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Heterometallic Molybdenum−Gold and Tungsten−Gold Clusters, $M_3(CO)_9(AuPPh_3)_3(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (M = Mo, W)

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Treatment of $[NMe_4]_3[M_3(CO)_9(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (**1**, M = Mo; **2**, M = W) with 3 equiv of $(Ph_3P)AuCl/TlPF_6$ affords $M_3(CO)_9(AuPPh_3)_3(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (**3**, M = Mo; **4**, M = W) in 80% and 89% yields, respectively. The molecular structures of **3** and **4** have been determined by X-ray diffraction methods. Complexes **3** and **4** are isomorphous. Variable-temperature $^{31}P\{H\}$ and ^1H NMR spectra for **3**, **4**, and related complex $[NMe_4][W_3(CO)_9(Au_2(\mu\text{-dppm}))(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (**6**) verify valence isomerization in these complexes at ambient conditions.

Introduction

Heteronuclear metal clusters have attracted considerable interest in the past as the reactivity of a metal center can often be modified by bonding to a heterometallic fragment.[1] Since the pioneering work of Lewis and Nyholm,[2] the area of heteronuclear gold clusters has expanded rapidly.[3] Although mixed-metal clusters containing "$M_x(CO)_yAu_z$" ($x \geq 3$ and $z \geq 2$) fragment are not uncommon,[4] to our knowledge, no such clusters for group 6 metals were reported in the literature, apparently due to the scarcity of group 6 metal carbonyl clusters.[5] We therefore chose $[NMe_4]_3[M_3(CO)_9(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (**1**, M = Mo; **2**, M = W)[5c] as our building blocks for such clusters since condensation reactions of anionic metal carbonyl clusters with electrophiles were found to be useful in construction of clusters with higher nuclearity.[6] In this paper we will describe the syntheses of unusual group 6 metal−gold clusters, $M_3(CO)_9(AuPPh_3)_3(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (**3**, M = Mo; **4**, M = W), and their interesting fluxional behavior in solution. Syntheses of several closely related clusters are also included in this report.

Experimental Section

General Procedure. Infrared measurements were made on a Perkin-Elmer 880 spectrophotometer. The NMR spectra were recorded on a Bruker MSL 200, AC200, or AMX 500 spectrometer. The ^1H and ^{31}P spectra are referenced to TMS and external 85% H_3PO_4, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

All operations were carried out under nitrogen with use of standard Schlenk techniques or a drybox. All solvents were purified by standard procedures or degassed prior to use. All the column chromatography was performed under N_2 by use of silica gel (230-400 mesh ASTM, Merck) as the stationary phase in a column 35 cm long and 2.5 cm in diameter. $[NMe_4]_3[M_3(CO)_9(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (**1**, M = Mo; **2**, M = W),[5c] $(Ph_3P)AuCl$,[7] and $(\mu\text{-dppm})(AuCl)_2$[8] were prepared according to the published procedures.

Syntheses of $M_3(CO)_9(AuPPh_3)_3(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (3, M = Mo; 4, M = W). Essentially the same procedures were followed for the syntheses of **3** and **4**, and only the preparation of **3** will be described in detail. To a CH_3CN solution (50 mL) of **1** (200 mg, 0.22 mmol) prechilled to −20 °C was added dropwise a THF solution (10 mL) of $(Ph_3P)AuCl$ (326 mg, 0.66 mmol) and $TlPF_6$ (234 mg, 0.66 mmol). After 30 min the solvent was removed and the residue was recrystallized from THF/hexane to give crude **3**, which was then chromatographed using CH_2Cl_2/hexane (3:1) as eluent to provide pure **3** as a red powder in 80% yield. Anal. Calcd for $C_{69}H_{60}O_{12}P_3Au_3Mo_3$: C, 40.47; H, 2.84. Found: C, 40.80, H, 2.81.

Orange red complex **4** was isolated in 89% yield. Anal. Calcd for $C_{69}H_{60}O_{12}P_3Au_3W_3$: C, 36.02; H, 2.52. Found: C, 36.25, H, 2.81.

