Synthesis and Characterization of Bi- and Trinuclear Molybdenum Carbonyl Compounds Obtained by Ligand Exchange Reactions of $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$

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The complex $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (**1**) has been synthesized by adding the photochemically generated $Mo(CO)_5THF$ adduct to a 6-fold excess of Et_4NOH in methanol. Complex **1** has been shown to undergo ligand exchange reactions at room temperature in the presence of alcohols more acidic than methanol, yielding binuclear complexes $[Et_4N]_3[Mo_2(CO)_6(OR)_3]$ or trinuclear complexes $[Et_4N]_3[Mo_3(CO)_9(OR)_3]$ depending on the alcohol used. The exchanges for the aromatic alcohols 4-aminophenol (**2**), 3-hydroxypyridine (**3**), 3-cyanophenol (**4**), and 4-cyanophenol (**5**) and the diols ethylene glycol (**6**) and 1,3-propanediol (**7**) were studied. These complexes have been characterized by infrared and ^1H and ^{13}C NMR spectroscopy. Complexes **1**, **2**, **5**, and **6** were also structurally characterized by X-ray crystallography.

Introduction

In the past two decades several group 6 polynuclear carbonyl complexes of general formula $[W_2(CO)_8(OR)_2]^{-2}$, $[M_2(CO)_6(OR)_3]^{-3}$ (M = Mo, W), and $[M_4(CO)_{12}(OR)_4]^{-4}$ (M = Cr, Mo, W) have been isolated and structurally characterized.[1−9] In these complexes the metal centers are bridged by either hydroxide, alkoxide, or aryloxide ligands. For example, in the tetraanion $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{-4}$ which possesses a cubane-like structure,[8] the $Cr(CO)_3$ fragments are held together by triply bridging methoxide groups.

In this family of compounds the occurrence of a metal−metal bond is seldom found; one unique example is observed in the complex $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$, whose structure contains a W−W bond, based on the reported bond length (2.939 Å) and the number of electrons required by the effective atomic number rule (EAN).[9] Even when compounds of this nature present unique features, there have been only a few attempts at studying their reactivities. Complexes of formula $[Me_4N]_3[M_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$ (M = Mo, W) have been used as building blocks for the generation of heteronuclear clusters in reactions with Ph_3PAu^+ and Bi^+.[10,11]

While there are a few examples of zerovalent Mo polynuclear complexes that contain a Mo−Mo bond,[12−15] there have not been any structural reports for alkoxide complexes containing a Mo−Mo bond. In this paper we extend our studies of the ligand exchange reactions of zerovalent group 6 metal[16] compounds to molybdenum and present the synthesis and characterization of the novel trinuclear compound $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (**1**), which contains a Mo−Mo bond. The reactivity of this complex in ligand substitution reactions with several different alcohols has been studied. The ligand substitution reactions proceed provided the incoming alcohol is more acidic than the afforded methanol, yielding binuclear complexes $[Et_4N]_3[Mo_2(CO)_6(OR)_3]$ or trinuclear complexes $[Et_4N]_3[Mo_3(CO)_9(OR)_3]$, which retain the Mo−Mo bond, depending on the nature of the alcohol used.

Experimental Section

General Considerations. All reactions were carried out under air-free conditions in an argon-filled gloved box or using standard Schlenk techniques. THF and diethyl ether were freshly distilled from sodium/benzophenone ketyl, and acetonitrile was freshly distilled from calcium hydride. All other reagents were purchased from Aldrich Chemical Co. or Sigma Chemical Co. and were used as received. Photolysis reactions were carried out with a 350 W mercury vapor lamp purchased from Ace Glass Inc. Infrared spectra were recorded on a

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Table 1. Crystal Data, Data Collection and Structure Refinement for 1, 2, 5, and 6

	1	**2**	**5**	**6**
empirical formula	$C_{36}H_{69}Mo_3N_3O_{12}$	$C_{50}H_{81}Mo_2N_7O_9$	$C_{53}H_{75}Mo_2N_7O_9$	$C_{78}H_{150}Mo_6N_6O_{30}$
fw	1023.76	1116.10	1146.08	2227.68
temperature, K	110(2)	293(2)	293(2)	110(2)
wavelength, Å	0.71073			
cryst syst	tetragonal	orthorhombic	orthorhombic	monoclinic
space group	$P4_2/ncm$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
unit cell dimens	$a = 11.7204(9)$ Å $b = 11.7204(9)$ Å $c = 31.957(4)$ Å $V = 4389.9(8)$ Å^3 $Z = 4$	$a = 11.8918(8)$ Å $b = 17.5341(12)$ Å $c = 26.049(2)$ Å $V = 5431.6(6)$ Å^3 $Z = 4$	$a = 15.089(3)$ Å $b = 19.243(2)$ Å $c = 19.329(3)$ Å $V = 5612.1(13)$ Å^3 $Z = 4$	$a = 10.039(4)$ Å $b = 44.65(2)$ Å $\beta = 90.14(2)$ $c = 21.756(8)$ Å $V = 9752(6)$ Å^3 $Z = 4$
density (calcd), Mg/m^3	1.549	1.365	1.356	1.517
abs coeff, mm^{-1}	0.903	0.520	0.505	0.824
cryst size, mm	0.34 × 0.23 × 0.19	0.35 × 0.30 × 0.20	0.52 × 0.25 × 0.19	0.25 × 0.23 × 0.15
θ range for data collection, deg	2.54 to 31.95	1.95 to 28.33	1.71 to 25.08	0.94 to 23.34
index ranges	$-16 \le h \le 17$ $-17 \le k \le 12$ $-47 \le l \le 35$	$-15 \le h \le 14$ $-21 \le k \le 22$ $-34 \le l \le 19$	$-2 \le h \le 18$ $0 \le k \le 22$ $-1 \le l \le 23$	$-10 \le h \le 6$ $-48 \le k \le 49$ $-23 \le l \le 24$
no. of reflns collected	59 326 [R(int) = 0.0428]	34 195 [R(int) = 0.0658]	5903 [R(int) = 0.0120]	36 294 [R(int) = 0.0484]
no. of ind reflns	4036 [2676 obs, $I > 2\sigma(I)$]	12 535 [8751 obs, $I > 2\sigma(I)$]	5761 [4790 obs, $I > 2\sigma(I)$]	12 531 [11 365 obs, $I > 2\sigma(I)$]
abs corr	SADABS	SADABS	Integration	SADABS
refinement	full-matrix least-squares on F^2			
no. of data/restraints/ params	4036/10/191	12535/3/682	5761/0/642	12531/164/1191
goodness-of-fit on F^2	1.085	1.015	1.070	1.030
final R indices (obs data)	R1 = 0.0622 wR2 = 0.1258	R1 = 0.0590 wR2 = 0.1403	R1 = 0.0494 wR2 = 0.1031	R1 = 0.0545 wR2 = 0.1404
R indices (all data)	R1 = 0.0944 wR2 = 0.1356	R1 = 0.0870 wR2 = 0.1541	R1 = 0.0659 wR2 = 0.1088	R1 = 0.0592 wR2 = 0.1445
abs structure param		−0.08(4)	−0.09(6)	
largest diff peak and hole, e/Å^3	0.915 and −1.407	2.193 and −0.474	0.549 and −0.380	1.890 and −0.657

