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Study on the Reaction between Metal–Metal-Bonded Compounds $[(\eta^5\text{-RC}_5\text{H}_4)\text{M(CO)}_3]_2$ and $\text{Co}_2(\text{CO})_8$. Synthesis and Characterization of the Tetrahedral Clusters $(\eta^5\text{-RC}_5\text{H}_4)\text{M(CO)}_2\text{Co}_3(\text{CO})_6(\mu\text{-CO})_3$ (M = Mo, W; R = Me_3Si, C(O)Me, CO_2Me, CO_2Et)

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Through the reaction of respective dimers $[(\eta^5\text{-RC}_5\text{H}_4)\text{M(CO)}_3]_2$ (**1a–f**) with $\text{Co}_2(\text{CO})_8$ in refluxing toluene, the cluster complexes of $(\eta^5\text{-RC}_5\text{H}_4)\text{M(CO)}_2\text{Co}_3(\text{CO})_6(\mu\text{-CO})_3$ (**2a–f**) (**2a** M = Mo, R = Me_3Si; **2b** M = Mo, R = CO_2Me; **2c** M = Mo, R = CO_2Et; **2d** M = W, R = C(O)Me; **2e** M = W, R = CO_2Me; **2f** M = W, R = CO_2Et), were prepared in 18–32% yields and characterized by C/H analysis, IR, ^{1}H NMR and MS spectroscopies. In addition, **2f** also could be prepared by reaction of **1f** with $\text{Co}_4(\text{CO})_{12}$ in 14% yield. The determination of single-crystal molecular structure of one repesentative, **2e**, showed that the molecule crystallizes in the triclinic space group $P\bar{1}$ with a = 8.679 (2) Å, b = 9.473 (3) Å, c = 13.817 (4) Å, α = 78.31 (3)°, β = 82.81 (3)°, γ = 85.44 (3)°, V = 1101.9 (7) Å^3, and Z = 2; final R = 0.046 for 3441 observed reflections.

Introduction

The chemistry of transition metal–metal-bonded compounds and of metal cluster complexes is of great interest and has become the subject of a large number of studies.[1–3] For group 6 transition metals, however, only a few metal–metal-bonded compounds with η^5-functional cyclopentadienyl ligands and the tetrahedral MCo_3 (M = Mo, W) cluster complexes which contain η^5-substituted cyclopentadienyl ligands have been investigated.[4–11] Recently, it was claimed that reaction of $[\text{Cp(CO)}_3\text{Mo}]_2$ with $\text{Co}_2(\text{CO})_8$ could most conveniently give the clusters of $\text{CpMo(CO)}_2\text{Co}_3(\text{CO})_6(\mu\text{-CO})_3$ in 25% yield, along with a trace of $\text{CpMo(CO)}_2\text{Co}_2(\text{CO})_4\text{Mo(CO)Cp}(\mu\text{-CO})_3$.[12] In order to explore the scope and limitations of this novel reaction and also to make the new MCo_3 (M = Mo, W) clusters of the type mentioned above, particularly the type containing η^5-functional cyclopentadienyl ligands, we initiated this study and now report our results.

Results and Discussion

When a mixture of bis[η^5-substituted cyclopentadienyltricarbonylmolybdenum(tungsten)] dimers **1a–f** and $\text{Co}_2(\text{CO})_8$ are refluxed in toluene for 10 h, the expected MCo_3 cluster complexes **2a–f** were obtained in 18–32% yields (Scheme I).

Thus, the results demonstrated some generality of this kind of reaction, regardless of the dimers used. The dimers, for instance, may contain either a Mo–Mo or W–W metal–metal bond and may also carry various substituents on the cyclopentadienyl ring. However, the second type of M_2Co_2 cluster complexes were not found in our experiments, which was contrary to the reaction carried out by Kaganovich and his co-workers.[12]

The cluster complexes **2a–f** are air-stable black solids, but their solutions are quite air-sensitive. The data of combustion analysis, IR, ^{1}H NMR, and MS are consistent with the structures shown in Scheme I.