Syntheses of $M_3(CO)_9(Au_2(\mu\text{-dppm}))(AuPPh_3)(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (5, M = Mo; 6, M = W). The same procedures were followed for the syntheses of **5** and **6**, and only the preparation of **6** will be described in detail. To a CH_3CN solution (75 mL) of **2** (250 mg, 0.22 mmol) prechilled to −20 °C was added dropwise a THF solution (10 mL) of $(\mu\text{-dppm})(AuCl)_2$ (183 mg, 0.22 mmol) and $TlPF_6$ (153 mg, 0.44 mmol). After 30 min at

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Table 1. Crystal Data for Complex 3

chem formula	$C_{69}H_{60}O_{12}P_3Au_2Mo_3$
fw	2052.87
cryst size, mm	0.13 × 0.13 × 0.22
color	red
cryst system	triclinic
space group	$P\bar{1}$
a, Å	12.187(2)
b, Å	15.219(3)
c, Å	22.720(7)
α, deg	81.81(2)
β, deg	85.05(2)
γ, deg	87.85(1)
V, Å^3	4154(2)
Z	2
ρ_{calc}, g cm^{-3}	1.641
F(000)	1956
λ(Mo Kα), Å	0.7107
μ, cm^{-1}	58.0
transm coeff	1.00−0.83
T, °C	+25
2θ max, deg	45
h,k,l range	−13 to 13, 0 to 16, −23 to 24
tot. reflns	11 453
unique reflns	10 832
obsd reflns ($I > 2.5\sigma(I)$)	5319
refined params	811
R;[a] R_w[b]	0.051; 0.077
GOF[c]	2.34

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + kF_o^2]$, where $k = 0.0001$. [c] Goodness of fit, $S = [(\sum w(|F_o| - |F_c|)^2/N_{obs} - N_{var})]^{1/2}$; N_{obs} = number of observed reflections, and N_{var} = number of variables.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Distances

Au1−Mo1	2.739(3)	Mo1−C2	1.85(3)
Au2−Mo2	2.788(3)	Mo1−C3	1.97(3)
Au3−Mo3	2.750(3)	Mo2−C4	1.90(3)
Mo2−Mo3	2.975(4)	Mo2−C5	1.92(3)
Au2−Au3	3.011(2)	Mo2−C6	1.96(3)
Au1−P1	2.253(9)	Mo3−C7	1.93(3)
Au2−P2	2.302(8)	Mo3−C8	1.95(3)
Au3−P3	2.280(7)	Mo3−C9	1.91(3)
Mo1−O10	2.28(2)	C1−O1	1.22(3)
Mo1−O12	2.27(2)	C2−O2	1.25(3)
Mo1−O14	2.13(2)	C3−O3	1.19(4)
Mo2−O10	2.23(2)	C4−O4	1.20(4)
Mo2−O12	2.25(2)	C5−O5	1.16(4)
Mo2−O14	2.09(2)	C6−O6	1.15(3)
Mo3−O10	2.22(2)	C7−O7	1.13(3)
Mo3−O12	2.17(2)	C8−O8	1.14(4)
Mo1−C1	1.87(3)	C9−O9	1.17(4)

Angles

Au2−Mo2−Mo3	67.42(8)	C4−Mo2−O14	91(1)
Au3−Mo3−Mo2	102.2(1)	C5−Mo2−C6	100(1)
Mo1−O14−Mo2	100.0(8)	C5−Mo2−O10	169(1)
Mo1−O12−Mo2	91.0(6)	C5−Mo2−O12	103(1)
Mo1−O12−Mo3	102.1(7)	C5−Mo2−O14	99(1)
Mo1−O10−Mo2	91.3(7)	C6−Mo2−O10	87(1)
Mo1−O10−Mo3	100.2(7)	C6−Mo2−O12	116(1)
Mo2−O10−Mo3	83.9(6)	C6−Mo2−O14	155(1)
Mo2−O12−Mo3	84.5(6)	O10−Mo2−O12	66.7(6)
Mo1−Au1−P1	166.3(2)	O10−Mo2−O14	75.8(7)
Mo2−Au2−P2	151.5(2)	O12−Mo2−O14	75.0(7)
Mo3−Au3−P3	170.3(2)	C7−Mo3−C8	77(1)
C1−Mo1−C2	81(1)	C7−Mo3−C9	76(1)
C1−Mo1−C3	76(1)	C7−Mo3−O10	106(1)
C1−Mo1−O10	167(1)	C7−Mo3−O12	104(1)
C1−Mo1−O12	105.0(9)	C8−Mo3−C9	102(1)
C1−Mo1−O14	96(1)	C8−Mo3−O10	165(1)
C2−Mo1−C3	102(1)	C8−Mo3−O12	97(1)
C2−Mo1−O10	107(1)	C9−Mo3−O10	93(1)
C2−Mo1−O12	168(1)	C9−Mo3−O12	161(1)
C2−Mo1−O14	95(1)	O10−Mo3−O12	68.4(7)
C3−Mo1−O10	111.2(9)	Mo1−C1−O1	178(2)
C3−Mo1−O12	89.7(9)	Mo1−C2−O2	171(2)
C3−Mo1−O14	159(1)	Mo1−C3−O3	165(3)
O10−Mo1−O12	65.6(6)	Mo2−C4−O4	177(2)
O10−Mo1−O14	73.8(7)	Mo2−C5−O5	172(3)
O12−Mo1−O14	73.9(7)	Mo2−C6−O6	162(3)
C4−Mo2−C5	81(1)	Mo3−C7−O7	174(3)
C4−Mo2−C6	76(1)	Mo3−C8−O8	171(2)
C4−Mo2−O10	108(1)	Mo3−C9−O9	172(2)
C4−Mo2−O12	166(1)		