ThermoMattson IR300 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer and referenced to the residual solvent peaks. When possible, ^{13}C assignments of the ligands were made by comparison with referenced shifts for the free ligands.[17] Solvent trace impurities in the ^{1}H and ^{13}C NMR spectra were assigned by comparison with referenced shifts for the solvents.[18]

Synthesis. Synthesis of $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (1). Method A. $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ was synthesized by the reaction of $Mo(CO)_5THF$ (produced by photolysis of 0.30 g of $Mo(CO)_6$ in 60 mL of THF) with a 6-fold excess of Et_4NOH 25% (w/w) methanol solution. Stirring of the solution for 16 h led to the precipitation of **1** as a yellow solid. After removing the solvent, the compound was washed three times with 20 mL of THF and dried under vacuum for 2 h, yielding 0.276 g (71%).

Method B. A 6-fold excess of 25% (w/w) Et_4NOH in methanol was added to a solution of $Mo(CO)_6$ (0.30 g, 1.1 mmol) in 20 mL of THF. The resulting solution was refluxed for 2 h, producing a yellow precipitate of **1**. After cooling to room temperature, the solvent was removed via cannula, and the solid obtained was washed three times with 20 mL of THF and dried under vacuum for 2 h. Yield: 0.303 g (77%). IR (cm^{-1}): CH_3CN ν (C−O) 1901 (w), 1870 (vs), 1757 (s), 1732 (s). ^{1}H NMR (CD_3CN): δ 4.08, 3.45 (s, s, 3H, 6H, OCH_3), 3.21 (m, 24H, $(CH_3CH_2)_4N$), 1.22 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 235.5, 235.4 (CO), 68.9, 66.7 (OCH_3), 52.8 ($(CH_3CH_2)_4N$), 7.5 ($(CH_3CH_2)_4N$).

General Synthesis of $[Et_4N]_3[Mo_2(CO)_6(OR)_3]$ (OR = 4-$OC_6H_4NH_2$ (2), 3-OC_5H_4N (3), 3-OC_6H_4CN (4), 4-OC_6H_4CN (5)). Complex **1** (0.100 g, 0.10 mmol) was dissolved in CH_3CN (20 mL), and a ROH solution (0.45 mmol in 15 mL of CH_3CN) was added. After stirring at room temperature, the solvent was reduced in vacuo to approximately 10 mL. The compound was precipitated from the resulting solution by addition of 60 mL of diethyl ether. The solid obtained, $[Et_4N]_3[Mo_2(CO)_6(OR)_3]$, was washed twice with 30 mL of THF and dried under vacuum for 2 h. Complexes **3**, **4**, and **5** were stirred for only 8 h, and complex **2** was stirred for 24 h. Complex **2** is light sensitive, decomposing in solution, but all the other complexes are stable in solution under inert atmosphere conditions. During the reaction the four-band pattern of the starting material slowly disappears and the two-band pattern of the product appears in the IR spectrum; no discernible intermediates are observed.

$[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4NH_2)_3]$ (2): violet powder; yield 0.105 g (67%). IR (cm^{-1}): CH_3CN ν(C−O) 1863 (s), 1724 (vs). ^{1}H NMR (CD_3CN): δ 7.29, 6.63, 6.50, 6.37 (d, d, d, d, 4H, 2H, 2H, 4H, $OC_6H_4NH_2$), 2.99 (m, 24H, $(CH_3CH_2)_4N$), 1.08 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 234.2 (CO), 163.5 ($OCC_5H_4NH_2$), 134.8 ($OC_5H_4CNH_2$), 121.2, 115.8 ($OCC_4H_4CNH_2$), 52.6 ($(CH_3CH_2)_4N$), 7.5 ($(CH_3CH_2)_4N$).

$[Et_4N]_3[Mo_2(CO)_6(3\text{-}OC_5H_4N)_3]$ (3): yellow powder; yield 0.089 g (59%). IR (cm^{-1}): CH_3CN ν(C−O) 1874 (s), 1737 (vs). ^{1}H NMR (CD_3CN): δ 8.73, 7.69, 7.58, 6.94 (m, m, m, m, 3H, 3H, 3H, 3H, OC_5H_4N), 3.02 (m, 24H, $(CH_3CH_2)_4N$), 1.09 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 233.5 (CO), 165.5 (OCC_4H_4N), 145.1−123.2 (OCC_4H_4N), 52.7 ($(CH_3CH_2)_4N$), 7.4 ($(CH_3CH_2)_4N$).

$[Et_4N]_3[Mo_2(CO)_6(3\text{-}OC_6H_4CN)_3]$ (4): yellow powder; yield 0.108 g (67%). IR (cm^{-1}): CH_3CN ν(C−O) 1877 (s), 1742 (vs); ν(C−N) 2222 (s). ^{1}H NMR (CD_3CN): δ 7.78, 7.13, 6.70 (m, m, m, 6H, 3H, 3H, OC_6H_4CN), 3.03 (m, 24H, $(CH_3CH_2)_4N$), 1.10 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 233.3 (CO), 170.0 (OCC_5H_4CN), 129.6−117.3 (OCC_5H_4CN), 111.5 (CN) 52.7 ($(CH_3CH_2)_4N$), 7.4 ($(CH_3CH_2)_4N$).

