film itself. These and other aspects of crown polymer film electrochemistry promise interesting further investigations.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843, and Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Insertion Reactions of Hexaalkoxydimolybdenum and -ditungsten Compounds with Organic Isocyanates. Syntheses and Structures of $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ and $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]$

MALCOLM H. CHISHOLM,*[1a] F. ALBERT COTTON,*[1b] KIRSTEN FOLTING,[1a] JOHN C. HUFFMAN,[1a]
A. L. RATERMANN,[1a] and EDWAR S. SHAMSHOUM[1b]

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Dimolybdenum and ditungsten hexaalkoxides react with phenyl isocyanates (2 equiv) in nonpolar solvents to form products involving insertion of the isocyanate into the metal alkoxide bond. The new products $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ (**1**) and $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ (**2**) have both been characterized by X-ray crystallography. Compound **1** crystallizes in space group *Pnab* with $a = 18.652$ (22) Å, $b = 10.808$ (11) Å, $c = 18.912$ (24) Å, and $Z = 4$ (at −55 °C). The molecule has a twofold axis of symmetry perpendicularly bisecting the Mo–Mo bond, and it consists of two cis bridging bidentate ligands and four isopropoxy groups. Each molybdenum atom is in the +3 oxidation state, and the Mo–Mo bond length is 2.221 (5) Å. Compound **2** crystallizes in space group $P\bar{1}$ with $a = 10.48$ (1) Å, $b = 11.38$ (1) Å, $c = 11.80$ (1) Å, $\alpha = 96.96$ (3)°, $\beta = 110.02$ (3)°, $\gamma = 106.93$ (3)°, $V = 1226$ (2) Å^3, and $Z = 1$. The molecule is centrosymmetric and consists of two trans bridging bidentate ligands and four *tert*-butoxy ligands. Each tungsten atom is in the +3 oxidation state, and the W–W bond length is 2.290 (1) Å. The bond distance in each compound is consistent with a bond order of 3, and the magnitude of the difference, 0.069 (5) Å, is as expected.

Introduction

The reactivity of metal–metal triple bonds of ditungsten and dimolybdenum alkoxides or amides has attracted considerable interest in recent years. Schrock and co-workers[2] have shown that $W_2(OCMe_3)_6$ reacts with various alkynes to give $(Me_3CO)_3W{\equiv}CR$, which catalytically metathesizes acetylenes. Chisholm and co-workers[3] have shown that acetylenes and peroxides oxidatively add to $M_2(OR)_6$ (M = Mo, W; R ≠ $OCMe_3$ when M = W). Cotton, Schwotzer, and Shamshoum[4] have shown that under more vigorous conditions still other, new types of products are obtained.

The insertions of various unsaturated organic molecules such as CO_2, isocyanates, and CS_2 into M–X (X = O, N) bonds are well-known processes. With respect to isocyanates, the reactants of interest here, Davies and co-workers,[5] and also Mehrotra and co-workers,[6] have demonstrated the insertion of isocyanates into a titanium alkoxide bond and into a niobium alkoxide bond. Later, Cotton, Chisholm, and co-workers[7] have also shown that CO_2 can insert into M–X (M = Mo, W; X = O, N) bonds of dinuclear species to form bridging bidentate ligands. In this report, we bring these two lines of work together and report the insertion products obtained from the reaction of phenyl isocyanate with $W_2(OCMe_3)_6$ and several $Mo_2(OR)_6$ compounds.

Experimental Section

Ditungsten hexa-*tert*-butoxide, $W_2(OCMe_3)_6$, was prepared[2] by Na/Hg reduction of WCl_4 in THF at −10 °C in the presence of $LiOCMe_3$, followed by recrystallization from hexane at −10 °C. Dimolybdenum hexaalkoxides were prepared[3] by first reacting $MoCl_3$ with $LiNMe_2$ (3 equiv) in THF to give $Mo_2(NMe_2)_6$, which was sublimed. Excess 2-propanol or 2,2-dimethyl-1-propanol was then added to a hexane solution of $Mo_2(NMe_2)_6$, and the $Mo_2(O\text{-}i\text{-}Pr)_6$ or $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$ products was recrystallized from hexane at −20 °C. All reactions were done under an argon atmosphere.

NMR spectra of the molybdenum products were recorded on a Varian HR-220 spectrometer at 16 °C in toluene-d_8 or benzene-d_6. Chemical shifts were calculated on the basis of the residual protons in the solvent and referenced to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer in a Nujol mull between CsI plates. Elemental analysis were done by Bernhardt Microanalytical Laboratories, West Germany. ^1H NMR spectra of $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ were recorded on a Varian XL-200 PET spectrometer in $CDCl_3$. The infrared spectrum was recorded on a Perkin-Elmer 783 infrared spectrophotometer.

