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Reactions of Metal–Metal Multiple Bonds. 12.[1] Reactions of Organic Halides (Cl, Br, I) with Hexaalkoxydimolybdenum and -ditungsten ($M{\equiv}M$) Compounds. Preparation and Characterization of Hexaneopentoxydibromo(pyridine)dimolybdenum ($M{=}M$)

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In hydrocarbon solvents at 20–25 °C, $M_2(OR)_6$ ($M{\equiv}M$) compounds do not react with primary or secondary alkyl halides (Cl, Br, I) but do react with the more labile halides such as CCl_4, CH_2Br_2, and allyl, benzyl, and trityl halides. A reactivity order W > Mo and C–Br > C–Cl is observed. In general when a reaction does occur, several products are formed including $M_2X_4(OR)_6$ (M–M) compounds. From the reaction between $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and benzal bromide, $PhCHBr_2$, the green crystalline compound $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ ($M{=}M$) has been isolated and shown to have an interesting highly distorted confacial bioctahedral molecular structure with one bridging bromide, two bridging alkoxy ligands, and Mo–Mo = 2.534 (1) Å. Crystal data: a = 19.137 (5) Å, b = 11.215 (2) Å, c = 11.303 (2) Å, α = 113.53 (1)°, β = 77.57 (1)°, γ = 95.42 (1)°, Z = 2 in the space group $P\bar{1}$.

Introduction

Metal–metal multiple bonds provide a reservoir of electrons for redox reactions.[2,3] In organometallic chemistry, the oxidative addition of alkyl halides to transition-metal complexes, generalized by the reaction sequence (1), has been extensively

$$L_nM + RX \rightarrow L_nM(R)(X) \qquad (1)$$

studied because of its involvement in catalytic reactions; e.g., the addition of methyl iodide to a rhodium(I) complex is a step in the Monsanto acetic acid synthesis.[4] We were thus stimulated to investigate the reactivity of $M_2(OR)_6$ compounds toward alkyl halides. We report here the results of a survey of these reactions.

Results and Discussion

A summary of our studies is given in Table I, from which it can be seen that $M_2(OR)_6$ compounds are rather unreactive toward carbon–halogen bonds in simple alkyl halides. Only organic halides with particularly active carbon–halide bonds, most notably those well-known for C–X bond homolysis, react, and when a reaction is observed, a mixture of products is generally obtained. The only easily characterized inorganic compounds are the $M_2(OR)_6X_4$ compounds (M = Mo,[5] W),[6,7] though these are not very stable. The other metal-containing species are insoluble in hydrocarbon solvents and are probably mixed oxo–alkoxy–halo metal-containing species, wherein the oxo ligand is formed from decomposition of an alkoxide.[8]

The only inorganic compound of interest that has been discovered in this work is $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$, formed in the reaction between $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and $PhCHBr_2$ (2 equiv). The coordinated pyridine serves to suppress a further oxidation. The only organic compounds that have been isolated in these reactions are derived from radical coupling, R–R, or radical H abstraction from the solvent, R–H. A change in the solvent from hexane to ethylbenzene favors the latter (R–H) at the expense of the former, as expected. The reactions involving tungsten compounds proceed roughly 6–10 times as fast as do reactions involving molybdenum analogues. This correlates well with the general trend of ease of oxidation of M–M multiple bonds, W > Mo.[9] Also, we find that C–Br are more reactive than C–Cl bonds: dichloromethane is suitable as a solvent for these dinuclear alkoxides, whereas dibromomethane acts as a brominating agent. This trend probably reflects the C–X bond strength, C–Cl > C–Br, although the weaker C–I bonds do not necessarily react, as evidenced by the fact that $Mo_2(O\text{-}i\text{-}Pr)_6$ may be dissolved in neat methyl iodide and recovered, unreacted, by subsequent crystallization.

We studied, by low-temperature ^1H NMR spectroscopy, solutions of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$ in toluene-d_8 with $BrCH_2CH_2Br$ and 2-bromopyridine and found no evidence of adduct formation. The only role established for adduct formation was the pyridine trapping of the Mo_2^{8+}-containing compound $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$. In the absence of pyridine, oxidation proceeds to give $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_4$.

