)		

Table III. Bond Angles (Deg) for the $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ Molecule

Mo(2)–Mo(1)–Cl(3)	136.5	Cl(6)–Mo(2)–O(27)	85.4 (1)
Mo(2)–Mo(1)–Cl(4)	138.4	O(7)–Mo(2)–O(11)	94.8 (1)
Mo(2)–Mo(1)–O(7)	47.3 (1)	O(7)–Mo(2)–O(23)	94.8 (2)
Mo(2)–Mo(1)–O(11)	47.4 (1)	O(7)–Mo(2)–O(27)	92.8 (1)
Mo(2)–Mo(1)–O(15)	96.7 (1)	O(11)–Mo(2)–O(23)	93.3 (1)
Mo(2)–Mo(1)–O(19)	95.8 (1)	O(11)–Mo(2)–O(27)	95.1 (1)
Cl(3)–Mo(1)–Cl(4)	85.1 (1)	O(23)–Mo(2)–O(27)	168.2 (1)
Cl(3)–Mo(1)–O(7)	89.1 (1)	Mo(1)–O(7)–Mo(2)	85.2 (1)
Cl(3)–Mo(1)–O(11)	176.1 (1)	Mo(1)–O(7)–C(8)	135.9 (4)
Cl(3)–Mo(1)–O(15)	85.5 (2)	Mo(2)–O(7)–C(8)	139.0 (4)
Cl(3)–Mo(1)–O(19)	85.7 (1)	Mo(1)–O(11)–Mo(2)	85.3 (1)
Cl(4)–Mo(1)–O(7)	174.3 (1)	Mo(1)–O(11)–C(12)	138.7 (3)
Cl(4)–Mo(1)–O(11)	91.0 (1)	Mo(2)–O(11)–C(12)	135.7 (3)
Cl(4)–Mo(1)–O(15)	85.5 (1)	Mo(1)–O(15)–C(16)	144.8 (4)
Cl(4)–Mo(1)–O(19)	84.9 (1)	Mo(1)–O(19)–C(20)	143.8 (3)
O(7)–Mo(1)–O(11)	94.7 (1)	Mo(2)–O(23)–C(24)	146.0 (3)
O(7)–Mo(1)–O(15)	94.1 (1)	Mo(2)–O(27)–C(28)	145.9 (3)
O(7)–Mo(1)–O(19)	94.7 (1)	O(7)–C(8)–C(9)	113.2 (6)
O(11)–Mo(1)–O(15)	93.8 (2)	O(7)–C(8)–C(10)	112.0 (5)
O(11)–Mo(1)–O(19)	94.3 (1)	C(9)–C(8)–C(10)	128.6 (6)
O(15)–Mo(1)–O(19)	167.5 (2)	O(11)–C(12)–C(13)	111.9 (5)
Mo(1)–Mo(2)–Cl(5)	138.0	O(11)–C(12)–C(14)	111.5 (4)
Mo(1)–Mo(2)–Cl(6)	136.0	C(13)–C(12)–C(14)	124.0 (6)
Mo(1)–Mo(2)–O(7)	47.5 (1)	O(15)–C(16)–C(17)	107.9 (5)
Mo(1)–Mo(2)–O(11)	47.3 (1)	O(15)–C(16)–C(18)	107.7 (6)
Mo(1)–Mo(2)–O(23)	96.8 (1)	C(17)–C(16)–C(18)	115.6 (8)
Mo(1)–Mo(2)–O(27)	95.0 (1)	O(19)–C(20)–C(21)	108.1 (4)
Cl(5)–Mo(2)–Cl(6)	85.9	O(19)–C(20)–C(22)	108.1 (4)
Cl(5)–Mo(2)–O(7)	90.6 (1)	C(21)–C(20)–C(22)	113.3 (4)
Cl(5)–Mo(2)–O(11)	174.6 (1)	O(23)–C(24)–C(25)	108.4 (5)
Cl(5)–Mo(2)–O(23)	85.3 (1)	O(23)–C(24)–C(26)	108.0 (4)
Cl(5)–Mo(2)–O(27)	85.6 (1)	C(25)–C(24)–C(26)	113.0 (5)
Cl(6)–Mo(2)–O(7)	176.1 (1)	O(27)–C(28)–C(29)	108.1 (4)
Cl(6)–Mo(2)–O(11)	88.8 (1)	O(27)–C(28)–C(30)	107.8 (4)
Cl(6)–Mo(2)–O(23)	86.5 (1)	C(29)–C(28)–C(30)	113.6 (4)