Preparations. $Mo_2(O\text{-}i\text{-}Pr)_4[N(Me)C(O)O\text{-}i\text{-}Pr]_2(py)_2$. $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.6 g, 1.10 mmol) was suspended in hexane (10 mL) and then frozen at liquid-nitrogen temperatures. The flask was evacuated and methyl isocyanate (2.20 mmol) was vacuum distilled into the flask from a calibrated vacuum gas line. The solution was warmed to 25 °C, and pyridine (1 mL) was added. Slow cooling to −15 °C produced a homogeneous mass of dark red crystals of $Mo_2(O\text{-}i\text{-}Pr)_4[(N(Me)C(O)O\text{-}i\text{-}Pr]_2(py)_2$. Yield: 80% based on molybdenum.

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(1) (a) Indiana University. (b) Texas A&M University.
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IR data: 2940 (s), 1600 (m), 1510 (s), 1480 (m), 1418 (m), 1312 (m), 1192 (s), 1120 (s), 1045 (m), 960 (s), 898 (s), 749 (m), 695 (m), 600 (m), 528 (m), 440 (m), 392 (w) cm^{-1}.

^{1}H NMR data: δ 1.32 (d, 6 H), 1.38 (d, 6 H), 1.42 (d, 6 H), 1.55 (d, 6 H), 1.78 (d, 6 H), 1.82 (d, 6 H, J = 6 Hz), 2.80 (s, 6 H), 4.78 (sep, 2 H), 5.00 (sep, 2 H), 6.62 (mult, 3 H), 8.41 (d, 2 H).

$Mo_2(OCH_2$-*t*-$Bu)_4[N(Me)C(O)OCH_2$-*t*-$Bu]_2(py)_2$. This compound was synthesized in essentially the same manner as that just described for the *i*-PrO compound.

IR data: 2905 (s), 1603 (w), 1562 (s), 1420 (w), 1330 (m), 1260 (w), 1220 (m), 1152 (m), 1115 (m), 1082 (s), 1042 (m), 1020 (m), 755 (m), 720 (w), 700 (m), 632 (m), 601 (m), 455 (w), 3950 (w) cm^{-1}.

^{1}H NMR data: δ 0.92 (s, 18 H), 0.94 (s, 18 H), 1.70 (s, 18 H), 1.71 (s, 18 H), 1.25 (s, 18 H), 1.26 (s, 18 H), 2.80 (s, 6 H), 2.81 (s, 6 H), 4.02, 4.04 (two overlapping AB quart, 8 H), 4.25, 4.58 (AB quart, 4 H), 4.42, 5.12 (AB quart, 4 H), 4.80, 4.26 (AB quart, 4 H), 5.08, 5.70 (AB quart, 4 H), 6.61 (mult, 12 H), 8.4 (overlapping d, 8 H).

$Mo_2(OCH_2$-*t*-$Bu)_4[N(C_6H_5)C(O)OCH_2$-*t*-$Bu]_2(py)_2$. $Mo_2(OCH_2$-*t*-$Bu)_6(py)_2$ (0.7 g, 0.801 mmol) was suspended in hexane (10 mL) and the mixture cooled to 0 °C. Phenyl isocyanate (0.174 mL, 1.60 mmol) was added via syringe to the stirred solution. The solution was warmed to 25 °C and then cooled to −15 °C to produce a homogeneous crop of red crystals of the product.

IR data: 2900 (s), 1601 (s), 1545 (s), 1335 (s), 1230 (m), 1210 (w), 1138 (w), 1064 (s), 1005 (s), 912 (m), 750 (m), 742 (m), 720 (m), 689 (m), 660 (w), 628 (w), 598 (w), 454 (w), 418 (m), 386 (m) cm^{-1}.

^{1}H NMR data: δ 0.85 (s, 18 H), 1.12 (s, 18 H), 1.22 (s, 18 H), 4.11, 4.14 (AB quart, 4 H), 4.25, 4.73 (AB quart, 4 H), 4.61, 5.08 (AB quart, 4 H), 6.6, 6.75, 7.25 (mult, 16 H), 8.40 (d, 4 H).

$Mo_2(O$-*i*-$Pr)_4[N(C_6H_5)C(O)O$-*i*-$Pr]_2(pyMe$-$4)_2$. This compound was synthesized in the manner as just given for the neopentyl compound.

IR data: 2910 (s), 1615 (w), 1595 (w), 1538 (s), 1400 (w), 1336 (w), 1315 (w), 1265 (w), 1250 (w), 1232 (m), 1210 (w), 1178 (w), 1152 (w), 1110 (w), 1070 (m), 1035 (w), 980 (m), 947 (m), 908 (w), 880 (w), 830 (w), 810 (m), 775 (m), 752 (m), 720 (w), 708 (w), 690 (m), 658 (w), 578 (m), 502 (m) cm^{-1}.

^{1}H NMR data: δ 1.14 (d, 6 H), 1.20 (d, 6 H), 1.40 (d, 6 H), 1.48 (d, 6 H), 1.58 (d, 6 H), 1.64 (d, 6 H), 5.10 (sep, 2 H), 5.26 (sep, 2 H), 6.68 (sep, 2 H), 6.52 (d, 4 H), 6.78, 7.10, 7.40 (mult, 12 H), 8.40 (d, 4 H).

