vital intercluster bridging that is no longer possible in the binary R_4X_6 structure.

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Supplementary Material Available: Tables of detailed data collection and refinement information and thermal displacement parameters for $Y_{10}I_{13}C_2$ (2 pages); observed and calculated structure factors for $Y_{10}I_{13}C_2$ (5 pages). Ordering information is given on any current masthead page.

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Synthesis of Cobalt–Tungsten Clusters with Tetrahedral Metallic Cores Using the Mixed-Metal Complex $CoW(CO)_7(\eta^5\text{-}C_5H_4Me)$ (Co–W) as a Cluster Building Block. X-ray Diffraction Study of the Sterically Crowded Tetrahedral Cluster $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$

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Cobalt–tungsten clusters with tetrahedral Co_xW_{4-x} (x = 1–3) cores are formed when $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$) or $Co_2(CO)_8$ is treated with $(OC)_4Co\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1b**). **1b** reacts with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ affording clusters $Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2b**) and $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3b**), whose structure was established by a single-crystal X-ray diffraction study. **3b** crystallizes in the monoclinic space group *C*2/*c* (No. 15) with a = 30.740 (6) Å, b = 9.706 (1) Å, c = 18.729 (4) Å, β = 91.78 (1)°, V = 5585 (3) Å^3, and Z = 8; refinement converged at R = 0.032, R_w = 0.041. The molecule contains a slightly flattened CoW_3 tetrahedral metallic core and has a pseudo-C_3 axis. The cobalt atom is ligated to three carbonyl ligands, while each tungsten atom is linked to a η^5-methylcyclopentadienyl ligand and two carbonyl groups. **3b** exhibits dynamic behavior that involves carbonyl ligand exchange; the ^{13}C NMR resonances of the $\eta^5\text{-}C_5H_4Me$ group are also temperature dependent. This cluster has C_3 symmetry in solution at −80 °C on the ^{13}C NMR time scale, but at or above 20 °C the effective symmetry is C_{3v}. The heterotrimetallic cluster $CoMoW_2(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3′**) was prepared by reacting **1b** with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$), and its ^{13}C NMR spectrum was also studied. The cluster $Co_3W(\mu_2\text{-}CO)_3(CO)_8(\eta^5\text{-}H_4Me)$ (**5b**) and an unidentified cobalt species formed when **1a** was treated with $Co_2(CO)_8$. The pyrolysis of **1b** and the reaction of $Co_2(CO)_8$ with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$) are described.

Introduction

A multitude of mixed-metal clusters have been characterized, and new species continue to be reported. Many heterometallic tetrahedral clusters containing combinations of the ubiquitous isolobal fragments $Ni(\eta^5\text{-}C_5H_5)$, $Co(CO)_3$, $M(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo, W), and RC are known,[1] but others remain elusive owing to the lack of readily available syntheses. Our current research involves reactions of heterobimetallic compounds;[2] our serendipitous preparation of Ni_3W and Ni_3Mo clusters from nickel–molybdenum and nickel–tungsten dinuclear species[3] led us to explore whether other mixed-metal complexes had potential as better routes to known clusters or as building blocks to new compounds. The dimetallatetrahedrane species $(OC)_4CO(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2R)W(CO)_2(\eta^5\text{-}C_5H_5)$ (R = Me, Ph) and related cobalt–molybdenum compounds are known.[4] The isolobal analogy suggests that tetrahedral clusters with Co_xW_{4-x} (x = 1–3) metallic cores should be accessible. Here we describe reactions of $(OC)_4C\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1b**) with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$) and $Co_2(CO)_8$ and the thermolysis of **1b**, all of which lead to mixed-metal clusters. The X-ray structure and VT ^{13}C NMR behavior of $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$, a cluster that results from the reaction of **1b** with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$), are presented, and a few reactions of the analogous cobalt–molybdenum complex $(OC)_4Co\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1a**) with some of these reagents are also discussed. We use **1a** and **1b** rather than their previously reported cyclopentadienyl analogues,[5] as the multiplet patterns exhibited by C_5H_4Me nuclei allow additional symmetry information to be gleaned from ^1H and ^{13}C NMR spectra.

Results and Discussion

(a) Reaction of $(OC)_4Co\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1b) with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$). (i) Reaction Products. $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ ($W\equiv W$) and **1b** react to form three compounds that were separated chromatographically. The dimeric tungsten species $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ was identified by IR spectroscopy. Two other products (**2b** and **3b**) were crystallized from hexanes. The dark colors of these complexes (**2b** is dark green; **3b** is purple) and their low solubilities and chromatographic mobilities are characteristic of metal clusters, and this was confirmed by spectroscopic analyses.

No meaningful MS data could be obtained for **2b** or **3b**: the clusters are involatile at low probe temperatures and decompose

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Table I. Crystallographic Data for $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3b**)

$W_3CoO_9C_{27}H_{21}$	space group $C2/c$ (No. 15)
fw 1099.95	T = 20 °C
a = 30.740 (6) Å	λ = 0.71073 Å
b = 9.706 (1) Å	ρ_{calc} = 2.616 g cm^{-3}
c = 18.729 (4) Å	μ = 132.22 cm^{-1}
β = 91.78 (1)°	transm coeff = 1.000–0.555
V = 5585 (3) Å^3	$R(F_o)$ = 0.032
Z = 8	$R_w(F_o)$ = 0.041

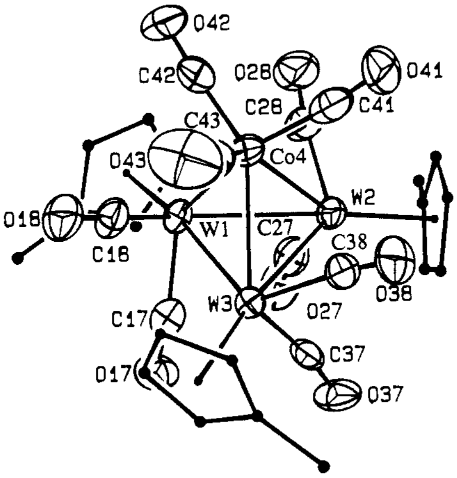
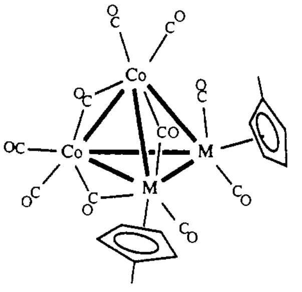
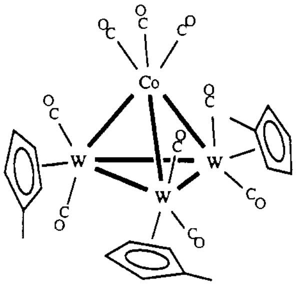


Figure 1. ORTEP plot of $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3b**) showing the thermal ellipsoids at the 50% probability level. Carbon atoms of the methylcyclopentadienyl ligand are shown as arbitrarily sized solid circles.

when vaporized at higher temperatures. The IR spectrum of **2b** showed ν(CO) bands at frequencies characteristic of terminal and μ_2-CO ligands, while that of **3b** revealed only terminal ν(CO) absorptions. ^1H NMR spectra for both species show signals for $\eta^5\text{-}C_5H_4Me$ groups. The aromatic protons resonate as a single set of AA′BB′ spin multiplets for both species. These data and analyses suggest that **2b** and **3b** are the clusters $Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ and $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$, respectively. While this work was in progress, a cyclopentadienylmolybdenum analogue of **2b**, the tetrahedral cluster $Co_2Mo_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$, was synthesized and characterized by X-ray diffraction.[6] IR data suggest that **2b** is isostructural with this species. The structures of **2b** and **3b** are shown as follows: eq 1 summarizes this reaction.



