Metal Alkoxides: Models for Metal Oxides. 16.[1] Synthesis and Characterization of a New Class of Homoleptic 12-Electron Molybdenum and Tungsten Alkoxide Clusters of Formula $M_4(OR)_{12}$: Structural Characterization of $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}\text{-}(HOCH_2\text{-}c\text{-}Bu)$

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Abstract: Addition of primary alcohols, RCH_2OH (>6 equiv), to hydrocarbon solutions of $M_2(O\text{-}t\text{-}Bu)_6$ compounds has led to the isolation of the first homoleptic series of cluster alkoxides $M_4(OCH_2R)_{12}$ for *both* M = Mo and W where R = *i*-Pr, Cy (Cy = cyclohexyl), Cp (Cp = cyclopentyl), and c-Bu (c-Bu = cyclobutyl). The NMR data (^1H and ^{13}C) indicate a common structural unit for this class of compounds containing a molecular mirror plane. For each $M_4(OCH_2R)_{12}$ compound there are eight types of alkoxide ligands in the integral intensity 2:2:2:2:1:1:1:1. Those having integral intensity two possess diastereotopic methylene protons, indicating that they do not lie on the mirror plane, whereas the other four alkoxides (1:1:1:1) are contained within the mirror plane. Though these compounds yield crystals from 1,2-dimethoxyethane, they failed to diffract beyond 10° indicating a molecular disorder within hexagonal packing of M_4 units. However, the cyclobutylmethoxide derivatives crystallize with an additional molecule of alcohol, $M_4(OCH_2\text{-}c\text{-}Bu)_{12}(HOCH_2\text{-}c\text{-}Bu)$, and the molecular structure of the molybdenum compound was determined by an X-ray study. Crystal data for $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}(HOCH_2\text{-}c\text{-}Bu)$ at −156 °C: $a = b = 19.952$ (7) Å, $c = 34.755$ (16) Å, $Z = 8$, $d_{calcd} = 1.43$ g cm⁻³, and space group $P4_1$. The unit cell contains two crystallographically independent molecules that are essentially equivalent with respect to M–M and M–O distances and angles. In each there is a central Mo_4 butterfly with a dihedral angle between the Mo_3 triangles of 132.5°. One wingtip metal atom is octahedrally coordinated by oxygen atoms of which three are terminal, two edge bridging, and one triply bridging. The backbone Mo–Mo atoms are evidently strongly bonded, Mo–Mo 2.47 Å, and are coordinated to two edge bridging alkoxides and one terminal alkoxide. The other wingtip Mo atom is similarly coordinated, and the unique molecule of alcohol is bound to one of the backbone Mo atoms, Mo–O ($HOCH_2\text{-}c\text{-}Bu$) = 2.34 (1) Å. In solution (benzene-d_6 and toluene-d_8) the NMR spectra are similar to those obtained for the other members of this class of compounds, $M_4(OCH_2R)_{12}$, with additional signals due to free $HOCH_2R$. This implies that the cyclobutylmethanol is weakly bonded and readily dissociates in solution. The present findings are compared with other 12-electron alkoxide supported clusters of molybdenum and tungsten.

Molybdenum and tungsten alkoxide clusters provide templates for organometallic chemistry.[2] The essential features that should be present in these alkoxide clusters include both coordinative unsaturation and redox flexibility at the metal centers.[3]

We have recently demonstrated that $W_2(O\text{-}i\text{-}Pr)_6$ (1) exists in reversible equilibrium with its 12-electron cluster, $W_4(O\text{-}i\text{-}Pr)_{12}$ (11), in solution at room temperature, eq 1,[4] whereas $Mo_2(O\text{-}i\text{-}Pr)_6$ is indefinitely stable with respect to cluster formation.[5] Even by
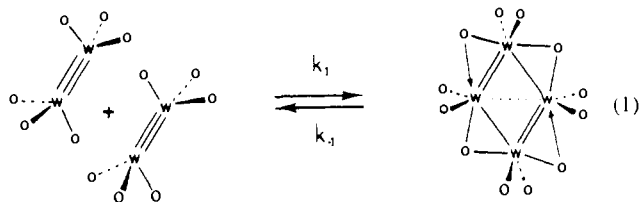
reducing the steric demands at the molybdenum center we were unable to induce the formation of new metal–metal bonds in $[Mo_2(O\text{-}i\text{-}Pr)_5(OMe)]_2$ (111), which instead retains isolated, unbridged Mo–Mo triple bonds.[5] We report here the isolation and characterization of members of a new class of 12-electron tetranuclear alkoxide clusters, IV–XI, together with the single-crystal X-ray diffraction structure of one derivative, $[Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}(HOCH_2\text{-}c\text{-}Bu)]$ (XI) (where c-Bu = cyclobutyl). This represents the first group of structurally related homoleptic alkoxide clusters for molybdenum and tungsten in oxidation state (+3). A preliminary aspect of this work has been published.[6] The new compounds are defined as follows: (IV), $W_4(OCH_2Cy)_{12}$;

(V), $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$; (VI), $W_4(OCH_2Cp)_{12}$; (VII), W_4-$(OCH_2\text{-}c\text{-}Bu)_{12}\cdot HOCH_2\text{-}c\text{-}Bu$; (VIII), $Mo_4(OCH_2Cy)_{12}$; (IX), $Mo_4(OCH_2\text{-}i\text{-}Pr)_{12}$; (X), $Mo_4(OCH_2Cp)_{12}$; (XI), $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}\cdot HOCH_2\text{-}c\text{-}Bu$; where Cy = cyclohexyl; *i*-Pr = isopropyl; Cp = cyclopentyl, and c-Bu = cyclobutyl.

Experimental Section

General Procedures. All preparations and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques together with a Vacuum Atmosphere's Company Dri-Lab System. Aromatic and aliphatic hydrocarbon solvents, diethyl ether, and 1,2-dimethoxyethane were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves prior to use. Alcohols and BH_3·Me_2S were purchased from Aldrich Chemical Company, and NMe_3 was obtained from Matheson. Isobutyl alcohol was dried and distilled from magnesium and stored over 4 Å molecular sieves prior to use; other alcohols were dried over sieves but not distilled prior to use. $^{13}CO_2$ (99 mol %) was purchased from MSD Isotopes. $M_2(O\text{-}t\text{-}Bu)_6$ and M_2-

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(1) For Part 15 see: Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.*, previous paper in this issue.

(2) Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 3146 and references therein.

(3) Reduced metal alkoxides of Mo and W may provide a complementary reaction chemistry with the heteropolyoxoanions. The latter may provide a good class of homogeneous oxidation catalysts: Pope, M. T. In *Heteropoly and Isopoly Oxometallates*; Springer: New York, 1983. Day, V. W.; Klemperer, W. G.; Schwartz, C.; Wang, R. C. *NATO Workshop Report*, in press. Faraji, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(4) Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1014. Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 7750.

(5) Chisholm, M. H.; Hammond, C. E.; Hampden-Smith, M. J.; Huffman, J. C.; Van Der Sluys, W. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 905.

(6) Chisholm, M. H.; Folting, K.; Hammond, C. E.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3314.

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$(NMe_2)_6$ (M = Mo and W) were prepared by the literature routes.[7]

Spectroscopic Instrumentation and Interpretation. ^1H and ^{13}C NMR were obtained on Varian XL300 and Bruker AM500 NMR spectrometers. ^1H and ^{13}C assignments were made with the aid of a variety of two-dimensional NMR experiments on the Bruker instrument. Typical acquisition parameters were as follows, COSY [512 W (4 scans) × 128]; XHCORR [1 K (84 scans) × 256]; JRES, [1 K (16 scans) × 128], using solutions containing about 70 mg of sample. The ^1H and ^{13}C NMR data are reported in detail because of their importance in interpretation of molecular structure of these molecules in solution. In future papers we will describe reactions involving this class of $M_4(OR)_{12}$ cluster and small molecules such as CO for which the spectroscopic data are of primary importance in determining the reaction mechanism and stereochemistry of products. The present data for the parent molecules will serve as a data base. The methylene and methine ^1H and ^{13}C NMR resonances of these species are diagnostic for this type of structure. For the case of the isobutoxide clusters, $M_4(OCH_2$-i-$Pr)_{12}$ (M = Mo, W), the connectivity of the ^1H and ^{13}C NMR resonances within all the isobutoxide ligands can be assigned. For the other derivatives, only the methylene and methine protons will be identified for simplicity. The NMR data are labeled as follows: (i) the eight types of alkoxide ligands will be labeled with superscripts 1–8; (ii) subscripts a–c will designate methylene (a), methine (b), or methyl (c) (in the case of isobutoxide only) ^1H or ^{13}C resonances; (iii) a prime over the subscript indicates one of a pair of diastereotopically related methylene or methyl resonances (e.g., methylene proton $H^4_{a'}$ is bonded to the same carbon atom as H^4_a of the alkoxide ligand arbitrarily number 4). Using this labeling scheme the NMR data are presented in this text for $W_4(OCH_2$-i-$Pr)_{12}$ (V). The data for other compounds are listed in the Supplementary Material.

Ultrahigh resolution ^{13}C NMR spectra were obtained in collaboration with Allerhand et al. on a Nicolet NT200 NMR instrument using techniques that have been previously described.[8] Infrared spectra were recorded on a Perkin Elmer 283 infrared spectrometer as Nujol mulls.

^{95}Mo NMR spectra were recorded on a Nicolet NT360 NMR spectrometer at 23.59 MHz, in 10-mm NMR tubes, containing approximately 1 g of material dissolved in 3 mL of toluene-d_8. Chemical shifts are reported relative to an external standard of 2 M $Na_2[MoO_4]$ solution in D_2O of pH 11. Typically 10^5 transients were acquired by adding together the FID's of individual experiments each consisting of 3000 transients to avoid memory overflow.

Molecular Weights. The molecular weight of $Mo_4(OCH_2$-i-$Pr)_{12}$ was measured by the freezing point depression method in benzene at two different concentrations. The values obtained were 1140 g at a concentration of 1.46×10^{-3} M and 1360 g at a concentration of 3.41×10^{-2} M. These values were obtained from three measurements at each concentration. The calculated molecular weight of $Mo_4(OCH_2$-i-$Pr)_{12}$ is 1263 g. The instrument was calibrated using biphenyl solutions of the two different concentrations.

Syntheses. $M_4(OCH_2R)_{12}$. All the compounds of molecular formula $M_4(OCH_2R)_{12}$ where M = Mo, W; R = cyclohexyl, isopropyl, or cyclopentyl were prepared in a virtually identical manner. A representative example of this procedure is given below, followed by the spectroscopic data for all the new compounds.

$W_4(OCH_2$-i-$Pr)_{12}$ (V). $W_2(O$-t-$Bu)_6$ (0.750 g, 0.93 mmol) was placed in a 30-mL Schlenk flask and dissolved in 3 mL of hexane at room temperature. An excess of isobutyl alcohol (1 mL) was added dropwise to the solution which rapidly turned deep purple. The mixture was stirred for 2 h, and then all the volatile components were removed in vacuo to give on some occasions a black solid or an oily black residue. ^1H NMR spectra of the crude material showed it to be essentially pure W_4-$(OCH_2$-i-$Pr)_{12}$. This compound is extremely soluble in most hydrocarbon solvents and attempts to crystallize it from any of pentane, hexane, toluene, diethyl ether, or mixtures of these solvents were unfruitful. However, by redissolving the residue in a small amount of 1,2-dimethoxyethane (~1.5 mL) a green solution was obtained and by cooling to ~20 °C over 12 h crystals of V were obtained. The solution was filtered at 0 °C to give 0.536 g of dark green crystalline material. The filtrate was concentrated to half its volume, and more crystalline material was isolated as above to yield a second crop, 0.112 g. The combined yield of V was 0.648 g, 86.4% yield based on tungsten.

$W_4(OCH_2$-i-$Pr)_{12}$ (V). ^1H NMR (23 °C, 500.13 MHz, C_6D_6) methylenes, CH_2, H^1_a, 5.08 ppm, d, 1 H, J_{a-b} = 6.1 Hz; H^2_a, 4.86 ppm, d × d, 1 H, $J_{a-a'}$ = 10.0 Hz, J_{a-b} = 7.2 Hz; $H^2_{a'}$, 4.63 ppm, d × d, 1 H, J_{a-b} = 5.8 Hz; H^3_a, 4.53 ppm, d, 1 H, J_{a-b} = 6.1 Hz; H^4_a, 4.50 ppm, d × d, 1

H, $J_{a-a'}$ = 6.9 Hz, J_{a-b} = 10.3 Hz; $H^4_{a'}$, 4.23 ppm, d × d, 1 H, J_{a-b} = 6.3 Hz; H^5_a, 4.48 ppm, d × d, 1 H, $J_{a-a'}$ = 9.7 Hz, J_{a-b} = 6.6 Hz; $H^5_{a'}$, 4.28 Hz; d × d, 1 H, J_{a-b} = 5.9 Hz; H^6_a = 4.15 ppm, d × d, 1 H, $J_{a-a'}$ = 10.0 Hz, J_{a-b} = 5.4 Hz; $H^6_{a'}$, 3.18 ppm, d × d, 1 H, J_{a-b} = 10.0 Hz; H^7_a, 3.88 ppm. d, 1 H, J_{a-b} = 6.9 Hz; H^8_a, 3.65 ppm, d, 1 H, J_{a-b} = 8.3 Hz; methines, CH, H^1_b, 3.29 ppm, m, 1 H; H^2_b, 2.43 ppm, m, 2 H; H^3_b, 2.07 ppm, m, 1 H; H^4_b, 1.99 ppm, m, 2 H; H^5_b, 1.97 ppm, m, 2 H; H^6_b, 2.25 ppm, m, 2 H; H^7_b, 1.76 ppm, m, 1 H; H^8_b, 1.68 ppm, m, 1 H; methyls, CH_3, H^1_c, 1.16 ppm, d, 6 H, J_{c-b} = 6.7 Hz; H^2_c, 1.12 ppm, d, 6 H, J_{c-b} = 6.2 Hz; $H^2_{c'}$, 1.12 ppm, d, 6 H, J_{c-b} = 6.0 Hz; H^3_c, 1.24 ppm, d, 6 H, J_{c-b} = 6.7 Hz; H^4_c, 1.11 ppm, d, 6 H, J_{c-b} = 5.7 Hz; $H^4_{c'}$, 1.09 ppm, d, 6 H, J_{c-b} = 6.2 Hz; H^5_c, 1.16 ppm, d, 6 H, J_{c-b} = 6.3 Hz; $H^5_{c'}$, 1.24 ppm, d, 6 H, J_{c-b} = 6.7 Hz; H^6_c, 1.01 ppm, d, 6 H, J_{c-b} = 6.5 Hz; $H^6_{c'}$, 0.96 ppm, d, 6 H, J_{c-b} = 6.8 Hz; H^7_c, 0.86 ppm, d, 6 H, J_{c-b} = 6.5 Hz; H^8_c, 0.86 ppm, d, 6 H, J_{a-b} = 6.4 Hz; ^{13}C NMR (23 °C, 125.76 MHz, C_6D_6) methylenes, CH_2, C^1_a, 80.0 ppm, 1C; C^2_a, 79.9 ppm, 2C; C^3_a, 72.4 ppm, 1C; C^4_a, 78.2 ppm, 2C; C^5_a, 74.7 ppm, 2C; C^6_a, 75.3 ppm, 2C; C^7_a, 82.5 ppm, 1C; C^8_a, 77.2 ppm, 1C; methines, CH: C^1_b, 28.6 ppm, 1C; C^2_b, 32.9 ppm, 2C; C^3_b, 34.1 ppm, 1C; C^4_b, 33.2 ppm, 2C; C^5_b, 32.7 ppm, 2C; C^6_b, 31.0 ppm, 2C; C^7_b, 32.2 ppm, 1C; C^8_b, 32.9 ppm, 1C; methyls, CH_3, C^1_c, 20.4 ppm, 1C; C^2_c, 19.8 ppm, 1C; $C^2_{c'}$, 19.9 ppm, 1C; C^3_c, 19.7 ppm, 1C; C^4_c, 21.9 ppm, 1C; $C^4_{c'}$, 20.4 ppm, 1C; C^5_c, 19.5 ppm, 1C; $C^5_{c'}$, 20.7 ppm, 1C; C^6_c, 19.5 ppm, 1C; $C^6_{c'}$, 19.2 ppm; C^7_c, 19.2 ppm, 1C; C^8_c, 19.3 ppm, 1C; IR ν (cm^{-1}) 1366 s, 1354 sh, 1341 sh, 1291 w, 1261 w, 1069 s, 1028 s, 977 m, 960 m, 944 m, 822 w, 661 m, 635 m, 467 w, 399 w. Elemental Anal. Calcd for $W_4O_{12}C_{48}H_{108}$: C, 35.73; H, 6.75. Found: C, 35.49; H, 6.57.