$Mo_2(O$-*i*-$Pr)_4[N(C_6H_5)C(O)O$-*i*-$Pr]_2$. $Mo_2(O$-*i*-$Pr)_6$ (0.7 g, 1.28 mmol) was suspended in hexane/toluene (10 mL/1 mL), and phenyl isocyanate (0.28 mL, 2.56 mmol) was added to the solution via syringe. The solution was stirred for 10 min, and pyridine (1.0 mL) was added. Slow cooling to −15 °C produced a homogeneous crop of crystals of the product suitable for X-ray structural analysis.

IR data: 2905 (s), 1548 (m), 1407 (m), 1322 (m), 1246 (m), 1234 (w), 1146 (w), 1104 (s), 1054 (m), 972 (s), 948 (m), 905 (w), 880 (w), 847 (w), 820 (w), 770 (w), 718 (w), 688 (w), 658 (w), 628 (w), 605 (m), 490 (w) cm^{-1}.

^{1}H NMR data: δ 1.18 (d, 6 H), 1.21 (d, 6 H), 1.38 (d, 6 H), 1.46 (d, 6 H) 1.56 (d, 6 H), 1.61 (d, 6 H), 5.08 (sep, 2 H), 5.23 (sep, 2 H), 6.54 (sep, 2 H), 6.78 (t, 4 H), 7.01 (d, 2 H), 7.25 (d, 4 H).

$W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$. $W_2(OCMe_3)_6$ (400 mg, 0.5 mmol) was dissolved in a 20 mL of toluene. The solution was cooled to −55 °C. At this temperature phenyl isocyanate (0.9 mL, 1.0 mmol) was added to the solution via syringe. The solution was stirred at this temperature for 2 h. Several minutes after the addition of PhNCO, the color of the solution changed from red to purple. The solution was allowed to warm to room temperature where it was stirred for 6 h. It was observed that at −15 °C the color began to change to brown, and the solution became completely brown when it reached room temperature. The toluene solution was filtered into a 25-mL storage tube where it was stripped down to 5 mL. Orange-red plates (compound **2**) were deposited from the brown solution during 3 days of cooling at −10 °C. The reaction is reproducible to give a homogeneous crystalline material in 80–90% yield based on tungsten.

IR data (KBr pellets): 3035 (w), 2950 (s), 2905 (w), 1685 (m), 1590 (m), 1531 (m), 1525 (m), 1430 (m), 1385 (w), 1360 (m), 1310 (m), 1255 (s), 1155 (s), 1080 (w), 1045 (w), 1020 (s), 800 (s), 745 (s), 690 (s), 670 (w).

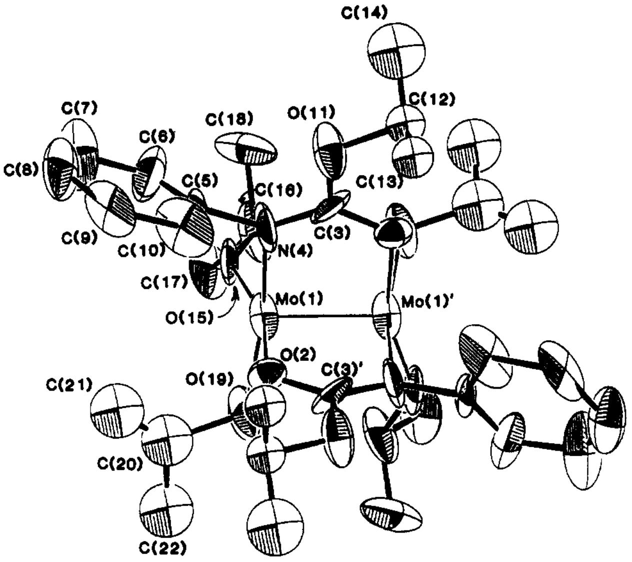

Figure 1. ORTEP drawing of $Mo_2(O$-*i*-$Pr)_4[N(C_6H_5)C(O)O$-*i*-$Pr]_2$ showing a view perpendicular to the metal–metal bond and giving the atom-numbering scheme used in the tables.

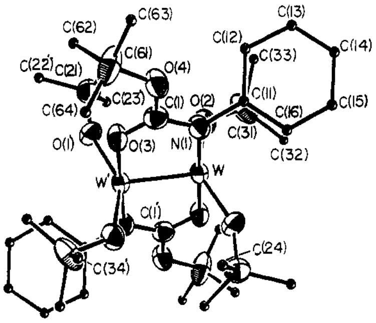

Figure 2. ORTEP drawing of the $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ molecule, giving the atom-labeling scheme. The methyl carbon atoms of the *tert*-butyl groups and the phenyl groups are represented by arbitrarily small spheres to avoid covering up other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

^{1}H NMR data: δ 7.0–7.75 (complex m, NPh), 1.25 (s, 4 terminal $OCMe_3$), 1.48 (s, 2 bridging $OCMe_3$).