$[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4CN)_3]$ (5): yellow powder; yield 0.097 g (60%). IR (cm^{-1}): CH_3CN ν(C−O) 1880 (s), 1747 (vs);

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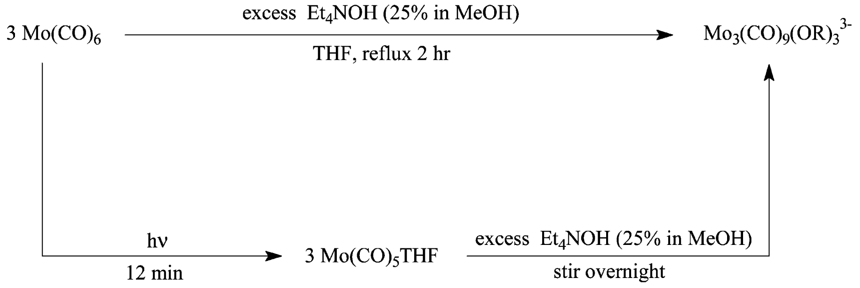
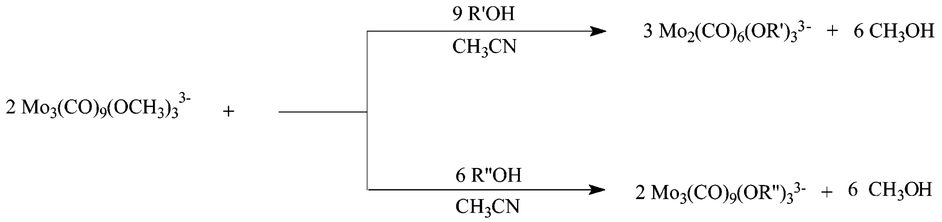
[18] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512−7515.

Scheme 1. Synthesis of Compound 1



Scheme 2. Ligand Exchange Reactions[a]



[a] R′OH = 4-$HOC_6H_4NH_2$, 3-HOC_5H_4N, 3-HOC_6H_4CN, 4-HOC_6H_4CN. R″OH = $HOCH_2CH_2OH$, $HO(CH_2)_3OH$.

ν(C−N) 2209 (s). ^{1}H NMR (CD_3CN): δ 7.56, 7.34 (m, m, 6H, 6H, OC_6H_4CN), 2.98 (m, 24H, $(CH_3CH_2)_4N$), 1.09 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 232.9 (CO), 174.0 (OCC_5H_4CN), 133.3−122.4 (OCC_5H_4CN), 95.0 (CN) 52.7 ($(CH_3CH_2)_4N$), 7.4 ($(CH_3CH_2)_4N$).

General Synthesis of $[Et_4N]_3[Mo_3(CO)_9(OR)_3]$ (R = CH_2CH_2OH (6), $(CH_2)_3OH$ (7)). Complex **1** (0.100 g, 0.10 mmol) was dissolved in CH_3CN (10 mL), and a ROH solution (0.30 mmol in 10 mL of CH_3CN) was added. After stirring at room temperature for 2 h, the solvent was reduced in vacuo to approximately 5 mL. The resulting solution was precipitated with 70 mL of diethyl ether. The oil obtained, $[Et_4N]_3[Mo_3(CO)_9(OR)_3]$, was washed twice with 30 mL of THF and dried under vacuum for 12 h. The oil can be converted to a solid by repeated washing with ether.

$[Et_4N]_3[Mo_3(CO)_9(OCH_2CH_2OH)_3]$ (6): yellow solid; yield 0.090 g (83%). IR (cm^{-1}): CH_3CN ν(C−O) 1907 (w), 1877 (vs), 1764 (s), 1743 (s). ^{1}H NMR (CD_3CN): δ 4.06−3.52 (m, 12H, OC_2H_4OH), 3.20 (m, 24H, $(CH_3CH_2)_4N$), 1.22 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 233.6 (CO), 79.7, 77.4 (OCH_2CH_2OH), 68.0, 66.2 (OCH_2CH_2OH), 52.8 ($(CH_3CH_2)_4N$), 7.5 ($(CH_3CH_2)_4N$).

$[Et_4N]_3[Mo_3(CO)_9(O(CH_2)_3OH)_3]$ (7): yellow powder; yield 0.078 g (69%). IR (cm^{-1}): CH_3CN ν(C−O) 1902 (w), 1872 (vs), 1759 (s), 1736 (s). ^{1}H NMR (CD_3CN): δ 4.28−3.43, 1.85, 1.59 (m, 18H, OC_3H_6OH), 3.21 (m, 24H, $(CH_3CH_2)_4N$), 1.23 (m, 36H, $(CH_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 234.6 (CO), 77.6, 75.8 ($OCH_2CH_2CH_2OH$), 63.9, 60.0 ($OCH_2CH_2CH_2OH$), 52.8 ($(CH_3CH_2)_4N$), 38.7, 36.5 ($OCH_2CH_2CH_2OH$), 7.5 ($(CH_3CH_2)_4N$).

X-ray Crystallography. Details of data collection and refinement are given in Table 1. Crystals of complexes **1**, **5**, and **6** were grown by vapor diffusion of ether into an acetonitrile solution at 5 °C. Crystals of complex **2** were grown at room temperature by vapor diffusion of THF into an acetonitrile solution. Yellow blocks for **1**, **5**, and **6** and a brown block for **2** were fixed to a cryo-loop in paratone oil and immediately placed in a nitrogen cold stream (110 K). Data for **1** was collected on a Bruker-Nonius X8 APEX diffractometer, a Bruker SMART 1000 X-ray diffractometer was used for **2** and **6**, and an Enraf-Nonius CAD4 diffractometer was used for **5**.

Data reduction was accomplished using SAINTPLUS (Bruker[19]) for **1**, **2**, and **6**, and XCAD for **5**. All structures were solved by direct methods using the SHELX[20] program suite, which provided the positions of the molybdenum atoms and some of the atoms of the ligands. Subsequent least-squares refinements revealed the positions of the remaining atoms in the structure. Unless noted otherwise, all non-hydrogen atoms were refined anisotropically. The absolute structure of **2** and **5** was deduced using the Flack parameter in SHELX.