Table IV. Fractional Coordinates for the $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	−54.1 (4)	−614.4 (5)	8900.2 (1)	11
Br(2)	1144 (1)	−1445 (1)	8117 (1)	19
Br(3)	−1471 (1)	−1523 (1)	6560 (1)	23
O(4)	−1124 (3)	−41 (4)	9295 (5)	12
C(5)	−2261 (5)	−91 (6)	8497 (8)	15
C(6)	−2691 (7)	981 (8)	8009 (9)	23
C(7)	−2587 (6)	−654 (7)	9424 (9)	21
O(8)	−185 (4)	445 (4)	7691 (5)	14
C(9)	−358 (6)	775 (6)	6245 (8)	18
C(10)	539 (8)	1427 (8)	6499 (10)	25
C(11)	−1375 (7)	1317 (8)	5453 (10)	28
O(12)	60 (4)	−1840 (4)	9834 (5)	15
C(13)	44 (7)	−2949 (6)	9787 (9)	23
C(14)	1010 (9)	−3342 (8)	11102 (11)	35
C(15)	−918 (11)	−3337 (8)	9725 (18)	39

Complete listings of bond distances and angles involving nonhydrogen atoms are given in Tables V and VI, respectively.

Table V. Bond Distances (Å) for the $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ Molecule

Mo(1)–Mo(1)′	2.739 (1)	O(8)–C(9)	1.470 (8)
Mo(1)–Br(2)	2.584 (1)	O(12)–C(13)	1.426 (9)
Mo(1)–Br(3)	2.579 (1)	C(5)–C(6)	1.499 (11)
Mo(1)–O(4)′	2.012 (4)	C(5)–C(7)	1.490 (10)
Mo(1)–O(4)	2.014 (4)	C(9)–C(10)	1.504 (11)
Mo(1)–O(8)	1.805 (5)	C(9)–C(11)	1.501 (11)
Mo(1)–O(12)	1.818 (5)	C(13)–C(14)	1.500 (14)
O(4)–C(5)	1.487 (8)	C(13)–C(15)	1.515 (13)

Table VI. Bond Angles (Deg) for the $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ Molecule

Mo(1)′–Mo(1)–Br(2)	139.6	O(4)–Mo(1)–O(12)	93.9 (2)
Mo(1)′–Mo(1)–Br(3)	136.8	O(4)′–Mo(1)–O(12)	93.4 (2)
Mo(1)′–Mo(1)–O(4)′	47.2 (1)	O(8)–Mo(1)–O(12)	168.9 (2)
Mo(1)′–Mo(1)–O(4)	47.1 (1)	Mo(1)′–O(4)–Mo(1)	85.7 (2)
Mo(1)′–Mo(1)–O(8)	95.7 (1)	Mo(1)–O(4)–C(5)	134.0 (4)
Mo(1)′–Mo(1)–O(12)	95.4 (1)	Mo(1)′–O(4)–C(5)	140.2 (4)
Br(2)–Mo(1)–Br(3)	83.6	Mo(1)–O(8)–C(9)	147.7 (4)
Br(2)–Mo(1)–O(4)′	92.4 (1)	Mo(1)–O(12)–C(13)	148.4 (5)
Br(2)–Mo(1)–O(4)	173.3 (1)	O(4)–C(5)–C(6)	109.3 (6)
Br(2)–Mo(1)–O(8)	85.8 (1)	O(4)–C(5)–C(7)	109.3 (6)
Br(2)–Mo(1)–O(12)	85.8 (1)	C(6)–C(5)–C(7)	116.0 (7)
Br(3)–Mo(1)–O(4)′	176.0 (1)	O(8)–C(9)–C(10)	108.1 (6)
Br(3)–Mo(1)–O(4)	89.7 (1)	O(8)–C(9)–C(11)	107.3 (6)
Br(3)–Mo(1)–O(8)	86.0 (2)	C(10)–C(9)–C(11)	115.0 (8)
Br(3)–Mo(1)–O(12)	85.8 (2)	O(12)–C(13)–C(14)	108.2 (7)
O(4)–Mo(1)–O(4)	94.3 (2)	O(12)–C(13)–C(15)	109.2 (7)
O(4)–Mo(1)–O(8)	93.5 (2)	C(14)–C(13)–C(15)	113.4 (9)
O(4)′–Mo(1)–O(8)	94.3 (2)		