Note on the Color Changes. In a separate experiment, the preparation just described for the ditungsten compound was repeated through the early stages where the color changes (red to purple to brown) occurred. After room temperature was reached and stirring was continued for 2 h, the solution was cooled to −60 °C and stirring continued. The brown color remained unchanged.

X-ray Crystallographic Procedures. The structures of single crystals containing **1** and **2** were determined by applying general procedures that have been described elsewhere.[8] Some further details are available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement for both compounds are summarized in Table I.

Tables II and III list the atomic coordnates for **1** and **2**, respectively, while Tables IV and V give important bond distances and angles for the two structures. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 1 and 2 show the structures and the atom-numbering schemes.

Results and Discussion

Synthetic Reactions. The addition of 2 equiv of organic isocyanates to $Mo_2(OR)_6$ (R = *i*-Pr, neopentyl), in the presence of pyridine, or to $W_2(OCMe_3)_6$ leads to remarkable

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(8) For compound **2**: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. For compound **1**: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table I

formula	$W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$	$Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$
fw	1020.62	784.65
space group	$P\bar{1}$	*Pnab*
a, Å	10.48 (1)	18.652 (22)
b, Å	11.38 (1)	10.808 (11)
c, Å	11.80 (1)	18.912 (24)
α, deg	96.96 (3)	
β, deg	110.02 (3)	
γ, deg	106.93 (3)	
V, Å^3	1226 (2)	3813 (2)
Z	1	4
d_{calcd}, g/cm^3	1.382	1.367
cryst size, mm	0.25 × 0.25 × 0.2	0.25 × 0.25 × 0.21
μ(Mo Kα), cm^{-1}	48.3	6.851
data colln instrum	CAD-4	Picker 4-circle
radiation (monochromated in incident beam)	Mo Kα	Mo Kα
orientation reflcns: no.; range (2θ), deg	25; $20 < 2\theta < 37$	50; $15 < 2\theta < 35$
temp, °C	25 ± 1	−55
scan method	θ–2θ	θ–2θ
data colln range (2θ), deg	4–50	6–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3012	1784
no. of parameters refined	246	
R^a	0.0373	0.099
$R_w{}^b$	0.0465	0.099
quality-of-fit indicator^c	1.31	1.43
largest shift/esd, final cycle	0.2	0.05
largest peak, e/Å^3	0.95	0.35

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	7602 (1)	967 (2)	4421 (2)	41
O(2)	8076 (8)	2592 (16)	5718 (9)	35
C(3)	8417 (14)	3008 (30)	5163 (16)	45
N(4)	8356 (12)	2413 (25)	4533 (10)	53
C(5)	8640 (14)	2964 (29)	3910 (12)	39
C(6)	9105 (17)	2201 (34)	3544 (16)	63
C(7)	9359 (23)	2753 (34)	2880 (17)	79
C(8)	9175 (23)	3827 (37)	2653 (17)	74
C(9)	8673 (22)	4486 (34)	3016 (18)	73
C(10)	8399 (19)	4155 (27)	3692 (18)	63
O(11)	8887 (12)	3885 (18)	5217 (8)	50
C(12)	8971 (15)	4514 (27)	5960 (15)	43 (7)
C(13)	8581 (32)	5532 (53)	5913 (29)	41 (13)
C(14)	9687 (44)	4587 (77)	5971 (42)	79 (23)
O(15)	8276 (10)	−303 (19)	4246 (8)	47
C(16)	8589 (19)	−1327 (28)	4582 (14)	63
C(17)	8380 (18)	−2470 (28)	4128 (15)	64
C(18)	9388 (15)	−1166 (33)	4650 (17)	70
O(19)	6759 (11)	202 (20)	4096 (9)	57
C(20)	6635 (20)	101 (35)	3322 (19)	73 (9)
C(21)	6971 (38)	612 (66)	2885 (39)	80 (19)
C(22)	5988 (40)	−634 (73)	3216 (38)	97 (20)
C(13)′	9647 (28)	3824 (56)	6254 (28)	37 (12)
C(14)′	9133 (30)	5889 (62)	5812 (28)	52 (14)
C(21)′	6809 (38)	−1162 (73)	3035 (37)	79 (19)
C(22)′	6006 (36)	592 (67)	3185 (36)	73 (18)