In IR spectrum of **2a** there are two groups of peaks, one between 2078 and 1949 cm^{-1} and the other ranging from 1882 to 1822 cm^{-1}, both characteristic of terminal and bridging carbonyls. However, for **2b–f** there are three kinds of peaks, one around 1700 cm^{-1}, indicating the existence of an ester or acyl carbonyl, the other two in the regions 2082–1926 and 1885–1818 cm^{-1}, also characteristic of terminal and bridging carbonyls, respectively. For ^{1}H NMR assignment of **2b–f**, it is evident that the downfield apparent triplet should be assigned to protons H(2) and H(5) and the upfield triplet to H(3) and H(4), but inversely for **2a**, since the substituents of the acetyl and ester groups on cyclopentadienyl ring are well-known electron-withdrawing groups and the Me_3Si substituent is an electron-releasing group.[13]

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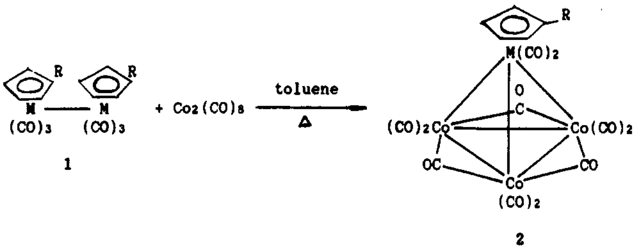
Scheme I



	a	b	c	d	e	f
M	Mo	Mo	Mo	W	W	W
R	Me3Si	CO2Me	CO2Et	C(O)Me	CO2Me	CO2Et

Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms for 2e

atom	*x*	*y*	*z*	B_{eq} (Å^2)
W(1)	0.78416 (5)	0.30370 (4)	0.34878 (4)	2.155 (7)
Co(1)	0.7105 (2)	0.3988 (2)	0.1607 (1)	2.83 (3)
Co(2)	0.9226 (2)	0.2078 (2)	0.1856 (1)	2.93 (3)
Co(3)	0.6449 (2)	0.1515 (2)	0.2395 (1)	2.76 (3)
C(1)	0.818 (1)	0.106 (1)	0.4197 (8)	3.2 (2)
O(1)	0.833 (1)	−0.0123 (9)	0.4692 (8)	4.6 (2)
C(2)	0.560 (1)	0.294 (1)	0.407 (1)	3.2 (2)
O(2)	0.4374 (9)	0.2896 (9)	0.4467 (7)	4.0 (2)
C(3)	0.667 (1)	0.579 (1)	0.168 (1)	4.1 (3)
O(3)	0.636 (1)	0.698 (1)	0.173 (1)	6.6 (3)
C(4)	0.680 (1)	0.402 (2)	0.034 (1)	4.4 (3)
O(4)	0.655 (1)	0.395 (1)	−0.0427 (8)	6.5 (3)
C(5)	1.084 (1)	0.161 (1)	0.252 (1)	4.1 (3)
O(5)	1.189 (1)	0.124 (1)	0.294 (1)	6.2 (3)
C(6)	0.998 (2)	0.175 (1)	0.066 (1)	5.0 (4)
O(6)	1.054 (2)	0.154 (2)	−0.010 (1)	10.2 (4)
C(7)	0.534 (1)	0.034 (1)	0.3358 (9)	3.3 (3)
O(7)	0.465 (1)	−0.042 (1)	0.3951 (8)	4.9 (2)
C(8)	0.577 (2)	0.095 (2)	0.139 (1)	5.6 (4)
O(8)	0.528 (2)	0.064 (2)	0.075 (1)	12.6 (4)
C(11)	0.514 (1)	0.336 (1)	0.216 (1)	4.0 (3)
O(11)	0.382 (1)	0.372 (1)	0.2288 (8)	5.0 (2)
C(12)	0.937 (1)	0.411 (1)	0.142 (1)	3.4 (3)
O(12)	1.027 (1)	0.501 (1)	0.1171 (8)	4.8 (2)
C(13)	0.835 (1)	0.023 (1)	0.233 (1)	3.4 (3)
O(13)	0.866 (1)	−0.1006 (9)	0.250 (1)	5.7 (3)
C(21)	0.818 (1)	0.385 (1)	0.4871 (9)	2.8 (2)
C(22)	0.966 (1)	0.337 (1)	0.4499 (8)	2.7 (2)
C(23)	1.009 (1)	0.430 (1)	0.3566 (9)	3.0 (2)
C(24)	0.888 (1)	0.534 (1)	0.337 (1)	3.2 (2)
C(25)	0.765 (1)	0.508 (1)	0.417 (1)	3.4 (3)
C(26)	0.733 (1)	0.339 (1)	0.588 (1)	3.2 (2)
O(27)	0.603 (1)	0.3823 (9)	0.6118 (7)	4.1 (2)
O(28)	0.8216 (9)	0.255 (1)	0.6490 (7)	3.9 (2)
C(29)	0.754 (2)	0.221 (2)	0.752 (1)	5.2 (4)