Finally, we should draw attention to the fact that alkyl halides and these metals alkoxides do not enter into the well-known ether syntheses:[8] MOR + R′X → MX + R′OR. A plausible rationale for this lies in the extensive RO-to-M π bonding that occurs in $M_2(OR)_6$ compounds.[10]

Solid-State and Molecular Structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$. In the space group $P\bar{1}$, there is one unique molecule in the asymmetric unit. Fractional coordinates are given in Table II; selected bond distances and angles are given in Table III and IV, respectively. An ORTEP view of the molecule giving the atom-numbering scheme used in the tables is given in Figure 1.

Each molybdenum atom is in a distorted octahedral environment, and the halves of the molecule are joined by two bridging alkoxy ligands and one bromide ligand. The molecule contains no elements of symmetry, and in a formal sense, the metal atoms are in different oxidation states, , Mo(1) being +3.5 and Mo(2) +4.5. The alkoxy bridge that is trans to the pyridine ligand is, however, principally associated with Mo(1), since the Mo(1)–O(23) distance, 2.062 (5) Å, is significantly shorter than the Mo(2)–O(23) distance, 2.118 (5) Å. The Mo–Mo distance, 2.534 (1) Å, is consistent with a $(Mo{=}Mo)^{8+}$ unit and may be compared to that in $(i\text{-}PrO)_3Mo(\mu\text{-}O\text{-}i\text{-}Pr)_2Mo(O\text{-}i\text{-}Pr)_3$, 2.525 (1) Å.[11] It is notably shorter than

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(1) Chisholm, M. H.; Corning, J. F.; Folting, K.; Huffman, J. C.; Ratermann, A. L.; Rothwell, I. P.; Streib, W. E. *Inorg. Chem.*, in press.

(2) Cotton, F. A; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982.

(3) Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1.

(4) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books, Mill Valley, CA, 1980.

(5) Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1981**, *20*, 871.

(6) Cotton, F. A.; DeMarco, D.; Kolthammer, B. W. S.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 3048.

(7) Reagan, W. J.; Brubaker, C. H. Jr., *Inorg. Chem.* **1970**, *9*, 827.

(8) Bradley, D. C.; Mehrotra, R. C.; Gaur, P. "Metal Alkoxides"; Wiley: New York, 1978.

(9) Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

(10) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

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Table I. Summary of Observations Concerning the Reactivity of $M_2(OR)_6$ Compounds toward a Variety of Organic Halides