The central $Mo_2O_6Br_4$ unit has virtual D_{2h} symmetry and a crystallographically imposed center of inversion relating the halves of the dimer. The $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ molecule has rigorous C_{2h} symmetry.

Remarks on Structure and Bonding in $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ Molecules. The angles subtended at molybdenum to the oxygen and halide atoms in both $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ and $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ are remarkably similar and deviate little from those required for a regular octahedral set of molybdenum atomic hybrid orbitals. The greatest deviation from linearity for a trans angle occurs for the mutually trans pair of terminal O-*i*-Pr ligands. Here the O–Mo–O angle is 168° (averaged), and the distortion bends these bonds away from the center of the molecule. This distortion no doubt results from steric repulsive interactions. Indeed space-filling models suggest that steric factors determine the arrangement of the isopropyl groups and thus confine the methyne protons of the bridging O-*i*-Pr ligands to the $Mo_2X_4O_2$ plane and bring about abnormally short CH···X nonbonding distances 2.48 Å (average) in $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ and 2.59 Å in $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$. It is this short distance that we believe is responsible for producing the anomalous deshielding of the methyne proton resonances of the bridging O-*i*-Pr ligands which occur at δ 7.90, 7.44, and 7.21 (δ relative to Me_4Si) when X = I, Br, and Cl, respectively.

The observed diamagnetic nature of the compounds and the short Mo-to-Mo distances, 2.731 (1) Å in $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ and 2.739 (1) Å in $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$, are consistent with the view that these compounds contain Mo–Mo single bonds. Whenever bridging groups are present, it is not possible to distinguish *unequivocally* between the direct coupling of electron spins (M–M bonding) and indirect coupling through bridges. However, for the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds the evidence for direct metal–metal bonding is virtually overwhelming.

1. Though Mo—Mo single bonds vary greatly in length depending upon oxidation state number and the character of the ligands present, the distance 2.73 Å is rather a normal value.[10]

2. The Mo—Mo distances in $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds may be compared to the Mo≡Mo bond distance, 2.222 (2) Å, in $Mo_2(OCH_2CMe_3)_6$[5] and to the Mo=Mo bond distances of 2.498 (1) and 2.523 (1) Å found in $Mo_2(O\text{-}t\text{-}Bu)_6(CO)$[11] and $Mo_2(O\text{-}i\text{-}Pr)_8$,[6] respectively. In both of the latter compounds, there are bridging OR ligands.

3. In both $[Mo(O\text{-}i\text{-}Pr)_3(NO)]_2$[12] and $[Mo(O\text{-}i\text{-}Pr)_3(NO)(HNMe_2)]_2$,[13] there are planar central $Mo_2(\mu\text{-}O)_2$ groups with Mo-to-Mo distances of 3.335 (2) and 3.390 (2) Å, respectively. On electronic grounds we have argued that these are nonbonding Mo-to-Mo distances.