Results and Discussion

Synthesis. The reaction of $Mo(CO)_5THF$, obtained by the photolysis of $Mo(CO)_6$ in THF, with a 6-fold excess of Et_4NOH (25% w/w in methanol solution) yields the trinuclear complex $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (**1**). This reaction pathway is analogous to the one reported by Darensbourg et al. for the synthesis of the binuclear tungsten complex $[Et_4N]_3[W_2(CO)_6(OMe)_3]$, starting with the photolysis of $W(CO)_6$.[1] A new synthetic route to complex **1** has also been found. In this method, complex **1** is obtained by refluxing a solution consisting of $Mo(CO)_6$ and a 6-fold excess of Et_4NOH (25% w/w in methanol) in 25 mL of THF for 2 h. These two different pathways for the synthesis of **1** are presented in Scheme 1.

The IR spectrum of complex **1** shows four CO stretching bands, which is different from the two-band pattern observed for the $W(CO)_3$ fragments found in the binuclear tungsten complexes $[Et_4N]_3[W_2(CO)_6(OR)_3]$;[1,16] however this four-band pattern has also been seen for the trinuclear complexes $[Et_4N]_3[M_3(CO)_9(OEt)_3]$ (M = Mo and W) synthesized by Ellis,[9] and as noted by Ellis the bands are broad, likely due to different stretching modes that have similar energies. Complex **1** has been shown to undergo ligand substitution with a variety of alcohols, yielding binuclear complexes $[Et_4N]_3[Mo_2(CO)_6(OR)_3]$ or trinuclear complexes $[Et_4N]_3[Mo_3(CO)_9(OR)_3]$ depending on the alcohol used.

The exchange of the methoxy ligand for the incoming alcohol is indicated by the shift to higher wavenumbers in the IR spectrum for the C−O stretches of the carbonyl groups, shown in Table 2. The binuclear complexes exhibit a two-band pattern consistent with the presence of the $Mo(CO)_3$ moiety of local C_{3v} symmetry, meanwhile the trinuclear complexes present the same four bands

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(19) *SAINTPLUS*, 6.02 ed.; Bruker AXS Inc.: Madison, WI, 1999.
(20) Sheldrick, G. M. *SHELX*, 6.10 ed.; Bruker AXS, Inc.: Madison, WI, 2000.

Table 2. Infrared Spectra in the Carbonyl Region for Compounds 1−7

compound[a]	ν(CO)
$[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (**1**)	1901 (w), 1870 (vs), 1757 (s), 1732 (s)
$[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4NH_2)_3]$ (**2**)	1863 (s), 1724 (vs)
$[Et_4N]_3[Mo_2(CO)_6(3\text{-}OC_5H_4N)_3]$ (**3**)	1874 (s), 1737 (vs)
$[Et_4N]_3[Mo_2(CO)_6(3\text{-}OC_6H_4CN)_3]$ (**4**)	1877 (s), 1742 (vs)
$[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4CN)_3]$ (**5**)	1880 (s), 1747 (vs)
$[Et_4N]_3[Mo_3(CO)_9(OCH_2CH_2OH)_3]$ (**6**)	1907 (w), 1877 (vs), 1764 (s), 1743 (s)
$[Et_4N]_3[Mo_3(CO)_9(O(CH_2)_3OH)_3]$ (**7**)	1902 (w), 1872 (vs), 1759 (s), 1736 (s)

[a] Spectra recorded in CH_3CN.

as seen in complex **1**. All of the complexes decompose rapidly in the presence of air, and as a result, satisfactory elemental analysis has not been possible; however ^1H and ^{13}C NMR spectra confirm bulk purity to the detection limit of the NMR spectrometer.

The ligand exchange reaction is facile for any of the complexes, provided the incoming alcohol has a lower pK_a than the leaving alcohol. For example, when 3 equiv of 4-cyanophenol is added to the complex $[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4NH_2)_3]$ (**2**) (pK_a = 10.80 for 4-aminophenol vs pK_a = 8.21 for 4-cyanophenol),[21] substitution occurs, resulting in the formation of the 4-cyanophenol derivate $[Et_4N]_3[Mo_2(CO)_6(4\text{-}OC_6H_4CN)_3]$ (**5**), but if instead, the reaction is carried out by addition of 3 equiv of 4-aminophenol to the 4-cyanophenol derivate (**5**), no ligand exchange is observed. The time of reaction is also of note; for substitution processes where the trinuclear core is retained, the substitution is complete within 2 h. For the formation of binuclear centers, where the trinuclear center has been destroyed, the required reaction time is much longer, at 8−24 h.

X-ray Crystallography. X-ray crystal structure determinations were carried out for compounds **1**, **2**, **5**, and **6**; suitable crystals for the other remaining complexes have not yet been obtained. Three molecules of Et_4N^+ are present to balance the charge of the anion. Hydrogen atoms were placed in calculated positions. All of the CO ligands are nearly linear in all complexes (Mo−C−O, 177.5° for **1**, 177.0° for **2**, 176.3° for **5**, 175.6° for **6**), and the $C-O_{(carbonyl)}$ bond lengths for these complexes are within the range of normally observed values.

A thermal ellipsoid drawing of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 3. Complex **1** contains a trimetallic core with the $Mo(CO)_3$ units held together by bridging methoxide groups. Two of the methoxides bridge in a μ_3 fashion, capping the triangle of Mo atoms, and the third bridges a Mo−Mo edge. The average Mo−O distance for the μ_3 mode is 2.25 Å; for the μ_2 mode the Mo−O distances are quite asymmetric at 2.191(9) Å for Mo1−O5 and 2.021(9) Å for Mo2−O5. The Mo−Mo bond distance is 3.078 Å for **1**, which represents a crystallographically imposed average between the true distances. This is illustrated by comparison with the structure of **6** (vide infra). The Mo−Mo−Mo bond angle is 72.0°. The nonbonded Mo1−Mo1a distance is 3.62 Å. The structure of **1** is highly disordered with respect to the μ_2 OMe; it is disordered along with a carbonyl (C6) over four positions.