Table II. Bond Distances (Å) between Non-Hydrogen Atoms for 2e[a]

W(1)–Co(1)	2.7108 (9)	W(1)–C(22)	2.315 (6)
W(1)–Co(2)	2.707 (1)	W(1)–C(23)	2.395 (6)
W(1)–Co(3)	2.7266 (9)	W(1)–C(24)	2.388 (6)
W(1)–C(1)	1.946 (8)	W(1)–C(25)	2.310 (7)
W(1)–C(2)	2.009 (7)	W(1)–Cp(1)[b]	1.998 (7)
W(1)–C(21)	2.261 (7)		
Co(1)–W(1)	2.7108 (9)	Co(1)–C(4)	1.799 (9)
Co(1)–Co(2)	2.481 (1)	Co(1)–C(11)	1.870 (7)
Co(1)–Co(3)	2.454 (1)	Co(1)–C(12)	1.958 (7)
Co(1)–C(3)	1.739 (7)		
Co(2)–W(1)	2.707 (1)	Co(2)–C(6)	1.78 (1)
Co(2)–Co(1)	2.481 (1)	Co(2)–C(12)	1.909 (7)
Co(2)–Co(3)	2.498 (1)	Co(2)–C(13)	1.918 (7)
Co(2)–C(5)	1.752 (8)		
Co(3)–W(1)	2.7266 (9)	Co(3)–C(8)	1.77 (1)
Co(3)–Co(1)	2.454 (1)	Co(3)–C(11)	2.001 (8)
Co(3)–Co(2)	2.498 (1)	Co(3)–C(13)	1.973 (7)
Co(3)–C(7)	1.788 (7)		
C(1)–O(1)	1.198 (8)	C(7)–O(7)	1.119 (8)
C(2)–O(2)	1.137 (8)	C(8)–O(8)	1.13 (1)
C(3)–O(3)	1.154 (9)	C(11)–O(11)	1.175 (9)
C(4)–O(4)	1.12 (1)	C(12)–O(12)	1.168 (9)
C(5)–O(5)	1.131 (9)	C(13)–O(13)	1.167 (8)
C(6)–O(6)	1.14 (2)		
C(21)–C(22)	1.397 (9)	C(24)–C(25)	1.43 (2)
C(21)–C(25)	1.437 (9)	C(26)–O(27)	1.194 (8)
C(21)–C(26)	1.50 (1)	C(26)–O(28)	1.319 (9)
C(22)–C(23)	1.429 (9)	O(28)–C(29)	1.452 (9)
C(23)–C(24)	1.397 (9)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp(1) is the center of the five-membered ring composed of C(21)–C(25) atoms.

The 70-eV EI mass spectra of **2a–f** did not show their respective molecular ion but showed the fragment ions $RC_5H_4MCo_3(CO)_n^+$ (n = 0–6) and $MCo_3(CO)_n^+$ (n = 0–7), both resulting from parent molecular ions by successive loss of a given number of carbonyls and the substituted cyclopentadienyl. In order to unambiguously confirm the structures of **2a–f**, the molecular structure of **2e** was determined by single-crystal X-ray diffraction.