2a, M = Mo
2b, M = W



3b

$$\begin{gathered}(OC)_4Co\text{-}W(CO)_3(\eta^5\text{-}C_5H_4Me)\ (\mathbf{1b}) + \\ [W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\ (W{\equiv}W) \rightarrow \\ Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2\ (\mathbf{2b}) + \\ CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3\ (\mathbf{3b}) + [W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2 \end{gathered} \tag{1}$$

(ii) X-ray Structural Determination of 3b. A single-crystal X-ray diffraction study of **3b** was undertaken to unambiguously establish the structure of this complex. Tables of crystal data parameters, atomic positional parameters, and key bond lengths and angles are collected in Tables I–III. An ORTEP plot of the structure is shown in Figure 1, while Figure 2 shows a "ball and stick" stereoview of the molecule, looking down onto the tritungsten plane.

Table II. Final Positional Parameters for Key Atoms of **3b** and Esd's in Parentheses

atom	x/a	y/b	z/c
W(1)	0.08702 (2)	0.24642 (5)	0.05502 (3)
W(2)	0.14280 (2)	0.27716 (6)	0.18525 (3)
W(3)	0.16026 (2)	0.05424 (5)	0.08232 (3)
Co(4)	0.08718 (6)	0.0551 (2)	0.16487 (9)
O(17)	0.1561 (4)	0.288 (1)	−0.0597 (5)
O(18)	0.0552 (3)	−0.028 (1)	−0.0151 (6)
O(27)	0.1558 (4)	0.520 (3)	0.0822 (6)
O(28)	0.0544 (4)	0.391 (1)	0.2340 (6)
O(37)	0.2351 (3)	0.267 (1)	0.0856 (6)
O(38)	0.1925 (3)	−0.073 (1)	0.2287 (5)
O(41)	0.0992 (4)	0.012 (2)	0.3172 (6)
O(42)	−0.0061 (3)	0.100 (2)	0.1661 (6)
O(43)	0.0799 (5)	−0.235 (1)	0.1318 (8)
C(17)	0.1335 (5)	0.259 (1)	−0.0143 (8)
C(18)	0.0693 (5)	0.068 (1)	0.0147 (8)
C(27)	0.1469 (5)	0.416 (2)	0.1169 (8)
C(28)	0.856 (5)	0.346 (2)	0.2122 (9)
C(37)	0.2041 (4)	0.192 (2)	0.0890 (7)
C(38)	0.1788 (5)	−0.017 (2)	0.1786 (7)
C(41)	0.0967 (5)	0.039 (2)	0.2572 (9)
C(42)	0.0309 (5)	0.090 (2)	0.1635 (8)
C(43)	0.0843 (5)	−0.123 (2)	0.1410 (9)

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **3b** with Esd's in Parentheses

	Distances		
W(1)–W(2)	2.9526 (7)	W(1)–W(3)	2.9561 (7)
W(1)–W(3)	2.9580 (7)	W(1)–Co(4)	2.771 (2)
W(2)–Co(4)	2.770 (2)	W(3)–Co(4)	2.767 (2)
W–$C_{Cp'}$	2.336[a]	W–C_{CO}	1.94[a]
Co–C_{CO}	1.76[a]	W–C_{CO}	2.757[a,b]
	Angles		
W(2)–W(1)–W(3)	60.08 (2)	W(1)–Co(4)–W(2)	64.39 (4)
W(1)–W(3)–W(2)	59.90 (2)	W(1)–Co(4)–W(3)	64.52 (4)
W(1)–W(2)–W(3)	60.02 (2)	W(2)–Co(4)–W(3)	64.59 (4)
W(1)–W(2)–Co(4)	57.82 (4)	W(1)–C(17)–O(17)	166 (1)
W(1)–W(3)–Co(4)	57.81 (4)	W(1)–C(18)–O(18)	171 (1)
W(2)–W(3)–Co(4)	57.76 (4)	W(2)–C(27)–O(27)	166 (1)
W(3)–W(2)–Co(4)	57.65 (4)	W(2)–C(28)–O(28)	173 (1)
W(2)–W(1)–Co(4)	57.78 (4)	W(3)–C(37)–O(37)	170 (1)
W(3)–W(1)–Co(4)	57.66 (4)	W(3)–C(38)–O(38)	170 (1)
Co(4)–C(41)–O(41)	170 (2)	W–W–Co	57.8[a]
Co(4)–C(42)–O(42)	173 (2)	W–Co–W	64.5[a]
Co(4)–C(43)–O(43)	173 (2)	W–C–O	169[a]
		Co–C–O	172[a]

[a] Mean values. [b] Closest nonbonded distance.

Complex **3b** consists of a flattened tetrahedral CoW_3 core—the cobalt atom is compressed slightly toward the W_3 plane. Each tungsten atom is coordinated to a η^5-methylcyclopentadienyl group and to two carbonyl ligands that lie above and below the W_3 plane (closer to and away from the cobalt atom). The disposition of these ligands results in no mirror planes being present in **3b**, but the molecule does contain a pseudo-C_3 axis of symmetry and the W_3 triangle is practically equilateral. The cobalt atom is bonded to three terminal carbonyl groups that are skewed so that their projections onto the W_3 plane do not bisect W–W bonds. Every atom in **3b** is electron precise, and the cluster as a whole has the expected 60-electron configuration.