Table III. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O\text{-}t\text{-}Bu)_4[N(C_6H_5)C(O)O\text{-}t\text{-}Bu]_2$ Molecule

atom	*x*	*y*	*z*	B,^{a} Å^2
W	0.12402 (3)	0.03972 (3)	0.05029 (3)	2.686 (7)
O(1)	0.1972 (5)	−0.0918 (5)	0.0843 (5)	3.6 (1)
O(2)	0.1758 (6)	0.2156 (5)	0.0410 (5)	3.8 (1)
O(3)	0.1445 (5)	0.0040 (5)	−0.1236 (5)	3.4 (1)
O4	0.0352 (6)	−0.0826 (6)	−0.3303 (5)	3.8 (1)
N(1)	0.1037 (6)	0.0792 (6)	0.2205 (6)	3.1 (2)
C(1)	0.0301 (8)	−0.0501 (7)	−0.2219 (7)	3.2 (2)
C(11)	0.2321 (9)	0.1483 (8)	0.3322 (7)	3.5 (2)
C(12)	0.3443 (9)	0.099 (1)	0.3634 (8)	4.7 (3)
C(13)	0.473 (1)	0.170 (1)	0.4668 (9)	5.5 (3)
C(14)	0.490 (1)	0.285 (1)	0.5369 (9)	5.7 (3)
C(15)	0.380 (1)	0.330 (1)	0.504 (1)	5.8 (3)
C(16)	0.248 (1)	0.2643 (9)	0.4030 (9)	4.8 (3)
C(21)	0.1850 (9)	−0.2207 (8)	0.0778 (9)	4.1 (2)
C(22)	0.341 (1)	−0.217 (1)	0.120 (1)	7.1 (4)
C(23)	0.092 (1)	−0.300 (1)	−0.057 (1)	5.8 (3)
C(24)	0.115 (1)	−0.266 (1)	0.167 (1)	6.5 (3)
C(31)	0.317 (1)	0.3030 (9)	0.0687 (9)	5.1 (3)
C(32)	0.429 (1)	0.239 (1)	0.098 (1)	6.5 (3)
C(33)	0.352 (1)	0.414 (1)	0.175 (1)	7.6 (4)
C(34)	0.304 (1)	0.355 (1)	−0.054 (1)	8.8 (4)
C(61)	0.1748 (9)	−0.059 (1)	−0.3483 (9)	5.4 (3)
C(62)	0.262 (1)	−0.128 (1)	−0.271 (1)	8.0 (3)
C(63)	0.118 (1)	−0.124 (1)	−0.4874 (8)	5.9 (3)
C(64)	0.259 (1)	0.082 (1)	−0.318 (1)	6.8 (3)
C(91)	0.081 (3)	0.493 (3)	0.582 (2)	18 (1)*
C(92)	0.200 (3)	0.539 (3)	0.550 (3)	9.5 (8)*
C(93)	0.095 (2)	0.530 (2)	0.460 (2)	10.8 (5)*
C(94)	0.010 (4)	0.466 (3)	0.654 (3)	11 (1)*
C(95)	0.166 (2)	0.492 (2)	0.672 (2)	15.0 (8)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

dinuclear products that form by insertions of isocyanate molecules into two M–O bonds, as shown in eq 1. Two of

$$M_2(OR)_6 + R'N{=}C{=}O \rightarrow M_2(OR)_4[N(R')C(O)OR]_2 \quad (1)$$

$$M = W,\ R = OCMe_3,\ R' = Ph$$

$$M = Mo,\ R = i\text{-}Pr,\ \text{neopentyl},\ R' = Me,\ Ph$$

the products, $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ and $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$, have been definitively identified by single-crystal X-ray study. Several other products (see Table VI and the Experimental Section), all containing molybdenum, were characterized by NMR, IR, and analytical data. All these compounds fit into the class of compounds $M_2(X)_4(YL)_2$ where X = OR or NMe_2 and YL is a type shown in I–V.[7,9,10] None of the reported products can be sublimed.

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(10) Chisholm, M. H.; Haitko, D. A.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1981**, *20*, 171.

Table IV. Selected Bond Angles (deg) for $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ and $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$

Mo(1)′-Mo(1)-O(2)	91.4 (5)	W′-W-O(1)	111.0 (2)
-O(15)	106.6 (5)	-O(2)	103.4 (2)
-O(19)	100.5 (6)	-O(3)	90.3 (1)
-N(4)	90.7 (5)	-N(1)	89.6 (2)
O(2)-Mo(1)-O(15)	161.6 (7)	O(1)-W-O(2)	144.5 (2)
-O(19)	80.4 (8)	-O(3)	85.9 (2)
-N(4)	78.4 (7)	-N(1)	95.4 (2)
O(15)-Mo(1)-O(19)	100.0 (9)	O(2)-W-O(3)	85.2 (2)
-N(4)	96.8 (8)	-N(1)	93.5 (2)
O(19)-Mo(1)-N(4)	156.2 (9)	O(3)-W-N(1)	178.6 (2)
Mo(1)-O(2)-C(3)	116 (2)	W-O(1)-C(21)	154.3 (5)
C(3)-O(11)-C(12)	117 (2)	W-O(2)-C(31)	127.1 (6)
Mo(1)-O(15)-C(16)	139 (2)	W-O(3)-C(1)	118.7 (5)
Mo(1)-O(9)-C(20)	119 (2)	C(1)-O(4)-C(61)	123.3 (7)
Mo(1)-N(4)-C(3)	118 (2)	W-N(1)-C(1)	119.4 (5)
-C(5)	117 (2)	W-N(1)-C(11)	119.5 (5)
C(3)-N(4)-C(5)	122 (3)		
O(2)-C(3)-O(11)	120 (3)		
-N(4)	123 (3)		
O(11)-C(3)-N(4)	117 (2)		