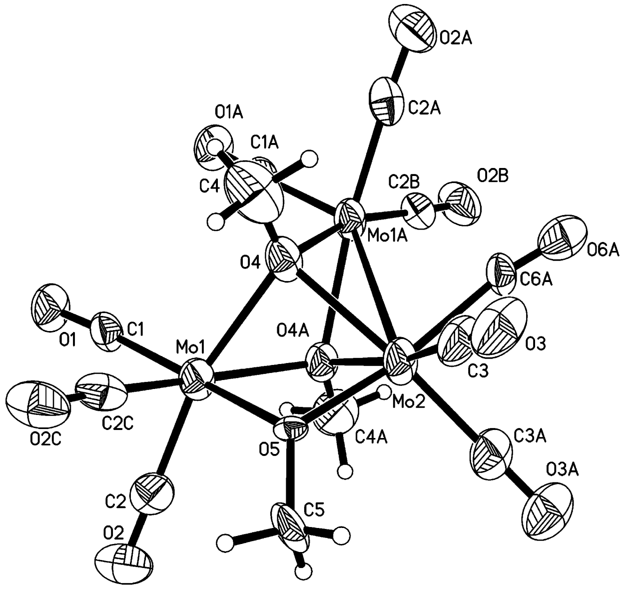

Figure 1. Thermal ellipsoid plot of **1** with atomic numbering scheme. Ellipsoids are shown at 40% probability.

Complexes **2** and **5** are isostructural and comparable to the previously reported $[Et_4N]_3[Mo_2(CO)_6(OPh)_3]$ complex.[2] Each contains a bimetallic Mo_2O_3 core with three terminal carbonyls on each of the molybdenum atoms. The average Mo−O distances are 2.22 Å for **2** and 2.25 Å for **5**, and the average Mo−C bond distances are 1.91 Å for **2** and 1.92 Å for **5**. These distances are comparable with those reported for the phenoxide complex (Mo−O, 2.25 Å; Mo−C 1.87 Å) and for the tetrameric cluster $[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)_3]_4$ (Mo−O, 2.25 Å; Mo−C, 1.91 Å).[7] The Mo−O−Mo bond angles, averaging 94.8° for **2** and 95.2° for **5**, are nearly the same as the 94.6° reported for the phenoxide.[2] The $O-C_{(ring)}$ average bond length is 1.35 Å for **2** and 1.32 Å for **5**, indicating the presence of some double-bond character and therefore the approximately trigonal planar geometry. The molybdenum metal centers are in a distorted octahedral geometry, analogous to that observed for the phenoxide complex.

The molecular structure of complex **2** is shown in Figure 2, and selected bond lengths and angles are provided in Table 4. The average C−N distance, 1.44 Å, is appropriate for an amine and equal to the 1.44 Å observed in the tungsten analogue complex $[Et_4N]_3[W_2(CO)_6(4\text{-}C_6H_4NH_2)_3]$.[16] The rings of the aminophenol ligands are twisted slightly with respect to the Mo−Mo axis with the bridging oxygen atom having a nearly trigonal planar geometry, the average angle around the oxygen being 119.4°. The Mo−O−C−C torsion angles for this compound range from −17.3° to 24.8°. Complex **2** has one cocrystallized molecule of acetonitrile and one distorted Et_4N^+ molecule with a 53:47 ratio for the two positions.

A thermal ellipsoid drawing of **5** is shown in Figure 3, and selected bond lengths and angles are given in Table 5. The average C−N distance, 1.14 Å, appropriate for a cyanide functionality, is similar to the one reported for the tungsten complex $[Et_4N]_3[W_2(CO)_6(4\text{-}C_6H_4CN)_3]$ (C−N, 1.15 Å).[16] For complex **5**, the average angle

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[21] Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421−6427.

Table 3. Selected Bond Lengths [Å][a] and Angles [deg] for 1

Mo(1)−O(5)	2.191(9)	Mo(1)−O(4)	2.249(3)
Mo(1)−Mo(2)	3.0781(7)	Mo(2)−O(5)	2.021(9)
Mo(2)−C(6)	2.08(2)	Mo(2)−O(4)	2.257(4)
O(4)−C(4)	1.37(1)	C(5)−O(5)	1.47(4)
Mo(1)−Mo(2)−Mo(1)#2	72.03(2)	C(2)−Mo(1)−O(5)#1	83.3(3)
C(2)#1−Mo(1)−O(5)#1	96.6(3)	C(1)−Mo(1)−O(5)	168.6(2)
C(2)−Mo(1)−O(4)	166.0(2)	C(2)#1−Mo(1)−O(4)	105.8(2)
C(1)−Mo(1)−O(4)	105.9(2)	O(5)#1−Mo(1)−O(4)	84.0(2)
O(5)−Mo(1)−O(4)	72.8(2)	O(4)−Mo(1)−O(4)#2	64.7(2)
C(2)−Mo(1)−Mo(2)	119.0(1)	C(1)−Mo(1)−Mo(2)	145.1(2)
C(3)#2−Mo(2)−C(3)	86.4(4)	C(3)#2−Mo(2)−O(5)	104.8(3)
C(3)−Mo(2)−O(5)	89.4(2)	C(3)#2−Mo(2)−C(6)#2	84.1(2)
O(5)−Mo(2)−C(6)#2	168.7(3)	C(3)#2−Mo(2)−O(4)	169.0(2)
C(3)−Mo(2)−O(4)	104.6(2)	O(5)#1−Mo(2)−O(4)	87.8(2)
O(5)−Mo(2)−O(4)	75.8(3)	C(6)#2−Mo(2)−O(4)	96.8(3)
O(4)−Mo(2)−O(4)#2	64.4(2)	C(3)−Mo(2)−Mo(1)	126.1(1)
O(5)#3−Mo(2)−Mo(1)	115.6(3)	C(6)#2−Mo(2)−Mo(1)	134.1(3)
C(6)−Mo(2)−Mo(1)	62.1(3)	O(4)−Mo(2)−Mo(1)	46.82(7)
O(5)#3−Mo(2)−Mo(1)#2	45.2(2)	C(4)−O(4)−Mo(1)	120.6(2)
Mo(1)−O(4)−Mo(1)#2	107.2(2)	C(4)−O(4)−Mo(2)	127.6(5)
Mo(1)−O(4)−Mo(2)	86.2(1)	C(5)−O(5)−Mo(2)	126.7(2)
C(5)−O(5)−Mo(1)	124.7(2)	Mo(2)−O(5)−Mo(1)	93.8(3)

[a] Estimated standard deviations are given in parentheses. Symmetry transformations used to generate equivalent atoms: #1 *y*, *x*, *z*; #2 −*x*+1/2, −*y*+1/2, *z*.