reactants			
metal alkoxide	organic halide	reaction conditions	results and observns
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	$(C_6H_5)H_2CBr$ (2 equiv)	hexane/25 °C/8 h	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2py$ and other minor products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	$(C_6H_5)HCBr_2$ (2 equiv)	hexane/25 °C/1 h	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2py$ and other minor products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	$(C_6H_5)_3CBr$ (2 equiv)	hexane/25 °C/5 min	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2py$ and other products
$Mo_2(O\text{-}t\text{-}Bu)_6$	$(C_6H_5)_3CBr$ (2 equiv)	toluene-d_8/25 °C/5 min	mixture of products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	$(C_6H_5)_3CCl$ (2 equiv)	toluene-d_8/25 °C/24 h	no reaction
		toluene-d_8/60 °C/1 h	mixture of products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	$C_6H_5CH_2Cl$ (4 equiv)	toluene-d_8/25 °C/48 h	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	$(CH_3)_2HCBr$ (4 equiv)	toluene-d_8/25 °C/48 h	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	CH_3I (neat)	reflux	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	CH_3I (2 equiv)	pentane/reflux and UV lamp/3.5 h	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	H_2CBr_2 (2 equiv)	hexane/40 °C/60 min	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2py$ and other minor products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	HCI_3	hexane/25 °C	mixture of products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	CBr_4	hexane/25 °C	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_4$ and other products
$Mo_2(O\text{-}i\text{-}Pr)_6$	CCl_4 (neat)	25 °C/48 h	$Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	CCl_4 (neat)	25 °C/48 h	$Mo_2(OCH_2\text{-}t\text{-}Bu)_6Cl_4$ and other minor products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	2-bromopyridine (2 equiv)	toluene-d_8/60 °C/1 h	no reaction/no coordination to $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$ at −85 °C
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6py_2$	BrHC=CHBr (cis and trans mixture; 2 equiv)	toluene-d_8/25 °C/24 h	no reaction
$Mo_2(O\text{-}i\text{-}Pr)_6$	CH_2=$CHCH_2Br$ (4 equiv)	toluene-d_8/25 °C/24 h	mixture of products
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	1,2-dibromoethane (2 equiv)	toluene-d_8/25 °C/15 h and 80 °C/1 h	no reaction/no coordination to $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$ at −85 °C
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	1,3-dibromopropane (2 equiv)	hexane/reflux/4.5 h	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	1,3-dichloropropane (2 equiv)	toluene-d_8/25 °C/24 h	no reaction
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	1,4-dichlorobutane (2 equiv)	toluene-d_8/25 °C/24 h	no reaction
$W_2(O\text{-}i\text{-}Pr)_6py_2$	$(C_6H_5)CH_2Br$ (2 equiv)	hexane/25 °C/4 h	$W_2(O\text{-}i\text{-}Pr)_6Br_4$ and $(C_6H_5)H_2CCH_2(C_6H_5)$
$W_2(O\text{-}i\text{-}Pr)_6py_2$	$(C_6H_5)CHBr_2$ (2 equiv)	hexane/25 °C/30 min	$W_2(O\text{-}i\text{-}Pr)_6Br_4$ and $(C_6H_5)HBrCCHBr(C_6H_5)$
$W_2(O\text{-}i\text{-}Pr)_6py_2$	$(C_6H_5)_3CBr$ (2 equiv)	toluene-d_8/25 °C/5 min	mixture of products
$W_2(O\text{-}i\text{-}Pr)_6py_2$	$(C_6H_5)_3CCl$ (2 equiv)	hexane/25 °C/1 h	mixture of products
$W_2(O\text{-}i\text{-}Pr)_6py_2$	$MeC_6H_4CH_2Cl$ (2 equiv)	toluene-d_8/25 °C/8 h and 60 °C/30 min	no reaction
$W_2(O\text{-}i\text{-}Pr)_6py_2$	BrHC=CHBr (cis and trans; 2 equiv)	hexane/25 °C/24 h	mixture of products
$W_2(O\text{-}i\text{-}Pr)_6py_2$	CH_2=$CHCH_2Br$ (2 equiv)	toluene-d_8/25 °C/30 min	mixture of products
$W_2(O\text{-}i\text{-}Pr)_6py_2$	CH_3I (large excess)	toluene-d_8/25 °C/24 h	no reaction
$W_2(O\text{-}i\text{-}Pr)_6py_2$	CH_2I_2 (4 equiv)	hexane/25 °C/12 h	mixture of products
$W_2(O\text{-}i\text{-}Pr)_6py_2$	CCl_4 (4 equiv)	hexane/25 °C/1 h	$W_2(O\text{-}i\text{-}Pr)_6Cl_4$ and some minor products

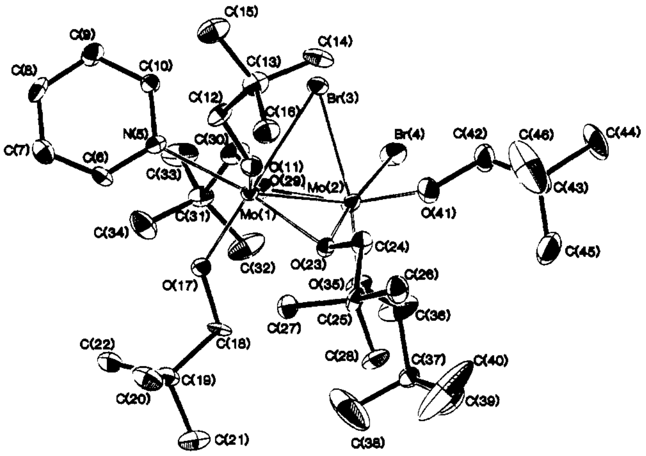

Figure 1. ORTEP view of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ molecule giving the atom-numbering scheme used in the tables.

the Mo–Mo single bond distance in $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$, 2.73 Å, which adopts an edge-shared octahedral geometry.[5] The Mo–Br (bridging) distances, 2.73 Å (average), are notably longer than the Mo–Br (bridging) distances in $Cs_3Mo_2Br_9$, 2.62 Å (average),[12] probably as a result of the trans influence[13] of the RO ligands. However, the long Mo–Br (bridging) distance, relative to the Mo–O (bridging) distances, makes for a highly distorted confacial bioctahedral $Mo_2O_6Br_2N$ moiety. It is also interesting to see one bridging and one terminal bromide ligand rather than two terminal bromides and three bridging alkoxides. The latter is seen in $(Ph_2CN_2)(i\text{-}PrO)(py)Mo(\mu\text{-}O\text{-}i\text{-}Pr)_3Mo(O\text{-}i\text{-}Pr)_2(N_2CPh_2)$.[14] One could argue that the observed structure results from a compromise of two opposing tendencies: (i) the metal atom's drive to form the strongest (shortest) M–M bond possible and (ii) the metal atom's desire to maximize RO-to-Mo π bonding. The former favors RO bridges, cf.[12] Mo–Mo = 2.82 Å in the d^3–d^3 anion $Mo_2Br_9^{3-}$, while the latter favors terminal RO ligands and halide bridges.