$W_4(OCH_2Cp)_{12}$ (VI). IR ν (cm^{-1}) 1366 s, 1337 w sh, 1260 w, 1169 w, 1068 vs, 1030 s, 1006 s, 963 w, 9402, 898 w, 749 w, 643 w, 585 w. Elemental Anal. Calcd for $W_4O_{12}C_{72}H_{131}$: C, 44.93; H, 6.86. Found: C, 44.87; H, 6.89.

$Mo_4(OCH_2$-i-$Pr)_{12}$ (IX). ^{95}Mo NMR (23 °C, 23.59 MHz, toluene-d_8) 2628 ppm, $\Delta\nu_{1/2}$ = 488 Hz; IR ν (cm^{-1}) 1364 s, 1352 m, 1104 m sh, 1064 s, 1042 s, 982 m, 957 w, 943 w, 820 w, 660 m, 664 m, 607 m, 479 w, 404 w. Elemental Anal. Calcd for $Mo_4O_{12}C_{48}H_{108}$: C, 45.71; H, 8.63; N, 0.00. Found: C, 45.48; H, 8.46; N, 0.05.

$Mo_4(OCH_2Cy)_{12}$ (VIII). IR ν (cm^{-1}) 1305 w, 1285 w, 1270 w, 1260 w, 1216 w, 1180 w, 1147 w, 1100 s, 1099 s, 1079 s, 1057 s, 1045 vs, 1024 s, 950 m, 913 w, 890 m, 840 m, 788 w, 777 w, 690 w, 655 m sh, 635 s br d, 595 m sh, 550 m, 475 w, 429 w, 295 w. Elemental Anal. Calcd for $Mo_4O_{12}C_{84}H_{156}$: C, 57.92; H, 9.02. Found: C, 57.62; H, 9.02.

$Mo_4(OCH_2Cp)_{12}$ (X). IR ν (cm^{-1}) 1364 s, 1335 m, 1310 w, 1170 w, 1055 s, 1000 sh, 970 m, 939 m, 897 m, 800 w, 650 m, 590 m, 470 w, 464 w. Elemental Anal. Calcd for $Mo_4O_{12}C_{72}H_{131}$: C, 54.96; H, 8.46. Found: C, 54.70; H, 8.32.

$W_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-$Bu)$ (VII), $W_2(O$-i-$Bu)_6$ (1.000 g, 1.24 mmol) was placed in a Schlenk flask and dissolved in 5 mL of hexane. Cyclobutylmethanol was added (1.5 mL), dropwise, while the solution was vigorously stirred at room temperature. The solution immediately changed color from deep red to deep purple. After stirring for 2 h, the volatile components were removed in vacuo leaving an oily purple residue. The residue was dissolved in 2 mL of 1,2-dimethoxyethane and cooled to −20 °C for 16 h. During this time a dark purple solid precipitated and was isolated by filtering the solution at 0 °C. The filtrate was concentrated to about a quarter of its original volume, and then a second crop was isolated by cooling to −20 °C and working up as above. The combined mass of material isolated was 1.030 g (5.6 mmol), a yield of 90.2% based on tungsten. The ^1H and ^{13}C NMR and IR spectroscopic data are reported below. On dissolution of a sample of the purple solid obtained in this way, 1 equiv of uncoordinated *free* cyclobutylmethanol per W_4-$(OCH_2$-c-$butyl)_{12}$ was observed by ^1H NMR spectroscopy. The resonances attributed to free $HOCH_2$-c-Bu were identified by their ^1H and ^{13}C chemical shifts. Furthermore, the addition of 20 μL of an authentic sample of the alcohol to a solution of 32 mg of VII dissolved in 0.5 mL of benzene-d_6 merely resulted in an increase in intensity of the signals attributed to dissociated $HOCH_2$-c-Bu.

$W_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-$Bu)$ (VII). ^1H NMR (23 °C, 500.13 MHz, C_6D_6) methylenes, CH_2, H^1_a, 5.13 ppm, d × d, 1 H, $J_{a-a'}$ = 10.4 Hz, J_{a-b} = 7.3 Hz; $C^1_{a'}$, 5.00 ppm, d × d, 1 H, J_{a-b} = 7.0 Hz; H^2_a, 5.05 ppm, d, 1 H, J_{a-b} = 6.1 Hz; H^3_a, 4.70 ppm, d, 1 H, J_{a-b} = 6.4 Hz; H^4_a, 4.57 ppm, d × d, 1 H, J_{a-b} = 6.8 Hz; $H^4_{a'}$, 4.35 ppm, d × d, 1 H, J_{a-b} = 6.5 Hz; H^5_a, 4.48 ppm, d × d, 1 H, $J_{a-a'}$ = 11.0 Hz, J_{a-b} = 6.8 Hz; $H^5_{a'}$, 2.34 ppm, d × d, 1 H, J_{a-b} = 6.0 Hz; H^6_a, 4.34 ppm d × d, 1 H, $J_{a-a'}$ = 10.7 Hz, J_{a-b} = 6.8 Hz; H^7_a, 4.09 ppm, d, 1 H, J_{a-b} = 6.8 Hz; H^8_a, 3.90 ppm, d, 1 H, J_{a-b} = 6.7 Hz; H^9_a, 3.69 ppm, d, 1 H, J_{a-b} = 6.6 Hz; methines, CH, H^1_b, 3.17 ppm, m, 2 H; H^2_b, 3.78 ppm, m, 1 H; H^3_b, 2.91 ppm, m, 1 H; H^4_b, 2.71 ppm, m, 2 H; H^5_b, 2.69 ppm, m, 2 H; H^6_b, 2.94 ppm, m, 2 H; H^7_b, 2.50 ppm, m, 1 H; H^8_b, 2.52 ppm, m, 1 H; H^9_b, 2.60, m, 1 H. Other resonances overlapping between 2.30 and 1.60 ppm. ^{13}C NMR (23 °C, 125.76 MHz, C_6D_6) methylenes, CH_2, C^1_a, 82.8 ppm, 2C; C^2_a 81.5 ppm, 1C; C^3_a, 75.0 ppm, 1C; C^4_a, 78.3 ppm, 2C; C^5_a, 76.9 ppm, 2C;

(7) Chisholm, M. H.; Haitko, D. A.; Murillo, C. A. *Inorganic Syntheses*; Fackler, J. R., Ed.; John Wiley and Sons: New York, 1982; Vol. XXI, pp 51–57, and references therein.

(8) Allerhand, A.; Maple, S. R. *Anal. Chem.* **1987**, *59*, 441A. Allerhand, A.; Addleman, R. E.; Osman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5809.

C_a^6, 77.2 ppm, 2C; C_a^7, 81.2 ppm, 1C; C_a^8, 78.7 ppm, 1C; C_a^9, 67.0, 1C; methines, CH, C_b^1, 39.2 ppm, 2C; C_b^2, 36.1 ppm, 1C; C_b^3, 41.6 ppm. 1C; C_b^4, 39.5 ppm 2C; C_b^5, 40.4 ppm, 2C; C_b^6, 38.3 ppm, 2C; C_b^7, 38.3 ppm, 1C; C_b^8, 39.4 ppm, 1C. Remaining resonances observed as sharp singlets between 28.2 and 25.0 ppm and from 19.4 to 18.7 ppm. IR ν (cm^{-1}) 1362 s, 1319 m, 1333 m, 1150 w, 1100 s, 1060 s, 1010 s, 972 m, 940 m, 912 w, 782 w, 650 m, 605 m, 589 m, 440 w. Elemental anal. Calcd for $W_4O_{13}C_{65}H_{118}$: C, 42.34; H, 6.45. Found: C, 42.15; H, 6.32.

Mo$_4$(OCH$_2$-c-Bu)$_{12}$(HOCH$_2$-c-Bu). Mo$_2$(O-t-Bu)$_6$ (0.805 g) was dissolved in 20 mL of pentane at 0 °C in a solvent-seal flask. Cyclobutylmethanol (1 mL) was added dropwise to the vigorously stirred solution which immediately turned dark green. The solution was stirred for 2.5 h after which the volatile components were removed in vacuo. A ^{1}H NMR spectrum of the crude material showed the reaction to be incomplete. The solid was redissolved in 20 mL of pentane, and another portion of cyclobutylmethanol (1 mL) was added. The reaction was stirred for 12 h, and then the volatile components were again removed in vacuo. The residue was redissolved in the minimum amount of 1,2-dimethoxyethane and cooled to −10 °C. After 1 month 0.150 g of large crystals were isolated by filtration at 0 °C. ^{1}H and ^{13}C NMR spectroscopy of this sample showed it to contain the cluster Mo$_4$(OCH$_2$-c-Bu)$_{12}$ together with 1 equiv of uncoordinated cyclobutylmethanol in benzene-d_6 solution. A sample of these crystals was submitted for a single-crystal X-ray diffraction study. The filtrate was concentrated, and a second crop of crystals was obtained and isolated by the procedure outlined above. The ^{1}H and ^{13}C NMR and IR spectroscopic data for this compound are reported below.

Mo$_4$(OCH$_2$-c-Bu)$_{12}$(HOCH$_2$-c-Bu) (XI). ^{1}H NMR (23 °C, 500.13 MHz, C$_6$D$_6$) methylenes, CH_2, H_a^1, 5.26 ppm, d, 1 H, J_{a-b} = 6.1 Hz; H_a^2, 5.19 ppm, d × d, 1 H, $J_{a-a'}$ = 10.6 Hz, J_{a-b} = 7.2 Hz; H_a^3, 5.09 ppm, d × d, 1 H, J_{a-b} = 7.1 Hz; H_a^3, 4.71 ppm, d, 1 H, J_{a-b} = 6.5 Hz; H_a^4, 4.56 ppm, d × d, 1 H, $J_{a-a'}$ = 10.6 Hz, J_{a-b} = 6.5 Hz; H_a^4, 4.33 ppm, d × d, 1 H, J_{a-b} = 6.0 Hz; H_a^5, 4.50 ppm, d × d, 1 H, $J_{a-a'}$ = 11.4 Hz, J_{a-b} = 6.4 Hz; H_a^5, 4.38 ppm, d × d, 1 H, J_{a-b} = 6.5 Hz; H_a^6, 4.46 ppm, d × d, 1 H, $J_{a-a'}$ = 10.7 Hz, J_{a-b} = 7.1 Hz; $H_{a'}^6$, 3.93 ppm, d × d, 1 H, J_{a-b} = 7.1 Hz; H_a^7, 4.39 ppm, d, 1 H, J_{a-b} = 6.8 Hz; H_a^8, 4.06 ppm, d, 1 H, J_{a-b} = 6.8 Hz; H_a^9, 3.52 ppm, d, 1 H, J_{a-b} = 6.8 Hz; methines, CH, H_b^1, 3.77 ppm, m, 1 H; H_b^2, 3.16 ppm, m, 2 H; H_b^3, 2.94 ppm, m, 1 H; H_b^4, 2.69 ppm, m, 2 H; 2.69 ppm, m, 2 H; H_b^6, 2.88 ppm, m, 2 H; H_b^7, 2.49 ppm, m, 1 H; H_b^8, 2.52 ppm. m, 1 H; H_a^9, 2.48 ppm, m, 1 H. Remaining resonances, broad overlapping multiplets between 2.32 and 1.97 ppm. ^{13}C NMR (23 °C, 125.76 MHz, C$_6$D$_6$) methylenes, CH_2, C_a^1, 83.0 ppm, 1C; C_a^2, 82.0 ppm, 2C; C_a^3, 76.3 ppm, 1C; C_a^4, 77.3 ppm, 2C; C_a^5, 80.2 ppm, 2C; C_a^6, 77.6 ppm, 2C; C_a^7, 81.3 ppm, 1C; C_a^8, 79.3 ppm, 1C; C_a^9, 66.8 ppm, 1C; methines, CH, C_b^1, 36.9 ppm, 1C; C_b^2, 39.9 ppm, 2C; C_b^3, 42.0 ppm, 1C; C_b^4, 40.7 ppm, 2C; C_b^5, 39.6 ppm, 2C; C_b^6, 38.8 ppm, 2C; C_b^7, 39.8 ppm, 1C; C_b^8, 39.2 ppm, 1C; C_b^9, 38.2 ppm, 1C. Remaining cyclobutyl resonances sharp singlets from 28.0–25.0 and 18.5–19.5 ppm. IR ν (cm^{-1}) 1362 s, 1313 w, 1235 w, 1095 sh, 1065 s, 1035 s, 995 sh, 980 sh, 955 m, 940 m, 915 w, 781 w, 645 m, 595 m, 580 m, 467 w. Elemental Anal. Calcd for Mo$_4$O$_{13}$C$_{65}$H$_{118}$: C, 52.34; H, 7.97. Found: C, 52.64; H, 7.61; N, <0.03.

Preparation of W(O*CH$_2$-i-Pr)$_{12}$ (*C = 99 mol % ^{13}C). (i) Preparation of HO*CH$_2$-i-Pr. The following synthesis was first carried out using unlabeled starting materials as a control. The procedure reported here is for the labeled material. *i*-PrMgBr (25 mL of 2 M) in THF (~80 mL) was placed in a 300-mL Schlenk flask under nitrogen, and then the solution was cooled to liquid nitrogen temperature with the tap closed. The flask was evacuated and connected to a calibrated vacuum manifold and 1 L of ^{13}CO$_2$ (99 mol % ^{13}C) was condensed into the 300-mL Schlenk flask. With the top of the calibrated manifold still open, the mixture was warmed to −78 °C (dry-ice–acetone bath) over about a 15-min period and then to 0 ° (ice bath) over 0.5 h. During this time a reaction took place, and a white precipitate was observed. The mixture was warmed to room temperature and stirred for 2 h to ensure that all the ^{13}CO$_2$ had been consumed. The volatile components of the flask were removed by distillation to a trap so that unreacted ^{13}CO$_2$ was recovered, and the flask was removed from the vacuum manifold. The glassy residue was redissolved in diethyl ether (in air, ~50 mL) and hydrolyzed with an excess of distilled water. The water layer was acidified with dilute nitric acid, and the organic products were extracted by separation of the ether layer and extraction of the aqueous layer with three 30-mL portions of diethyl ether. The organic extracts were combined and dried over magnesium sulfate. The ether was removed by distillation at atmospheric pressure to leave a colorless liquid (3.5 g). ^{1}H and ^{13}C NMR spectra showed this crude product to be virtually pure [^{13}C$_1$]isobutyric acid. The crude acid was redissolved in diethyl ether and added slowly to an excess (3 mL) of BH$_3$·Me$_2$S, dissolved in 30 mL of diethyl ether (under N$_2$). A vigorous reaction ensued with some gas evolution, and some white precipitate was formed. When all the acid had been added (~1 h), the solution was

stirred for 18 h to ensure complete reaction. The products were hydrolyzed by adding a small excess of distilled water and finally a small amount (0.5 mL) of dilute nitric acid. The organic layer was separated, and the aqueous layer was extracted with three 15-mL portions of ether; the extracts were combined and dried. The diethyl ether was removed by distillation at atmospheric pressure, and ^{1}H and ^{13}C NMR spectra of the crude product (3.2 g) showed that it contained mainly [^{13}C$_1$]isobutyl alcohol together with some diethyl ether and THF impurities. The crude product was distilled at atmospheric pressure, and the fraction that boiled between 98–105 °C (lit. value = 108 °C, unlabeled) was collected. The distilled product was spectroscopically pure (^{1}H and ^{13}C NMR), and 1.5 g of [^{13}C$_1$]isobutyl alcohol was isolated, a yield of 49.3% based on ^{13}CO$_2$. This product was stored over 4 Å molecular sieves. The undistilled residue gave some evidence of decomposition (by ^{1}H and ^{13}C NMR) but still mainly contained [^{13}C$_1$]isobutyl alcohol.