The statistically equal tungsten–tungsten distances in the molecule (2.956 Å, average) are typical of W–W single bonds. Cobalt–tungsten bonds in **3b** (2.769 ± 0.002 Å) lie in the middle of the range reported for other such bonds[1b,4,7-21] (Table IV). The

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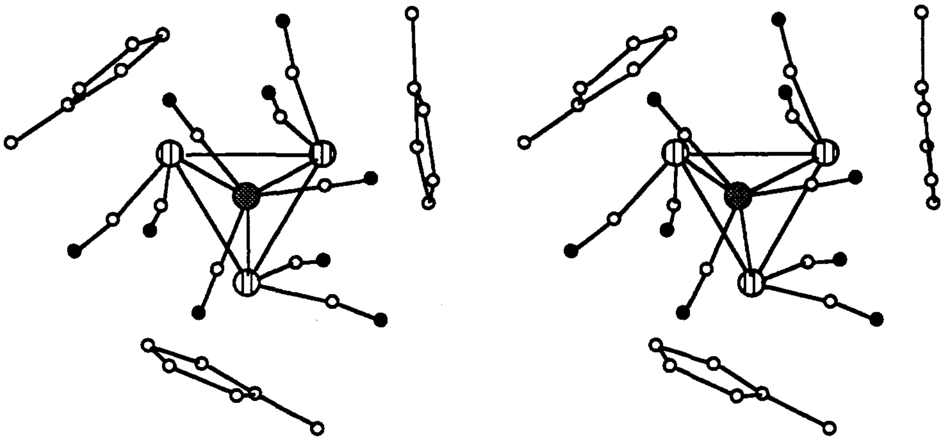

Figure 2. Stereoplot of **3b**, showing the view perpendicular to the W_3 plane.

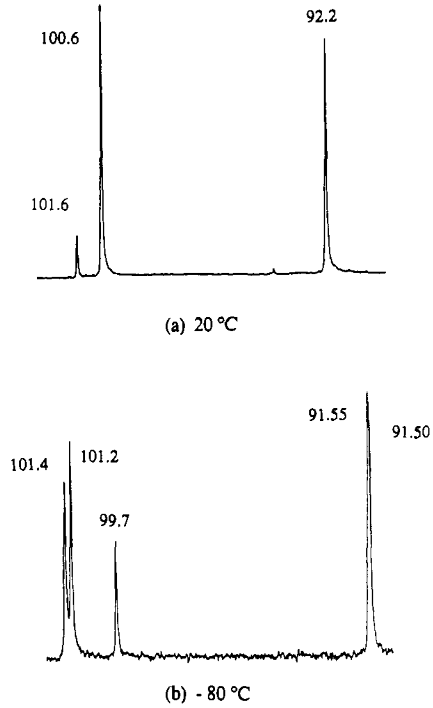

Figure 3. Appearance of the aromatic η^5-C_5H_4Me group carbon atom resonances of **3b** in the $^{13}C\{^1H\}$ NMR spectra: (a) 20 °C; (b) −80 °C.

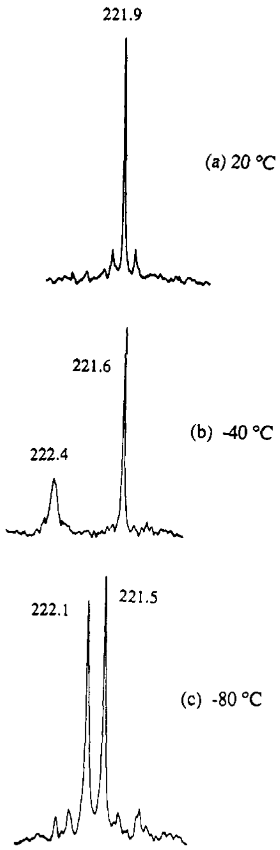

Figure 4. Appearance of the carbonyl ligand resonances of **3b** in the $^{13}C\{^1H\}$ NMR spectra: (a) 20 °C; (b) −40 °C; (c) −80 °C. Note the magnitude of the ^{183}W satellites in (a) and (c) and their absence in (b).

M–C–O (M = Co, W) angles in the molecule are all significantly less than 180° (some as low as 166°), indicating that weak semibridging interactions are present. These interactions decrease in the order W–C(O)···W > W–C(O)···Co ≫ Co–C(O)···W: the first two classes of interactions have asymmetry parameters[22] in the 0.42–0.51 range.

Deviations from linearity are observed in M–C–O groups in the related tetrahedral clusters $Ir_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$[23] and $Ir_2W_2(CO)_{10}(\eta^5\text{-}C_5H_5)_2$,[23a,24] and three carbonyl ligands bridge the edges of a Co_2Mo triangle in the cluster $Co_2Mo_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$.[6] As **3b** is one of the most sterically congested

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Table IV. Selected Cobalt–Tungsten Bonds

complex	Co–W, Å	ref
(a) Dinuclear Systems		
$CoW(\mu\text{-}PhC_2Me)(CO)_5(\eta^5\text{-}C_5H_5)$	2.693 (1)	4
$CoW\{\mu\text{-}C_4(CF_3)_4\}(CO)_3(\eta^5\text{-}C_5H_5)$	2.664 (1)	7
$CoW(\mu\text{-}CR)(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)^a$	2.758 (1)	8
$[CoW(\mu\text{-}C_4R_2Me_2)(\mu\text{-}CO)(CO)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]^{+\,a}$	2.552 (1)	9
$CoW\{\mu\text{-}C_4R_2(Et)(OH)\}(CO)_4(\eta^5\text{-}C_5H_5)^a$	2.702 (1)	10
$CoW(\mu\text{-}CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_5H_5)^b$	2.356 (0)!	11
$CoW(\mu\text{-}C_3R_2O)(CO)_5(\eta^5\text{-}C_5H_5)$	2.669 (1)	12
$CoW(\mu\text{-}C_4RMe_2O)(CO)_6(PPh_3)$	2.737 (1)	13
$[CoW\{\mu\text{-}C_4Me_2Ph(OH)\}(CO)_6(PPh_3)]^+$	2.660 (1)	13
(b) Polynuclear Systems		
$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta^5\text{-}C_5H_5)^a$	2.672 (1)	1b
$Co_2W(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta^5\text{-}C_5H_5)$	2.792 (1), 2.730 (1)	14
$CoRuW(\mu_3\text{-}\eta^2\text{-}C{=}CH^tBu)(CO)_8(\eta^5\text{-}C_5H_5)$	2.723 (3)	15
$Co_2W(\mu\text{-}PEt_2)_3(CO)_5(\eta^5\text{-}C_5H_5)$	2.684 (1), 2.995 (1)	10
$Co_2W(\mu_3\text{-}C_4REt_2O\}(\mu\text{-}CO)(CO)_4\{PPh_2CEt{=}CHEt\}^a$	2.809 (1), 2.784 (1)	10
$Co_2RuW(\mu_4\text{-}C_2Ph)(\mu\text{-}CO)(CO)_{10}(\eta^5\text{-}C_5H_5)$	2.775 (1)	16
$Co_2RuW(\mu_3\text{-}CR)(\mu\text{-}CO)_2(CO)_8(\eta^5\text{-}C_5H_5)^a$	2.675 (2), 2.739 (2)	16
$Co_2W(\mu\text{-}C_4Et_4)(\mu\text{-}C_2Et_2)(CO)_8$	2.732 (1), 2.673 (1)	17
$[Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]^-$	2.767 (2), 2.769 (2)	18
$Co_2W(\mu\text{-}S)(\mu\text{-}SCNEt_2)(C_2Ph_2)(CO)_4(S_2CNEt_2)$	2.701 (1), 2.601 (1)	19
$Co_2W\{\mu_3\text{-}CSC(CF_3)C(CF_3)\}(\mu_2\text{-}S)(dmpe)(CO)_7$	2.727 (1), 2.744 (1)	20
$Co_3W(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)$	2.716 (1), 2.725 (1), 2.706 (1)	21
$CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$	2.770 (2), 2.767 (2), 2.771 (2)	this work

^{a}R = C_6H_4Me-4. ^{b}Formal Co–W triple bond.

tetrahedral clusters known, these interactions probably stem from the severe steric congestion present (i.e. interligand repulsion), rather than from electronic effects.