^1H NMR spectra obtained in toluene-d_8 in the range −40 to +20 °C reveal that the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ molecule

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

(12) Saillant, R.; Jackson, R. B.; Streib, W. E.; Folting, K.; Wentworth, R. A. D. *Inorg. Chem.* **1971**, *10*, 1453.

(13) Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1972**, *10*, 335.

(14) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1229.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	1957.2 (3)	448 (1)	8004 (1)	11
Mo(2)	2270.5 (3)	925 (1)	10217 (1)	15
Br(3)	1105.0 (4)	−613 (1)	9617 (1)	17
Br(4)	1601.9 (4)	1969 (1)	12629 (1)	24
N(5)	1035 (3)	855 (6)	7270 (6)	15
C(6)	1159 (4)	1347 (7)	6339 (7)	16
C(7)	639 (4)	1638 (8)	5847 (8)	21
C(8)	−67 (4)	1430 (8)	6335 (8)	21
C(9)	−213 (4)	879 (8)	7259 (7)	19
C(10)	346 (4)	617 (7)	7710 (7)	14
O(11)	2002 (3)	−1292 (5)	6726 (5)	17
C(12)	1460 (4)	−2046 (7)	6069 (7)	19
C(13)	1496 (4)	−3508 (7)	5730 (8)	20
C(14)	1428 (4)	−3771 (8)	6967 (8)	23
C(15)	877 (4)	−4126 (8)	5036 (9)	28
C(16)	2203 (4)	−4053 (8)	4811 (8)	23
O(17)	2485 (2)	1493 (5)	7159 (5)	15
C(18)	3109 (4)	2287 (7)	7470 (7)	16
C(19)	3397 (4)	2905 (8)	6485 (8)	20
C(20)	3578 (5)	1862 (8)	5106 (8)	27
C(21)	4073 (4)	3647 (9)	6876 (9)	31
C(22)	2866 (4)	3851 (8)	6512 (8)	23
O(23)	2909 (2)	23 (5)	8320 (5)	14
C(24)	3221 (4)	−1246 (7)	7843 (7)	17
C(25)	3905 (4)	−1396 (7)	6846 (7)	17
C(26)	4190 (4)	−2777 (8)	6456 (8)	24
C(27)	3771 (4)	−1282 (8)	5615 (7)	20
C(28)	4465 (4)	−396 (8)	7431 (8)	24
O(29)	1632 (3)	1950 (5)	9730 (5)	15
C(30)	983 (4)	2706 (8)	10396 (8)	21
C(31)	1107 (4)	4113 (7)	10557 (8)	19
C(32)	1711 (5)	4681 (9)	11303 (9)	34
C(33)	408 (4)	4819 (8)	11369 (8)	29
C(34)	1261 (5)	4214 (9)	9222 (8)	28
O(35)	3007 (3)	2169 (6)	10509 (5)	23
C(36)	3231 (5)	2971 (11)	11714 (9)	42
C(37)	3984 (4)	3450 (7)	11499 (7)	18
C(38)	4055 (12)	4133 (20)	10624 (19)	142
C(39)	4148 (5)	4372 (10)	12820 (10)	41
C(40)	4473 (7)	2356 (14)	10956 (14)	91
O(41)	2615 (3)	−407 (6)	10547 (5)	26
C(42)	2480 (5)	−825 (11)	11619 (10)	40
C(43)	3058 (5)	−1696 (8)	11518 (8)	28
C(44)	2858 (6)	−2023 (10)	12751 (9)	42
C(45)	3764 (5)	−976 (11)	11522 (10)	39
C(46)	3148 (9)	−2947 (10)	10277 (10)	64

Table III. Selected Bond Distances (Å) for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ Molecule