−20 °C a THF solution (10 mL) of $(Ph_3P)AuCl$ (106 mg, 0.22 mmol) and $TlPF_6$ (77 mg, 0.22 mmol) was added dropwise. The solution was stirred at the same temperature for another 30 min, and the solvent was removed. The residue was washed with Et_2O, recrystallized from THF/hexane, and chromatographed. Orange powdery **6** was isolated in 56% yield (260 mg) from the reddish band eluted by CH_2Cl_2/hexane (3:1) after removal of the solvent. Anal. Calcd for $C_{58}H_{52}O_{12}P_3Au_3W_3$: C, 32.01; H, 2.41. Found: C, 31.66, H, 2.21.

Orange complex **5** was isolated in 43% yield. Anal. Calcd for $C_{58}H_{52}O_{12}P_3Au_3Mo_3$: C, 36.44; H, 2.74. Found: C, 36.05, H, 2.92.

Syntheses of $[NMe_4][W_3(CO)_9(Au_2(\mu\text{-dppm}))(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (7). To a CH_3CN solution (75 mL) of **2** (250 mg, 0.22 mmol) prechilled to −20 °C was added dropwise a THF solution (10 mL) of $(\mu\text{-dppm})(AuCl)_2$ (183 mg, 0.22 mmol) and $TlPF_6$ (153 mg, 0.44 mmol). The solution was stirred at the same temperature for 40 min and filtered. The filtrate was pumped dry and washed with Et_2O. The solid was further recrystallized from THF/Et_2O to provide **7** as red crystals in 65% yield (250 mg). Anal. Calcd for $C_{44}H_{49}NO_{12}P_2Au_2W_3$: C, 29.50; H, 2.76; N, 0.78. Found: C, 29.11, H, 2.50; N, 0.65.

Syntheses of $[NMe_4]_2[W_3(CO)_9(AuPPh_3)(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (8). To a CH_3CN solution (150 mL) of **2** (400 mg, 0.34 mmol) prechilled to −20 °C was added dropwise a THF solution (10 mL) of $(Ph_3P)AuCl$ (170 mg, 0.34 mmol) and $TlPF_6$ (120 mg, 0.34 mmol) over a period of 30 min. After 30 min at −20 °C the solution was warmed to room temperature and stirred for 1 h. After filtration the filtrate was pumped dry to give an orange solid. The solid was washed with THF and MeOH and dried in vacuo to give yellow-orange powdery **8** in 30% yield (158 mg). Anal. Calcd for $C_{41}H_{54}N_2O_{12}PAuW_3$: C, 32.41; H, 3.34; N, 1.72. Found: C, 32.28; H, 3.28; N, 1.69.

Syntheses of $[NMe_4][W_3(CO)_9(AuPPh_3)_2(\mu\text{-OEt})(\mu_3\text{-OEt})_2]$ (9). To a CH_3CN solution (50 mL) of **2** (250 mg, 0.22 mmol) prechilled to −20 °C was added dropwise a THF solution (10 mL) of $(Ph_3P)AuCl$ (213 mg, 0.44 mmol) and $TlPF_6$ (153 mg, 0.44 mmol). After 30 min at −20 °C the solution was warmed to room temperature and stirred for 1 h. The solution was filtered, and the filtrate was pumped dry to give a red solid. Recrystallization of the red solid from THF/hexane gave **9** in 52% yield (221 mg). Anal. Calcd for $C_{55}H_{57}NO_{12}P_2Au_2W_3$: C, 34.86; H, 2.85; N, 0.69. Found: C, 34.61; H, 3.11; N, 0.65.

Syntheses of $Mo_3(CO)_9(Au_2(\mu\text{-dppm}))(HgMe)(\mu\text{-OEt})(\mu_3\text{-OEt})_2$ (10). Orange complex **10** was synthesized by the same procedure as for the synthesis of **6** except that MeHgCl was used instead of $(PPh_3)AuCl$. Yield: 46%. Anal. Calcd for $C_{41}H_{40}O_{12}P_2Au_2HgMo_3$: C, 29.50; H, 2.42. Found: C, 29.81; H, 2.65.