HO*CH$_2$CHMe$_2$. ^{1}H NMR methylene, *CH_2, 3.25 ppm, d × d, 2 H, $^1J_{H-C}$ = 143 Hz, $^1J_{H-H}$ = 6 Hz; methine, CH, 1.62 ppm, m, 1 H; methyl, $CHMe_2$, 0.81 ppm, t, 6 H, $^1J_{H-H}$ = 7 Hz; OH, 1.75 ppm, br, ~1 H; ^{13}C NMR methylene, *CH_2, 69.4 ppm, s, J_{C-H} = 140 Hz; methyl, CH, 31.0 ppm, d, J_{C-C} = 35 Hz; methyl, $CHMe_2$, 19.0 ppm.

(ii) Preparation of W$_4$(O*CH$_2$-i-Pr)$_{12}$. W$_2$(NMe$_2$)$_6$ (1.000 g, 1.58 mmol) was suspended in 5 mL of toluene, and a solution of 1.5 g (an excess) of the [^{13}C$_1$]isobutyl alcohol in 8 mL of toluene was added over about 10 min. The solution turned deep red-purple as the amide dissolved and the solution was stirred for 2 h at room temperature with the flask open to a nitrogen vent. The volatile components were vacuum distilled into a trap (to recover unreacted alcohol) and a red-purple oil obtained. ^{13}C NMR spectra of a sample of the crude oil were consistent with formation of W$_2$(O*CH$_2$-i-Pr)$_6$(NMe$_2$H)$_2$. The oil was redissolved in 8 mL of toluene and stirred for 10 h at room temperature. During this time the solution turned black, and when the volatile components were removed, an oily black solid was obtained. The ^{1}H and ^{13}C NMR spectra of a sample of this crude material showed it to be W$_4$(O*CH$_2$-i-Pr)$_{12}$. The crude product was taken up in 2 mL of 1,2-dimethoxyethane and stored at −20 °C for 16 h during which time black crystals were formed. The solution was filtered at 0 °C, the volume of the filtrate was reduced by half, and the flask was replaced at −20 °C to yield a second crop of black crystals. W$_4$(O*CH$_2$-i-Pr)$_{12}$ (0.827 g) was isolated, a yield of 64.6% based on tungsten. The volatile components were removed from the filtrate, and the residue (which appears spectroscopically pure) was saved. The crystallized material was characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and by elemental analysis. This material was used for the ultrahigh resolution ^{13}C NMR experiment in an attempt to observe two bond couplings between the 99 mol % ^{13}C-labeled isobutoxide resonances and ^{183}W.

W$_2$(O*CH$_2$-i-Pr)$_6$(NMe$_2$H)$_2$. ^{13}C NMR methylenes, CH_2, 79.6 ppm, 2C; 74.4 ppm, 1C.

W$_4$(O*CH$_2$-i-Pr)$_{12}$ (Where *C = 99 mol % ^{13}C Labeled). ^{13}C NMR (23 °C, 125 MHz, C$_6$D$_6$) methylene carbon chemical shifts (C_a^n) same as above. Methines, CH, C_b^1, 28.6 ppm, 1C, J_{b-a} = 37 Hz; C_b^2, 32.9 ppm, 2C, J_{b-a} = 37 Hz; C_b^3, 34.3 ppm, 1C, J_{b-a} = 36 Hz; C_b^4, 33.2 ppm, 2C, J_{b-a} = 37 Hz; C_b^5, 32.8 ppm, 2C, J_{b-a} = 38 Hz; C_b^6, 31.1 ppm, 2C, J_{b-a} = 38 Hz; C_b^7, 32.2, 1C, J_{b-a} = 37 Hz; C_b^8, 32.9 ppm. 1C, J_{b-a} = 37 Hz.

Ultrahigh Resolution ^{13}C NMR Data (40 MHz, Toluene/Toluene-d_8, 70/30, 26 °C). C_a^2, J_{C-w} = 4.93 Hz; C_a^1, J_{C-w} ~ 4.0 Hz; C_a^2, J_{C-w} ~ 4.0 Hz; C_a^8, J_{C-w} = 6.94 Hz; C_a^4, J_{C-w} = 3.84 Hz; ^6_a, J_{C-w} = <3.4 Hz; C_a^5, $C-w$ = 6.43 Hz; C_a^3, J_{C-w} = 1.93 Hz; IR ν (cm^{-1}) 1360 m, 1350 m, 1288 w, 1258 w, 1043 s. 1005 s, 955 m, 936 m, 893 w, 812 w. 665 m, 635 m, 465 w, 390 w. Elemental Anal. Calcd for W$_4$O$_{12}$^{13}C$_{12}$C$_{36}$H$_{108}$: C, 35.47; H, 6.70. Found: C, 35.56; H, 6.58.

W$_2$(OCH$_2$-i-Pr)$_6$(PMe$_3$)$_2$. W$_2$(O-t-Bu)$_6$ (0.500 g, 0.62 mmol) was dissolved in 5 mL of hexane in a Schlenk flask at room temperature. The flask was cooled to liquid nitrogen temperature and evacuated, and a large excess (>10 equiv) of PMe$_3$ was condensed in from a calibrated vacuum manifold. The flask was warmed to −78 °C (dry-ice/acetone bath), and nitrogen was readmitted. An excess of isobutyl alcohol (1 mL) was added dropwise to the flask, and the color immediately changed from red to deep orange-brown. The mixture was warmed to room temperature and then stirred for 2 h. The volatile compounds were removed in vacuo to give a dark brown residue. Repeated attempts to crystallize (or precipitate) the product from hexane, pentane, diethyl ether, or THF at −78 °C were unsuccessful. However, by redissolving the residue in 1,2-dimethoxyethane and cooling to −20 °C for 3 days, a small amount of red/orange material precipitated (20.2 mg, 0.23 mmol), 37.5% yield. ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy as well as elemental analysis were used to identify this solid as W$_2$(OCH$_2$-i-Pr)$_6$(PMe$_3$)$_2$. The solvent was removed from the filtrate in vacuo. and the residue obtained had the same spectroscopic parameters as the solid isolated from this reaction.

W$_2$(OCH$_2$-i-Pr)$_6$(PMe$_3$)$_2$. ^{1}H NMR (23 °C, 300 MHz, C$_6$D$_6$) methylenes, CH_2, H_a^1, ppm, d, 4 H, J_{a-b} = 5.6 Hz; H_a^2, 3.86 ppm, d × d, 8

H, $J_{a-a'}$ = 11.0 Hz, J_{a-b} = 6.2 Hz; $H_{a'}^2$, 3.83 ppm, d × d, 8 H, J_{a-b} = 6.2 Hz; methines, CH, H_b^1, 2.18 ppm, m, 2 H; H_b^2, 1.94 ppm, m, 4 H; methyls, CH_3, H_c^1, 1.52 ppm, d, 12 H, J_{c-b} = 6.2 Hz; H_c^2, 1.05 ppm, d, 12 H, J_{b-c} = 6.0 Hz; $H_{c'}^2$, 1.02 ppm, d, 12 H, J_{b-c} = 6.0 Hz; PMe_3, 1.52 ppm, d, 18 H, J_{H-P} = 6.3 Hz; ^{13}C NMR (23 °C, 75.42 MHz, C_6D_6) methylenes, CH_2, C_a^1, 75.8 ppm, 1C; C_a^2, 76.0 ppm, 2C; methines, CH, C_b^1, 33.4 ppm, 1C; C_b^2, 32.5 ppm, 2C; methyls, CH_3, C_c^1, 20.2 ppm, 2C; C_c^2, 20.1 ppm 2C; $C_{c'}^2$, 19.9 ppm, 2C; $P(CH_3)_3$, 15.8 ppm, 3C, J_{C-P} = 24 Hz. Elemental Anal. Calcd for $W_2O_6P_2C_{30}H_{72}$: C, 37.58; H, 7.57. Found: C, 37.47; H, 7.38.

Attempted Preparation of $M_2(OCH_2$-i-$Pr)_6(py)_2$. (i) M = W. W_2-$(NMe_2)_6$ (0.500 g, 0.79 mmol) was placed in a Schlenk flask, and 3 mL of each of pentane and pyridine were added. Isobutyl alcohol (0.6 mL) was added dropwise over 10 min, and the solution turned deep orange-red. After stirring for 8 h at room temperature the volatile components were removed in vacuo, and a sample of the oily residue was dissolved in pyridine-d_5. A ^1H NMR spectrum revealed the presence of only $W_4(OCH_2$-i-$Pr)_{12}$ (analogous to an authentic sample) in solution.

(ii) M = Mo. $Mo_2(NMe_2)_6$ (0.330 g) was treated in an analogous manner to (i) above with the identical amounts of solvents and reagents. On addition of the alcohol, the solution turned deep purple, and after stirring for 8 h the volatile components were removed in vacuo. A ^1H NMR spectrum of a sample of the oily residue indicated the presence of a small amount of $Mo_2(OCH_2$-i-$Pr)_6(py)_2$, but mainly $Mo_4(OCH_2$-i-$Pr)_{12}$ (analogous to an authentic sample).

$Mo_2(OCH_2Cy)_6(NMe_3)_2$. $Mo_2(NMe_2)_6$ (0.853 g, 1.9 mmol) was suspended in 1 mL of hexane in a Schlenk flask. The flask was cooled to −196 °C and evacuated, and a large excess of NMe_3 (2 mL at 0 °C) was condensed in from a calibrated vacuum manifold. The solution was warmed to 0 °C (caution: NMe_3 boils at +5 °C), and an excess of cyclohexylmethanol (1 mL) was added. The brown solution was stirred at 0 °C for 4 h under nitrogen and then cooled to −78 °C (dry-ice/acetone). After 3 days, some red/brown crystals had formed. They were filtered at 0 °C, and the filtrate was replaced at −78 °C. A second crop of crystals was obtained to give a combined mass of 0.387 g of Mo_2-$(OCH_2Cy)_6(NMe_3)_2$, 46.0% yield. Attempts to crystallize more material from the filtrate were unsuccessful, and further attempts to work up the solution resulted in formation of $Mo_4(OCH_2Cy)_{12}$. The solid isolated from this reaction was shown to be $Mo_2(OCH_2Cy)_6(NMe_3)_2$ by ^1H NMR spectroscopy. The elemental analysis obtained for the crystals was low in nitrogen, consistent with other observations. ^1H NMR (23 °C, 500 MHz, C_6D_6) methylenes, CH_2, H_a^1, 5.4 ppm, m, 4 H; H_a^1, 4.95 ppm, m, 4 H; H_a^2, 4.57 ppm, m, 4 H; methines, CH, H_b^1, 2.00 ppm, m, 4 H; H_b^2, 1.32 ppm, m. Remaining resonances overlapping multiplets from 2.3 ppm to 0.70 ppm. IR ν (cm^{-1}) 1102 m, 1088 s, 1077 s, 1057 s, 1046 vs, 1025 s, 1005 s, 985 s, 952 m, 893 s, 840 m, 655 m, 632 m, 581 m, 536 m, 500 w. Elemental Anal. Calcd for $Mo_2O_6N_2C_{48}H_{96}$: C, 58.28; H, 9.78; N, 2.83. Found: C, 58.22; H, 9.14; N, 0.69.

Evidence for Elimination of NMe_3 from $Mo_2(OCH_2Cy)_6(NMe_3)_2$. A sample of $Mo_2(OCH_2Cy)_6(NMe_3)_2$ (32 mg) was placed in an extended 5-mm NMR tube under a dynamic vacuum, and the solid was heated by use of an oil bath maintained at 70 °C for 5 h. After slowly cooling to room temperature the NMR tube was placed in a dry-ice-acetone bath, 0.5 mL of toluene-d_8 were added, and the sample was sealed under nitrogen. The sample was placed in an NMR probe previously cooled to −40 °C. A ^1H NMR spectrum at this temperature revealed only the presence of $Mo_4(OCH_2Cy)_{12}$ and, most significantly, the absence of a resonance due to free NMe_3. On warming the sample to room temperature, no evidence for any NMe_3 could be found. By contrast, samples of $Mo_2(OCH_2Cy)_6(NMe_3)_2$ in toluene-d_8 formed $Mo_4(OCH_2Cy)_{12}$ in solution over a period of about 4 h, and the resonance of liberated NMe_3 was clearly visible in the ^1H NMR spectrum. The above observations are consistent with the loss of NMe_3 from $Mo_2(OCH_2Cy)_6(NMe_3)_2$ to form $Mo_4(OCH_2Cy)_{12}$.

Reactions of $W_4(O$-i-$Pr)_{12}$ with $HOCH_2$-i-Pr. $W_4(O$-i-$Pr)_{12}$ (100 mg, 0.07 mmol) was placed in a 30-mL Schlenk flask and cooled to 0 °C. A cooled (0 °C) solution of 1.3 mL of isobutyl alcohol in 1 mL of toluene was added dropwise over a period of 0.2 h with rapid stirring. The green solution was stirred at 0 °C for a total of 0.5 h. The volatile components were then removed in vacuo at 0 °C to give a green solid. The complete contents of the flask were dissolved in benzene-d_6, and a ^1H NMR spectrum obtained at room temperature within 5 min of preparing the sample. The ^1H NMR spectrum showed *only* the presence of resonances attributable to $W_4(OCH_2$-i-$Pr)_{12}$, identical with an authentic sample. No isopropoxide resonances could be observed.

X-ray Crystallographic Studies. General operating procedures have been described.[9]

$Mo_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-$Bu)$. A suitable crystal was selected and transferred to the goniostat, where it was cooled to −156 °C for characterization and data collection. A systematic search of a limited

hemisphere of reciprocal space yielded a set of reflections that exhibited $4/m$ symmetry. The general condition of $1 = 4n$ for 001 led to the choice of the tetragonal space group $P4_1$ (no. 76). Data collection were carried out using the parameters given in Table I. A total of 11 293 reflections (including extinctions and standard reflections) were collected. Inspection of plots of the standards showed no systematic trends. After the usual data processing and averaging of equivalent reflections a unique set of 9263 reflections remained. Of these 7977 were considered observed by the criterion $F > 3.00\sigma(F)$.

The structure was solved by the usual combination of direct methods and Fourier techniques. The eight Mo atoms in the asymmetric unit were located from the E-map, and the remaining atoms in the structure were located in successive difference Fouriers. The asymmetric unit contains two independent Mo_4 units each with a total of 82 atoms. The molecules are numbered in an identical fashion: atoms in molecule A are labeled with A and the ones in molecule B with B. No hydrogen atoms were located, and none were introduced in calculated positions due to the large number of parameters. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on the Mo atoms and individual isotropic thermal parameters on all other atoms. The final R was 0.05.

The final difference Fourier was essentially featureless, the largest peaks were approximately 0.70 e/Å^3 and were located in the vicinity of the Mo atoms. It was not possible to locate the hydrogen atoms on the two OH groups O(59)A and O(59)B. Inspection of the stereo diagrams of the molecules (VERSORT) seem to indicate a possible hydrogen bond between O(59)A and O(35)A of 2.55 Å and in the B molecule between O(59)B and O(35)B of 2.60 Å.
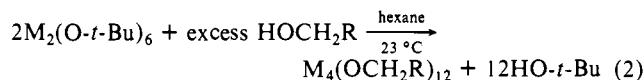
The two independent molecules in the asymmetric unit are almost identical differing only slightly in the relative orientation of the cyclobutyl groups.

Since the molecules are so similar only molecule A was used for the illustrations.

Results and Discussion

Synthesis and Characterization of $M_4(OCH_2R)_{12}$ Compounds. The new class of metal (3+) alkoxide compounds were prepared by treatment of hexane solutions of the dimetal hexakistertiary-butoxides with an excess of any of the following primary alcohols, $HOCH_2R$, where R = cyclohexyl (Cy), isopropyl (i-Pr), cyclopentyl (Cp), or cyclobutyl (c-Bu), according to eq 2. After stirring

$$2M_2(O\text{-}t\text{-}Bu)_6 + \text{excess } HOCH_2R \xrightarrow[\text{23 °C}]{\text{hexane}}$$
$$M_4(OCH_2R)_{12} + 12HO\text{-}t\text{-}Bu \quad (2)$$

the deep green or deep purple solutions for 4 h, the volatile components were removed in vacuo and the following products were crystallized by redissolving the residue in 1,2-dimethoxy-ethane and crystallizing at −20 °C: $W_4(OCH_2Cy)_{12}$ (IV), W_4-$(OCH_2$-i-$Pr)_{12}$ (V), $W_4(OCH_2Cp)_{12}$ (VI), $W_4(OCH_2$-c-$Bu)_{12}$-$(HOCH_2$-c-$Bu)$ (VII), $Mo_4(OCH_2Cy)_{12}$ (VIII), $Mo_4(OCH_2$-i-$Pr)_{12}$ (IX), $Mo_4(OCH_2Cp)_{12}$ (X), $Mo_4(OCH_2$-c-$Bu)_{12}$-$(HOCH_2$-c-$Bu)$ (XI), respectively. Compounds VII and XI were shown by NMR spectroscopy (see later) and combustion analysis (see Experimental Section) to contain one molecule of alcohol (presumably coordinated in the solid state) for each $M_4(OCH_2R)_{12}$ cluster unit. This was also confirmed by a single-crystal X-ray diffraction analysis of XI. The elemental analysis data define the empirical cluster formula as $M(OCH_2R)_3$ for the complexes IV–VI and VIII–X and $[M(OCH_2R)_3]_4$·$HOCH_2R$ for VII and XI.