A	B	distance	A	B	distance
Mo(1)	Mo(2)	2.534 (1)	Mo(2)	O(29)	2.045 (5)
Mo(1)	Br(3)	2.736 (1)	Mo(2)	O(35)	1.872 (5)
Mo(1)	O(11)	1.905 (5)	Mo(2)	O(41)	1.883 (6)
Mo(1)	O(17)	1.887 (5)	O(11)	C(12)	1.417 (9)
Mo(1)	O(23)	2.062 (5)	O(17)	C(18)	1.439 (9)
Mo(1)	O(29)	2.020 (5)	O(23)	C(24)	1.443 (9)
Mo(1)	N(5)	2.257 (6)	O(29)	C(30)	1.454 (9)
Mo(2)	Br(3)	2.720 (1)	O(35)	C(36)	1.431 (10)
Mo(2)	Br(4)	2.584 (1)	O(41)	C(42)	1.431 (10)
Mo(2)	O(23)	2.118 (5)			

Table IV. Selected Bond Angles (deg) for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ Molecule

A	B	C	angle
Mo(2)	Mo(1)	Br(3)	62.0 (0)
Mo(2)	Mo(1)	O(11)	119.6 (2)
Mo(2)	Mo(1)	O(17)	112.4 (2)
Mo(2)	Mo(1)	O(23)	53.7 (1)
Mo(2)	Mo(1)	O(29)	51.9 (1)
Mo(2)	Mo(1)	N(5)	136.7 (2)
Br(3)	Mo(1)	O(11)	84.1 (2)
Br(3)	Mo(1)	O(17)	168.8 (1)
Br(3)	Mo(1)	O(23)	95.2 (1)
Br(3)	Mo(1)	O(29)	73.9 (1)
Br(3)	Mo(1)	N(5)	94.0 (2)
O(11)	Mo(1)	O(17)	106.9 (2)
O(11)	Mo(1)	O(23)	84.8 (2)
O(11)	Mo(1)	O(29)	157.9 (2)
O(11)	Mo(1)	N(5)	90.3 (2)
O(17)	Mo(1)	O(23)	88.0 (2)
O(17)	Mo(1)	O(29)	94.9 (2)
O(17)	Mo(1)	N(5)	84.1 (2)
O(23)	Mo(1)	O(29)	99.8 (2)
O(23)	Mo(1)	N(5)	169.1 (2)
O(29)	Mo(1)	N(5)	88.4 (2)
Mo(1)	Mo(2)	Br(3)	62.7 (0)
Mo(1)	Mo(2)	Br(4)	134.5 (0)
Mo(1)	Mo(2)	O(23)	51.7 (1)
Mo(1)	Mo(2)	O(29)	51.0 (1)
Mo(1)	Mo(2)	O(35)	109.8 (2)
Mo(1)	Mo(2)	O(41)	120.2 (2)
Br(3)	Mo(2)	Br(4)	89.2 (0)
Br(3)	Mo(2)	O(23)	94.4 (1)
Br(3)	Mo(2)	O(29)	74.0 (1)
Br(3)	Mo(2)	O(35)	169.7 (2)
Br(3)	Mo(2)	O(41)	87.5 (2)
Br(4)	Mo(2)	O(23)	173.8 (1)
Br(4)	Mo(2)	O(29)	88.7 (1)
Br(4)	Mo(2)	O(35)	92.3 (2)
Br(4)	Mo(2)	O(41)	91.1 (2)
O(23)	Mo(2)	O(29)	97.2 (2)
O(23)	Mo(2)	O(35)	85.1 (2)
O(23)	Mo(2)	O(41)	84.0 (2)
O(29)	Mo(2)	O(35)	95.9 (2)
O(29)	Mo(2)	O(41)	161.5 (2)
O(35)	Mo(2)	O(41)	102.6 (2)
Mo(1)	Br(3)	Mo(2)	55.3 (0)
Mo(1)	O(11)	C(12)	128.8 (4)
Mo(1)	O(17)	C(18)	128.8 (4)
Mo(1)	O(23)	Mo(2)	74.6 (2)
Mo(1)	O(23)	C(24)	126.8 (4)
Mo(2)	O(23)	C(24)	123.6 (4)
Mo(1)	O(29)	Mo(2)	77.1 (2)
Mo(1)	O(29)	C(30)	136.5 (4)
Mo(2)	O(29)	C(30)	134.9 (4)
Mo(2)	O(35)	C(36)	129.4 (5)
Mo(2)	O(41)	C(42)	135.3 (5)

is fluxional. The low-temperature spectra are consistent with expectations based on the solid-state molecular structure. There are six neopentoxy groups of equal integral intensity, and the methylene protons of each group are diastereotopic as expected for a $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ molecule lacking any element of symmetry.