Crystallographic Studies. Crystals of **3** and **4** were grown by slow diffusion of hexane into a concentrated solution of relevant complexes in THF. Crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonious CAD4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) with the $\theta-2\theta$ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. All data reduction and refinements were carried out on a DecAlpha 3000/400 computer using NRCVAX[9] programs. Intensities were collected and corrected for decay, absorption (empirical, ψ-scan), and *Lp* effects. Each structure was solved by direct methods[10] and refined on F by using full-matrix least-squares techniques. An

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Table 3. IR Spectra in the ν(CO) Region and ^{1}H and ^{31}P{H} NMR Spectra of Compounds

compd	ν(CO)^a (cm^{-1})	δ (ppm)^{b,c} [J (Hz)]	δ (ppm)^{d,e} (J (Hz))
3	1953 m, 1931 vs, 1853 sh, 1826 s, 1810 sh	7.59−7.41 (m, 45 H, Ph), 4.72 (q, 2 H, J_{H-H} = 6.9, μ-OCH$_2$), 3.71 (q, 4 H, J_{H-H} = 6.9, μ_3-OCH$_2$), 1.56 (t, 3 H, J_{H-H} = 6.9, CH$_3$), 1.07 (t, 6 H, J_{H-H} = 6.9, CH$_3$)	52.3 (s, 2 P), 51.3 (s, 1 P)
4	1954 m, 1928 vs, 1850 sh, 1820 s, 1800 sh	7.58−7.39 (m, 45 H, Ph), 4.91 (q, 2 H, J_{H-H} = 6.9, μ-OCH$_2$), 3.91 (q, 4 H, J_{H-H} = 6.9, μ_3-OCH$_2$), 1.51 (t, 3 H, J_{H-H} = 6.9, CH$_3$), 1.03 (t, 6 H, J_{H-H} = 6.9, CH$_3$)	60.7 (s, 2 P), 59.7 (s, 1 P)
5	1945 m, 1920 vs, 1840 sh, 1815 s, br	7.72−7.30 (m, 35 H, Ph), 5.04 (q, 2 H, J$_{H-H}$ = 7.2, μ-OCH$_2$), 4.29 (t, 2 H, $^2J_{P-H}$ = 12.0, CH$_2$), 4.20 (dq, 2 H, $^2J_{H-H}$ = 10.5, $^3J_{H-H}$ = 7.0, μ_3-OCH$_2$), 4.06 (dq, 2 H, $^2J_{H-H}$ = 10.5, $^3J_{H-H}$ = 7.0, μ_3-OCH$_2$), 1.61 (t, 3 H, J_{H-H} = 7.2, CH$_3$), 1.20 (t, 6 H, J_{H-H} = 7.0, CH$_3$)	54.6 (s, 1 P, PPh$_3$), 53.2 (d, 1 P, J_{P-P} = 83, PPh$_2$), 50.1 (d, 1 P, J_{P-P} = 83, PPh$_2$)
6	1949 m, 1922 vs, 1841 sh, 1821 s, br	7.69−7.31 (m, 35 H, Ph), 5.06 (q, 2 H, J_{H-H} = 7.2, μ-OCH$_2$), 4.31 (t, 2 H, $^2J_{P-H}$ = 12.0, CH$_2$), 4.20 (dq, 2 H, $^2J_{H-H}$ = 10.5, $^3J_{H-H}$ = 7.0, μ_3-OCH$_2$), 4.08 (dq, 2 H, $^2J_{H-H}$ = 10.5, $^3J_{H-H}$ = 7.0, μ_3-OCH$_2$), 1.64 (t, 3 H, J_{H-H} = 7.2, CH$_3$), 1.21 (t, 6 H, J_{H-H} = 7.0, CH$_3$)	62.6 (s, 1 P, PPh$_3$), 61.5 (d, 1 P, J_{P-P} = 86, PPh$_2$), 58.1 (d, 1 P, J_{P-P} = 86, PPh$_2$)
7	1931 m, 1908 vs, 1895 sh, 1815 s, br	7.90−7.32 (m, 20 H, Ph), 4.73 (q, 2 H, J_{H-H} = 6.6, μ-OCH$_2$), 4.28 (m, 4 H, μ_3-OCH$_2$), 3.83 (m, 2 H, CH$_2$), 3.10 (s, 12 H, NCH$_3$), 1.47 (t, 3 H, J_{H-H} = 6.6, CH$_3$), 1.19 (t, 6 H, J_{H-H} = 6.6, CH$_3$)	52.8 (d, 1 P, J_{P-P} = 88), 51.3 (d, 1 P, J_{P-P} = 88)
8	1953 m, 1922 vs, 1886 s, 1800 vs, br	7.78−7.40 (m, 30 H, Ph), 4.81 (q, 2 H, J_{H-H} = 6.9, μ-OCH$_2$), 4.01 (q, 4 H, J_{H-H} = 6.9, μ_3-OCH$_2$), 3.33 (s, 12 H, NCH$_3$), 1.49 (t, 3 H, J_{H-H} = 6.9, CH$_3$), 1.14 (t, 6 H, J_{H-H} = 6.9, CH$_3$)	62.0 (s)
9	1909 m, 1889 s, 1871 vs, 1788 sh, 1753 vs, br	7.72−7.52 (m, 15 H, Ph), 4.47 (q, 2 H, J_{H-H} = 7.2, μ-OCH$_2$), 3.80 (q, 4 H, J_{H-H} = 7.2, μ_3-OCH$_2$), 3.08 (s, 24 H, NCH$_3$), 1.35 (t, 3 H, J_{H-H} = 7.2, CH$_3$), 1.13 (t, 6 H, J_{H-H} = 7.2, CH$_3$)	59.6 (s)
10	1963 m, 1950 sh, 1932 vs, 1855 sh, 1830 s	7.92−7.35 (m, 20 H, Ph), 4.87 (q, 2 H, J_{H-H} = 6.9, μ-OCH$_2$), 4.43 (t, 2 H, $^2J_{P-H}$ = 12.0, CH$_2$), 4.02 (m, 2 H, μ_3-OCH$_2$), 3.92 (m, 2 H, μ_3-OCH$_2$), 1.65 (t, 3 H, J_{H-H} = 6.9, CH$_3$), 1.19 (t, 6 H, J_{H-H} = 6.9, CH$_3$), 0.96 (s, 3 H, HgCH$_3$)	54.3 (d, 1 P, J_{P-P} = 84), 50.5 (d, 1 P, J_{P-P} = 84)