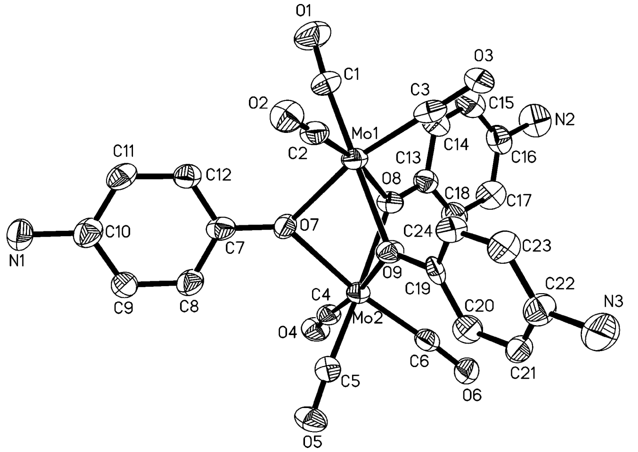

Figure 2. Thermal ellipsoid plot of **2** with atomic numbering scheme. Ellipsoids are shown at 40% probability. Hydrogen atoms are omitted for clarity.

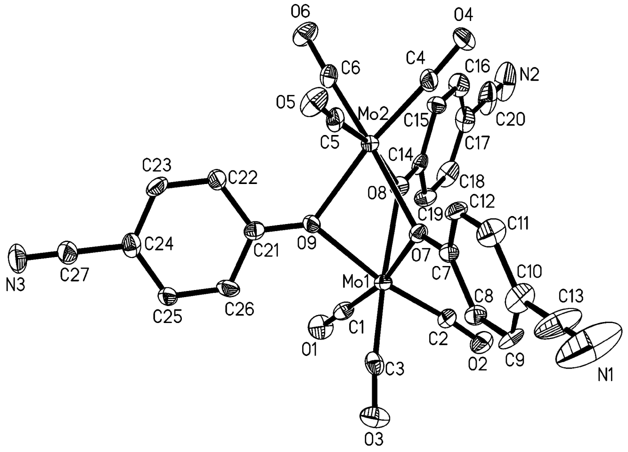

Figure 3. Thermal ellipsoid plot of **5** with atomic numbering scheme. Ellipsoids are shown at 40% probability. Ring hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths [Å][a] and Angles [deg] for 2

Mo(1)−O(8)	2.208(4)	Mo(1)−O(9)	2.211(3)
Mo(1)−O(7)	2.221(4)	Mo(2)−O(9)	2.223(3)
Mo(2)−O(8)	2.232(4)	Mo(2)−O(7)	2.248(4)
O(7)−C(7)	1.368(7)	O(8)−C(13)	1.345(7)
O(9)−C(19)	1.344(6)	N(1)−C(10)	1.420(8)
N(2)−C(16)	1.452(8)	N(3)−C(22)	1.459(8)
C(1)−Mo(1)−O(7)	106.1(2)	C(3)−Mo(1)−O(7)	167.6(2)
C(2)−Mo(1)−O(7)	100.5(2)	O(8)−Mo(1)−O(7)	71.0(1)
O(9)−Mo(1)−O(7)	72.4(1)	C(4)−Mo(2)−O(7)	101.6(2)
C(5)−Mo(2)−O(7)	105.0(2)	C(6)−Mo(2)−O(7)	172.1(2)
O(9)−Mo(2)−O(7)	71.6(1)	O(8)−Mo(2)−O(7)	70.1(1)
C(7)−O(7)−Mo(1)	130.7(3)	C(7)−O(7)−Mo(2)	133.9(3)
Mo(1)−O(7)−Mo(2)	94.1(1)	O(7)−C(7)−C(8)	120.6(5)

[a] Estimated standard deviations are given in parentheses.

Table 5. Selected Bond Lengths [Å][a] and Angles [deg] for 5

Mo(1)−O(8)	2.245(5)	Mo(1)−O(9)	2.252(5)
Mo(1)−O(7)	2.262(5)	Mo(2)−O(8)	2.230(5)
Mo(2)−O(9)	2.239(5)	Mo(2)−O(7)	2.246(5)
O(7)−C(7)	1.319(9)	O(8)−C(14)	1.314(9)
O(9)−C(21)	1.321(9)	N(1)−C(13)	1.15(1)
N(2)−C(20)	1.14(1)	N(3)−C(27)	1.13(1)
C(3)−Mo(1)−O(7)	99.1(3)	C(2)−Mo(1)−O(7)	106.6(3)
C(1)−Mo(1)−O(7)	169.0(3)	O(8)−Mo(1)−O(7)	71.7(2)
O(9)−Mo(1)−O(7)	71.0(2)	C(6)−Mo(2)−O(7)	169.8(3)
C(4)−Mo(2)−O(7)	101.6(3)	C(5)−Mo(2)−O(7)	100.6(3)
O(8)−Mo(2)−O(7)	72.2(2)	O(9)−Mo(2)−O(7)	71.6(2)
C(7)−O(7)−Mo(2)	130.7(5)	C(7)−O(7)−Mo(1)	133.3(5)
Mo(2)−O(7)−Mo(1)	94.7(2)	N(1)−C(13)−C(10)	178(2)
N(2)−C(20)−C(17)	179(1)	N(3)−C(27)−C(24)	178(1)

[a] Estimated standard deviations are given in parentheses.

around the oxygen of the 4-cyanophenol ligand is 119.9°, and the Mo−O−C−C torsion angles for this compound range from −1.3° to 14.4°. One molecule of acetonitrile is present in **5**.