Concluding Remarks. Though we have found no evidence for the formation of metal–carbon bonds akin to eq 1, we have found that a number of organic halides act as "relatively" mild reagents for the halogenation of the $(M{\equiv}M)^{6+}$ unit in $M_2(OR)_6$ compounds. The presence of pyridine serves as a suitable Lewis base to suppress oxidation of the $(Mo{=}Mo)^{8+}$ center in the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ molecule.[15] It is also understandable that a $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2$ molecule would be coordinatively unsaturated and labile to disproportionation by halide ligand transfer reactions of the type noted previously:[5] $2Mo_2(O\text{-}i\text{-}Pr)_6X_2 \rightarrow Mo_2(O\text{-}i\text{-}Pr)_6 + Mo_2X_4(O\text{-}i\text{-}Pr)_6$.

Experimental Section

General Procedures. All preparations and manipulations were carried out by using dry and oxygen-free atmospheres (N_2) and solvents. At the bench, Schlenk techniques were used, while other operations were carried out in a Vacuum Atmospheres Co. Dri Lab Assembly.

^1H NMR spectra were obtained on a Varian HR-220 spectrometer, using toluene-d_8 as solvent. Infrared spectra were obtained from Nujol mulls, using CsI plates with a Perkin-Elmer 283 spectrophotometer. Elemental analyses were obtained from Alfred Bernhardt Microan-

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(15) Chetcuti, M. J.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

Table V. Summary of Crystallographic Data for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ Molecule

formula	$C_{35}H_{71}Br_2Mo_2NO_6$
fw	953.64
space group	$P\bar{1}$
a, Å	19.137 (5)
b, Å	11.215 (2)
c, Å	11.303 (2)
α, deg	113.53 (1)
β, deg	77.57 (1)
γ, deg	95.42 (1)
Z	2
V, Å^3	2171.94
d(calcd), g/cm^3	1.458
cryst size, mm	0.13 × 0.20 × 0.25
cryst color	green
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromator
linear abs coeff, cm^{-1}	24.23
max abs cor	0.7130
min abs cor	0.7960
temp, °C	−164
instrument	Picker 4-circle diffractometer locally modified and interfaced
detector aperture	3.0 mm wide × 4.0 mm high; 22.5 cm from crystal
sample to source dist, cm	23.5
takeoff angle, deg	2.0
scan speed, deg/min	4.0
scan width, deg	1.8 + 0.692 tan θ
bkgd counts, s	5 at each end of scan
2θ range, deg	6–45
data collcd	7231 total
no. of unique data	5708
no. of unique data with $F_o > 2.33\sigma(F_o)$	2273
$R(F)$	0.050
$R_w(F)$	0.048
goodness of fit	1.404
largest Δ/σ	0.05

alytisches Laboratorium, Elbach, West Germany, using drybox sampling procedures.

Materials. The dimetal hexaalkoxides $M_2(OR)_6$ or their pyridine adducts $M_2(OR)_6(py)_2$ were prepared as described previously for M = Mo[16,17] and W.[18] Organic halides were obtained from commercial sources and distilled and stored over sieves prior to use.

Preparation of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$. $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (1.0 g, 1.14 mmol) was dissolved in pentane (10 mL), and $PhCHBr_2$ (0.38 mL, 2.28 mmol) was added via a microsyringe. The solution was reduced in volume by evaporation for 30 min at 25 °C under a partial vacuum. A fine green powder precipitated from the solution and was collected by filtration and dried in vacuo. Toluene (1 mL) was added to the filtrate, and this solution was cooled slowly to −15 °C, yielding green crystals suitable for the X-ray study. These were also collected by filtration and dried in vacuo; combined yield 200 mg, 206 mmol (18% based on Mo). Anal. Calcd for $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$: C, 44.26; H, 7.13; N, 1.47. Found: C, 44.04; H, 7.23; N, 1.41.

IR data: 2900 s, 1600 m, 1472 m, 1460 m, 1442 m, 1390 m, 1360 m, 1280 M, 1200 s, 1125 s, 1038 s, 1018 s, 1000 s, 970 s, 900 s, 755 m, 700 m, 692 w, 645 w, 645 w, 595 s, 525 s, 468 m, 440 m, 412 w, 332 w cm^{-1}.