[a] Measured in CH$_2$Cl$_2$ solution except **9**, which was in CH$_3$CN. [b] Measured in acetone-d_6 except **9**, which was in CD$_3$CN. [c] Reported in ppm relative to δ(Me$_4$Si) 0 ppm. [d] Measured in THF-d_8 solution except **9**, which was in CD$_3$CN. [e] Reported in ppm relative to δ (85% H$_3$PO$_4$) 0 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet.

E-map from the starting set with the highest combined figure of merit revealed coordinates for Mo (or W) and Au atoms. The remaining non-H atoms were located from successive difference Fourier maps. For **3**, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the structure factor calculation in idealized positions with d_{C-H} = 0.95 Å. The selected interatomic distances and bond angles are given in Table 2. The atom C13 in **3** is disordered and has an occupancy of 60%. The atom C15 in **4** is also disordered and has an occupancy of 50%. All crystal data for **4** are given in the Supporting Information.

Results and Discussion

It took more than 2 days for the reaction to go to completion in our initial trials to synthesize M$_3$(CO)$_9$(AuPPh$_3$)$_3$(μ-OEt)(μ_3-OEt)$_2$ (**3**, M = Mo; **4**, M = W) from reaction of [NMe$_4$]$_3$[M$_3$(CO)$_9$(μ-OEt)(μ_3-OEt)$_2$] (**1**, M = Mo; **2**, M = W)[5c] with (Ph$_3$P)AuCl. Besides, the yields of **3** and **4** were variable and generally lower than 20%. By use of (Ph$_3$P)Au$^+$ (prepared in situ from (PPh$_3$)AuCl and TlPF$_6$), an electrophile frequently used for incorporation of gold atoms into metal complexes,[11] we were able to synthesize **3** and **4** in good yields. Furthermore, we were able to isolate two air-sensitive complexes, [NMe$_4$]$_2$[W$_3$(CO)$_9$(AuPPh$_3$)(μ-OEt)(μ_3-OEt)$_2$] (**8**) and [NMe$_4$][W$_3$(CO)$_9$(AuPPh$_3$)$_2$(μ-OEt)(μ_3-OEt)$_2$] (**9**), if stoichiometric amounts of the metal cations were used. Complexes M$_3$(CO)$_9$(Au$_2$(μ-dppm))(AuPPh$_3$)(μ-OEt)(μ_3-OEt)$_2$ (**5**, M = Mo; **6**, M = W), [NMe$_4$][W$_3$(CO)$_9$(Au$_2$(μ-dppm))(μ-OEt)(μ_3-OEt)$_2$] (**7**), and Mo$_3$(CO)$_9$(Au$_2$(μ-dppm))(HgMe)(μ-OEt)(μ_3-OEt)$_2$ (**10**) could also be synthesized by use of Au$_2$(μ-dppm)$^{2+}$.