Table V. Selected Bond Distances (Å) for $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ and $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$

Mo(1)-Mo(1)′	2.221 (5)	W-W′	2.290 (1)
-O(2)	2.18 (2)	W-O(1)	1.895 (5)
-O(15)	1.91 (2)	W-O(2)	1.942 (5)
-O(9)	1.88 (2)	W-O(3)	2.139 (5)
-N(4)	2.13 (3)	W-N(1)	2.100 (6)
O(2)-C(3)	1.30 (3)	O(4)-C(1)	1.311 (9)
O(11)-C(3)	1.31 (3)	-C(61)	1.502 (10)
O(11)-C(12)	1.56 (3)	O(3)-C(1)	1.268 (9)
O(15)-C(16)	1.40 (3)	N(1)-C(1)	1.350 (9)
O(7)-C(20)	1.48 (4)	-C(11)	1.444 (10)
N(4)-C(3)	1.34 (4)	O(1)-C(21)	1.424 (9)
N(4)-C(5)	1.43 (3)	O(2)-C(31)	1.424 (10)

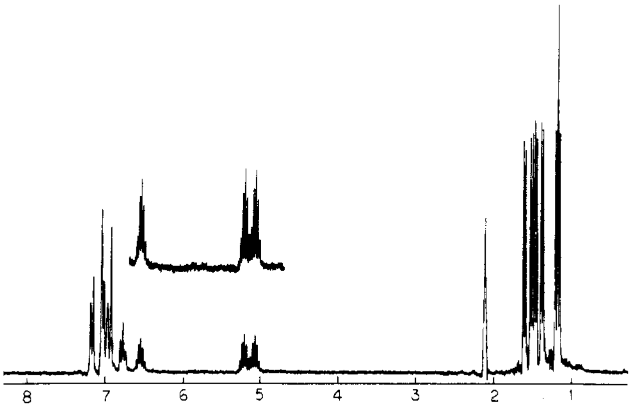


Figure 3. ^1H NMR spectrum of $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ recorded at 220 MHz and 16 °C in toluene-d_8 solution.

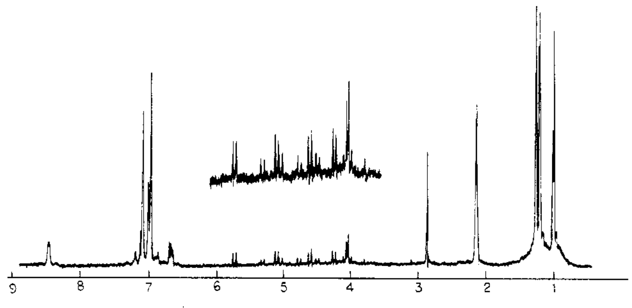
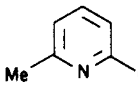
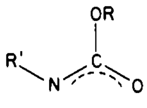


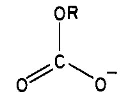
Figure 4. ^1H NMR spectrum of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4[NMeC(O)OCH_2\text{-}t\text{-}Bu]_2$ recorded at 220 MHz and 16 °C in toluene-d_8 showing the presence of two isomers.



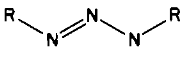
I



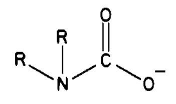
II



III



IV

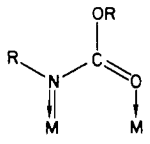


V

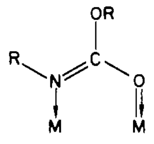
The insertion of an organic isocyanate into the metal alkoxide bond to form a ligand of type II is comparable to the insertion of CO_2 into bonds of $Mo_2(OR)_6$ form a ligand of type III,[7] i.e., a carbonate monoester. In both cases, the two bridging bidentate lignads are cis to each other in the $Mo_2X_4(YL)_2$ product. However, from the reaction of PhNCO with $W_2(O\text{-}t\text{-}Bu)_6$ a product having trans geometry was obtained. We shall return to this point later. It is also to be noted that while the insertion reaction of CO_2 is reversible, the insertion of isocyanates is irreversible.