^{1}H NMR data (−45 °C): δ 0.95 (s, 9 H), 0.99 (s, 9 H), 1.01 (s, 9 H), 1.10 (s, 9 H), 1.16 (s, 9 H), 1.28 (s, 9 H); δ 5.0–5.8 (12 H, AB quartet overlapping); δ 5.95, 6.7, 9.1 (pyridine).

$Mo_2(O\text{-}i\text{-}Pr)_6X_4$ compounds (X = Br, Cl) were prepared in an analogous manner to that described above using a variety of organic halides (see Table I) and were characterized by a comparison of IR and ^{1}H NMR spectra with the previous reported data for these compounds. The tungsten analogues showed similar spectroscopic properties.

^{1}H NMR data (16 °C): for $W_2(O\text{-}i\text{-}Pr)_6Br_4$, δ 1.02 (d, 24 H), 1.45 (d, 12 H), 5.80 (sept, 4 H), 7.20 (sept 2 H, J_{HH} = 7.0 Hz); for $W_2(O\text{-}i\text{-}Pr)_6Cl_4$, δ 0.95 (d, 24 H), 1.70 (d, 12 H), 5.50 (sept, 4 H), 7.30 (sept, 2 H).

X-ray Structural Determination. General operating procedures and computational techniques have been described previously.[19]

Structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$. Crystal and experimental data are summarized in Table V. A crystal of rather irregular dimensions was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cold stream of the diffractometer. The crystal was characterized in the usual manner, and the data collection proceeded normally.

The structure was solved by a combination of direct methods and Fourier techniques. A difference Fourier synthesis after isotropic refinement located the majority of the hydrogen atoms, although several were ill-placed or missing. For this reason, all hydrogen atoms were included as fixed atom contributors for the remaining refinement. All methyl hydrogens were assumed to be staggered. The final difference Fourier synthesis was essentially featureless, with the largest residual being 0.42 e/Å^3.

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Registry No. $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$, 89689-43-0; $W_2(O\text{-}i\text{-}Pr)_6Br_4$, 89689-44-1; $W_2(O\text{-}i\text{-}Pr)_6Cl_4$, 85202-70-6; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$, 81987-92-0; $Mo_2(O\text{-}t\text{-}Bu)_6$, 60764-63-8; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 62521-24-8; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_4$, 89689-45-2; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Cl_4$, 89689-46-3; $Mo_2(O\text{-}i\text{-}Pr)_6Br_4$, 76037-12-2; $Mo_2(O\text{-}i\text{-}Pr)_6Cl_4$, 76037-13-3; $(C_6H_5)H_2CBr$, 100-39-0; $(C_6H_5)HCBr_2$, 618-31-5; $(C_6H_5)_3CBr$, 596-43-0; $(C_6H_5)_3CCl$, 76-83-5; $C_6H_5CH_2Cl$, 100-44-7; $(CH_3)_2HCBr$, 75-26-3; CH_3I, 74-88-4; H_2CBr_2, 74-95-3; HCI_3, 75-47-8; CBr_4, 558-13-4; CCl_4, 56-23-5; *cis*-BrHC=CHBr, 590-11-4; *trans*-BrHC=CHBr, 590-12-5; CH_2=$CHCH_2Br$, 106-95-6; $MeC_6H_4CH_2Cl$, 26519-66-4; CH_2I_2, 75-11-6; $(C_6H_5)H_2CCH_2(C_6H_5)$, 103-29-7; $(C_6H_5)HBrCCHBr(C_6H_5)$, 5789-30-0; Mo, 7439-98-7; 2-bromopyridine, 109-04-6; 1,2-dibromoethane, 106-93-4; 1,3-dibromopropane, 109-64-8; 1,3-dichloropropane, 142-28-9; 1,4-dichlorobutane, 110-56-5.

Supplementary Material Available: Listings of atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and structure factor amplitudes and stereoviews for $Mo_2(OCH_2\text{-}t\text{-}Bu)_6Br_2(py)$ (47 pages). Ordering information is given on any current masthead page. The complete structural report, MSC No. 82011, is available from the Indiana University Chemistry Library, in microfiche form only, for $2.50.

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

(17) Leonelli, J. Ph.D. Thesis, Indiana University, 1982.

(18) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

(19) Caulton, K. G.; Huffman, J. C.; Lewis, L. N. *Inorg. Chem.* **1980**, *19*, 2755.