4. A comparison with the $[Nb(OMe)_5]_2$ structure[14] is particularly pertinent. Niobium and molybdenum are sister elements differing only in one valence electron. In the compounds $[Nb(OMe)_5]_2$ and $Mo_2(O\text{-}i\text{-}Pr)_6X_4$, the metal atoms are in oxidation state number +5 and in octahedral coordination environments. The metal–oxygen distances are similar; the only major difference concerns the structural parameters of the central $M_2(\mu\text{-}O)_2$ units. For $[Nb(OMe)_5]_2$ there are two conformers in the unit cell which yield an averaged Nb-to-Nb distance of 3.5 Å and an average Nb–O–Nb angle of 110°. This contrasts with the much shorter Mo-to-Mo distance [2.735 Å (averaged)] and more acute Mo–O–Mo angle (85°) found in the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ molecules. These structural differences arise because the dimers are of the type d^0–d^0 (Nb–Nb) and d^1–d^1 (Mo–Mo), which correspond to M–M bond orders of 0 and 1, respectively. The M–M bond in $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ is easily pictured as a σ bond arising from the overlap of two t_{2g}-type d orbitals which, in an octahedral geometry, have lobes directed between the oxygen atoms that bridge the two molybdenum atoms.

Aside from the structural evidence of the M–M bond, there is chemical evidence for its existence. $[Nb(OMe)_5]_2$ reacts with pyridine and many other donor molecules[15] to give mononuclear adducts of the form $Nb(OMe)_5L$. On the other hand $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ dissolves in pyridine-d_5 without cleavage of the dimer: the ^1H NMR spectrum is essentially the same as that obtained in toluene-d_8.

5. Finally in 1969 Cotton[16] noted: "For any particular element it is possible empirically to locate a transition region within the entire range of its known formal oxidation states in which M–M bonding gains ascendency. With molybdenum the influence of the nature of the bridging ligands is clearly shown by the fact that with oxygen and chlorine the threshold of M–M bonding is reached at different oxidation states. Structural evidence for Mo–Mo bonding in the $Mo_2(\mu\text{-}O)_2$ system is found[17] for the Mo(5+) anion $Mo_2(O)_4(C_2O_4)_2(H_2O)_2^{2-}$ whereas both structural[18] and magnetic[19] evidence show that there is no Mo-to-Mo bond in Mo_2Cl_{10}." The structural characterization of the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds is thus particularly noteworthy. We now see that for a mixed-halide alkoxide of Mo^{5+}, through the agency of bridging alkoxide ligands, Mo–Mo bonds are formed.

The last point of interest in the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ structures concerns the extremely short Mo–O distances, 1.81 Å (averaged), associated with the terminal O-*i*-Pr ligands. This is

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

(11) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

(12) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.

(13) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *Inorg. Chem.* **1980**, *19*, 2762.

(14) Pinkerton, A. A.; Schwarzenbach, D.; Hubert-Pfalzgraf, L. G.; Reiss, J. G. *Inorg. Chem.* **1976**, *15*, 1196.

(15) Reiss, J. G.; Hubert-Pfalzgraf, L. G. *J. Chim. Phys. Phys.-Chim. Biol.* **1973**, *70*, 646.

(16) Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240.

(17) Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *4*, 1377.

(18) Sands, D. E.; Zalkin, A. *Acta Crystallogr.* **1959**, *12*, 723.