(iii) ^{13}C VT NMR Spectrum and Dynamic Behavior of 3b. The natural-abundance ^{13}C NMR spectrum of **3b** varies significantly with temperature. At and above 20 °C, three signals are seen for the aromatic η^5-C_5H_4Me carbon atoms. These resonances are broadened at −40 °C, and at −80 °C five sharp signals are observed for these carbon atoms (Figure 3). The three ligands remain symmetry related, and a single signal is noted for their methyl groups at all temperatures.

The equivalence of the three η^5-C_5H_4Me groups on the ^{13}C NMR time scale suggests that **3b** has at least C_3 symmetry over the −80 to +20 °C range. Three signals are observed for the aromatic η^5-C_5H_4Me carbon atoms at 20 °C, indicating that the cluster now has C_{3v} symmetry. At −80 °C, five signals are seen for these carbon atoms: each dienyl group is no longer effectively bisected by a mirror plane, and **3b** now exhibits only C_3 symmetry.

Carbonyl ligand resonances are also temperature dependent. A single resonance flanked by ^{183}W satellites ($^1J_{WC}$ = 89 Hz) is observed at both +20 and +65 °C. At −40 °C, an additional broad signal is noted, and at −80 °C, the spectrum shows two sharp signals in approximately a 1:1 intensity ratio. Their coupling constants ($^1J_{WC}$ = 179 and 156 Hz) indicate direct linkages to tungsten (Figure 4).

Complex **3b** is undergoing a fluxional process on the NMR time scale that involves carbonyl ligand exchange. No signals are seen for cobalt-bound carbonyl ligands, presumably because of ^{59}Co quadrupolar broadening,[25] and all observed carbonyl resonances are assigned to tungsten-bound carbonyl ligands. The two carbonyl ligand signals observed at −80 °C are attributed to ligands that lie above and below the W_3 plane (closer to and away from the cobalt atom).

At −40 °C these ligands appear to be undergoing slow site exchange, as both signals are broad and tungsten-183 satellites are absent. The resonance observed at 20 °C (and 65 °C) shows a small $^1J_{WC}$ coupling of 89 Hz, a value approximately half of the mean ^{183}W–^{13}C value seen at −80 °C. This rules out localized exchange of the carbonyl ligands on a particular tungsten atom. As the chemical shift observed for this resonance is close to the mean chemical shift for the −80 °C signals, involvement of the cobalt-bound ligands in this fluxional process is also unlikely at this temperature.

The majority of tungsten nuclei in **3b** are spin inactive: if the tungsten-bound carbonyl ligands were exchanging with each other, the observed value of J_{WC} would be one-third and not half of the low-temperature average value,[26] at variance with what is observed. Global carbonyl group scrambling (involving the cobalt atom as well) would lead to even smaller ^{183}W–^{13}C coupling (approximately one-fourth of the mean value seen at −80 °C if $^2J_{WC} \approx 0$).

We do not fully understand the fluxional process or processes that lead to the single carbonyl resonance observed at 20 °C and the magnitude of $^1J_{WC}$. *Pairwise* exchange of two carbonyl ligands along all three tungsten–tungsten edges (global tungsten exchange) would give rise to the observed coupling constant of 89 Hz at 20 °C if each pair of carbonyl ligands remains localized on a particular W–W edge. The η^5-methylcyclopentadienyl groups may act as steric barriers to the scrambling of the carbonyl groups around the W_3 triangle perimeter.[27] Alternatively, all tungsten-bound carbonyl ligands may be exchanging with each other. This would also explain the effective C_{3v} symmetry observed for the cluster at 20 °C, but the magnitude of J_{WC} at this temperature is hard to rationalize. The observed intensities of the ^{183}W–^{13}C satellites (≈14% for pairwise tungsten ligand exchange, ≈21% for global tungsten ligand exchange) should be diagnostic, but the experimental data are not conclusive. Data for the analogous $CoMoW_2$ cluster (reported below), coupled with these data, make global tungsten carbonyl exchange the more likely dynamic process, despite the anomalous value of J_{WC} at ambient and elevated temperatures.

(iv) Synthesis and Spectroscopic Data of the Heterotrimetallic Cluster $CoMoW_2(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (3′). To clarify the dynamic behavior of **3b**, the analogous cluster with a molybdenum atom replacing one of the tungsten atoms was synthesized, effectively reducing the symmetry of **3b**. The cobalt–molybdenum dinuclear species $(OC)_4Co\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1a**) was reacted with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W), yielding small quantities of

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(25) Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, 1971; p 61.

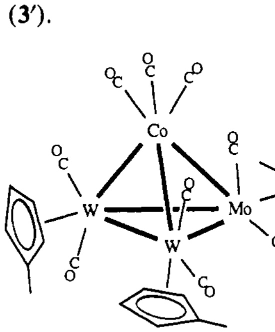
(26) This assumes that $^2J_{WC}$ = 0 and that the coupling constants involved have the same sign.

(27) Carbonyl ligand induced rocking of the η^5-C_5H_4Me ligands about their centroid–tungsten axes would generate C_{3v} symmetry for the cluster by creating effective mirror planes that bisect each ligand. A similar process was proposed for the alkyne-bridged species $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}\eta^2,\eta^2\text{-}RC_2R)M(CO)_2(\eta^5\text{-}C_5H_4Me)$ (Ni–M; M = Mo, W): Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298.