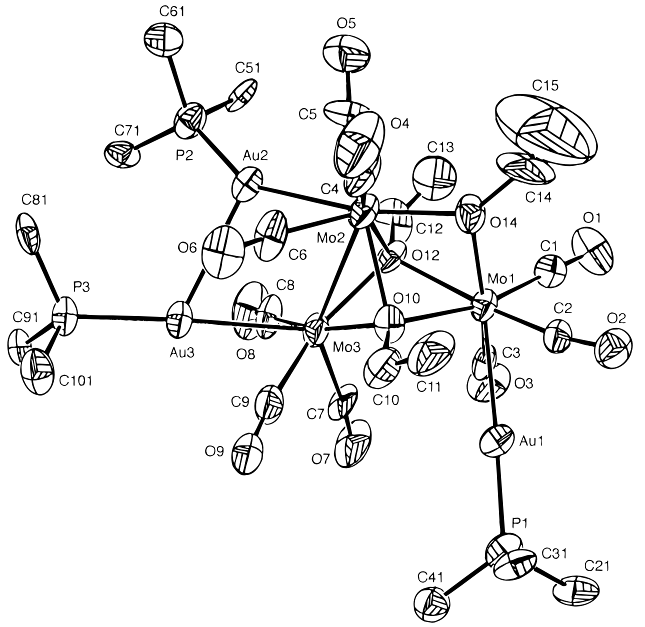

Figure 1. ORTEP drawing of Mo$_3$(CO)$_9$(AuPPh$_3$)$_3$(μ-OEt)(μ_3-OEt)$_2$. Only the ipso carbons of the phenyl groups are shown for clarity. The ellipsoids are drawn with 50% probability boundaries.

Molecular Structure of M$_3$(CO)$_9$(AuPPh$_3$)$_3$(μ-OEt)(μ_3-OEt)$_2$ (3, M = Mo; 4, M = W). Complexes **3** and **4** are isostructural,[12] and an ORTEP drawing of **3** is shown in Figure 1. The original "Mo$_3$(OEt)$_3$" core in **1**[5c] was retained: (1) There exists only one metal−metal bond (Mo2−Mo3 = 2.975(4) Å). (2) Two of the ethoxide ligands are triply bridged and the third ethoxide ligand

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[12] Complex **4** was isomorphous with **3**. Crystal data for **4**: C$_{69}$H$_{60}$O$_{12}$P$_3$Au$_3$W$_3$, space group $P\bar{1}$, a = 12.178(1) Å, b = 15.192(3) Å, c = 22.710(3) Å, α = 81.58(1)°, β = 85.06(1)°, γ = 87.86(1)°, Z = 2, R = 0.064, R_w = 0.072.

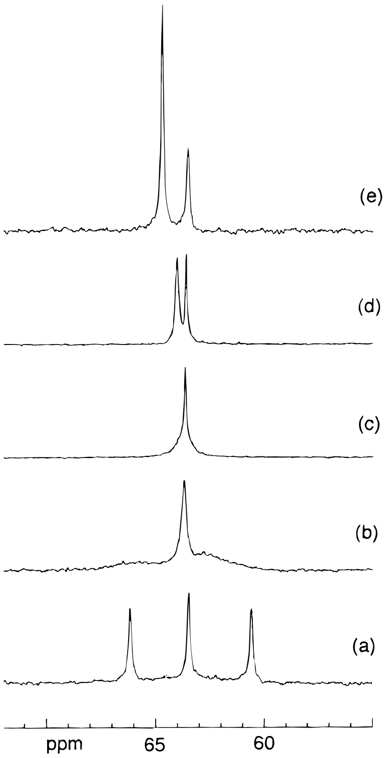


Figure 2. Variable-temperature $^{31}P\{H\}$ NMR spectra of complex **4** in THF-d_8 at (a) 183, (b) 213, (c) 233, (d) 253, and (e) 298 K.