(19) Klemm, W.; Steinberg, H. *Z. Anorg. Allg. Chem.* **1936**, *227*, 193.

significantly shorter (by 0.06 Å or more) than any other Mo–OR distance yet reported. Indeed these distances are only slightly longer than the oxo–molybdenum distance, 1.801 (9) Å, reported[20] for the green isomer of $MoOCl_2(PPhEt_2)_3$. This distance has been considered to be a Mo–O double-bond distance when compared to shorter distances, ca. 1.69 Å, normally associated with Mo–O triple bonds.[21] For the $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds, the short Mo–OR(terminal) distances testify to the ability of the alkoxy ligand to respond to the increased needs of a metal to receive π-electron density as its oxidation state is increased and/or as ligands are replaced by poorer π donors.[22]

Conclusions

In this work we have shown that oxidative additions to a compound containing a $M{\equiv}M$ bond can occur with concomitant changes in M—M bond order from 3 to 2 and 1. Previously we have shown[23] that reductive elimination from a dimolybdenum center can bring about a metal-to-metal bond-order change from 3 to 4. The prospects for dinuclear transition-metal chemistry[3] are thus further emphasized. The generality and/or limitations of such transformations remains to be established, however.

Experimental Section

General Procedures. All preparations and operations were carried out under a dry and oxygen-free atmosphere or in vacuo with the use of standard Schlenk techniques.[24] Hexane, toluene, and benzene were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, phenyl ether, and sodium. Carbon tetrachloride was distilled over P_2O_5 under a nitrogen atmosphere. Samples were stored and handled in a Vacuum Atmospheres Co. Dri Lab system.

NMR spectra were obtained from a Varian Associates XL-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 273 infrared spectrophotometer. Mass spectra were obtained on an AEI MS 902 by the method of direct insertion, courtesy of Mr. Peter Cook, Queen Mary College, London.

Materials. $Mo_2(O\text{-}i\text{-}Pr)_6$ and $Mo_2(O\text{-}t\text{-}Bu)_6$ were prepared as described previously.[5] *i*-PrOO-*i*-Pr and *t*-BuOO-*t*-Bu were prepared by reacting CH_3SO_3R (R = *t*-Bu and *i*-Pr, respectively) with H_2O_2 in alkaline medium.[25,26] $CD_3CHBrCD_3$ was prepared by the reaction between PBr_3 and $CD_3CHOHCD_3$. The latter compound was made from the reaction between acetone-d_6 (Merck Sharp and Dohme) and $LiAlH_4$, followed by acid hydrolysis.

High-purity Cl_2 was purchased from Matheson and was used without further purification. I_2 was purified by sublimation. Solutions of bromine in carbon tetrachloride were standardized by addition of KI followed by titration of the liberated I_2 with standard solutions of $Na_2S_2O_3$.

$Mo_2(O\text{-}i\text{-}Pr)_6$ + *i*-PrOO-*i*-Pr. $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.54 g, 0.97 mmol) was dissolved in hexane (50 mL). To this yellow solution was added *i*-PrOO-*i*-Pr (0.5 mL, 5.0 mmol). The solution immediately began to turn green, and upon stirring overnight (ca. 12 h) it became blue. The solvent was stripped, and the remaining solids were sublimed at 80 °C (10^{-3} torr). The ^1H NMR spectrum, IR spectrum, and mass spectrum of the blue sublimate corresponded to those of $Mo_2(O\text{-}i\text{-}Pr)_8$. Trace quantities of unreacted $Mo_2(O\text{-}i\text{-}Pr)_6$ were detected.

In a similar situation, $Mo_2(O\text{-}i\text{-}Pr)_6$ and *t*-BuOO-*t*-Bu and $Mo_2(O\text{-}t\text{-}Bu)_6$ and each of *t*-BuOO-*t*-Bu and *i*-PrOO-*i*-Pr were found not to react: though the solution took on a green appearance, only the $Mo_2(OR)_6$ compounds were recovered upon sublimation.

$Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$. $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.462 g, 0.85 mmol) was dissolved in CCl_4 (175 mL) in a 500-mL round-bottomed flask. Cl_2 (1.70 mmol) was condensed into a Urey tube to provide a pressure of 0.68 atm at 22 °C by way of calibrated vacuum manifold. The Urey tube was connected to the flask containing the hexane solution of $Mo_2(O\text{-}i\text{-}Pr)_6$ under 1 atm (nitrogen gas + solvent vapor) by a glass tube fitted with stopcocks. The chlorine gas was then allowed to slowly diffuse toward the hexane solution of $Mo_2(O\text{-}i\text{-}Pr)_6$. After 3 days the solution was brown and red-brown crystals had formed at the bottom of the reaction vessel. These were recrystallized from toluene to give red crystals of $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$. The results of several analyses varied considerably, depending largely upon the age of the sample. E.g.: Anal. Calcd: C, 31.39; H, 6.15; Cl, 20.61. Found: C, 25.87; H, 5.67; Cl, 23.13. Crystals for X-ray studies were freshly prepared and kept cold (ca. −15 °C) prior to mounting in the liquid-nitrogen boil-off cold stream. Infrared data obtained from a Nujol mull between CsI plates: 260 m, 305 m, 410 m, 435 w, 454 m, 499 s, 596 m, 612 w, 639 s, 728 w, 833, 868 s, 897 s, 960 vs, 989 s, 1098 vs, 1134 m, 1169 m, 1262 w, 1310 s, 1320 m, 2900 vs cm^{-1}. ^1H NMR data obtained from toluene-d_8 solutions at 100 MHz (22 °C): δ 0.94 (d, 12 H), 1.73 (d, 6 H), 5.58 (septet, 2 H), 7.21 (septet, 1 H, J_{HH} = 7.0 Hz) (δ relative to Me_4Si).

Addition of 1 equiv of Cl_2 to $Mo_2(O\text{-}i\text{-}Pr)_6$ in CCl_4 gave only a mixture $Mo_2(O\text{-}i\text{-}Pr)_6$ and $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ under analogous conditions to those described above. Addition of greater than 2 equiv of Cl_2 led to destruction of $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$ and formation of hydrocarbon-insoluble products.

$Mo_2(O\text{-}i\text{-}Pr)_6Br_4$. $Mo_2(O\text{-}i\text{-}Pr)_6$ (1.161 g, 2.12 mmol) was dissolved in CCl_4 (80 mL). The solution was cooled to 0 °C in an ice bath, and a solution of Br_2 in CCl_4 (4.24 mmol of Br_2) was added slowly by syringe. The solution immediately turned green and then red as an orange precipitate formed. The solution was stirred and warmed to room temperature, and the orange precipitate was collected by filtration and then crystallized from toluene. The results of several elemental analyses were erratic and inconclusive. [E.g.: Anal. Calcd for $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$: C, 24.96; H, 4.89; Br, 36.91. Found: C, 25.12; H, 4.79; Br, 33.68.] The crystals for X-ray studied were freshly prepared, kept cold (ca. −15 °C), and taken directly from the mother liquor to the point of data collection in the liquid-nitrogen boil-off cold stream. The crystals grown from toluene evidently contain toluene in the unit cell. This solvent is lost if the crystals are dried in vacuo, since they then fail to diffract X-rays and they show no evidence of toluene in the infrared, ^1H NMR, or mass spectrum. IR data obtained from a Nujol mull between CsI plates: 280 w, 328 w, 399 m, 430 w, 445 m, 491 s, 583 m, 597 w, 629 vs, 721 w, 805 m, 823 s, 863 s, 888 s, 895 s, 943 vs, 982 s, 1014 s, 1092 vs, 1130 s, 1161 s, 1259 m, 1316 s, 1367 s, 2940 vs cm^{-1}. ^1H NMR data obtained from toluene-d_8 at 100 MHz (22 °C): δ 0.91 (d, 12 H), 1.55 (d, 6 H), 5.68 (septet, 2 H), 7.44 (septet, 1 H, J_{HH} = 7.0 Hz) (δ relative to Me_4Si).