A. Solid-State Structure of $Mo_4(OCH_2$-c-$Bu)_{12}$·$HOCH_2$-c-Bu (XI). Attempts to determine the single-crystal X-ray diffraction structures of VI, V, VIII, IX, and X were unfruitful because the crystals obtained only diffracted to small angles, and it was concluded that the structure consisted of hexagonal close packed molecules with a molecular disorder.

The crystal of XI contained eight molecules in the unit cell with two independent Mo_4 clusters in the asymmetric unit. The two independent molecules are virtually identical having small differences in the relative orientations of the cyclobutyl groups. A best molecular fit computation was performed fitting the molybdenum atoms of the two independent molecules, and this is shown in a figure in the Supplementary Material. Since the two independent molecules are so similar, only one type is used for the figures in this paper. A ball-and-stick drawing that emphasizes the coordination geometry at the molybdenum centers is shown
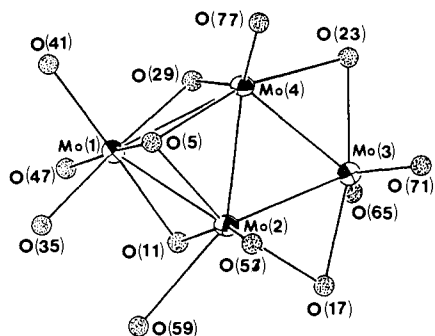
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Figure 1. A ball-and-stick drawing of the central Mo_4O_{13} skeleton of the $Mo_4(OCH_2-c-Bu)_{12}(HOCH_2-c-Bu)$ molecule giving the atom number scheme used in the tables. The complete atom number scheme is shown in drawings in the Supplementary Material.
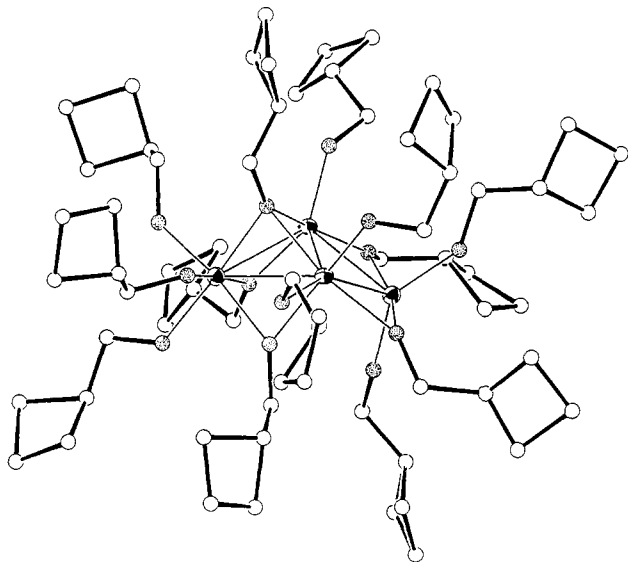

Figure 2. A ball-and-stick drawing of the $Mo_4(OCH_2-c-Bu)_{12}$-$(HOCH_2-c-Bu)$ molecule emphasizing the octahedral MoO_6 unit at $Mo(1)$.
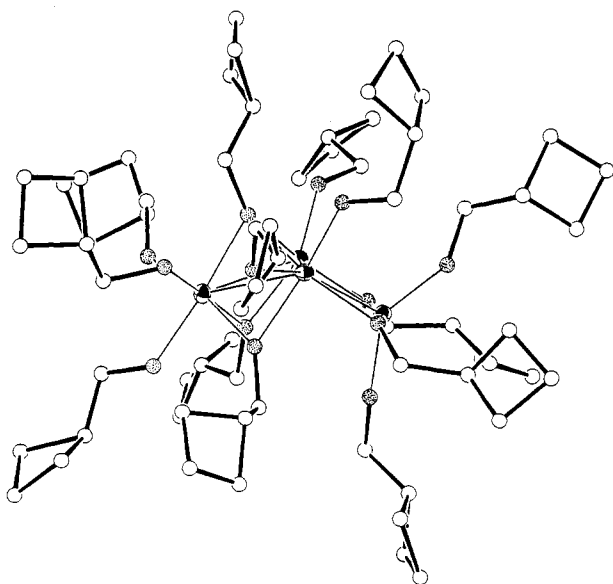
Figure 3. A ball-and-stick drawing of the $Mo_4(OCH_2-c-Bu)_{12}$-$(HOCH_2-c-Bu)$ molecule emphasizing the central Mo_4 butterfly. The dihedral angle between the two Mo_3 triangles is 132.5°.

in Figure 1. Figures 2 and 3 demonstrate the butterfly geometry of metal atoms as well as the orientations of the cyclobutyl-methoxide ligands. The crystallographic data are given in Table

Table I. Summary of Crystal Data

empirical formula	$C_{65}H_{118}Mo_4O_{13}$
color of crystal	black
crystal dimensions (mm)	0.40 × 0.35 × 0.35
space group	$P4_1$
cell dimensions	
temp (°C)	−156
$a = b$ (Å)	19.952 (7)
c (Å)	34.755 (16)
Z (molecules/cell)	8
vol (Å³)	13835.24
calcd density (gm/cm³)	1.432
wavelength (Å)	0.71069
mol wt	1491.40
linear absorptn coeff (cm⁻¹)	7.467
detector to sample distance (cm)	22.5
sample to source distance (cm)	23.5
average ω scan width at half weight	0.25
scan speed (deg/min)	6.0
scan width (deg + dispersion)	1.3
individual background (sc)	5
aperture size (mm)	3.0 ≥ 4.0
2θ range (deg)	6–45
total no. of reflcns collected	11293
no. of unique intensities	9263
no. of $F > 0.0$	8759
no. of $F?3.0\sigma(F)$	7977
$R(F)$	0.0570
$Rw(F)$	0.0575
goodness of fit for the last cycle	1.105
maximum δ/σ for last cycle	0.05

Table II. Selected Bond Distances (Å) for the Two Crystallographically Independent Molecules A and B, $Mo_4(OCH_2-c-Bu)_{12}(HOCH_2-c-Bu)$

bond distances in molecule A			bond distances in molecule B		
A	B	distance	A	B	distance
Mo(1)A	Mo(2)A	2.6637 (16)	Mo(1)B	Mo(2)B	2.6757 (23)
Mo(1)A	Mo(4)A	2.6810 (16)	Mo(1)B	Mo(4)B	2.6901 (23)
Mo(1)A	O(5)A	2.111 (9)	Mo(1)B	O(5)B	2.108 (9)
Mo(1)A	O(11)A	2.048 (9)	Mo(1)B	O(11)B	2.041 (9)
Mo(1)A	O(29)A	2.080 (9)	Mo(1)B	O(29)B	2.099 (10)
Mo(1)A	O(35)A	1.967 (9)	Mo(1)B	O(35)B	1.968 (10)
Mo(1)A	O(41)A	1.913 (10)	Mo(1)B	O(41)B	1.907 (10)
Mo(1)A	O(47)A	2.011 (9)	Mo(1)B	O(47)B	2.004 (10)
Mo(2)A	Mo(3)A	2.5071 (18)	Mo(2)B	Mo(3)B	2.5128 (23)
O(2)A	Mo(4)A	2.4751 (18)	Mo(2)B	Mo(4)B	2.4614 (23)
Mo(2)A	O(5)A	2.078 (9)	Mo(2)B	O(5)B	2.091 (9)
Mo(2)A	O(11)B	2.053 (9)	Mo(2)B	O(11)B	2.061 (9)
Mo(2)A	O(17)A	2.105 (9)	Mo(2)B	O(17)B	2.114 (10)
Mo(2)A	O(53)A	1.956 (9)	Mo(2)B	O(53)B	1.930 (10)
Mo(2)A	O(59)A	2.342 (10)	Mo(2)B	O(59)B	2.349 (10)
Mo(3)A	Mo(4)A	2.4788 (19)	Mo(3)B	Mo(4)B	2.4730 (24)
Mo(3)A	O(17)A	2.018 (9)	Mo(3)B	O(17)B	2.009 (10)
Mo(3)A	O(23)A	2.057 (9)	Mo(3)B	O(23)B	2.073 (9)
Mo(3)A	O(65)A	1.937 (10)	Mo(3)B	O(65)B	1.915 (10)
Mo(3)A	O(71)A	1.876 (9)	Mo(3)B	O(71)B	1.880 (10)
Mo(4)A	O(5)A	2.163 (9)	Mo(4)B	O(5)B	2.110 (9)
Mo(4)A	O(23)A	2.105 (9)	Mo(4)B	O(23)B	2.105 (10)
Mo(4)A	O(29)A	2.026 (9)	Mo(4)B	O(29)B	2.026 (10)
Mo(4)A	O(77)A	1.923 (10)	Mo(4)B	O(77)B	1.920 (10)

1 and the pertinent bond distances and angles in Tables 11 and 1II, respectively. Atomic positional parameters are given in Table IV.

The molecule consists of a butterfly arrangement of metal atoms where Mo(1) and Mo(3) are defined as the wingtip metal atoms and Mo(2) and Mo(4) as the backbone metal atoms, with a dihedral angle between the triangular faces of 132.5°. One triangular face is capped with a triply bridging alkoxide ligand, and each backbone-to-wingtip metal atom edge is bridged by alkoxide ligands. Mo(2) possesses one terminal alkoxide ligand and is also coordinated to another oxygen atom at a distance of 2.34 Å, in the range we have previously observed for metal-to-alcohol oxygen distances.[12] Mo(1) has coordination number 6 with respect to alkoxide ligands such that the Mo(1)-6(O) moiety

is a distorted octahedron. Mo(3) and Mo(4) are four-coordinate with respect to oxygen atoms. Mo(2) is five-coordinate with respect to oxygen atoms. The coordinated alcohol ligand takes up the axial position of the square-based pyramid that is missing for the Mo(4)–4(O) moiety.

The molybdenum–molybdenum distances within the cluster are quite remarkable and require some comment. The relevant distances are given in Table II. The distances within the triangle defined by Mo(2), Mo(3), and Mo(4) are markedly shorter than those of the triangle defined by Mo(1), Mo(2), and Mo(4) Typical bond lengths for Mo–Mo single, double, and triple bonds are of the order 2.73 Å (e.g., in $Mo_2Cl_4(O\text{-}i\text{-}Pr)_6$), 2.52 Å (e.g., in $Mo_2(O\text{-}i\text{-}Pr)_8$), and 2.22 Å (e.g., in $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$), respectively (note that the first two examples contain alkoxide bridged metal–metal bonds).[12] The metal-to-metal distances for the atoms within the triangle Mo(4), Mo(3), and Mo(2) are consistent with some multiple bond character and can be compared to the metal–metal distances of 2.53 Å within the cluster $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$, although the latter is no doubt constrained by the presence of *both* triply bridging oxo and alkoxo ligands. The distances Mo(1)–Mo(4) and Mo(1)–Mo(2) are closer to single bond separations, although, as always, the presence of bridging ligands complicates the simple assignment of bond order.

The metal–oxygen bond distances all lie within the expected ranges, 1.88–2.01 Å for terminal alkoxides and 2.03–2.16 Å for the doubly and triply bridging alkoxides.[12] The Mo–oxygen distance between Mo(2) and O(59) of 2.34 Å, the ligand believed to be coordinated cyclobutylmethanol, is notably longer than any other Mo–O distance in the molecule. The presence of one molecule of coordinated alcohol for each cluster unit in the solid state is also consistent with the solution NMR results discussed below where it was observed that 1 equiv of free alcohol was liberated when the crystalline materials VII and XI were dissolved in benzene-d_6. The reasons why only one molecule of alcohol and not two should be coordinated (the other to Mo(4)) remains unclear at this stage. The observation that the molecular symmetry of the cluster formed on dissolution of a sample of the crystals of XI used for the structure determination is identical with that of all the other complexes of this class supports the idea that the solid-state structure is related to the species characterized spectroscopically in solution.

B. Solution Structure of Compunds IV–XI. In solution, the ^1H and ^{13}C NMR spectroscopic data for *all* the complexes IV–XI are consistent with a common, stereochemically rigid cluster framework. The methylene, and to a lesser extent the methine, ^1H and ^{13}C NMR resonances of the alkoxide ligands are sensitive probes of the cluster geometry, and their assignments and connectivity have been examined in detail (see Experimental Section). In the ^1H NMR spectrum, there is evidence for eight types of alkoxide ligands from the methylenic proton resonances which occur in the relative ratios of 1:1:1:1:2:2:2:2. The methylenic resonances of relative intensity one occur as doublets coupled to the single methine proton, while the resonances due to the alkoxide ligands of relative intensity two arise from diastereotopic methylene protons and can easily be identified by their additional geminal coupling constants. In most cases the individual proton chemical shifts could be distinguished using the chemical shift dispersion of a 500 MHz instrument. Figure 4 shows a two-dimensional ^1H NMR chemical shift correlated contour plot of $Mo_4(OCH_2\text{-}i\text{-}Pr)_{12}$ obtained at 500.13 MHz. The four types of diastereotopic alkoxide ligands of relative intensity two consisting of eight individual methylenic proton resonances can be identified by the four off-diagonal contours (marked H_a^2, H_a^4, H_a^5, H_a^6 in Figure 4) within the methylene region. This assignment is confirmed by noting that the pairwise related methylenic protons are coupled to the same methyne protons, respectively, e.g., between the pair H_a^2, H_a^2, and H_b^2 (see Experimental Section for definition of terms). The nondiastereotopic methylene protons exhibit single crosspeaks to the methine region. Therefore, there are a total of 12 off-diagonal elements between methylene and methyne protons, and, together with the equivalent relative intensities of methylene resonances, a minimum cluster nuclearity of tetranuclear can be
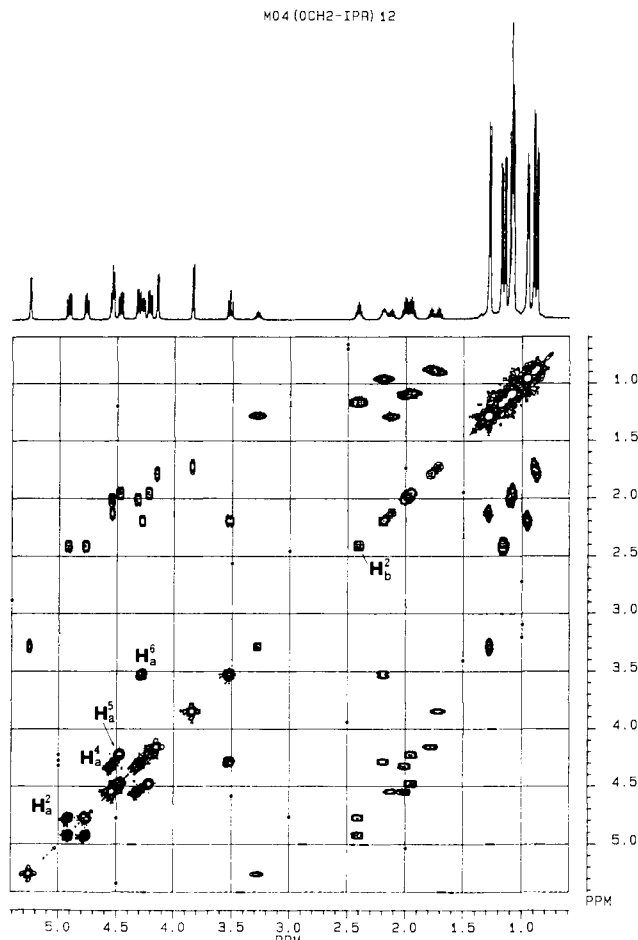

Figure 4. A 2D ^1H NMR chemical shift correlated contour plot (COSY) for $Mo_4(OCH_2\text{-}i\text{-}Pr)_{12}$ recorded in benzene-d_6 at 500.13 MHz and 23 °C.

set, i.e., the molecular formula in solution must be $[M_4(OCH_2R)_{12}]_n$.