In addition to the X-ray characterizations of two of the compounds, all of the reactions were monitored and products carefully studied by NMR spectroscopy. In all cases it was shown in this way that yields are essentially quantitative. The use of pyridine in the reactions with molybdenum is not essential, but it does help to provide crystalline products. All six of the compounds reported have NMR spectra consistent with their known or assumed structures. For $W_2(O\text{-}t\text{-}Bu)_4[N(C_6H_5)C(O)O\text{-}t\text{-}Bu]_2$, the ^1H spectrum shows, in addition to complex multiplets characteristic of the phenyl groups, two signals, in a 1:2 intensity ratio, which can be assigned to the two types of *t*-Bu hydrogen atoms expected for a centrosymmetric, trans structure. Four of the five molybdenum compounds have spectra of which that shown in Figure 3 for $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2(pyMe\text{-}4)_2$ is typical. This spectrum rules out the centrosymmetric, trans structure seen in the tungsten compound and also eliminates a trans structure in which the bridging ligands are both oriented the same way, since three pairs of diastereotopic methylene protons would be expected. It is, in its entirety, consistent with the type of cis structure found in the crystalline compound. In the case of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4[N(Me)C(O)OCH_2\text{-}t\text{-}Bu]_2$ at 16 °C there is evidently a second isomer present in a ratio of ca. 1:2 relative to the major one, as may be seen in Figure 4. A systematic examination of all possible isomers, including two with chelating RNC(O)OR ligands, leads to the plausible suggestion that the second isomer is also of cis stereochemistry but with both bridging ligands oriented in the same direction.

The infrared spectra were also examined. Those of the molybdenum products do not show any strong bands assignable to C=O stretches above 1600 cm^{-1}. All show a strong band between 1510 and 1562 cm^{-1}, which is probably assignable to C=O stretching that has been lowered because resonance form VIb is important as well as VIa. The C=O stretch has been found between 1680 and 1690 cm^{-1} in monodentate trialkyl germyl carbamates[5] and between 1635 and 1695 cm^{-1} in monodentate trialkyl stannyl carbamates.[11] The infrared spectrum of the tungsten compound has a C=O stretch at



VIa



VIb

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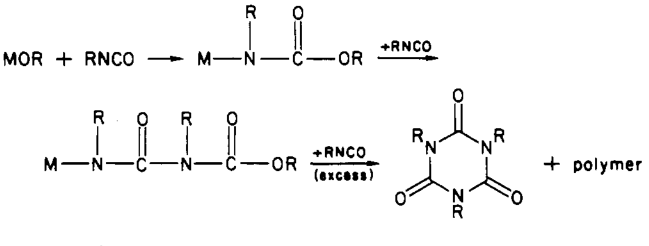
[11] Ishii, Y.; Itoh, K.; Nakamura, A.; Sadai, S. *J. Chem. Soc., Chem. Commun.* **1967**, 224.

Table VI. Analytical Data for $Mo_2(OR)_4[NR'C(O)OR](py)_2$ Compounds

	% C		% H		% N	
compd	calcd	found	calcd	found	calcd	found
$Mo_2(O\text{-}i\text{-}Pr)_4[MeNC(O)O\text{-}i\text{-}Pr]_2(py)_2$	45.41	45.45	7.32	7.12	7.11	7.16
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4[MeNC(O)OCH_2\text{-}t\text{-}Bu]_2(py)_2$	52.41	52.74	8.51	8.56	5.82	5.72
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4[(C_6H_5)NC(O)OCH_2\text{-}t\text{-}Bu](py)_2$	58.41	58.23	7.75	7.89	5.01	5.17
$Mo_2(O\text{-}i\text{-}Pr)_4[(C_6H_5)NC(O)O\text{-}i\text{-}Pr]_2(pyMe\text{-}4)_2$	54.41	53.52	6.81	6.94	5.82	6.04
$Mo_2(O\text{-}i\text{-}Pr)_4[(C_6H_5)NC(O)O\text{-}i\text{-}Pr]_2$	49.01	48.79	6.63	6.47	3.57	3.68

Scheme I



1685 cm^{-1}, which indicates the greater importance of resonance VIa in that case.

In our studies we have been interested in obtaining simple dinuclear insertion products and have succeeded. It should be noted, however, that further reactions leading to a cyclo trimer and also to polymers of some kind (Scheme I) have also been observed under some conditions, especially when excess isocyanate is used. Reactions of this type have previously been noted with $Ti(OR)_4$ and $R_3Sn(OR)$ compounds.[5]

Structural characterization (vide infra) of one representative compound of molybdenum and the tungsten compound containing *t*-BuO groups revealed the remarkable fact that the stereochemistry of the products is different for the two metallic elements. While this difference could be due to the difference in the metal atoms, it might also be a result of the different steric requirements of the different OR groups in the two cases. All of the molybdenum compounds contain either $OCHMe_2$ or OCH_2CMe_3 groups, which are sterically less demanding than the $OCMe_3$ group. This raises the question of whether it is the size of the $OCMe_3$ groups that favors the trans structure in the tungsten compound. A direct test of this steric argument could be made by preparing and structurally characterizing either the $OCMe_3$ compound of molybdenum or one of the $OCHMe_2$ or OCH_2CMe_3 compounds of tungsten. The second approach is less attractive since the simple $W_2(OR)_6$ compounds with these alkoxide groups are not available. It has been found that $Mo_2(OCMe_3)_6$ reacts readily with PhNCO, but the product has so far proved reluctant to crystallize. However, it may be noted that in the reaction of CO_2 with $Mo_2(OCMe_3)_6$, which we studied several year ago,[7] a cis product was obtained, $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$. Thus, the question of what determines stereochemistry in these reactions is one that requires further study.