The molecular structure of complex **6** is shown in Figure 4, and selected bond lengths and angles are provided in Table 6. The original trinuclear core of complex **1** is retained in **6**; the Mo1−Mo2 distance is 2.916 Å, demonstrating the presence of a single bond.[12,13] The nonbonded distance between Mo1 and Mo3 is 3.26 Å, and the nonbonded Mo2−Mo3 distance is 3.54 Å. Averaging the bonded distance, 2.916 Å, with the nonbonded distance, 3.26 Å, yields 3.09 Å, which is very close to the distance found in complex **1**; this supports the assessment that the Mo−Mo bond length in **1** is best

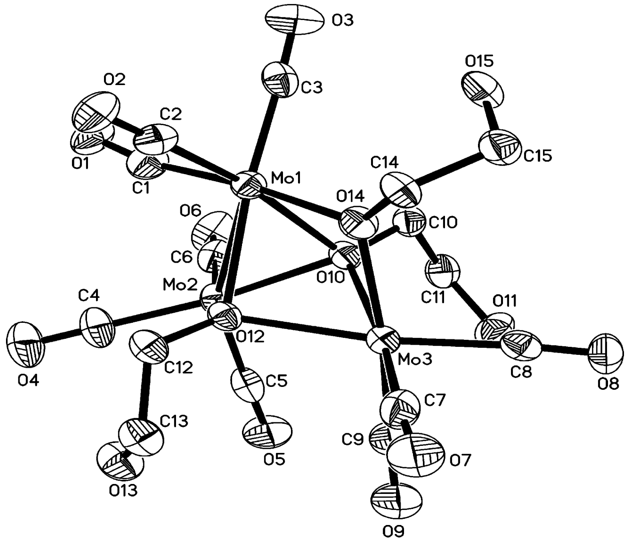

Figure 4. Thermal ellipsoid plot of **6** with atomic numbering scheme. Ellipsoids are shown at 40% probability. Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Lengths [Å][a] and Angles [deg] for 6

Mo(1)−C(2)	1.927(8)	Mo(1)−C(3)	1.94(1)
Mo(1)−C(1)	1.960(8)	Mo(1)−O(14)	2.133(4)
Mo(1)−O(10)	2.244(5)	Mo(1)−O(12)	2.262(5)
Mo(1)−Mo(2)	2.916(1)	Mo(2)−C(4)	1.910(8)
Mo(2)−C(6)	1.919(9)	Mo(2)−C(5)	1.930(9)
Mo(2)−O(10)	2.221(4)	Mo(2)−O(12)	2.224(4)
Mo(3)−C(8)	1.914(8)	Mo(3)−C(9)	1.930(8)
Mo(3)−C(7)	1.94(1)	Mo(3)−O(14)	2.177(5)
Mo(3)−O(12)	2.268(4)	Mo(3)−O(10)	2.304(5)
O(10)−C(10)	1.417(9)	O(12)−C(12)	1.418(9)
O(14)−C(14)	1.412(8)		
C(2)−Mo(1)−C(3)	87.5(3)	C(2)−Mo(1)−C(1)	80.8(3)
C(3)−Mo(1)−C(1)	79.8(3)	C(2)−Mo(1)−O(14)	97.8(2)
C(3)−Mo(1)−O(14)	106.2(2)	C(1)−Mo(1)−O(14)	173.7(3)
C(2)−Mo(1)−O(10)	168.1(3)	C(3)−Mo(1)−O(10)	103.8(3)
C(1)−Mo(1)−O(10)	104.6(3)	O(14)−Mo(1)−O(10)	75.7(2)
C(2)−Mo(1)−O(12)	102.5(3)	C(3)−Mo(1)−O(12)	169.6(2)
C(1)−Mo(1)−O(12)	98.7(3)	O(14)−Mo(1)−O(12)	75.6(2)
O(10)−Mo(1)−O(12)	66.4(2)	C(2)−Mo(1)−Mo(2)	127.6(2)
C(3)−Mo(1)−Mo(2)	122.3(2)	C(1)−Mo(1)−Mo(2)	65.9(2)
O(14)−Mo(1)−Mo(2)	111.0(1)	O(10)−Mo(1)−Mo(2)	48.9(1)
O(12)−Mo(1)−Mo(2)	48.9(1)	C(4)−Mo(2)−C(6)	85.4(3)
C(4)−Mo(2)−C(5)	85.1(3)	C(6)−Mo(2)−C(5)	84.9(3)
C(4)−Mo(2)−O(10)	167.6(3)	C(6)−Mo(2)−O(10)	101.9(3)
C(5)−Mo(2)−O(10)	105.4(2)	C(4)−Mo(2)−O(12)	102.8(3)
C(6)−Mo(2)−O(12)	161.7(3)	C(5)−Mo(2)−O(12)	111.9(3)
O(10)−Mo(2)−O(12)	67.5(2)	C(4)−Mo(2)−Mo(1)	118.5(2)
C(6)−Mo(2)−Mo(1)	111.7(2)	C(5)−Mo(2)−Mo(1)	151.2(2)
O(10)−Mo(2)−Mo(1)	49.6(1)	O(12)−Mo(2)−Mo(1)	50.0(1)
C(8)−Mo(3)−C(9)	85.2(3)	C(8)−Mo(3)−C(7)	81.6(3)
C(9)−Mo(3)−C(7)	82.6(4)	C(8)−Mo(3)−O(14)	101.1(2)
C(9)−Mo(3)−O(14)	173.7(3)	C(7)−Mo(3)−O(14)	98.4(3)
C(8)−Mo(3)−O(12)	171.1(3)	C(9)−Mo(3)−O(12)	99.1(3)
C(7)−Mo(3)−O(12)	106.6(3)	O(14)−Mo(3)−O(12)	74.6(2)
C(8)−Mo(3)−O(10)	106.1(3)	C(9)−Mo(3)−O(10)	104.5(3)
C(7)−Mo(3)−O(10)	169.7(3)	O(14)−Mo(3)−O(10)	73.68(17)
O(12)−Mo(3)−O(10)	65.3(2)	C(10)−O(10)−Mo(2)	124.5(4)
C(10)−O(10)−Mo(1)	121.4(4)	Mo(1)−O(14)−Mo(3)	98.4(2)
Mo(2)−O(10)−Mo(1)	81.6(2)	C(10)−O(10)−Mo(3)	123.6(4)
Mo(2)−O(10)−Mo(3)	102.9(2)	Mo(1)−O(10)−Mo(3)	91.6 (2)
C(12)−O(12)−Mo(2)	125.5(4)	C(12)−O(12)−Mo(1)	118.7(4)
Mo(2)−O(12)−Mo(1)	81.1(2)	C(12)−O(12)−Mo(3)	123.5(4)
Mo(2)−O(12)−Mo(3)	104.0(2)	Mo(1)−O(12)−Mo(3)	92.1(2)
C(14)−O(14)−Mo(1)	133.7(4)	C(14)−O(14)−Mo(3)	127.3(4)

[a] Estimated standard deviations are given in parentheses.

described as an average. Two of the glycoxide ligands in **6** bridge the Mo triangle in a μ_3 fashion with an average bond length of 2.25 Å, and the third one bridges the Mo1−Mo3 edge, with Mo−O bond lengths of 2.133(4) and 2.177(5) Å, respectively. For complex **6**, the average angle around the oxygen of the doubly bridged ethylene glycol ligand is 119.8°, indicative of a trigonal planar geometry and sp^2 hybridization at the oxygen. This geometry can be rationalized by realizing that the Mo−O(μ_2) bond lengths are about 0.1 Å shorter than the Mo−O(μ_3) bond lengths, suggesting at least partial double-bond character, which would require sp^2 hybridization. The geometry around the oxygen of the triply bridged ligands is that of a distorted tetrahedron, with an average angle around the oxygen of 107.5 Å, as expected for an sp^3 hybrid. One of the triply bridged ethylene glycol ligands is disordered, with a 60:40 ratio for the two positions. Two independent trianions are present in the unit cell for complex **6**, with the only major difference being the lack of disorder in the second trianion (Mo4).