The ^{13}C NMR spectra of these compounds were also consistent with these observations. Eight types of methylenic carbons were observed in the approximate ratio 1:1:1:1:2:2:2:2. Two-dimensional heteronuclear $^{13}C\text{–}^1H$ chemical shift correlated experiments clearly confirm not only the presence of eight different types of alkoxide ligands but also the assignment that the resonances of relative intensity two arise from diastereotopic alkoxide ligands. Figure 5 shows an expansion of the two-dimensional $^{13}C\text{–}^1H$ chemical shift correlated contour plot for $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}$ to show the methylenic region. This experiment was optimized to determine correlations between ^{13}C nuclei and their directly attached protons. The ^{13}C resonances labeled C_a^2, C_a^2, C_a^6, and C_a^4 are of approximate relative intensity two, and each possess two chemically inequivalent directly attached protons, while ^{13}C resonances C_a^1, C_a^7, C_a^8, and C_a^3, of approximate relative intensity one, are attached to one type of methylenic proton. Similar arguments were used to determine the connectivity between the methine ^1H and ^{13}C resonances of all the new compounds, and in the case of $M_4(OCH_2\text{-}i\text{-}Pr)_{12}$ molecules the connectivity of all the ^1H and ^{13}C nuclei within every alkoxide ligand could be determined. In cases where any ambiguity of assignment existed, two-dimensional *J*-resolved ^1H NMR experiments were used to separate chemical shifts from homonuclear coupling constants.

Complexes VII and XI showed a slightly different behavior. On dissolving the isolated crystalline material in benzene-d_6 ^1H NMR resonances were obtained that were consistent with the same molecular geometry for the cluster in solution, but in addition ^1H NMR resonances similar to those of free cyclobutylmethanol were observed in each case. On addition of an authentic sample of cyclobutylmethanol to a benzene-d_6 solution of isolated VII, the resonances originally attributed to the dissociated alcohol increased in intensity, confirming their assignment to uncoordinated alcohol.

Table III. Selected Bond Angles (deg) for the Two Crystallographically Independent Molecules A and B, Mo$_4$(OCH$_2$-c-Bu)$_{12}$(HOCH$_2$-c-Bu)

bond angles for molecule A				bond angles for molecule B			
Mo(2)A	Mo(1)A	Mo(4)A	55.17 (4)	Mo(2)B	Mo(1)B	Mo(4)B	54.61 (4)
Mo(2)A	Mo(1)A	O(5)A	49.98 (25)	Mo(2)B	Mo(1)B	O(5)B	50.13 (24)
Mo(2)A	Mo(1)A	O(11)A	49.58 (25)	Mo(2)B	Mo(1)B	O(11)B	49.60 (26)
Mo(2)A	Mo(1)A	O(29)A	90.23 (24)	Mo(2)B	Mo(1)B	O(29)B	89.33 (26)
Mo(2)A	Mo(1)A	O(35)A	87.73 (25)	Mo(2)B	Mo(1)B	O(35)B	90.5 (3)
Mo(2)A	Mo(1)A	O(41)A	139.5 (3)	Mo(2)B	Mo(1)B	O(41)B	138.8 (3)
Mo(2)A	Mo(1)A	O(47)A	130.62 (28)	Mo(2)B	Mo(1)B	O(47)B	130.1 (3)
Mo(4)A	Mo(1)A	O(5)A	52.03 (25)	Mo(4)B	Mo(1)B	O(5)B	50.40 (25)
Mo(4)A	Mo(1)A	O(11)A	87.71 (25)	Mo(4)B	Mo(1)B	O(11)B	87.37 (26)
Mo(4)A	Mo(1)A	O(29)A	48.35 (25)	Mo(4)B	Mo(1)B	O(29)B	48.13 (26)
Mo(4)A	Mo(1)A	O(35)A	132.41 (25)	Mo(4)B	Mo(1)B	O(35)B	132.3 (3)
Mo(4)A	Mo(1)A	O(41)A	96.5 (3)	Mo(4)B	Mo(1)B	O(41)B	93.3 (3)
Mo(4)A	Mo(1)A	O(47)A	134.79 (28)	Mo(4)B	Mo(1)B	O(47)B	134.8 (3)
O(5)A	Mo(1)A	O(11)A	99.2 (3)	O(5)B	Mo(1)B	O(11)B	99.5 (4)
O(5)A	Mo(1)A	O(29)A	99.6 (3)	O(5)B	Mo(1)B	O(29)B	97.8 (4)
O(5)A	Mo(1)A	O(35)A	82.0 (3)	O(5)B	Mo(1)B	O(35)B	82.8 (4)
O(5)A	Mo(1)A	O(41)A	90.3 (4)	O(5)B	Mo(1)B	O(41)B	90.3 (4)
O(5)A	Mo(1)A	O(47)A	173.1 (4)	O(5)B	Mo(1)B	O(47)B	174.6 (4)
O(11)A	Mo(1)A	O(29)A	87.3 (3)	O(11)B	Mo(1)B	O(29)B	86.7 (4)
O(11)A	Mo(1)A	O(35)A	88.5 (4)	O(11)B	Mo(1)B	O(35)B	92.7 (4)
O(11)A	Mo(1)A	O(41)A	170.3 (4)	O(11)B	Mo(1)B	O(41)B	167.8 (4)
O(11)A	Mo(1)A	O(47)A	81.0 (4)	O(11)B	Mo(1)B	O(47)B	80.5 (4)
O(29)A	Mo(1)A	O(35)A	175.6 (4)	O(29)B	Mo(1)B	O(35)B	179.2 (4)
O(29)A	Mo(1)A	O(41)A	89.0 (4)	O(29)B	Mo(1)B	O(41)B	84.8 (4)
O(29)A	Mo(1)A	O(47)A	87.3 (4)	O(29)B	Mo(1)B	O(47)B	87.6 (4)
O(35)A	Mo(1)A	O(41)A	95.1 (4)	O(35)B	Mo(1)B	O(41)B	95.8 (4)
O(35)A	Mo(1)A	O(47)A	81.1 (4)	O(35)B	Mo(1)B	O(47)B	91.9 (4)
O(41)A	Mo(1)A	O(47)A	89.8 (4)	O(41)B	Mo(1)B	O(47)B	90.5 (4)
Mo(1)A	Mo(2)A	Mo(3)A	106.75 (5)	Mo(1)B	Mo(2)B	Mo(3)B	106.85 (6)
Mo(1)A	Mo(2)A	Mo(4)A	62.77 (4)	Mo(1)B	Mo(2)B	Mo(4)B	62.99 (5)
Mo(1)A	Mo(2)A	O(5)A	51.06 (25)	Mo(1)B	Mo(2)B	O(5)B	50.69 (24)
Mo(1)A	Mo(2)A	O(11)A	49.40 (25)	Mo(1)B	Mo(2)B	O(11)B	48.97 (26)
Mo(1)A	Mo(2)A	O(17)A	134.81 (25)	Mo(1)B	Mon2)B	O(17)B	135.50 (27)
Mo(1)A	Mo(2)A	O(53)A	134.3 (3)	Mo(1)B	Mo(2)B	O(53)B	133.8 (3)
Mo(1)A	Mo(2)A	O(59)A	86.70 (24)	·Mo(1)B	Mo(2)B	O(59)B	84.98 (24)
Mo(3)A	Mo(2)A	Mo(4)A	59.67 (5)	Mo(3)B	Mo(2)B	Mo(4)B	59.62 (6)
Mo(3)A	Mo(2)A	O(5)A	114.56 (25)	Mo(3)B	Mo(2)B	O(5)B	113.16 (25)
Mo(3)A	Mo(2)A	O(11)A	93.74 (25)	Mo(3)B	Mo(2)B	O(11)B	94.02 (27)
Mo(3)A	Mo(2)A	O(17)A	50.97 (24)	Mo(3)B	Mo(2)B	O(17)B	50.59 (26)
Mo(3)A	Mo(2)A	O(53)A	102.40 (28)	Mo(3)B	Mo(2)B	O(53)B	103.5 (3)
Mo(3)A	Mo(2)A	O(59)A	151.53 (26)	Mo(3)B	Mo(2)B	O(59)B	153.91 (26)
Mo(4)A	Mo(2)A	O(5)A	55.92 (25)	Mo(4)B	Mo(2)B	O(5)B	54.49 (24)
Mo(4)A	Mo(2)A	O(11)A	93.38 (24)	Mo(4)B	Mo(2)B	O(11)B	93.36 (26)
Mo(4)A	Mo(2)A	O(17)A	110.61 (24)	Mo(4)B	Mo(2)B	O(17)B	110.20 (27)
Mo(4)A	Mo(2)A	O(53)A	105.86 (27)	Mo(4)B	Mo(2)B	O(53)B	106.5 (3)
Mo(4)A	Mo(2)A	O(59)A	145.78 (25)	Mo(4)B	Mo(2)B	O(59)B	143.60 (25)
O(5)A	Mo(2)A	O(11)A	100.1 (3)	O(5)B	Mo(2)B	O(11)B	99.4 (4)
O(5)A	Mo(2)A	O(17)A	163.7 (3)	O(5)B	Mo(2)B	O(17)B	161.9 (4)
O(5)A	Mo(2)A	O(53)A	85.0 (4)	O(5)B	Mo(2)B	O(53)B	85.6 (4)
O(5)A	Mo(2)A	O(59)A	93.5 (4)	O(5)B	Mo(2)B	O(59)B	92.4 (3)
O(11)A	Mo(2)A	O(17)A	89.3 (3)	O(11)B	Mo(2)B	O(17)B	90.6 (4)
O(11)A	Mo(2)A	O(53)A	159.3 (4)	O(11)B	Mo(2)B	O(53)B	158.3 (4)
O(11)A	Mo(2)A	O(59)A	75.8 (3)	O(11)B	Mo(2)B	O(59)B	76.0 (3)
O(17)A	Mo(2)A	O(53)A	90.9 (4)	O(17)B	Mo(2)B	O(53)B	90.7 (4)
O(17)A	Mo(2)A	O(59)A	101.8 (3)	O(17)B	Mo(2)B	O(59)B	104.7 (4)
O(53)A	Mo(2)A	O(59)A	83.9 (4)	O(53)B	Mo(2)B	O(59)B	82.7 (4)
Mo(2)A	Mo(3)A	Mo(4)A	59.53 (5)	Mo(2)B	Mo(3)B	Mo(4)B	59.16 (7)
Mo(2)A	Mo(3)A	O(17)A	54.16 (27)	Mo(2)B	Mo(3)B	O(17)B	54.4 (3)
Mo(2)A	Mo(3)A	O(23)A	113.83 (26)	Mo(2)B	Mo(3)B	O(23)B	113.48 (27)
Mo(2)A	Mo(3)A	O(65)A	109.2 (3)	Mo(2)B	Mo(3)B	O(65)B	110.3 (3)
Mo(2)A	Mo(3)A	O(71)A	109.5 (3)	Mo(2)B	Mo(3)B	O(71)B	109.8 (3)
Mo(4)A	Mo(3)A	O(17)A	113.65 (27)	Mo(4)B	Mo(3)B	O(17)B	113.5 (3)
Mo(4)A	Mo(3)A	O(23)A	54.35 (26)	Mo(4)B	Mo(3)B	O(23)B	54.32 (27)
Mo(4)A	Mo(3)A	O(65)A	110.8 (3)	Mo(4)B	Mo(3)B	O(65)B	108.9 (3)
Mo(4)A	Mo(3)A	O(71)A	106.7 (3)	Mo(4)B	Mo(3)B	O(71)B	107.3 (3)
O(17)A	Mo(3)A	O(23)A	167.4 (4)	O(17)B	Mo(3)B	O(23)B	167.8 (4)
O(17)A	Mo(3)A	O(65)A	89.3 (4)	O(17)B	Mo(3)B	O(65)B	92.9 (4)
O(17)A	Mo(3)A	O(71)A	96.5 (4)	O(17)B	Mo(3)B	O(71)B	95.4 (4)
O(23)A	Mo(3)A	O(65)A	91.8 (4)	O(23)B	Mo(3)B	O(65)B	91.0 (4)
O(23)A	Mo(3)A	O(71)A	91.5 (4)	O(23)B	Mo(3)B	O(71)B	89.9 (4)
O(65)A	Mo(3)A	O(71)A	135.8 (4)	O(65)B	Mo(3)B	O(71)B	135.7 (4)
Mo(1)A	Mo(4)A	Mo(2)A	62.06 (4)	Mo(1)B	Mo(4)B	Mo(2)B	62.40 (5)
Mo(1)A	Mo(4)A	Mo(3)A	107.05 (5)	Mo(1)B	Mo(4)B	Mo(3)B	107.58 (6)
Mo(1)A	Mo(4)A	O(5)A	50.28 (24)	Mo(1)B	Mo(4)B	O(5)B	50.33 (24)
Mo(1)A	Mo(4)A	O(23)A	135.22 (25)	Mo(1)B	Mo(4)B	O(23)B	137.34 (26)

Table III (Continued)