Table V. IR Data

		freq, cm^{-1}	
	color	Nujol mull	hexanes
1a	purple		2075 (s), 2058 (vw), 2044 (vw), 2021 (s), 1987 (s), 1977 (s), 1959 (w), 1944 (s), 1941 (s), 1918 (vw), 1913 (vw)
1b	purple	2074 (s), 2018 (s), 1994 (sh), 1985 (s), 1976 (s), 1958 (s), 1920 (s), 1911 (s), 1888 (s)	2076 (s), 2021 (s), 1989 (s), 1978 (s), 1957 (m), 1937 (s), 1930 (s), 1910 (m), 1899 (w)
2a	green	2050 (s), 2016 (s), 1987 (s), 1980 (sh), 1935 (s), 1887 (s), 1841 (w), 1810 (m), 1796 (m)	2054 (s), 2024 (s), 1991 (s), 1983 (s), 1957 (m), 1933 (s), 1889 (s), 1852 (sh), 1848 (w), 1819 (w), 1807 (w)
2b	green	2037 (s), 2004 (sh), 1998 (s), 1978 (s), 1962 (s), 1946 (s), 1925 (s), 1877 (s), 1843 (m), 1807 (m), 1792 (m), 1775 (s)	2054 (s), 2024 (s), 2011 (vw), 1989 (m), 1980 (m), 1954 (w), 1931 (m), 1883 (m), 1850 (w), 1806 (w), 1790 (w)
3b	purple	2000 (m), 1991 (m), 1954 (m), 1939 (m), 1928 (s), 1915 (sh), 1898 (s), 1850 (s), 1808 (m)	2001 (m), 1947 (s), 1916 (m), 1901 (m), 1864 (m)
3′	blue	2001 (s), 1947 (s), 1928 (s), 1917 (s), 1898 (s), 1863 (s), 1846 (s)	2004 (s), 1949 (vs), 1920 (sh), 1916 (m), 1898 (m), 1863 (s), 1846 (s)
4	green	2081 (s), 2043 (s), 2012 (vs), 1814 (s)	2075 (s), 2052 (s), 2030 (s), 2013 (s), 1821 (s)
5a	green	2077 (s), 2023 (s), 1997 (s) 1977 (s), 1952 (s), 1941 (s), 1873 (s), 1839 (s), 1821 (s)	2080 (s), 2041 (s), 2033 (s), 2024 (s), 2003 (s), 1995 (s), 1979 (m), 1951 (s), 1893 (w), 1864 (s), 1836 (s)
5b	purple	2087 (m), 2076 (w), 2041 (sh), 2033 (s), 2022 (s), 1995 (s), 1973 (m), 1946 (m), 1931 (m), 1873 (w), 1851 (m), 1839 (m)	2079 (m), 2041 (s), 2033 (m), 2024 (m), 2000 (m), 1993 (m), 1976 (w), 1944 (m), 1890 (w), 1864 (w), 1836 (w)

$Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2b**) and larger amounts of **3b**. A new dark blue-purple complex was also isolated, later characterized as the heterotrimetallic cluster $CoMoW_2(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3′**).



3′

No meaningful mass spectrum was obtained for **3′** (cf. **3b**), but analytical data and IR and NMR spectroscopy indicate that it is formulated correctly as shown. Its IR spectrum is quite similar to that of **3b**. The ^1H NMR spectrum of **3′** shows two methyl group resonances in a 1:2 ratio: some aromatic $\eta^5\text{-}C_5H_4Me$ protons of the $(\eta^5\text{-}C_5H_4Me)$–W ligands are fortuitously coincident, in different solvents (an AA′BB′ pattern is observed in acetone-d_6, while ABCC′ spectra are seen in benzene-d_6 and chloroform-d_1, even on a 500-MHz instrument).

The ^{13}C NMR spectrum of **3′** is in accord with the ^1H NMR data. Eight resonances were seen for the $\eta^5\text{-}C_5H_4Me$ carbon atoms. The $(\eta^5\text{-}C_5H_4Me)$–Mo carbon atoms appear as three signals in a 2:2:1 relative ratio, and five signals, in a 2:2:2:2:2 relative ratio, are noted for the $(\eta^5\text{-}C_5H_4Me)$–W carbon atoms. This indicates that **3′** has an effective mirror plane that bisects the $(\eta^5\text{-}C_5H_4Me)$–Mo ligand and reflects the two $(\eta^5\text{-}C_5H_4Me)$–W groups into each other. In addition, these data confirm that isochronous proton resonances observed for some of the $\eta^5\text{-}C_5H_4Me$ protons in the ^1H NMR spectrum are coincidental. One resonance is observed for the carbonyl ligands at 20 °C, implying that the molybdenum- and tungsten-bound carbonyl groups are undergoing site exchange. As the symmetry of **3b** is higher than that of **3′**, a similar process is more likely in **3b**, suggesting that carbonyl exchange between three, and not two, tungsten atoms is prevalent in that cluster.

(v) Reaction of 1b with Excess $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W). In the reaction of **1b** with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W), the ditungsten compound scavenges a carbonyl ligand and is carbonylated to form $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$, reacting similarly to the reagent trimethylamine *N*-oxide. To ensure that sufficient $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W) would be present to react with **1b** after the carbonyl-scavenging reaction, the reaction of the triply bonded complex with **1b** in a 2:1 ratio was attempted. This resulted in higher yields of **3b** (≈37%). The only other species formed under these conditions (apart from traces of another product) was $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$, and **2b** was not produced at all (eq 2). In a separate reaction, CO was bubbled overnight

$$\begin{gathered}(OC)_4Co\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)\ (\mathbf{1b}) + \\ 2[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\ (W{\equiv}W) \rightarrow \\ CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3\ (\mathbf{3b}) + [W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2\end{gathered} \quad (2)$$

through a solution of **3b**. IR analysis of the reaction mixture showed that **2b** and $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ were not produced.

(b) Reactions of $(OC)_4Co\text{–}M(CO)_3(\eta^5\text{-}C_5H_4Me)$ (M = Mo (1a), M = W (1b)) with $Co_2(CO)_8$. (i) Reaction of 1b. $Co_2(CO)_8$ reacts with **1b** affording a mixture of products. Chromatographic separation afforded a purple species and green mixture containing **2b** and a new species (**4**). The small quantities and similar solubility properties of **2b** and **4** prevented their clean separation, and **4** remains to be isolated pure and fully characterized. Three pointers lead us to believe that **4** contains no tungsten and that methylcyclopentadienyl ligand transfer from tungsten to cobalt may have taken place:[28] (1) ^1H NMR data for **4** reveal a single set of $\eta^5\text{-}C_5H_4Me$ signals, whose chemical shifts (Table VI) differ significantly from those of the other clusters reported here. (2) MS data for **4** reveal no characteristic tungsten isotope pattern, indicating a lack of tungsten. (3) The reaction of $Co_2(CO)_8$ with **1a**, discussed in the next section, also afforded traces of **4**,[29] clearly demonstrating the absence of tungsten in this species. These data suggest that **4** is a homonuclear cobalt cluster.

The mass spectrum of the purple species (**5b**) exhibits a parent peak with an *m/e* ratio of 748 and an isotopic envelope pattern

Table VI. ^1H NMR Data (Chloroform-d_1)[a]

complex	C_5H_4Me[a]	C_5H_4Me
$(OC)_4Co\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1a**)	5.44, 5.39	2.12
$(OC)_4Co\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1b**)	5.47, 5.35	2.28
$Co_2Mo_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2a**)	5.17, 4.94	2.02
$Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2b**)	5.22, 5.00	2.20
$CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3b**)	5.11, 4.93	2.20
$CoMoW_2(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (**3′**)[b]	5.093[c] (2 H), 5.076[c] (2 H) 5.00,[c] 4.93[c] (4 H), 4.86[d]	2.19[c] (6 H) 2.04[d] (3 H)
$Co_3Mo(\eta_2\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (**5a**)	5.29, 4.91	1.97
$Co_3W(\eta_2\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (**5b**)	5.35, 5.00	2.17
4	6.084, 6.079	2.53

[a] AA′BB′ multiplets; each integrates to 2 H unless stated. [b] 500-MHz ^1H NMR spectrum. [c] $\eta^5\text{-}C_5H_4Me$–W; aromatic protons appear as ABCC′ multiplets. [d] $\eta^5\text{-}C_5H_4Me$–Mo.