NMR Spectroscopy. In the ^{1}H NMR spectrum of each of the compounds a proper integration was attained versus the protons of the Et_4N cation.

The ^{1}H NMR spectrum of complex **1** shows two singlets for the protons in the OCH_3 ligands, with an integration ratio of 2:1. The ^{13}C NMR spectrum shows two resonances at 235.4 and 235.5 ppm that correspond to the metal carbonyl carbons. The carbons of the methoxide groups appear as single signals at 68.9 and 66.7 ppm, in a 2:1 ratio.

In the ^{1}H NMR spectrum of complex **2**, a significant asymmetry is observed. The proton resonances of two of the rings appear as equivalent, but the resonance for the third ring is quite different for the other two. The ^{13}C NMR spectrum shows a single peak at 234.2 ppm for the metal carbonyl carbons. The $C_{(ring)}$−O appear as a single signal at 163.5 ppm and the C−NH_2 at 134.8 ppm. The $OCC_4H_4CNH_2$ carbons appear as single signals at 121.2 and 115.8 ppm.

For complex **3**, the ^{1}H NMR spectrum shows, as we expected, that all the positions in the ring are inequivalent; due to this, four signals with an integration ratio of 3:3:3:3 are observed. Additional splitting is due to asymmetry in the molecule. In the ^{13}C NMR spectrum, the metal carbonyl carbons appear at 233.5 ppm, and the $C_{(ring)}$−O is at 165.5 ppm. The unsubstituted carbons in the 3-hydroxypyridine ligand are present between 145.1 and 123.2 ppm.

For the complex **4**, the ^{1}H NMR spectrum shows that all the positions in the ring are inequivalent. Two of the signals appear very close, making it impossible to separate for integration; due to this, the integration ratios are 6:3:3. In the ^{13}C NMR, the metal carbonyl carbons appear at about 233.3 ppm, and the $C_{(\mathrm{ring})}$−O is at 170.0 ppm. There is a single C−N peak at 111.5 ppm. The other signals for the unsubstituted carbons in the 3-cyanophenol ligand appear between 129.6 and 117.3 ppm.

The ^{1}H NMR spectrum of complex **5** shows only two doublets in the aromatic region, which indicates a very symmetric environment for the protons in the ring. The metal carbonyl carbons appear at 232.9 ppm in the ^{13}C NMR spectrum, and the $C_{(ring)}$−O for the 4-cyanophenol ligand is at 174.0 ppm. There is a single C−N resonance at 95.0 ppm. The unsubstituted carbons of the 4-cyanophenol have two sets of peaks at 133.3 and 122.4 ppm in a 1:1 ratio.

All the complexes with a trinuclear (**6** and **7**) structure are highly asymmetric, which can be seen in the NMR spectra, especially in the ^{1}H NMR spectrum. For complex **6**, two sets of resonances corresponding to the 12 protons expected for the trisubstituted product are present. The metal carbonyl carbons appear in the ^{13}C NMR spectrum at 233.6 ppm, and the $C{-}O_{(bridge)}$ of the ethylene glycol ligand is at 79.7 and 77.4 ppm, in a 2:1 ratio. The remaining two signals corresponding to the remaining CH_2 groups in the ligand are also observed in a 1:2 ratio at 68.0 and 66.2 ppm, respectively.

In the ^{1}H NMR spectrum for complex **7**, six different sets of resonances are observed, indicating, as expected, that two of the propanediol ligands are equivalent and the third one is not. The integration ratios are 2:2:8:4:2, which gives the 18 protons expected for this molecule. The ^{13}C NMR spectrum shows one resonance for the metal carbonyl carbons at 234.6 ppm. The $C{-}O_{(bridge)}$ appears as two resonances in a 1:2 ratio at 77.6 and 75.8 ppm, respectively. Similarly, the resonances attributed to the other carbons in the ligand are also present in a 1:2 ratio, with signals at 63.9 and 60.0 ppm for the carbons attached to the terminal OH groups and signals at 38.7 and 36.5 ppm for the middle carbon.

Conclusion

Our continued interest in group 6 carbonyl complexes has led to the development of many complexes in which the metal centers are bridged by alkoxide and aryloxide ligands. We have presented a unique complex, $[Et_4N]_3[Mo_3(CO)_9(OMe)_3]$ (**1**), that includes bridging methoxides in addition to a Mo−Mo bond. Complex **1** has been shown to undergo ligand substitution reactions, incorporating additional functionality into the complex. The substitution reactions are facile, provided the incoming alcohol is more acidic than the afforded methanol. By using ligands with diverse functionalities we have been able to synthesize complexes with different structural motifs.

The ligand exchange reaction is not exclusive for the methoxide ligand; we have demonstrated that as long as the incoming ligand has a lower pK_a than the leaving alcohol, the reaction will proceed. Future research is focusing on the reaction of carboxylic acids with compound **1**. It has been found that when compound **1** is reacted in a 1:3 ratio with carboxylic acids, the trinuclear complex is destroyed and stable carboxylate-containing derivatives are formed. These derivatives have the general formula $Mo(CO)_3(NCCH_3)(\eta^2\text{-}O_2CR)^-$. The presence of the labile ligand acetonitrile will allow us to form larger species by displacement with connecting ligands such as 4,4′-bipyridine.

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Supporting Information Available: A listing of the final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **1**, **2**, **5**, and **6** as well as ^{1}H and ^{13}C NMR spectra of the reported compounds is available free of charge via the Internet at http://pubs.acs.org.

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