|	bond angles for molecule A				bond angles for molecule B		
Mo(1)A	Mo(4)A	O(29)A	50.13 (25)	Mo(1)B	Mo(4)B	O(29)B	50.49 (28)
Mo(1)A	Mo(4)A	O(77)A	129.7 (3)	Mo(1)B	Mo(4)B	O(77)B	128.0 (3)
Mo(2)A	Mo(4)A	Mo(3)A	60.81 (5)	Mo(2)B	Mo(4)B	Mo(3)B	61.22 (5)
Mo(2)A	Mo(4)A	O(5)A	52.72 (24)	Mo(2)B	Mo(4)B	O(5)B	53.77 (24)
Mo(2)A	Mo(4)A	O(23)A	113.32 (25)	Mo(2)B	Mo(4)B	O(23)B	114.34 (26)
Mo(2)A	Mo(4)A	O(29)A	97.10 (25)	Mo(2)B	Mo(4)B	O(29)B	97.32 (27)
Mo(2)A	Mo(4)A	O(77)A	118.3 (3)	Mo(2)B	Mo(4)B	O(77)B	115.2 (3)
Mo(3)A	Mo(4)A	Mo(5)A	112.54 (24)	Mo(3)B	Mo(4)B	O(5)B	114.04 (25)
Mo(3)A	Mo(4)A	O(23)A	52.56 (25)	Mo(3)B	Mo(4)B	O(23)B	53.12 (26)
Mo(3)A	Mo(4)A	O(29)A	98.20 (26)	Mo(3)B	Mo(4)B	O(29)B	97.7 (3)
Mo(3)A	Mo(4)A	O(77)A	115.5 (3)	Mo(3)B	Mo(4)B	O(77)B	115.0 (3)
O(5)A	Mo(4)A	O(23)A	163.6 (3)	O(5)B	Mo(4)B	O(23)B	164.4 (4)
O(5)A	Mo(4)A	O(29)A	99.7 (4)	O(5)B	Mo(4)B	O(29)B	100.0 (4)
O(5)A	Mo(4)A	O(77)A	88.1 (4)	O(5)B	Mo(4)B	O(77)B	84.8 (4)
O(23)A	Mo(4)A	O(29)A	90.1 (4)	O(23)B	Mo(4)B	O(29)B	91.2 (4)
O(23)A	Mo(4)A	O(77)A	93.1 (4)	O(23)B	Mo(4)B	O(77)B	93.1 (4)
O(29)A	Mo(4)A	O(77)A	139.4 (4)	O(29)B	Mo(4)B	O(77)B	141.7 (4)
Mo(1)A	O(5)A	Mo(2)A	79.0 (3)	Mo(1)B	O(5)B	Mo(2)B	79.2 (3)
Mo(1)A	O(5)A	Mo(4)A	77.7 (3)	Mo(1)B	O(5)B	Mo(4)B	79.3 (3)
Mo(1)A	O(5)A	C(6)A	126.1 (8)	Mo(1)B	O(5)B	C(6)B	132.7 (8)
Mo(2)A	O(5)A	Mo(4)A	71.4 (3)	Mo(2)B	O(5)B	Mo(4)B	71.7 (3)
Mo(2)A	O(5)A	C(6)A	126.2 (8)	Mo(2)B	O(5)B	C(6)B	119.3 (8)
Mo(4)A	O(5)A	C(6)A	150.1 (8)	Mo(4)B	O(5)B	C(6)B	146.0 (8)
Mo(1)A	O(11)A	Mo(2)A	81.0 (3)	Mo(1)B	O(11)B	Mo(2)B	81.4 (3)
Mo(1)A	O(11)A	C(12)A	134.6 (8)	Mo(1)B	O(11)B	C(12)B	136.7 (9)
Mo(2)A	O(11)A	C(12)A	141.7 (8)	Mo(2)B	O(11)B	C(12)B	140.1 (9)
Mo(2)A	O(17)A	Mo(3)A	74.9 (3)	Mo(2)B	O(17)B	Mo(3)B	75.1 (3)
Mo(2)A	O(17)A	C(18)A	145.4 (8)	Mo(2)B	O(17)B	C(18)B	147.6 (9)
Mo(3)A	O(17)A	C(18)A	132.8 (9)	Mo(3)B	O(17)B	C(18)B	135.1 (9)
Mo(3)A	O(23)A	Mo(4)A	73.1 (3)	Mo(3)B	O(23)B	Mo(4)B	72.6 (3)
Mo(3)A	O(23)A	C(24)A	136.7 (9)	Mo(3)B	O(23)B	C(24)B	131.4 (9)
Mo(4)A	O(23)A	C(24)A	146.3 (9)	Mo(4)B	O(23)B	C(24)B	142.2 (9)
Mo(1)A	O(29)A	Mo(4)A	81.5 (3)	Mo(1)B	O(29)B	Mo(4)B	81.4 (4)
Mo(1)A	O(29)A	C(30)A	132.9 (8)	Mo(1)B	O(29)B	C(30)B	130.6 (8)
Mo(4)A	O(29)A	C(30)A	144.9 (8)	Mo(4)B	O(29)B	C(30)B	147.1 (9)
Mo(1)A	O(35)A	C(36)A	122.4 (8)	Mo(1)B	O(35)B	C(36)B	122.8 (8)
Mo(1)A	O(41)A	C(42)A	134.6 (9)	Mo(1)B	O(41)B	C(42)B	128.5 (10)
Mo(1)A	O(47)A	C(48)A	125.3 (8)	Mo(1)B	O(47)B	C(48)B	128.3 (8)
Mo(2)A	O(53)A	C(54)A	128.6 (9)	Mo(2)B	O(53)B	C(54)B	133.9 (9)
Mo(2)A	O(59)A	C(60)A	130.0 (8)	Mo(2)B	O(59)B	C(60)B	126.0 (8)
Mo(3)A	O(65)A	C(66)A	157.2 (9)	Mo(3)B	O(65)B	C(66)B	168.5 (9)
Mo(3)A	O(71)A	C(2)A	141.3 (9)	Mo(3)B	O(71)B	C(72)B	141.6 (9)
Mo(4)A	O(77)A	C(78)A	133.0 (9)	Mo(4)B	O(77)B	C(78)B	129.6 (9)
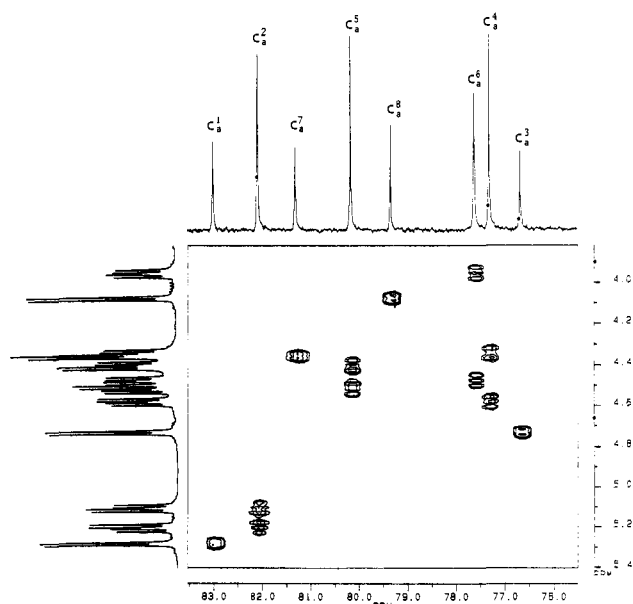
Figure 5. A portion of the $^{13}C-^{1}H$ 2D heteronuclear chemical shift correlated contour plot (XHCORR) for $W_4(OCH_2$-c-Bu)$_{12}$(HOCH$_2$-c-Bu) in benzene-d_6 at 125.76 MHz and 23 °C.

It was determined, by ^1H NMR integration, that 1 equiv of free alcohol per $M_4(OCH_2$-c-Bu)$_{12}$ cluster was liberated on dissolution of VII or XI in benzene-d_6. The result is consistent with the elemental analysis data for the isolated solids VII and XI (see Experimental Section) and led to the formulation for the isolated materials as $M_4(OCH_2$-c-Bu)$_{12}$·HOCH$_2$-c-Bu. We were fortunate in obtaining a single-crystal X-ray diffraction structure of $Mo_4(OCH_2$-c-Bu)$_{12}$(HOCH$_2$-c-Bu), XI, which confirmed this assignment.

On cooling toluene-d_8 solutions of crystalline VII and XI to −90 °C, broadening of many of the methine resonances was observed in the ^1H NMR spectra as well as a downfield shift of the alcohol proton from 3.72 to 7.28 ppm. However, no clear evidence was obtained for a species consistent with the X-ray structural data in which the mirror plane of symmetry was lost. Similarly, a toluene-d_8 solution of VII containing 5 equiv of PMe$_3$ showed no clear-cut evidence for formation of $W_4(OCH_2$-c-Bu)$_{12}$(PMe$_3$) at low temperatures (−90 °C) although some methylene resonances were broadened. It is also noteworthy that these cluster compounds remain intact in the presence of PMe$_3$, which provides evidence that they do *not* exist in reversible equilibrium with their dinuclear counterparts as observed for 11 (see eq 1).

It is clear from the solution spectroscopic data that the cluster molecules IV–XI, [$M_4(OCH_2R)_{12}]_n$, contain a mirror plane of symmetry and eight types of alkoxide ligands. The four types of relative intensity one lie in the mirror plane, and the four types of relative intensity two are related by the mirror plane. Molecular weight determinations using IX confirm that the clusters are tetranuclear, i.e., $M_4(OCH_2R)_{12}$ in benzene solution. The solution structures can be related to the solid-state structure of XI by

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $Mo_4(OCH_2\text{-c-Bu})_{12}(HOCH_{12}\text{-c-Bu})$

atom	10^4x	10^4y	10^4z	$10B_{iso}$	atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)A	6943 (1)	3419 (1)	4378*	15	C(78)A	5644 (7)	992 (7)	4210 (4)	20 (3)
Mo(2)A	7664 (1)	2335 (1)	4549 (1)	14	C(79)A	5001 (7)	1104 (7)	3979 (4)	22 (3)
Mo(3)A	7048 (1)	1731 (1)	5073.8 (5)	14	C(80)A	4494 (8)	495 (8)	4036 (5)	32 (3)
Mo(4)A	6432 (1)	2199 (1)	4515.9 (5)	13	C(81)A	3927 (8)	1035 (8)	4121 (5)	33 (3)
O(5)A	7095 (4)	2529 (4)	4061 (3)	16 (2)	C(82)A	4484 (8)	1579 (8)	4151 (5)	31 (3)
C(6)A	7330 (7)	2485 (7)	3654 (4)	19 (3)	Mo(1)B	8099 (1)	1642 (1)	9281.4 (4)	16
C(7)A	7085 (7)	1882 (7)	3447 (4)	24 (3)	Mo(2)B	7283 (1)	2618 (1)	9524.9 (5)	15
C(8)A	6398 (8)	1871 (8)	3236 (5)	26 (3)	Mo(3)B	7832 (1)	3143 (1)	10101 (1)	16
C(9)A	6763 (8)	1516 (8)	2897 (5)	26 (3)	Mo(4)B	8492 (1)	2863 (1)	9521 (1)	16
C(10)A	7449 (8)	1796 (8)	3048 (5)	30 (3)	O(5)B	7904 (4)	2593 (4)	9041 (3)	13 (2)
O(11)A	7602 (4)	3248 (4)	4819 (3)	14 (2)	C(6)B	7634 (8)	2805 (8)	8665 (5)	25 (3)
C(12)A	7739 (7)	3569 (7)	5178 (4)	18 (3)	C(7)B	8121 (8)	2712 (8)	8337 (5)	28 (3)
C(13)A	8457 (7)	3839 (7)	5166 (4)	22 (3)	C(8)B	8651 (9)	3294 (9)	8264 (5)	35 (4)
C(14)A	8607 (7)	446 (7)	4909 (5)	23 (3)	C(9)B	8342 (10)	3418 (10)	7873 (6)	48 (4)
C(15)A	9020 (8)	4730 (8)	5246 (5)	31 (3)	C(10)B	7780 (8)	2903 (8)	7936 (5)	27 (3)
C(16)A	8665 (8)	4289 (8)	5525 (5)	31 (3)	O(11)B	7419 (4)	1653 (4)	9720 (3)	16 (2)
O(17)A	8042 (4)	1916 (4)	5061 (3)	17 (2)	C(12)B	7269 (7)	1247 (8)	10042 (5)	26 (3)
C(18)A	8542 (8)	1971 (8)	5358 (5)	25 (3)	C(13)B	6552 (8)	1000 (8)	10024 (5)	28 (3)
C(19)A	8491 (8)	1363 (8)	5624 (5)	30 (3)	C(14)B	6371 (9)	480 (9)	9700 (6)	37 (4)
C(20)A	8968 (9)	1332 (9)	5967 (6)	38 (4)	C(15)B	5939 (9)	129 (9)	9999 (5)	36 (4)
C(21)A	9028 '0)	559 (10)	5889 (6)	46 (4)	C(16)B	6347 (9)	458 (9)	10319 (5)	35 (4)
C(22)A	8758 (11)	687 (11)	5480 (7)	52 (5)	O(17)B	6859 (5)	2897 (5)	10059 (3)	22 (2)
O(23)A	6026 (5)	1710 (4)	4999 (3)	18 (2)	C(18)B	6312 (8)	2826 (8)	10327 (5)	26 (3)
C(24)A	5457 (7)	1619 (7)	5234 (4)	23 (3)	C(19)B	6276 (8)	3453 (8)	10571 (5)	29 (3)
C(25)A	5500 (8)	938 (8)	5442 (5)	27 (3)	C(20)B	5702 (10)	3462 (10)	10879 (6)	49 (4)
C(26)A	4977 (8)	774 (8)	5753 (5)	33 (3)	C(21)B	5644 (11)	4213 (10)	10801 (6)	49 (4)
C(27)A	5553 (9)	434 (10)	5995 (6)	42 (4)	C(22)B	5993 (10)	4101 (10)	10398 (6)	44 (4)
C(28)A	6054 (8)	830 (8)	5749 (5)	25 (3)	O(23)B	8852 (5)	3299 (4)	10032 (3)	19 (2)
O(29)A	6187 (4)	3098 (4)	4747 (3)	16 (2)	C(24)B	9386 (8)	3269 (8)	10294 (5)	26 (3)
C(30)A	5814 (7)	3425 (7)	5040 (4)	21 (3)	C(25)B	9420 (7)	3922 (7)	10518 (5)	23 (3)
C(31)A	5142 (8)	3661 (7)	4880 (5)	24 (3)	C(26)B	9937 (9)	3896 (9)	10873 (5)	35 (3)
C(32)A	4540 (8)	3156 (8)	4864 (5)	26 (3)	C(27)B	9368 (11)	4218 (11)	11114 (6)	51 (5)
C(33)A	4073 (9)	3772 (9)	4975 (5)	38 (4)	C(28)B	8860 (9)	4025 (9)	10827 (5)	37 (4)
C(34)A	4695 (8)	4128 (8)	5135 (5)	30 (3)	O(29)B	8811 (5)	1946 (5)	9690 (3)	19 (2)
O(35)A	7703 (4)	3725 (4)	4063 (3)	15 (2)	C(30)B	9175 (7)	1573 (7)	9958 (4)	18 (3)
C(36)A	7783 (8)	4425 (8)	3945 (5)	25 (3)	C(31)B	9877 (8)	1368 (8)	9801 (4)	24 (3)
C(37)A	8316 (9)	4452 (9)	3649 (5)	37 (4)	C(32)B	10480 (8)	1844 (8)	9839 (5)	29 (3)
C(38)A	8421 (9)	5131 (9)	3437 (6)	41 (4)	C(33)B	10933 (9)	1195 (9)	9900 (6)	39 (4)
C(39)A	8456 (10)	4731 (11)	3056 (7)	51 (5)	C(34)B	10295 (8)	832 (8)	10019 (5)	29 (3)
C(40)A	8131 (10)	4116 (10)	3251 (6)	43 (4)	O(35)B	7425 (5)	1352 (5)	8903 (3)	19 (2)
O(41)A	6270 (5)	3697 (5)	4020 (3)	23 (2)	C(36)B	7400 (7)	681 (7)	8752 (4)	23 (3)
C(42)A	5897 (8)	3371 (8)	3722 (5)	29 (3)	C(37)B	6971 (8)	685 (8)	8395 (5)	27 (3)
C(43)A	5181 (8)	3370 (8)	3827 (5)	25 (3)	C(38)B	6995 (9)	−8 (9)	8180 (5)	36 (4)
C(44)A	4738 (8)	3212 (8)	3461 (5)	32 (3)	C(39)B	7580 (9)	311 (9)	7914 (6)	38 (4)
C(45)A	4597 (9)	3974 (9)	3412 (5)	39 (4)	C(40)B	7313 (8)	1007 (8)	8043 (5)	32 (3)
C(46)A	4839 (8)	4094 (8)	3835 (5)	31 (3)	O(41)B	8852 (5)	1537 (5)	8948 (3)	24 (2)
O(47)A	6886 (5)	4315 (5)	4641 (3)	20 (2)	C(42)B	9353 (8)	2011 (8)	8854 (5)	31 (3)
C(48)A	6427 (7)	4841 (7)	4542 (5)	23 (3)	C(43)B	9844 (10)	1751 (10)	8555 (6)	44 (4)
C(49)A	6477 (9)	5379 (9)	4843 (5)	37 (4)	C(44)B	9485 (13)	1490 (13)	8191 (8)	67 (6)
C(50)A	7120 (11)	5806 (11)	4876 (7)	54 (5)	C(45)B	10030 (12)	935 (13)	8177 (8)	66 (6)
C(51)A	6677 (11)	6439 (11)	4944 (7)	55 (5)	C(46)B	10162 (10)	1021 (10)	8611 (6)	48 (4)
C(52)A	6080 (11)	6059 (11)	4757 (7)	55 (5)	O(47)B	8218 (5)	705 (5)	9478 (3)	21 (2)
O(53)A	8040 (5)	1597 (5)	4248 (3)	19 (2)	C(48)B	8731 (7)	252 (7)	9358 (4)	21 (3)
C(54)A	8485 (8)	1096 (8)	4367 (5)	28 (3)	C(49)B	8711 (8)	−329 (8)	9634 (5)	27 (3)
C(55)A	8582 (10)	544 (10)	4063 (6)	46 (4)	C(50)B	8108 (10)	−821 (10)	9628 (6)	45 (4)
C(56)A	7942 (9)	196 (9)	3893 (5)	36 (4)	C(51)B	8631 (10)	−1410 (10)	9671 (6)	44 (4)
C(57)A	8259 (10)	224 (10)	3510 (6)	49 (4)	C(52)B	9205 (8)	−937 (9)	9568 (5)	35 (3)
C(58)A	8749 (10)	801 (9)	3657 (6)	42 (4)	O(53)B	6848 (5)	3365 (5)	9275 (3)	22 (2)
O(59)A	8595 (5)	2928 (5)	4320 (3)	23 (3)	C(54)B	6486 (7)	3922 (7)	9409 (4)	20 (3)
C(60)A	9120 (7)	2718 (7)	4064 (4)	24 (3)	C(55)B	6522 (8)	4481 (8)	9121 (5)	28 (3)
C(61)A	9770 (7)	2725 (7)	4272 (4)	23 (3)	C(56)B	7739 (8)	4715 (8)	8963 (5)	30 (3)
C(62)A	10046 (8)	3407 (8)	4432 (5)	28 (3)	C(57)B	6944 (8)	4733 (8)	8552 (5)	31 (3)
C(63)A	10765 (9)	3184 (9)	4318 (5)	35 (3)	C(58)B	6304 (8)	4328 (8)	8690 (5)	30 (3)
C(64)A	10447 (8)	2658 (8)	4026 (5)	26 (3)	O(59)B	6437 (5)	2005 (5)	9214 (3)	21 (2)
O(65)A	6968 (5)	2314 (5)	5517 (3)	23 (2)	C(60)B	5897 (8)	2279 ()	8991 (5)	28 (3)
C(66)A	6650 (7)	2636 (7)	5830 (4)	18 (3)	C(61)B	5327 (9)	2408 (9)	9235 (5)	33 (3)
C(67)A	6989 (8)	2462 (8)	6200 (5)	30 (3)	C(62)B	4922 (9)	1777 (9)	9417 (5)	35 (4)
C(68)A	6709 (9)	2836 (9)	6567 (5)	38 (4)	C(63)B	4295 (10)	2228 (10)	9384 (6)	48 (4)
C(69)A	7426 (9)	2879 (9)	6713 (6)	40 (4)	C(64)B	4635 (11)	2651 (11)	9051 (7)	52 (5)
C(70)A	7677 (8)	2775 (8)	6297 (5)	33 (3)	O(65)B	7999 (5)	2480 (5)	10488 (3)	23 (2)
O(71)A	7110 (5)	803 (5)	4994 (3)	21 (2)	C(66)B	8227 (8)	2075 (8)	10796 (5)	27 (3)
C(72)A	6901 (8)	290 (8)	4731 (5)	25 (3)	C(67)B	7690 (9)	1980 (9)	11096 (6)	38 (4)
C(73)A	7283 (8)	−343 (8)	4817 (5)	32 (3)	C(68)B	7916 (11)	1629 (11)	11474 (6)	51 (5)
C(74)A	7100 (9)	−713 (9)	5200 (5)	36 (4)	C(69)B	7415 (10)	2114 (10)	11689 (6)	48 (4)
C(75)A	6978 (12)	−1351 (12)	4970 (8)	68 (6)	C(70)B	7444 (11)	2571 (11)	11324 (7)	53 (5)
C(76)A	6998 (9)	−956 (9)	4584 (6)	42 (4)	O(17)B	7960 (5)	4074 (5)	10096 (3)	24 (2)
O(77)A	6072 (5)	1550 (5)	4163 (3)	21 (2)	C(72)B	7942 (7)	4680 (7)	9930 (4)	18 (3)