Crystal Structures. The structure of the $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$ molecules in the crystal is shown in Figure 1 and that of $W_2(O\text{-}t\text{-}Bu)_4[N(C_6H_5)C(O)O\text{-}t\text{-}Bu]_2$ in Figure 2, and important bond distances and angles in both molecules are listed in Tables IV and V. The molybdenum molecule resides on a crystallographic axis of twofold symmetry, which is a perpendicular bisector of the Mo–Mo bond. The two bridging $C_6H_5NC(O\text{-}i\text{-}Pr)O$ ligands point in opposite directions, and the two metal atoms are equivalent. The idealized symmetry of the molecule can be no higher than C_2 since two O-*i*-Pr ligands are trans to nitrogen atoms and two are trans to oxygen atoms. The tungsten molecule resides on a crystallographic center of inversion, with the bridging ligands again oppositely directed and all four alkoxide groups equivalent. The idealized symmetry here is D_{2h}.

Despite these differences in stereochemistry, the two molecules are very much alike. Each involves two four-coordinated metal atoms in formal oxidation state +3 linked by a triple bond. The M–M bond lengths are each in the ranges that are typical for such bonds.[12] The difference in bond lengths, 0.069 (5) Å, is also typical for a closely related pair of compounds. The lengths of the M–OR bonds range from 1.88 (2) to 1.972 (5) Å, but the variations have no evident significance and all are within the expected range. The M–O–C angles, with the exception of the W–O(1)–C(21) angle, which is 154°, deviate little from 120°, i.e., are suggestive of sp^2 hybridization at oxygen. As with other alkoxides of molybdenum and tungsten, there is a correlation of shorter M–O distances with larger M–O–C angles as a result of increased oxygen p to metal d π bonding.

Concluding Remarks. The mechanism—or mechanisms—by which these interesting molecules are formed are still unknown. In the case of several of the molybdenum compounds it was observed that when only a 1:1 mole ratio of RNCO to $Mo_2(OR)_6$ is used, the $Mo_2(OR)_6$ can be recovered essentially quantitatively. This suggests that perhaps a 1:1 adduct s formed reversibly as the initial step. We also have preliminary evidence that this may be the case in the reaction of PhNCO with $W_2(O\text{-}t\text{-}Bu)_6$, where there is a rapidly formed purple intermediate that then slowly and irreversibly gives the product when an additional 1 mol of PhNCO is present. It appears that it may be possible to conduct more detailed studies of this purple intermediate and thus garner at least partial information on the mechanistic course of these reactions. We therefore do not wish to engage in any speculations about the mechanism at this time.

Acknowledgment. We thank the National Science Foundation for support of the work at Texas A&M University and Indiana University. A.L.R. was the 1982/1983 Indiana University Sohio Fellow.

Registry No. $Mo_2(O\text{-}i\text{-}Pr)_4[N(Me)C(O)O\text{-}i\text{-}Pr]_2(py)_2$, 93134-11-3; $Mo_2(OCH_2\text{-}t\text{-}Bu)_4[N(Me)C(O)OCH_2\text{-}t\text{-}Bu]_2(py)_2$, isomer I, 93110-40-8; $Mo_2(OCH_2\text{-}t\text{-}Bu)_4[N(Me)C(O)OCH_2\text{-}t\text{-}Bu]_2(py)$, isomer II, 93110-41-9; $Mo_2(OCH_2\text{-}t\text{-}Bu)_4[N(C_6H_5)C(O)OCH_2\text{-}t\text{-}Bu]_2(py)_2$, 93110-42-0; $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2(pyMe\text{-}4)_2$, 93110-43-1; $Mo_2(O\text{-}i\text{-}Pr)_4[N(C_6H_5)C(O)O\text{-}i\text{-}Pr]_2$, 93110-44-2; $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$, 93110-45-3; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; *i*-PrOH, 67-63-0; *t*-$BuCH_2OH$, 75-84-3; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 62521-24-8; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$, 81987-92-0; $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2$, 88609-64-7; $W_2(OCMe_3)_6$, 57125-20-9; *t*-BuOH, 75-65-0; Mo, 7439-98-7; W, 7440-33-7; methyl isocyanate, 624-83-9; phenyl isocyanate, 103-71-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete bond lengths and bond angles, and observed and calculated structure factors for both compounds, VERSORT drawings of the dimolybdenum compound, and a more detailed account of the crystallographic work (35 pages). Ordering information is given on any current masthead page.

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(12) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms", Wiley: New York, 1982; Chapter 5.