is doubly bridged between Mo1 and Mo2. There are three Mo−Au bonds and the bond distances (Mo1−Au1 = 2.739(3), Mo2−Au2 = 2.788(3), Mo3−Au3 = 2.750(3) Å) are within those reported for Mo−Au or W−Au in the literature (2.698 - 2.824 Å).[3a] The Au2−Au3 distance (3.011(2) Å) is well within those (2.72−3.10 Å) observed in heteronuclear clusters.[13] Hoffmann[14] suggested that two Au(0) atoms in close proximity had a tendency to form an Au−Au bond. Therefore, the presence of a Mo2−Mo3 metal−metal bond might assist the formation of a Au2−Au3 bond. Atoms Mo2, Mo3, Au2, and Au3 form a puckered four-membered ring which is rare in M_2Au_2 clusters and is similar to that found in $Fe_2Au_2(CO)_8(\mu$-dppm).[15] The dihedral angle between the two Mo(2)Au(2)Au(3) and Mo(3)Au(2)Au(3) triangles is 36.8(1)°. Another interesting feature of **3** is that, including the metal−metal bond, all molybdenum atoms have a coordination number of 7 or 8.

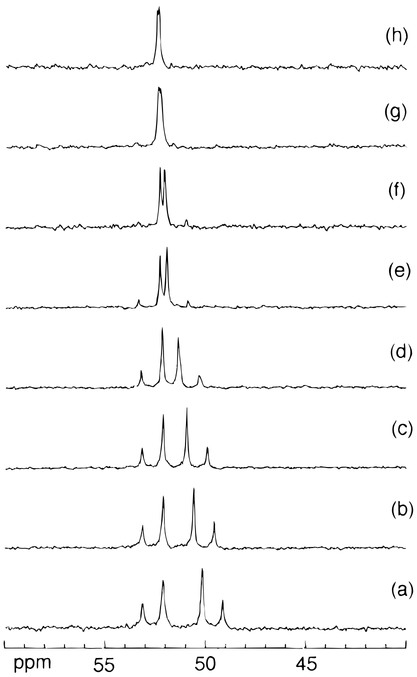
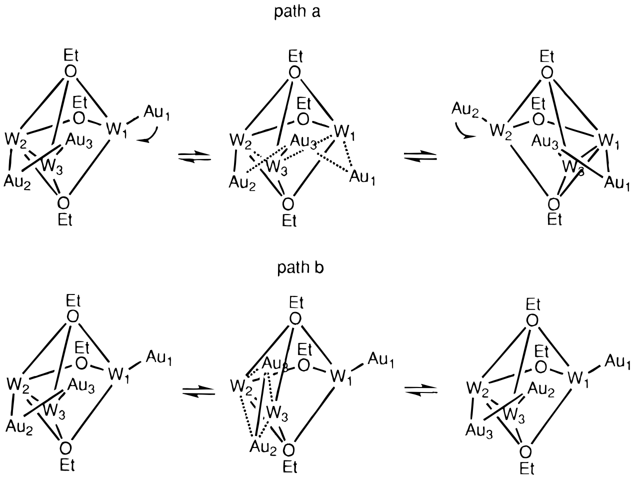


Figure 3. Variable-temperature $^{31}P\{H\}$ NMR spectra of complexe **6** in THF-d_8 at (a) 213, (b) 233, (c) 253, (d) 273, (e) 303, (f) 313, (g) 323, and (h) 333 K.

Scheme 1



Fluxionality. Rigorously speaking, the three phosphorus atoms should be magnetically inequivalent because of the dissimilarity of the coordination core for each W or Mo atom. However, we observed only two ^{31}P NMR signals with a 2:1 ratio at room temperature (Table 3). In view of the common stereochemical nonrigidity found in polynuclear gold complexes,[16] we performed the variable-temperature $^{31}P\{H\}$ NMR studies for **4**, and the spectra are shown in Figure 2. By a lowering of the temperature, the signal of intensity one (δ 63.5) remained static whereas the signal of intensity two (δ 64.6) broadened and eventually collapsed (−60 °C) to two separate signals of equal intensities (δ 66.1 and 60.5). The ^1H NMR spectra are also consistent with the fluxional behavior of **4** and suggest that bridging ethoxide ligands are not involved in exchange behavior. At room temperature the two μ_3-OEt ligands are magnetically equivalent and are distinct from the μ_2-OEt ligand in the ^1H NMR spectra. As the temperature is lowered, the CH_2 peaks of the μ_2-OEt ligand are broadened, albeit the chemical shifts of which remain invariant down to −60 °C. In contrast to μ_2-OEt, at −60 °C the CH_2 peaks of the μ_3-OEt ligands collapse into four broad peaks which correspond to the solid structure of **4**. A plausible exchange mechanism, “a”, is depicted in Scheme 1. In mechanism “a”, concomitant breakage of W2−W3 and Au2−Au3 bonds and formation of W1−W3 and Au1−Au3 bonds would render P1 and P2 to be magnetically equivalent. This type of valence isomerization is equivalent to a racemization process and is similar to that[17] described for $Mn_2(AuPPh_3)_2(\mu_4$-PCy)-$(CO)_8$. A second mechanism, “b”, is also depicted in Scheme 1. In “b”, P2 and P3 become equivalent through