Table IV (Continued)

atom	10^4x	10^4y	10^4z	$10B_{iso}$	atom	10^4x	10^4y	10^4z	$10B_{iso}$
C(73)B	7471 (8)	5247 (8)	10030 (5)	27 (3)	C(78)B	9162 (8)	4181 (8)	9311 (5)	27 (3)
C(74)B	7364 (9)	5367 (9)	10484 (5)	35 (4)	C(79)B	9839 (8)	4132 (8)	9105 (5)	26 (3)
C(75)B	7944 (9)	5915 (9)	10463 (5)	36 (4)	C(80)B	10338 (8)	4654 (8)	9277 (5)	30 (3)
C(76)B	7843 (9)	5943 (9)	10028 (5)	36 (4)	C(81)E	10747 (15)	4043 (15)	9417 (9)	86 (7)
O(77)B	8753 (5)	3618 (5)	9212 (3)	23 (2)	C(82)B	10286 (9)	3533 (9)	9251 (6)	37 (4)

removing the molecule of coordinated alcohol to form a higher symmetry species (see diagram for XII below) which is consistent with the NMR spectroscopic data obtained in solution.
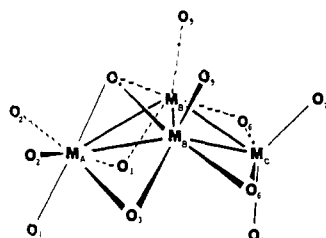
XII

The butterfly cluster now has three types of molybdenum atoms, wingtip, Mo$_A$ and Mo$_C$, and backbone, Mo$_B$. A mirror plane passes through the following atoms: O$_1$, Mo$_A$, O$_4$, Mo$_C$, O$_7$, and O$_8$. The mirror plane then relates the remaining alkoxide ligands to form four pairs of which each methylene group would be diastereotopic. This explanation is consistent with the observation of eight types of alkoxide ligands in solution in the ratio 1:1:1:1:2:2:2:2 with the alkoxide ligands of relative intensity two containing diastereotopic groups.

In order to obtain more information about the structure of these clusters in solution we prepared the isotopically labeled species W$_4$(O*CH$_2$-i-Pr)$_{12}$ where *C = 99% ^{13}C to examine the ultrahigh resolution ^{13}C NMR spectrum of the methylene carbons. We have previously observed[10] that *terminal* alkoxide ligand α-carbon nuclei exhibit a relatively large two-bond ^{183}W–O–^{13}C coupling, e.g., 5.9 Hz in W$_2$(O-t-Bu)$_6$, whereas *bridging* alkoxide ligand α-carbons exhibit two much smaller two-bond ^{183}W–O–^{13}C couplings in the range ∼2–3 Hz. In the case of W$_4$(O*CH$_2$-i-Pr)$_{12}$ there are some marked differences in the magnitudes of the two-bond ^{183}W–O–^{13}C *J* values for the different alkoxide ligands. Of the nondiastereotopic ligands, the former $^2J_{^{183}W–O–^{13}C}$ values are 4.93, ∼4 (slightly obscured by coincident diastereotopic ^{13}C resonances), 6.93, and 1.93 Hz. This would be consistent with three terminal alkoxide ligands and one bridging alkoxide ligand. Of the diastereotopic alkoxide ligands, the methylene resonances with ^{183}W–O–^{13}C couplings of 6.43 and ∼4 Hz are consistent with terminal alkoxide ligands and those with couplings of 3.84 and <3.4 Hz are consistent with bridging alkoxide ligand. These data are not unambiguous, and an absolute distinction between bridging and terminal alkoxide ligands is not possible. However, it seems that the assignments made above are consistent with the structure XII. For example, the nondiastereotopic methylene with the two-bond ^{183}W–O–^{13}C coupling of 1.93 Hz may be assigned to the triply bridging alkoxide ligand. This methylene ^{13}C resonance had ^{183}W satellites that have relatively large intensity (i.e., >14% by comparison with other resonances), although it was not possible to integrate them accurately due to overlap with the central resonance.

The ^{95}Mo NMR spectrum of Mo$_4$(OCH$_2$-i-Pr)$_{12}$ exhibited only a single broad resonance at 2628.4 ppm, downfield of Na$_2$MoO$_4$. Although the spectrum was measured on two separate occasions, it was not possible to resolve any fine structure. This chemical shift is in the region similar to that previously observed for Mo$_2$(OR)$_6$ compounds.[11] No other resonances were observed over

Scheme I

II　　　　　　　　　　　　　XII
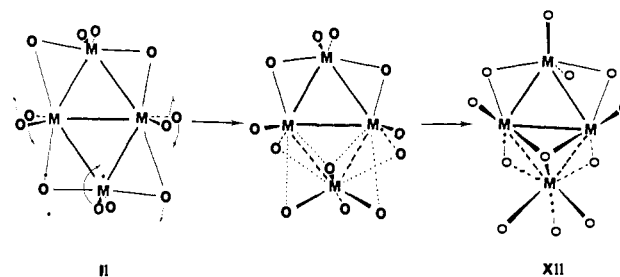
a chemical shift range of 3700–2200 ppm.

Comments of Cluster Bonding. This new class of M$_4$(OCH$_2$R)$_{12}$ compounds are members of a growing series of 12e$^-$ tetranuclear metal clusters. Although only two structurally different examples of homoleptic metal alkoxide tetranuclear 12e$^-$ clusters have been unequivocally characterized thus far,[4,5] there exist examples that contain heteroligands, especially halides.[13] These include a distorted M$_4$ rhombus in W$_4$(μ-O-i-Pr)$_4$(O-i-Pr)$_8$, II, a square M$_4$ moiety in Mo$_4$(μ-O-i-Pr)$_8$Cl$_4$, XIII, and a symmetrical C_{2v} M$_4$ butterfly in Mo$_4$(μ_3-O-i-Pr)$_2$(μ-O-i-Pr)$_4$(O-i-Pr)$_2$X$_4$, where X = Br and I, shown in XIV below.
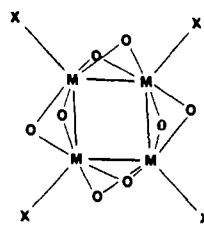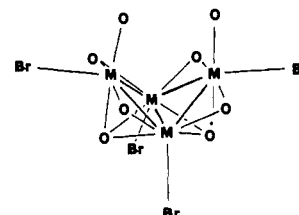
XIII　　　　　　　　　　　　XIV

Perhaps the most remarkable feature of the present cluster system, XII, is the arrangement of the alkoxide ligands to form a cluster in which one metal atom is octahedrally coordinated at the expense of the coordination environment of the other metal atoms. The thermodynamic driving force for an octahedral environment is well-known in reduced molybdenum and tungsten oxides,[14] polyoxoanion systems,[3] and in the structures of metal alkoxides.[15] There are a variety of ways the cluster bonding electrons may be distributed about the butterfly cluster. By simply assuming each metal center of XII has retained a +3 oxidation could lead to metal–metal bonding configuration similar to that of II, with alternating single and double metal–metal bonds and a small interaction between the backbone metal atoms. This is clearly *not* the case. In contrast to all previously characterized 12-electron alkoxides of Mo or W, the present class shows a distinct asymmetry with respect to metal–alkoxide and metal–metal bonding. A mixed-valence structure is represented in XV below that is consistent with the idea that Mo(A) is in the +4 oxidation state and forms only metal–metal single bonds to the

(9) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, 23.

(10) Allerhand, A.; Maple, S. R.; Chisholm, M. H.; Hampden-Smith, M. J., results to be published.

(11) Young, C. G.; Kober, E. M.; Enemark, J. H. *Polyhedron* **1987**, 6, 255. Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, 68, 169.

(12) Chisholm, M. H. *Polyhedron* **1983**, 2, 681 and references therein.

(13) Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, 104, 4389. Chisholm, M. H.; Clark, D. L.; Folting, K.; Errington, R. J.; Huffman, J. C. *Inorg. Chem.* **1988**, 27, 2071.

(14) McCarley, R. E. *ACS Symp. Ser.* **1983**, 211, 273.

(15) Bradley, D. C.; Mehrotra, R. C.; Gaur, P. D. In *Metal Alkoxides*; Academic Press: 1978.
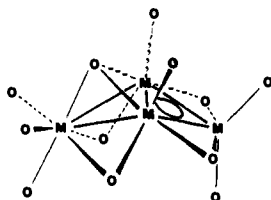
XV

backbone molybdenum atoms. The remaining eight cluster electrons are shared, or delocalized, over the other triangle to form M–M bonds of bond order one and one-third. This is the first time we have seen an intramolecular valence disproportionation in an alkoxide cluster of molybdenum and tungsten although a number of mixed valent dinuclear alkoxides are known, e.g., $Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$.[16]

The structure depicted by XII can be related to the rhomboidal $W_4(O\text{-}i\text{-}Pr)_{12}$ structure, Il. Indeed, the local geometry about Mo_C in XII (Mo(3) in Figure 1) is the same as that of the wingtip tungsten atoms in II. The M_4O_{12} unit of Il can easily be transformed to that of XII by the opening and closing of various bridges as shown in Scheme I.

The 12 electrons in M_4 alkoxide clusters are accommodated in M–M bonds in a variety of geometries. In the square (D_{4h}) $Mo_4(\mu\text{-}O\text{-}i\text{-}Pr)_8Cl_4$ molecule the four Mo–Mo distances of 2.38 Å are indicative of some M–M multiple bond order, while in the C_{2v} Mo_4 butterfly $Mo_4(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_2Br_4$ there are four Mo–Mo distances of 2.51 Å (av) and one slightly shorter distance between the backbone Mo atoms, 2.48 Å. This is consistent with the slightly greater M–M bonding expected for backbone–backbone interactions based on MO calculations.[17] It is also worth noting that a number of tetranuclear halide clusters of molybdenum have been prepared by McCarley and co-workers with varying cluster electron counts ranging from 12 to 16.[18] However, in none of these clusters is there such asymmetry with respect to ligand-to-metal bonding.

Application of Bond Length–Bond Order Relationships. Nonlinear bond strength–bond length relationships have been proposed for element–oxygen bonds and find use as independent checks on certain solid-state structural preferences, as a means of (i) detecting secondary bonding effects and (ii) determining the valency distribution in mixed-valence compounds.[19] The bond strength–bond length relationships that have been developed for molybdenum and oxygen find profitable use for both coordination compounds and solid-state oxides with and without metal–metal bonds.[20] Specifically, these have been used by McCarley[21] in studies on lower valent molybdenum oxides such as $NaMo_4O_6$ and $Ca_{5.45}Mo_{18}O_{32}$.

The equation relating Mo–O bond lengths and valency of Mo is

$$S(\text{Mo–O}) = [d(\text{Mo–O})/1.882]^{-6.0}$$

where S = bond strength in valency units and $d(\text{Mo–O})$ = observed bond distance in Å. The value 1.882 Å is taken to represent a standard single bond distance between molybdenum and oxygen. The sum of the values of $S(\text{Mo–O})$ about each metal represent the formal oxidation state of that molybdenum atom. For the structurally characterized compound $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}$-$(HOCH_2\text{-}t\text{-}Bu)$, there are two crystallographically similar but independent molecules in the unit cell. As is seen in Table V the

(16) Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 2514.

(17) Bursten, B. E.; Clark, D. L.; Chisholm, M. H. *Inorg. Chem.* **1988**, *27*, 2084.

(18) Aufdembrink, B. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2474. Stensvad, S.; Helland, B. J.; Babich, M. W.; Jacobson, R. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 6257.

(19) Brown, I. D.; Shannon, R. D. *Acta Crystalogr.* **1973**, *A29*, 266.

(20) Bart, J. C. J.; Ragaini, V. *Inorg. Chim. Acta.* **1979**, *36*, 261. Brown, I. D.; Wu, K. K. *Acta Crstallogr.* **1976**, *B32*, 5105.

(21) McCarley, R. E. *Polyhedron* **1986**, *5*, 51. See, also: Cheetham, A. K., et al. *J. Am. Chem. Soc.* **1988**, *110*, 3295.

Table V. Summary of Bond Length–Bond Strength Calculations and the Assignment of Oxidation States in $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}(HOCH_2\text{-}c\text{-}Bu)$

bond	valency units $s(\text{Mo–O})$	
	molecule A	molecule B
Mo(1)–O(5)	0.502 (13)	0.506 (13)
Mo(1)–O(11)	0.602 (16)	0.615 (16)
Mo(1)–O(29)	0.549 (14)	0.520 (15)
Mo(1)–O(35)	0.767 (22)	0.765 (24)
Mo(1)–O(41)	0.901 (35)	0.924 (29)
Mo(1)–O(47)	0.672 (18)	0.686 (21)
$\Sigma s[\text{Mo(1)–O}]$ =	3.99 (2)	4.02 (2)
Mo(2)–O(5)	0.552 (14)	0.532 (14)
Mo(2)–O(11)	0.593 (16)	0.580 (15)
Mo(2)–O(17)	0.511 (13)	0.498 (14)
Mo(2)–O(53)	0.793 (23)	0.860 (2)
$\Sigma s[\text{Mo(2)–O}]$ =	2.45 (2)	2.47 (2)
Mo(3)–O(17)	0.658 (18)	0.676 (20)
Mo(3)–O(23)	0.587 (16)	0.560 (15)
Mo(3)–O(65)	0.841 (27)	0.901 (29)
Mo(3)–O(71)	1.019 (3)	1.006 (33)
$\Sigma s[\text{Mo(3)–O}]$ =	3.10 (2)	3.14 (2)
Mo(4)–O(5)	0.434 (11)	0.504 (13)
Mo(4)–O(23)	0.511 (13)	0.511 (15)
Mo(4)–O(29)	0.643 (17)	0.563 (19)
Mo(4)–O(770)	0.879 (28)	0.887 (28)
$\Sigma s[\text{Mo(4)–O}]$ =	2.47 (2)	2.54 (2)

formal oxidation for Mo(1) is determined to be +4.0 for both molecules, while the other wing-tip Mo atom, Mo(3), that is coordinated to four oxygen atoms, has an oxidation state of +3.1(1). The backbone Mo atoms Mo(2) and Mo(4) are effectively +2.5 each, although when the Mo–O bond of distance 2.342 (10) to the alcohol ligand is included the oxidation state of Mo(2) is increased by +0.25 valence units.