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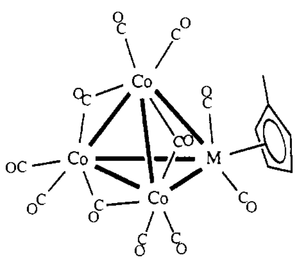
(28) Loss of coordinated $\eta^5\text{-}C_5H_5$ ligands from metals in electron-precise organometallic species is rare but not unprecedented: Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.

(29) Chetcuti, M. J.; Gordon, J. C. Unpublished results.

in agreement with **5b** being the cluster Co$_3$W(μ_2-CO)$_3$(CO)$_8$(η^5-C$_5$H$_4$Me), whose structure is shown. Ions corresponding to successive loss of eight CO ligands are seen in the mass spectrum. Other data support this formulation: IR spectra indicate terminal and μ_2-CO ligands are present, while ^{1}H NMR spectra show resonances for one chemically distinct type of η^5-C$_5$H$_4$Me ligand.



5a, M = Mo
5b, M = W

An X-ray diffraction study of the cluster Co$_3$W(μ_2-CO)$_3$(CO)$_8$(η^5-C$_5$H$_5$) has just been reported.[21] IR data for **5b** are close to those reported for this species but are shifted to slightly lower wavenumbers, as anticipated when a η^5-methylcyclopentadienyl ligand replaces a η^5-cyclopentadienyl group, and indicate that **5b** and this complex are isostructural. The related molybdenum cluster Co$_3$Mo(μ_2-CO)$_3$(CO)$_8$(η^5-C$_5$H$_5$) was synthesized by a circuitous route, and its structure was also established crystallographically.[30] This species and the concurrently formed Co$_2$Mo$_2$(μ_2-CO)$_3$(CO)$_7$(η^5-C$_5$H$_5$)$_2$ were also obtained when [Mo(CO)$_3$(η^5-C$_5$H$_5$)]$_2$ was reacted with Co$_2$(CO)$_8$ in refluxing heptane and its structure was redetermined.[6]

$$\begin{aligned}&\text{(OC)}_4\text{Co-W(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{1b}) + \text{Co}_2\text{(CO)}_8 \rightarrow\\ &\quad \text{Co}_2\text{W}_2(\mu_2\text{-CO})_3\text{(CO)}_7(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\ (\mathbf{2b}) + \mathbf{4} +\\ &\qquad \text{Co}_3\text{W}(\mu_2\text{-CO})_3\text{(CO)}_8(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{5b})\end{aligned} \quad (3)$$

(ii) Reaction of 1a with Co$_2$(CO)$_8$. The reaction of these two reagents parallels that of **1b** with cobalt carbonyl. Complexes characterized from this reaction include the molybdenum analogues of **2b** and **5b**, the clusters Co$_2$Mo$_2$(μ_2-CO)$_3$(CO)$_7$(η^5-C$_5$H$_4$Me)$_2$ (**2a**) and Co$_3$Mo(μ_2-CO)$_3$(CO)$_8$(η^5-C$_5$H$_4$Me) (**5a**). Traces of **4** were recovered, establishing the absence of tungsten in this complex. **4** could not be separated from **2a**, and neither complex was obtained pure. However the close peak to peak correspondence between IR spectra of **2a** and **2b** clearly indicates the isostructural nature of these two clusters.

(c) Reaction of Co$_2$(CO)$_8$ with [W(CO)$_2$(η^5-C$_5$H$_4$Me)]$_2$ (W≡W) and Thermolysis of 1b. Equimolar solutions of Co$_2$(CO)$_8$ and [W(CO)$_2$(η^5-C$_5$H$_4$Me)]$_2$ (W≡W) reacted to yield **2b** and **5b**. Minor quantities of **1b**, Co$_2$(CO)$_8$, and [W(CO)$_3$(η^5-C$_5$H$_4$Me)]$_2$ were also recovered (eq 4). The analogous reaction with the dimolybdenum species [Mo(CO)$_2$(η^5-C$_5$H$_5$)]$_2$ (Mo≡Mo) was attempted by Curtis, but interestingly, cobalt–molybdenum clusters related to **2b** and **5b** were not obtained.[31] Clusters with Co$_2$Mo$_2$ and Co$_3$Mo tetrahedral cores were obtained when Co$_2$(CO)$_8$ was treated with the μ-phosphido complex Mo$_2$(μ-CO){μ-C$_6$H$_4$(P^{t}Bu)$_2$}(η^5-C$_5$H$_5$)$_2$ (Mo≡Mo).[32] Pyrolysis of **1b** in toluene afforded **5b** with [W(CO)$_3$(η^5-C$_5$H$_4$Me)]$_2$ as the only products (eq 5).

$$\begin{aligned}&\text{Co}_2\text{(CO)}_8 + [\text{W(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2\ (\text{W}\equiv\text{W}) \rightarrow\\ &\quad \text{(OC)}_4\text{Co-W(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{1b}) +\\ &\quad \text{Co}_2\text{W}_2(\mu_2\text{-CO})_3\text{(CO)}_7(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\ (\mathbf{2b}) +\\ &\qquad \text{Co}_3\text{W}(\mu_2\text{-CO})_3\text{(CO)}_8(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{5b})\end{aligned} \quad (4)$$

$$\begin{aligned}&\text{(OC)}_4\text{Co-W(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{1b}) \rightarrow\\ &\quad \text{Co}_3\text{W}(\mu_2\text{-CO})_3\text{(CO)}_8(\eta^5\text{-C}_5\text{H}_4\text{Me})\ (\mathbf{5b}) +\\ &\qquad [\text{W(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2\end{aligned} \quad (5)$$

Conclusions. Reactions of **1b** with dicobalt or ditungsten species are good synthetic routes to new tetrahedral clusters that have Co$_x$W$_{4-x}$ (x = 1–3) metallic cores. Some cyclopentadienyl tungsten–iridium and cobalt–molybdenum analogues of these cluster exist, and spectroscopic data suggest their structures mirror those of the η^5-C$_5$H$_4$Me–tungsten clusters reported here. The solid-state structure of **3b** shows effective C_3 symmetry for the cluster: there are no bridging carbonyl ligands, and the weak semibridging interactions present are believed to result from severe steric crowding. This presumably accounts for the nonexistence of the W$_4$ tetrahedral cluster species W$_4$(CO)$_8$(η^5-C$_5$H$_5$)$_4$. In solution, our data indicate that **3b** has C_{3v} symmetry on ^{13}C NMR time scales at or above ambient temperatures but the symmetry is lowered to C_3 at −80 °C. Reactions of these Co$_x$W$_{4-x}$ clusters and the use of other heterobimetallic species in mixed-metal cluster synthesis are under investigation.