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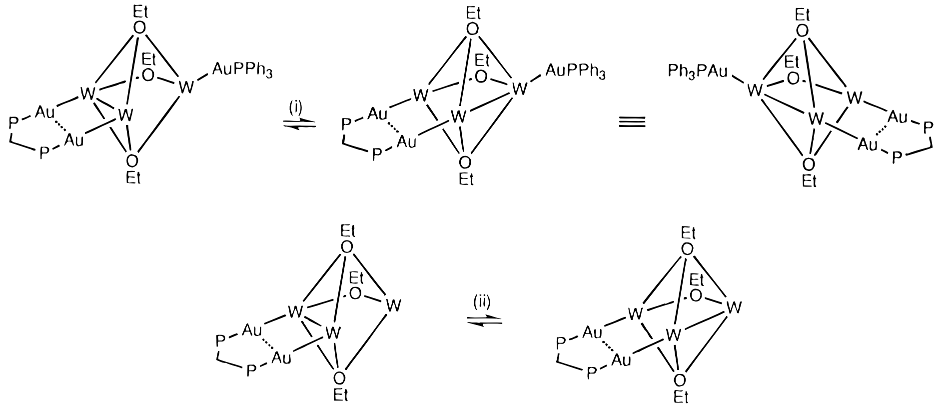
Scheme 2



concomitant formation of Au3−W2 and Au2−W3 and breakage of Au3−W3 and Au2−W2 bonds. The mechanism "b" is less favored due to the equivalence of the methylene protons of the μ_3-OEt ligands in the ^{1}H NMR spectra at 25 °C. Valence isomerization involving concomitant breakage of W2−W3 and formation of W1−W3 likely also occurs in complexes $W_3(CO)_9(Au_2(\mu$-dppm$))(AuPPh_3)(\mu$-OEt$)(\mu_3$-OEt$)_2$ (**6**)[14] and $[NMe_4][W_3(CO)_9(Au_2(\mu$-dppm$))(\mu$-OEt$)(\mu_3$-OEt$)_2]$ (**7**)[14] on the basis of the following observations: (i) The same product **6** is obtained from either sequential addition of $Au_2(\mu$-dppm$)^{2+}$ and $(Ph_3P)Au^+$ to **2** or sequential addition of $(Ph_3P)Au^+$ and $Au_2(\mu$-dppm$)^{2+}$ to **2**. (ii) There is no exchange between the two magnetically inequivalent phosphorus atoms of the complex **7** in the temperature range of −60 to 60 °C; however, the chemical shift of one of the phosphorus atoms remains almost invariant and that of the other is getting closer to the first one as the temperature increases (Figure 3). (iii) The two methylene protons of μ_3-OEt ligands remain diastereotopic for both **6** and **7**. Scheme 2 illustrates our rationalization of these observations.

In the temperature range of −70 to 25 °C, the complex $[NMe_4][W_3(CO)_9(AuPPh_3)_2(\mu$-OEt$)(\mu_3$-OEt$)_2]$ (**9**) exhibits only one signal in the $^{31}P\{H\}$ NMR, and the methylene protons of μ_3-OEt ligands are magnetically equivalent in the ^{1}H NMR spectra, implying that the two Au atoms of **9** are bonded to the W1 and W2 atoms and the valence isomerization process is not frozen at −70 °C.

Conclusion. Polyanionic metal carbonyls, $[M_3(CO)_9(\mu$-OEt$)(\mu_3$-OEt$)_2]^-$ (M = Mo; W), are useful building blocks for constructing mixed-metal (M/Au) carbonyls of higher nuclearity. Interesting valence isomerization was found to occur in these clusters due to proximity of metal atoms. Isolation of $Mo_3(CO)_9(Au_2(\mu$-dppm$))(HgMe)(\mu$-OEt$)(\mu_3$-OEt$)_2$ indicates that syntheses of mixed-metal clusters other than gold is possible. Our future research will also aim at extension of the strategy in this report to other polynuclear polyanions for the syntheses of mixed-metal clusters with peripheral coinage metals.

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Supporting Information Available: Listings of crystal data, atomic coordinates (including hydrogen atoms), thermal parameters, and bond distances and angles for complex **3** and all crystal data for complex **4** and an ORTEP view of **4** (24 pages). Ordering information is given on any current masthead page.

OM950711J

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