The final fractional coordinates with equivalent isotropic thermal parameters are listed in Table I. Tables II and III list the bond lengths and bond angles, respectively. The perspective view of **2e** is presented in Figure 1.

As seen from Figure 1, the molecule has a tetrahedral core MCo_3, which carries eight terminal carbonyls [each two being on Co(1), Co(2), Co(3), and W(1)], three bridging carbonyls [each across Co(1)–Co(2), Co(2)–Co(3), and Co(1)–Co(3)], and an η^5-$MeO_2CC_5H_4$ ligand bonded to the W atom. Thus, the molecular structure of **2e** is similar to that of the parent complex, η^5-$C_5H_5W(CO)_2Co_3(CO)_6(\mu$-$CO)_3$.[14] The related bond lengths for the cluster core of **2e** are compared with those of the parent complex[14] in Table IV. From Table IV it may be seen that the triangular base of the WCo_3 tetrahedron Co(1)–Co(2)–Co(3) in both complexes is equilateral and the distances of the W atom to each Co atom of the base are basically equal. The latter are somewhat longer than each side of the triangle Co(1)–Co(2)–Co(3); thus the metallatetrahedrane WCo_3 is elongated along the symmetrical axis through W and the center of the triangle. For complex **2e**, according to the bond lengths of Co(1)–C(12), Co(2)–C(12); Co(2)–C(13), Co(3)–C(13); and Co(3)–C(11), Co(1)–C(11), two of the three bridging carbonyls, i.e., C(12)–O(12) and C(13)–O(13), are symmetrically bridged across Co(1)–Co(2) and Co(2)–Co(3), while the third C(11)–O(11) is slightly unsymmetrically bridged across Co(1)–Co(3).

The cyclopentadienyl ring of **2e** is tilted to the triangular base Co(1)–Co(2)–Co(3) and gives a dihedral angle of 36.2 (5)°. In addition, the π-system of subtituent MeO_2C is not fully conjugated with the cyclopentadienyl π-system since the dihedral angle between the ring C_5H_4 and the plane C(26)–O(27)–O(28) is quite large (17.75°) and the bond length of C(21)–C(26) [1.50 (1) Å] is very close to that of a normal C–C single bond.

At the present stage we are not clear about the mechanism of this cluster formation reaction. However, it is believed that the formation of **2a–f** was the consequence of isolobal[15] displacement of the $Co(CO)_3$ unit in $Co_4(CO)_{12}$ by free radical fragments derived from $RC_5H_4M(CO)_2$; $Co_4(CO)_{12}$ and $RC_5H_4M(CO)_2$ were formed in situ

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Table III. Bond Angles (deg) between Non-Hydrogen Atoms for 2e[a]