Experimental Section

(a) General Remarks. All manipulations were carried out under a nitrogen atmosphere with Schlenk or vacuum-line techniques. Solvents were predried over 4-Å molecular sieves. Diethyl ether, toluene, and hexanes were distilled over sodium or sodium benzophenone ketyl. Dichloromethane was distilled over CaH$_2$. The syntheses of **1a** and **1b** were based on an improved synthesis of the related species (OC)$_4$Co–Mo(CO)$_3$(η^5-C$_5$H$_5$).[33]

NMR spectra were recorded on a GE GN-300 (or, for **3′**, on a Varian BXR-500S) spectrometer at 20 °C, in chloroform-d_1 unless stated otherwise. Cr(acac)$_3$ (0.01–0.05 M) was used for the ^{13}C NMR spectra as a shiftless relaxation reagent. IR spectra were obtained on an IBM IR-32 FT instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Mass spectra were obtained on a Finnegan-Matt instrument. All parent ions show the appropriate isotopomer pattern.

(b) X-Ray Diffraction Study of CoW$_3$(CO)$_9$(η^5-C$_5$H$_4$Me)$_3$ (3b). A dark purple crystal of **3b**, grown from hexanes solution at −20 °C, was mounted in a glass capillary tube and placed on an Enraf-Nonius CAD-4 diffractometer at 20 ± 1 °C. Cell constants and an orientation matrix were obtained from least-squares refinement of 25 reflections with $19 < \theta < 22°$. Systematic absences of $h0l$, $l = 2n$, indicated that the space group was $C2/c$. Three representative reflections monitored every 83 min showed no decay over the total data collection period.

Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.[34] Of the total 3903 unique reflections, 2831 with $I > 3\sigma(I)$ were used in refinement. The structure was solved on a VAX computer using SDP/VAX software and the structure solution package SHELX-86.[35] Remaining atoms were located from succeeding Fourier maps. Hydrogen atoms, located and added to the structure factor calculations, were not refined. Scattering factors were from Cromer and Waber,[36] and anomalous dispersion effects were included in F_c.[37,38] The highest peak in the final difference Fourier had a height of 1.70 e/Å^3 with an estimated error based on ΔF of 0.20.

(c) Syntheses. (i) Reaction of (OC)$_4$Co–W(CO)$_3$(η^5-C$_5$H$_4$Me) (1b) with [W(CO)$_2$(η^5-C$_5$H$_4$Me)]$_2$ (W≡W). **1b** (155 mg, 0.30 mmol) and [W(CO)$_2$(η^5-C$_5$H$_4$Me)]$_2$ (W≡W) (191 mg, 0.30 mmol) were dissolved in toluene (20 mL) in a Schlenk tube equipped with a stirrer bar and a septum cap. The stirred red solution slowly turned purple when kept for 2 h at 75 °C under a fast nitrogen purge. The solvent was then removed, the residue was dissolved in a hexanes/ether mixture, and the solution was subjected to chromatography on silica gel. Hexane elution afforded [W(CO)$_3$(η^5-C$_5$H$_4$Me)]$_2$. Addition of ether sequentially yielded a purple and a green band. Concentration and cooling (−20 °C) yielded purple-black CoW$_3$(CO)$_9$(η^5-C$_5$H$_4$Me)$_3$ (**3b**) (75 mg, 0.068 mmol, 23%) and green Co$_2$W$_2$(μ_2-CO)$_3$(CO)$_7$(η^5-C$_5$H$_4$Me)$_2$ (**2b**) (15 mg, 0.016 mmol, 5%), respectively. Anal. Calcd for **2b**, C$_{22}$H$_{14}$O$_{10}$Co$_2$W$_2$: C, 28.60; H, 1.53. Found: C, 28.62; H, 1.43. Data for **3b** are as follows. ^{13}C{^{1}H} NMR (ppm in acetone-d_6): 20 °C, δ 221.9 (W-CO, J_{WC} = 89 Hz), 101.6 [C(1), C$_5$H$_4$Me], 100.6 and 92.2 (2 C each, C$_5$H$_4$Me), 12.5 (Me);

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−40 °C, δ 222.4 (*C*O, vbr), 221.6 (*C*O), 100.5 [C(1), C_5H_4Me], 101.0 and 91.7 (br, 2 C each, C_5H_4Me), 12.4 (Me); −80 °C, 222.1 (W–*C*O, $^1J_{WC}$ = 156 Hz), 221.5 (W–*C*O, $^1J_{WC}$ = 179 Hz), 99.7 [C(1), C_5H_4Me], 101.4, 101.2, 91.55, 91.50 (1 C each, C_5H_4Me), 12.4 (Me). The 65 °C spectral parameters (benzene-d_6) were not significantly different from those recorded in acetone-d_6 at 20 °C. Anal. Calcd for $C_{27}H_{21}O_9CoW_3$: C, 29.48; H, 1.92. Found: C, 29.58; H, 1.76.

(ii) Reaction of $(OC)_4Co{-}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1a) with $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W). **1a** (178 mg, 0.30 mmol) and $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W) (191 mg, 0.30 mmol) were dissolved in toluene (20 mL) in a Schlenk tube equipped with a magnetic flea and capped with a rubber septum. The red solution did not change color when kept for ≈1.5 h at 25 °C under a fast nitrogen purge, so the reaction mixture was heated and maintained at 55 °C for a further 6 h, turning purplish black during this period. The solvent was then removed, the residue was dissolved in a ether/hexanes/dichloromethane mixture (2:1:1), and the solution was subjected to chromatography on silica gel. Elution with hexanes (with increasing quantities of ether added slowly) afforded a red, a purple, and a green band. The red band was shown by IR and ^1H NMR spectroscopy to be a mixture of **1a**, **1b**, and $MM'(CO)_6(\eta^5\text{-}C_5H_4Me)_2$ (M–M′; M, M′ = Mo or W); the green (third) solution subsequently afforded crystals of **2b** (35 mg, ≈5%). The second solution contained a mixture of two complexes. It was pumped to dryness and redissolved in a ether/hexanes/dichloromethane mixture (5:10:1), and the solution was subjected to careful chromatography. Slow elution with hexanes afforded greenish blue and purple bands. Recrystallization from hexanes afforded **3′** (35 mg, 12%) and **3b** (20 mg, 6%), respectively. Data for **3′** are as follows. $^{13}C\{^1H\}$ NMR (ppm in chloroform-d_1 at 20 °C): δ 222.9 (Mo, W–*CO*'s), 103.9 [C(1), Mo–C_5H_4Me], 100.8 (2 C, C_5H_4Me), 100.5 [C(1), W–C_5H_4Me], 99.9 (2 C, C_5H_4Me), 99.8 (2 C, C_5H_4Me), 93.7 (2 C, C_5H_4Me), 91.2 (2 C, C_5H_4Me), 91.1 (2 C, C_5H_4Me), 12.6 (Mo–C_5H_4*Me*), 12.4 (W–C_5H_4*Me*). Anal. Calcd for $C_{27}H_{21}O_9CoMoW_2$: C, 32.04; H, 2.09. Found: C, 31.94; H, 1.99.