Under analogous conditions to those described above, the addition of 1 equiv of Br_2 to $Mo_2(O\text{-}i\text{-}Pr)_6$ gave green solutions which slowly turned orange as $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ was precipitated from solution. The mother liquor contained only $Mo_2(O\text{-}i\text{-}Pr)_6$. Addition of greater than 2 equiv of Br_2 gave only $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ and unreacted Br_2 in the CCl_4 solution.

$Mo_2(O\text{-}i\text{-}Pr)_6I_4$. $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.790 g, 1.44 mmol) was dissolved in hexane (30 mL). To this solution, cooled to ca. 0 °C, was added dropwise I_2 (0.531 g, 2.88 mmol) dissolved in hexane (ca. 100 mL). The solution turned green, and a brown precipitate formed. The precipitate was collected by filtration, was dried under vacuum, and is formulated as $Mo_2(O\text{-}i\text{-}Pr)_6I_4$ on the basis of its properties which are similar to those of the other $Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds (X = Cl and Br). From the green hexane solution, green crystals have been obtained, and these are the subject of continuing studies. The brown solids were thermally unstable, and elemental analyses were not sought. ^1H NMR data for $Mo_2(O\text{-}i\text{-}Pr)_6I_4$ obtained in toluene-d_8 at 100 MHz (22 °C): δ 1.07 (d, 12 Hz); 2.00 (d, 6 H); 5.72 (septet, 2 H); 7.90 (septet, 1 H, J_{HH} = 7.0 Hz) (δ relative to Me_4Si). IR data obtained from a Nujol mull between CsI plates in the range 200–1500 cm^{-1}: 250 m, 300 w, 402 m, 442 w, 456 m, 500 s, 590 m, 612 w, 640 s, 725 m, 830 s, 862 s, 898 s, 956 vs, 990 s, 1093 vs, 1134 m, 1168 m, 1308 s, 1340 w cm^{-1}.

Thermal Stability of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$. A solid sample of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ was heated in vacuo to 60 °C. The sample rapidly darkened with the evolution of a gas, giving within 1 h a black molybdenum-containing substance which was insoluble in all common

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(20) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686.

(21) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(22) Huffman, J. C.; Molloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(23) Chisholm, M. H.; Haitko, D. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6262. Chisholm, M. H.; Haitko, D. A. *Ibid.* **1979**, *101*, 6984.

(24) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

(25) Williams, H. R.; Masher, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 2984.

(26) Pryor, W. A.; Hustun, D. M.; Fricke, J. R.; Pickering, J. L.; Cuiffavin, C. *J. Am. Chem. Soc.* **1964**, *86*, 4237.

organic solvents. The volatile product of this decomposition was identified as *i*-PrBr.

Attempts to obtain a mass spectrum of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ by the method of direct insertion yielded $i\text{-}PrBr^+$ (*m/e* at 122 and 124) as the ion of high mass.

NMR tube samples of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ in toluene-d_8 stored at ca. 0 °C showed significant quantities of *i*-PrBr. When heated to +60 °C, rapid decomposition occurred, yielding black solids and *i*-PrBr, which was identified by ^1H NMR spectroscopy.

Addition of $(CD_3)_2CHBr$ to a toluene-d_8 solution of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ showed no exchange of isopropyl groups of the type shown below, which would be expected if elimination of *i*-PrBr was reversible.

$$Mo_2(OCH(CH_3)_2)_6Br_4 + (CD_3)_2CHBr(\text{excess}) \rightarrow Mo_2(OCH(CD_3)_2)_6Br_4 + (CH_3)_2CHBr \quad (4)$$

X-ray Structural Determinations. General operating procedures and computational techniques have been described previously.[27]

$Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$. A crystal of dimensions 0.22 × 0.18 × 0.28 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cold stream of the diffractometer. The structure data from 30 reflections at −172 °C with Mo Kα (λ = 0.71069 Å) were a = 20.722 (6) Å, b = 9.617 (2) Å, c = 14.747 (4) Å, β = 96.02 (1)°, V = 2922.6 (1) Å^3, Z = 4, d_{calcd} = 1.578, and space group $P2_1/a$.