Co(1)–W(1)–Co(2)	54.51 (3)	Co(2)–W(1)–Cp(1)[b]	120.9 (2)
Co(1)–W(1)–Co(3)	53.65 (3)	Co(3)–W(1)–C(1)	78.1 (2)
Co(1)–W(1)–C(1)	128.9 (2)	Co(3)–W(1)–C(2)	73.7 (2)
Co(1)–W(1)–C(2)	93.2 (2)	Co(3)–W(1)–Cp(1)	171.1 (2)
Co(1)–W(1)–Cp(1)	117.5 (1)	C(1)–W(1)–C(2)	87.7 (3)
Co(2)–W(1)–Co(3)	54.74 (3)	C(1)–W(1)–Cp(1)	110.1 (2)
Co(2)–W(1)–C(1)	85.9 (2)	C(2)–W(1)–Cp(1)	109.5 (3)
Co(2)–W(1)–C(2)	128.2 (3)		
W(1)–Co(1)–Co(2)	62.68 (4)	Co(3)–Co(1)–C(3)	143.1 (3)
W(1)–Co(1)–Co(3)	63.50 (3)	Co(3)–Co(1)–C(4)	101.3 (3)
W(1)–Co(1)–C(3)	97.9 (3)	Co(3)–Co(1)–C(11)	53.1 (2)
W(1)–Co(1)–C(4)	161.5 (3)	Co(3)–Co(1)–C(12)	109.6 (2)
W(1)–Co(1)–C(11)	83.6 (2)	C(3)–Co(1)–C(4)	100.7 (5)
W(1)–Co(1)–C(12)	78.3 (3)	C(3)–Co(1)–C(11)	95.5 (3)
Co(2)–Co(1)–Co(3)	60.82 (3)	C(3)–Co(1)–C(12)	96.1 (4)
Co(2)–Co(1)–C(3)	141.1 (2)	C(4)–Co(1)–C(11)	95.6 (3)
Co(2)–Co(1)–C(4)	101.3 (3)	C(4)–Co(1)–C(12)	98.5 (3)
Co(2)–Co(1)–C(11)	113.7 (2)	C(11)–Co(1)–C(12)	159.8 (4)
Co(2)–Co(1)–C(12)	49.3 (2)		
W(1)–Co(2)–Co(1)	62.81 (4)	Co(3)–Co(2)–C(5)	128.9 (3)
W(1)–Co(2)–Co(3)	63.02 (3)	Co(3)–Co(2)–C(6)	115.6 (3)
W(1)–Co(2)–C(5)	85.7 (3)	Co(3)–Co(2)–C(12)	109.6 (3)
W(1)–Co(2)–C(6)	169.3 (3)	Co(3)–Co(2)–C(13)	51.0 (3)
W(1)–Co(2)–C(12)	79.2 (2)	C(5)–Co(2)–C(6)	102.1 (4)
W(1)–Co(2)–C(13)	91.0 (2)	C(5)–Co(2)–C(12)	102.0 (4)
Co(1)–Co(2)–Co(3)	59.04 (3)	C(5)–Co(2)–C(13)	93.9 (4)
Co(1)–Co(2)–C(5)	140.1 (3)	C(6)–Co(2)–C(12)	91.7 (3)
Co(1)–Co(2)–C(6)	106.9 (3)	C(6)–Co(2)–C(13)	95.9 (3)
Co(1)–Co(2)–C(12)	51.0 (3)	C(12)–Co(2)–C(13)	160.5 (3)
Co(1)–Co(2)–C(13)	109.6 (3)		
W(1)–Co(3)–Co(1)	62.84 (3)	Co(2)–Co(3)–C(7)	138.9 (3)
W(1)–Co(3)–Co(2)	62.24 (3)	Co(2)–Co(3)–C(8)	106.3 (3)
W(1)–Co(3)–C(7)	100.9 (2)	Co(2)–Co(3)–C(11)	108.3 (3)
W(1)–Co(3)–C(8)	162.4 (3)	Co(2)–Co(3)–C(13)	49.1 (2)
W(1)–Co(3)–C(11)	80.9 (2)	C(7)–Co(3)–C(8)	96.3 (4)
W(1)–Co(3)–C(13)	89.3 (2)	C(7)–Co(3)–C(11)	105.1 (3)
Co(1)–Co(3)–Co(2)	60.13 (3)	C(7)–Co(3)–C(13)	97.2 (3)
Co(1)–Co(3)–C(7)	148.5 (2)	C(8)–Co(3)–C(11)	91.0 (4)
Co(1)–Co(3)–C(8)	100.2 (3)	C(8)–Co(3)–C(13)	92.3 (5)
Co(1)–Co(3)–C(11)	48.3 (3)	C(11)–Co(3)–C(13)	157.1 (3)
Co(1)–Co(3)–C(13)	108.7 (2)		
W(1)–C(1)–O(1)	175.5 (7)	Co(1)–C(11)–O(11)	144.4 (6)
W(1)–C(2)–O(2)	174.7 (7)	Co(3)–C(11)–O(11)	137.0 (6)
Co(1)–C(3)–O(3)	179.4 (7)	Co(1)–C(12)–Co(2)	79.8 (3)
Co(1)–C(4)–O(4)	174.3 (8)	Co(1)–C(12)–O(12)	138.0 (6)
Co(2)–C(5)–O(5)	176.3 (7)	Co(2)–C(12)–O(12)	142.3 (6)
Co(2)–C(6)–O(6)	177 (2)	Co(2)–C(13)–Co(3)	80.0 (3)
Co(3)–C(7)–O(7)	178.5 (7)	Co(2)–C(13)–O(13)	143.2 (6)
Co(3)–C(8)–O(8)	177 (1)	Co(3)–C(13)–O(13)	136.9 (5)
Co(1)–C(11)–Co(3)	78.6 (3)		
C(22)–C(21)–C(25)	108.7 (6)	C(21)–C(25)–C(24)	106.3 (6)
C(22)–C(21)–C(26)	128.5 (6)	C(21)–C(26)–O(27)	123.9 (6)
C(25)–C(21)–C(26)	122.1 (6)	C(21)–C(26)–O(28)	111.7 (6)
C(21)–C(22)–C(23)	108.2 (6)	O(27)–C(26)–O(28)	124.2 (7)
C(22)–C(23)–C(24)	108.1 (7)	C(26)–O(28)–C(29)	115.2 (6)
C(23)–C(24)–C(25)	108.8 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp(1) is the center of the five-membered ring composed of C(21)–C(25) atoms.