(iii) Reaction of $(OC)_4Co{-}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1b) with $Co_2(CO)_8$. $Co_2(CO)_8$ (0.26 mmol; 1.2 mL of a 0.215 M toluene solution) was added to a solution of **1b** (135 mg, 0.26 mmol) in toluene (15 mL). A metallic mirror deposited from the dark solution after 3-h reflux. The solvent was removed, the residue dissolved in a hexane/ether mixture (3:1), and the solution passed through a silica gel column. $Co_2(CO)_8$ eluted first (hexanes). A green band was eluted by using a hexanes/ether mixture, and the final (purple-brown) band was collected by using pure diethyl ether. Concentration and cooling to −20 °C afforded crystals from both solutions. Green crystals consisting of an approximately 1:1 mixture of $Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2b**) and **4** were obtained from the second band (70 mg of **2b** and **4**). Crystals of $Co_3W(\mu_2\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (**5b**) were harvested from the final band (50 mg, 0.050 mmol, 19%). Data for **4** are as follows. MS: *m/e* 553, 581. Anal. Found: C, 33.58; H, 1.44. Data for **5b** are as follows. MS: *m/e* 748 (M^+) and peaks corresponding to $(M - nCO)^+$, *n* = 1–9. Anal. Calcd for $C_{17}H_7O_{11}Co_3W$: C, 27.30; H, 0.94. Found: C, 27.44; H, 0.82.

(iv) Reaction of $(OC)_4Co{-}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1a) with $Co_2(CO)_8$. **1a** (230 mg, 0.54 mmol) was added to $Co_2(CO)_8$ (180 mg, 0.54 mmol) in toluene (20 mL). The red-brown solution was refluxed gently for 1 h, the now brown mixture was pumped to dryness and dissolved in a hexanes/ether mixture (1:1), and the solution was subjected to silica gel chromatography using hexanes as the initial eluting solvent. After the elution of $Co_2(CO)_8$ and traces of $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$, a green and a red-brown band were recovered with addition of some ether. The green band was subsequently found to contain **2a** and **4**. While these two compounds could not be separated, data for pure **2a** could be deduced from spectra of the mixture. The final red-brown band contained **5a**, which was crystallized and recovered as purple black crystals. Anal. Calcd for **5a**, $C_{17}H_7O_{11}Co_3Mo$: C, 30.94; H, 1.07. Found: C, 31.07; H, 1.03.

(v) Reaction of $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (W≡W) with $Co_2(CO)_8$. Toluene (40 mL) was added to a mixture of $[W(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ (350 mg, 0.55 mmol) and $Co_2(CO)_8$ (190 mg, 0.55 mmol) in a Schlenk tube equipped with a stirrer bar and a pierced septum cap. After being stirred for 6 h under a vigorous nitrogen purge, the dark brown solution was pumped to dryness. The residue was dissolved in a mixture of solvents, and the solution was subjected to silica gel chromatography. Three species eluted with hexanes. These were identified as unreacted $Co_2(CO)_8$, $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$, and **1b**. A green band eluted with the addition of diethyl ether to the hexanes. Concentration and cooling of the solution to −20 °C afforded crystals of $Co_2W_2(\mu_2\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4Me)_2$ (**2b**) (85 mg, 0.091 mmol, 16.5%). The final product, $Co_3W(\mu_2\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_4Me)$ (**5b**) (15 mg, 0.015 mmol), eluted off the column with almost pure ether and was crystallized from hexanes.

(vi) Attempted Reaction of $CoW_3(CO)_9(\eta^5\text{-}C_5H_4Me)_3$ (3b) with CO. **3b** (15 mg, 0.014 mmol) was dissolved in dichloromethane (≈3 mL), and the solution was stirred for 1 day under a CO atmosphere. No changes in the solution IR spectrum were noted, so the dichloromethane was removed, toluene (5 mL) was added, and the solution was magnetically stirred under a CO atmosphere at 55–60 °C for several days. After vacuum removal of the toluene, a dichloromethane solution IR spectrum of the residue only revealed IR bands assignable to **3b**: no new bands were noted.

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Supplementary Material Available: Full tables of crystal data and data collection parameters, positional parameters for all atoms, anisotropic thermal parameters, bond lengths, and bond angles (16 pages); structure factor listings (13 pages). Ordering information is given on any current masthead page.

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Dirhenium Complexes Derived from the Ligand 2-Mercaptoquinoline (2-mqH). Structure of $[Re_2Cl_3(\mu\text{-dppm})_2(2\text{-mq})]PF_6$ (dppm = $Ph_2PCH_2PPh_2$)

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The triply bonded dirhenium complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) react with 2-mercaptoquinoline (2-mqH) to afford the 1:1 adducts $Re_2X_4(dppm)_2(2\text{-mqH})$, in which the 2-mqH ligand (in its zwitterionic form) is probably bound in a monodentate fashion through its deprotonated thiol donor. These complexes undergo a reversible one-electron transfer to give $[Re_2X_4(dppm)_2(2\text{-mqH})]^+$ (isolable as their PF_6^- salts). This oxidation is followed by the slow elimination of HX to give paramagnetic $[Re_2X_3(\mu\text{-dppm})_2(2\text{-mq})]PF_6$, in which, in addition to two bridging dppm ligands, there is also a bridging 2-mq ligand bound through its N and S atoms. A single-crystal X-ray structure determination of the chloride complex has been carried out at 20 °C. Crystal data are as follows: monoclinic space group $P2_1/c$, a = 13.594 (3) Å, b = 20.185 (3) Å, c = 21.691 (4) Å, β = 104.459 (9)°, V = 5763 (3) Å^3, Z = 4. The structure was refined to R = 0.030 (R_w = 0.037) for 5705 data with $I > 3.0\sigma(I)$. The Re–Re distance is 2.2540 (5) Å, and the hydrogen atom on the carbon atom adjacent to the nitrogen of the quinoline ring forms a close contact with one of the rhenium atoms (the Re–H distance is 2.3 (1) Å). These compounds are the first multiply bonded dirhenium complexes that contain Re–thiol bonds.

Introduction

Multiply bonded dimetal complexes that contain bridging monoanionic ligands based upon bridging N–C–O⁻ and N–C–N⁻ units are well-known, whereas complexes that contain the corresponding N–C–S⁻ unit are comparatively rare.[1] Thus, in the case of the quadruply bonded dimolybdenum(II) core, only the complexes $Mo_2(dmmp)_4$ (dmmpH = 4,6-dimethyl-2-mercapto-

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