Therefore, using the existing bond length–bond strength relationships for molybdenum and oxygen, we find a numerical method for establishing the nature of the charge delocalization in the clusters of structural type XII. The formal oxidation states +4, +3, and two +2.5 give a central M_4^{12+} core, a 12-electron cluster in which the oxidation states of the wingtip metal atoms are greater than those of the backbone.

It is interesting to apply the same type of calculation to the rhomboidal $W_4(O\text{-}i\text{-}Pr)_{12}$ cluster of structural type Il, and when we make the assumption that W–O and Mo–O bond distances are equivalent, which is good to within one or two hundredths of an Å, we find this gives +3.5 and +2.5 for the wingtip and backbone W atoms, respectively.

McCarley[21] has used the empirical formula

$$n_e(\text{M–M}) = \Sigma n(\text{M–M})$$

to determine the number of electrons used by a given metal in a cluster to form M–M bonds. A single bond radius $d(\text{Mo–Mo})$ was taken to be 2.614 Å. By using this procedure the electrons used in M–M bonding in $Mo_4(OCH_2\text{-}t\text{-}Bu)_{12}(HOCH_2\text{-}t\text{-}Bu)$ are for Mo(1) 1.76 and Mo(3) 2.66 and by the backbone Mo atoms, Mo(2) 3.57 and Mo(4) 3.62. Again this formalism of counting electrons provides a complementary picture of M–M bonding within the 12-electron Mo_4^{12+} core. Using the same single bond distance for a W–W bond gives 2.78 and 2.13 electrons available for M–M bonding by the backbone and wingtip W atoms, respectively, in $W_4(O\text{-}i\text{-}Pr)_{12}$.

Mechanism of Cluster Formation. We have recently described the base-free alcoholysis reactions of $W_2(O\text{-}t\text{-}Bu)_6$ that lead to the formation of new $W_2(OR)_6$ species (where R = $CH_2\text{-}t\text{-}Bu$, Cy, $i\text{-}Pr$).[22] Whereas solutions of $W_2(O\text{-}i\text{-}Pr)_6$ exist in equilibrium

(22) Chisholm, M. H.; Hampden-Smith, M. J. National Meeting of the American Chemical Society, New Orleans, LA, September 1987; Abst. Inorg. 44. Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* submitted for publication.
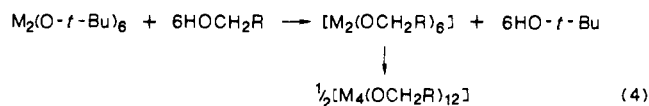
12-Electron Mo and W Alkoxide Clusters

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with the corresponding cluster, $W_4(O\text{-}i\text{-}Pr)_{12}$ (see eq 1), $W_2(OCy)_6$ was found to be completely inert with respect to cluster formation. This has been attributed to the large steric demand of the cyclohexoxide ligand compared to isopropoxide. By further reducing the steric demands of the alkoxide ligands we had expected to obtain either higher aggregates of M^{III} alkoxide clusters (hexanuclear or octanuclear for example) or examples of new structural types of existing nuclearity. Oxidative addition of alcohol to form higher oxidation state metal alkoxide clusters is unlikely because these processes are base promoted.[23] Since no evidence for new dinuclear species $M_2(OCH_2R)_6$ was obtained in the alcoholysis reactions according to eq 2, we sought to determine if dinuclear species were present in such solutions. Isobutyl alcohol $(HOCH_2\text{-}i\text{-}Pr)$ was added to a hexane solution of $W_2(O\text{-}t\text{-}Bu)_6$ containing a large excess of PMe_3. The solution immediately turned dark red/brown, the typical color of $W_2(OR)_6L_2$ species, in contrast to the deep purple color of $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$. On working up the solution, $W_2(OCH_2\text{-}i\text{-}Pr)_6(PMe_3)_2$ was isolated, and no evidence was obtained for any cluster formation. In an attempt to isolate an example of a Lewis base-free dinuclear species $M_2(OCH_2R)_6$, the target molecule $Mo_2(OCH_2Cy)_6$ was chosen for two reasons: (i) molybdenum(III) alkoxides are more inert with respect to cluster formation than their tungsten analogues and (ii) the rate of cluster formation is reduced as the steric demands of the alkoxide ligands increase.

Attempts to isolate pure $Mo_2(OCH_2Cy)_6$ by performing the alcoholysis reaction, eq 3, at low temperature (-78 °C) were unfruitful because of the very high solubility of these complexes and the low volatility of the alcohols involved. The yellow solutions, probably containing the dinuclear species, generated at low temperature turned green on workup, and only the cluster species were isolated. A second approach was taken employing the initial formation of a Lewis base-stabilized dinuclear complex. We have previously used this approach to prepare $W_2(O\text{-}i\text{-}Pr)_6$,[4] where a suitable Lewis base was NMe_3. Treatment of a solution of $Mo_2(NMe_2)_6$ with cyclohexylmethanol at 0 °C in the presence of a large excess of NMe_3 resulted in a deep red color and after concentrating the solution and cooling overnight, the red-brown crystals of $Mo_2(OCH_2Cy)_6(NMe_3)_2$ were obtained. On dissolving these crystals in benzene-d_6 solution at room temperature, the ^1H NMR spectrum (500 MHz, 25 °C) obtained was consistent with a dinuclear species with coordinated NMe_3 and rapid rotation about the metal–metal triple bond. However, on standing for a period of about 4 h, the compound completely reacted to form the $Mo_4(OCH_2Cy)_{12}$ cluster together with free NMe_3, as shown by ^1H NMR spectroscopy. It appears that in the absence of an *excess* of Lewis base, the Lewis base free dinuclear compound is long-lived enough for successful dimerization to occur, see eq 3.

$$Mo_2(OCH_2Cy)_6(NMe_3)_2 \ \rightleftharpoons \ Mo_2(OCH_2Cy)_6 \ + \ 2NMe_3$$
$$\downarrow$$
$$Mo_4(OCH_2Cy)_{12} \qquad (3)$$
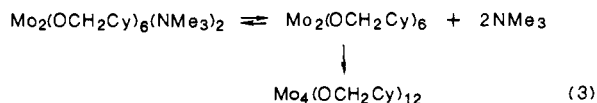
A crystalline sample (32 mg) of $Mo_2(OCH_2Cy)_6(NMe_3)_2$ was placed in a reaction vessel which was evacuated and heated in an oil bath at 70 °C over 5 h under a dynamic vacuum in order to remove any liberated NMe_3. [In the solid state, the rate of cluster formation is likely to be a lot slower than in solution.] During this time the dark solid lightened considerably, and when it had cooled it was dissolved in toluene-d_8 at -78 °C and sealed under nitrogen. A ^1H NMR spectrum taken at -40 °C showed only the presence of the $Mo_4(OCH_2Cy)_{12}$ cluster, and there was no evidence of any resonance due to dissociated NMe_3. These trapping experiments using Lewis base ligands provide convincing evidence that $M_2(OCH_2R)_6$ species are first formed in the alcoholysis of $M_2(O\text{-}t\text{-}Bu)_6$ compounds as depicted below.

It has already been noted that the cluster species formed from the dimerization of $W_2(O\text{-}i\text{-}Pr)_6$ has a different structure from those in the present study. The question therefore arises, are the

$$M_2(O\text{-}t\text{-}Bu)_6 \ + \ 6HOCH_2R \ \longrightarrow \ [M_2(OCH_2R)_6] \ + \ 6HO\text{-}t\text{-}Bu$$
$$\downarrow$$
$$\tfrac{1}{2}[M_4(OCH_2R)_{12}] \qquad (4)$$

two clusters II and XII formed mutually exclusively or are they directly related (i.e., one formed from the other). Since no other ^1H NMR resonances were observed in the conversion of Mo_2-$(OCH_2Cy)_6(NMe_3)_2$ to $Mo_4(OCH_2Cy)_{12}$, it can be assumed that if an intermediate species is formed, it is (a) formed in concentrations below the sensitivity of NMR spectroscopy and/or (b) is rapidly converted to the cluster of geometry XII. In order to examine the possibility that upon the coupling of two Mo_2-$(OCH_2R)_6$ molecules the *first formed* cluster species might be analogous to II, we conducted an independent alcoholysis reaction involving $W_4(O\text{-}i\text{-}Pr)_{12}$ (II). A 50:50 toluene–isobutyl alcohol mixture was added to pure $W_4(O\text{-}i\text{-}Pr)_{12}$, ($W_2(O\text{-}i\text{-}Pr)_6$ free) at 0 °C such that a solution was formed that was identical in concentration $[W_4(O\text{-}i\text{-}Pr)_{12}]$ with those previously used to measure the kinetic data for cluster formation and dissociation.[4] After stirring the reactants for only 0.5 h at 0 °C, the volatile components were removed, and the whole of the dry residue dissolved in benzene-d_6. At room temperature ^1H NMR spectrum indicated only the presence of $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$.

Since, under these conditions the extent of dissociation of $W_4(O\text{-}i\text{-}Pr)_{12}$ to $2W_2(O\text{-}i\text{-}Pr)_6$ is negligible, the new butterfly tetranuclear cluster XII has been formed *directly* from the previously known rhomboidal cluster unit II. Thus, if the dimerization of $Mo_2(OCH_2R)_6$ compounds proceeds first via a planar rhomboidal cluster analogous to II it would subsequently rapidly rearrange to the new butterfly cluster type XII as shown in eq 5 below. However, we cannot establish that a rhomboidal cluster of type II is actually a precursor to XII in a reaction starting from two $M_2(OCH_2R)_6$ ($M\equiv M$) molecules.

$$5 \quad 2M_2(OCH_2R)_6 \ \rightarrow \quad \rightarrow \quad (5)$$
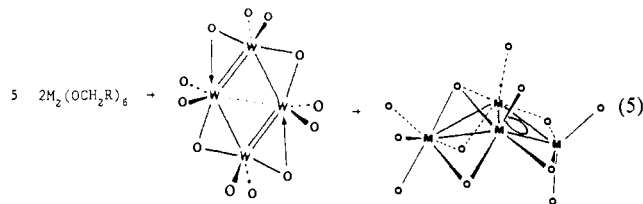
Conclusions

The work describes a new class of $12e^-$ tetranuclear metal alkoxide clusters $M_4(OCH_2R)_{12}$ that have been prepared in high yield by simple alcoholysis reactions between $M_2(O\text{-}t\text{-}Bu)_6$ and the appropriate primary alcohols $(HOCH_2R)$. The cluster compounds are the first examples of homoleptic alkoxide clusters that exist for both molybdenum and tungsten. The solid-state structure of $Mo_4(OCH_2\text{-}c\text{-}Bu)_{12}(HOCH_2\text{-}c\text{-}Bu)$ reveals that an interesting ligand redistribution has taken place on formation of these compounds. One metal atom has achieved an octahedral geometry at the expense of the coordination environment of the remaining metal atoms. This, we hope, will allow us a unique opportunity to examine the mechanism of activation of small molecules by tetranuclear metal alkoxide clusters that may serve as models for fragments of reduced metal oxides. Note that three of the metal atoms in $M_4(OR)_{12}$ compounds of type XII are coordinatively unsaturated, and the ability of the cyclobutylmethoxide cluster to coordinate a single molecule of cyclobutylmethanol testifies to the metal atoms desire to bind donor ligands. The presence of the M–M bonding electrons should allow for π-acid ligands to bind, and the presence of the tetranuclear metal center provides for template or ensemble effects.[24] It will be particularly interesting to compare the reactivity of these $M_4(OCH_2R)_{12}$ compounds with their dinuclear $M_2(OR)_6$ counterparts toward activation of carbon monoxide and alkynes.

Finally we note that the structures of the homoleptic alkoxides of molybdenum and tungsten of empirical formula $M(OR)_3$ differ from those seen for $M = Al$ and Cr,[15] in that in addition to the

(23) Chisholm, M. H.; Huffman, J. C.; Smith, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 202.

(24) Shriver, D. F.; Sailor, M. J. *Acc. Chem. Res.* **1988**, *21*, 374.

desire to maximize M–O bonding, the metal atoms (M = Mo and W) also want to maximize M–M bonding. Hence for $[M(OR)_3]_n$, where $n = 2$, the ethane-like $O_3M \equiv MO_3$ geometry, I, with the M–M bonding configuration $\sigma^2\pi^4$, is preferred over the $[Al(OR)_3]_2$ structure involving two fused MO_4 tetrahedra. For $n = 3$, there is no known example for M = Mo or W—perhaps not surprisingly since $n = 3$ yields nine electrons available for M–M bonding which would necessarily lead to paramagnetism and would not maximize M–M bonding. For $n = 4$, there are 12 cluster electrons that can be accommodated in a variety of structures as seen for $W_4(O-i-Pr)_{12}$, 11, $Mo_4Cl_4(O-i-Pr)_8$, XIII, and $Mo_4Br_4(O-i-Pr)_8$, XIV, and in the new homoleptic class $M_2(OCH_2R)_{12}$, XII. The preference for XII over structures II, XIII, and XIV appears to represent a situation wherein one metal atom achieves the maximum number of M–O bonds, namely six for M = W and Mo, while the other three metal atoms maximize their M–M bonding at the expense of M–O bonding.

Competitive Intramolecular [4 + 2] Cycloaddition and Tandem [2 + 2] Cycloaddition/[3,3]-Sigmatropic Rearrangement Sequence of Allenyl 3-Vinyl-2-cyclohexenyl Ethers: Evidence for Switching of the Reaction Pathway by the Substituent Effects[†]

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Abstract: The base-catalyzed intramolecular cycloaddition reactions (*t*-BuOK, *t*-BuOH, 83 °C) of variously substituted propargyl 3-vinyl-2-cyclohexenyl ethers have been investigated. The reaction proceeded smoothly via the initial isomerization to the corresponding allenyl ethers followed by the intramolecular Diels–Alder ([4 + 2]) reaction and/or tandem [2 + 2] cycloaddition, [3,3]-sigmatropic rearrangement ([2 + 2] + [3,3]) depending upon the substitution pattern. The C(2) substituent showed a remarkable switching effect. While the compounds bearing no substituents at C(2) (**1a,b, 21, 22**) underwent selectively the [4 + 2] cycloaddition, the 2-substituted compounds (**1c,d**) performed exclusively the tandem [2 + 2], [3,3] reactions. On the other hand, the C(6) substituents also influenced the reaction pathway in a unique manner. While the reaction of the 1,6-trans compounds (**15, 20**) gave exclusively the [2 + 2] + [3,3] products, the similar reaction of the 1,6-cis isomers (**14, 19**) resulted in a concomitant formation of [4 + 2] and [2 + 2] + [3,3] products. In the latter case, the allene intermediates (**36, 37**) could be isolated. The structure–reactivity relationship in the intramolecular cycloadditions of the allenyl ethers was discussed in detail.

The ability of allenes to undergo either inter- or intramolecular cycloaddition reactions with various unsaturated functionalities provides a convenient route for the construction of complex ring systems.[2] The intramolecular Diels–Alder reaction utilizing appropriate allenic dienophiles has proved to be an extraordinarily useful synthetic tool because of unusual facilitation of cycloaddition as well as a high degree of stereochemical control due to the unique geometry of allene molecules.[3-10]

Recently, we have reported a remarkable substituent effect in the intramolecular cycloaddition reaction of allenyl 3-vinyl-2-cyclohexenyl ethers (**2**) prepared in situ by the base-catalyzed

rearrangement of the corresponding propargyl ethers **1** (Scheme I).[7] The key feature of the substituent effect is switching of the

(1) (a) Kyushu University. (b) Shionogi & Co., Ltd.
(2) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley, New York, 1984.
(3) Hayakawa, K.; Yodo, M.; Ohsuki, S.; Kanematsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6735.
(4) (a) Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Lett.* **1985**, *26*, 2689. (b) Yamaguchi, Y.; Hayakawa, K. *J. Chem. Soc., Chem. Commun.* **1987**, 515. (c) Yamaguchi, Y.; Yamada, H.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1987**, *52*, 2040.
(5) (a) Hayakawa, K.; Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 1837. (b) *Ibid.* **1987**, *28*, 5895.
(6) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 947.