from $Co_2(CO)_8$ and $[RC_5H_4M(CO)_3]_2$, respectively. Thus, the mechanism may be one as shown in Scheme II.

The facts which support the mechanism proposed in Scheme II are (1) under our experimental conditions $Co_4(CO)_{12}$ might be formed from $Co_2(CO)_8$[16] and a trace of $Co_4(CO)_{12}$ was always separated from our reaction mixture, (2) **2f** was prepared by reaction of $Co_4(CO)_{12}$ with **1f**, (3) the isolobal displacement of the $Co(CO)_3$ unit in the clusters containing $Co(CO)_3$ by the corresponding fragments derived from organometallic compounds is a well-known process,[12,14,17-24] and (4) the mononuclear radical species $CpM(CO)_3$ are usually present in equilibrium with $[CpM(CO)_3]_2$.[25] Vahrenkamp[17] has already proposed a reasonable free radical displacement mechanism for some similarly isolobal displacement reactions. Although there are so many supporting facts, the detailed mechanism for this specific reaction still needs further study.

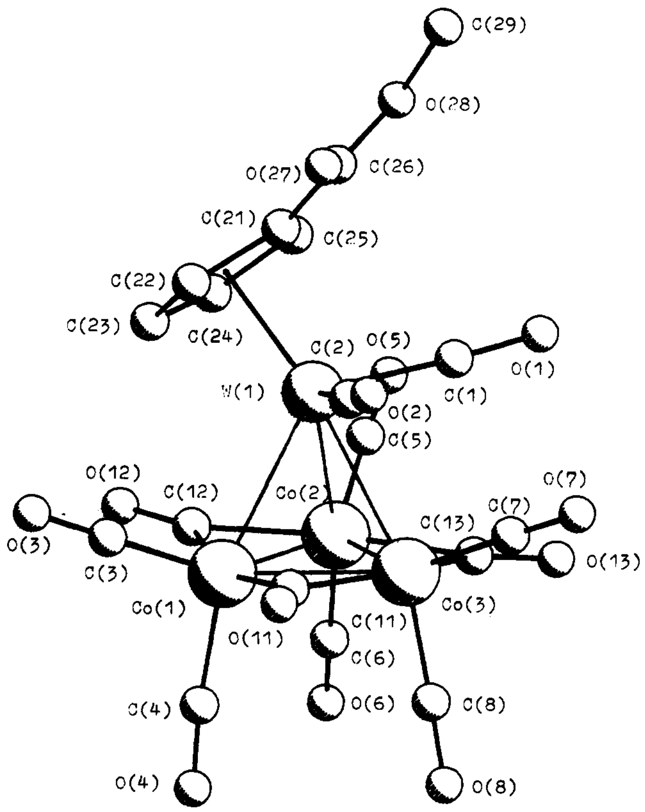

Figure 1. Perspective view of **2e** with atomic numbering scheme.