A total of 6928 reflections were collected including redundancies and were reduced to 5175 unique amplitudes by using standard moving-crystal, moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0° + dispersion, single background time at extremes of scan = 5 s, aperture size = 5° < 2θ < 50°. The number of reflections with $F > 2.33\sigma(F)$, on the basis of counting statistics, was 4285. Due to the nearly uniform size of the crystal and to low linear absorption coefficient (μ = 12.35 cm^{-1}), no absorption correction was applied.

The structure was solved with the use direct methods. Hydrogen atoms were apparent in a difference Fourier synthesis based on phases from the nonhydrogen atoms. Since several of the hydrogen atom parameters diverged upon refinement, they were placed in idealized positions [d(C–H) = 0.95 Å; $B_{iso} = 1 + B_{iso}$ of connected atom] and fixed during the final cycles of the full-matrix refinement. The final residuals are R_F = 0.0422 and R_{wF} = 0.0476. The goodness of fit for the last cycle was 1.05, and the maximum Δ/σ was 0.05.

Several atoms located on the periphery of the molecule possess rather large anisotropic thermal parameters, the largest being C(17) with an isotropic equivalent[28] of 12.1 Å^{-2}. These excessive parameters are attributed to thermal motion as opposed to disorder or sample decomposition, as evidenced by the facts that the hydrogen atoms were located in the course of refinement and four reflections chosen as standards and monitored during data collection exhibited only statistical fluctuations. Errors based on the variance–covariance matrix are larger by nearly 50% for those atoms with "large" thermal parameters compared to errors not involving these atoms.

$Mo_2(O\text{-}i\text{-}Pr)_6Br_4$. Crystallization of $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$ from toluene gave crystals which decrepitated upon drying in vacuo. Consequently, crystals were grown in toluene solution, and a crystal was selected and taken directly from the mother liquor to the goniostat by using inert-atmosphere handling techniques. The crystal dimensions were 0.08 × 0.20 × 0.48 mm. All data were collected at −171 °C.

The structure data obtained from 44 reflections at −171 °C with Mo Kα (λ = 0.71069 Å) were a = 15.204 (5) Å, b = 12.849 (5) Å, c = 10.535 (3) Å, β = 120.76 (1)°, V = 1768.6 (1) Å^3, Z = 4, and d_{calcd} = 1.638 g cm^{-3}, and space group $P2_1/a$.

A total of 4155 reflections were collected and reduced to 3134 unique amplitudes by using standard moving-crystal, moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0° + dispersion, single background time at extremes of scan = 10 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were 5° < 2θ < 50°. The number of reflections with $F > 2.33\sigma(F)$, on the basis of counting statistics, was 2618. The data were corrected for absorption: linear absorption coefficient = 51.924 cm^{-1}, with minimum and maximum corrections of 0.149 and 0.616, respectively.

The structure was solved with use of direct methods and lies on a center of symmetry. A disordered solvent molecule was located and refined isotropically. (Details are given in the supplementary material.) All hydrogen atoms (other than those associated with the solvent molecule) were also located and refined. The final residuals are R_F = 0.0477 and R_{wF} = 0.0472. The goodness of fit for the last cycle was 1.250, and the maximum Δ/σ was 0.05.

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Registry No. $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$, 76037-13-3; $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$, 76037-12-2; $Mo_2(O\text{-}i\text{-}Pr)_6I_4$, 76037-11-1; $Mo_2(O\text{-}i\text{-}Pr)_8$, 66526-46-3; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; *i*-PrOO-*i*-Pr, 16642-57-2; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2.

Supplementary Material Available: Tables of observed and calculated structure factors and isotropic parameters (32 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports 7928 and 7963, are available in microfiche form only from the Indiana University Library.

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[27] Caulton, K. G.; Huffman, J. C.; Lewis, L. N. *Inorg. Chem.* **1980**, *19*, 2755.

[28] Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.