Experimental Section

All reactions were carried out under prepurified nitrogen atmosphere using standard Schlenk or vacuum line techniques. Toluene was predried over sodium chips and distilled from sodium–benzophenone ketyl under nitrogen. Column chromatography and TLC were carried out by using silica gel of 300–400 mesh and silica gel G (10–40 μm), respectively. $Co_2(CO)_8$ was purchased from Strem Chemical Inc., and $Co_4(CO)_{12}$ was, according to literature,[16] prepared by heating a toluene solution of $Co_2(CO)_8$ for 3 h at 85–96 °C. $[(\eta^5\text{-}RC_5H_4)M(CO)_3]_2$ (**1a–f**) were prepared by the oxidative coupling reaction of $(\eta^5\text{-}C_5H_4)M(CO)_3^-$ with $Fe_2(SO_4)_3$/HOAc.[9,10] IR spectra were recorded on a NICOLET FT-IR 5DX infrared spectrophotometer; ^1H NMR spectra were recorded on either a JEOL JNM-PMX 60S1 or JEOL FX 90Q NMR spectrometer. C/H analyses and MS

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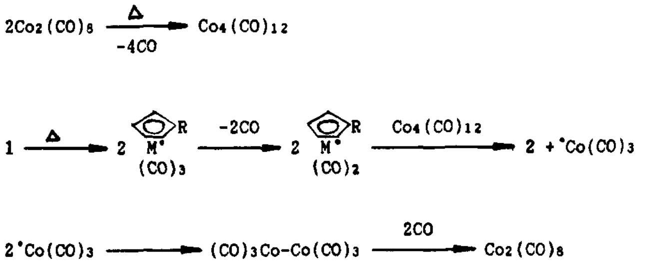
Table IV. Comparison of the Bond Lengths of the Cluster Core in 2e and Its Parent Complex[14]

cluster	Co(1)–Co(2)	Co(2)–Co(3)	Co(1)–Co(3)	W(1)–Co(1)	W(1)–Co(2)	W(1)–Co(3)
2e	2.481 (1)	2.498 (1)	2.454 (1)	2.7108 (9)	2.707 (1)	2.7266 (9)
parent complex	2.472 (2)	2.474 (2)	2.506 (2)	2.716 (1)	2.725 (1)	2.706 (1)

Scheme II



determinations were performed by a 240C analyzer and HP 5988A spectrometer, respectively. Melting points were determined on a Yanaco micro melting point apparatus MP-500.

Preparation of 2a. Into a 100-mL two-necked flask fitted with a magnetic stir bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube were added 317 mg (0.5 mmol) of $[(\eta^5\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and heated under refluxing for 10 h. Solvent was removed under reduced pressure and the residue extracted by CH_2Cl_2. The extracts were subjected to chromatographic separation on a silica gel column. Elution with 3:1 petroleum ether/CH_2Cl_2, followed by evaporation of solvents and drying under vacuum line gave a trace of $Co_4(CO)_{12}$ and 68 mg (18%) of **2a** as a black solid. Sample for analysis was further purified by recrystallization from 3:1 petroleum ether/CH_2Cl_2. **2a**; mp > 250 °C dec. Anal. Calcd for $C_{19}H_{13}Co_3MoO_{11}Si$: C, 31.78; H, 1.82. Found: C, 32.01; H, 1.80. IR (KBr disk): ν(terminal $C\equiv O$) 2078 (s), 2035 (vs), 2019 (s), 1996 (s),1949 (s); ν(bridging carbonyls), 1882 (m), 1845 (m), 1822 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.17 [s, 9 H, $Si(CH_3)_3$], 4.95 [t, 2 H, H(2), H(5)], 5.68 [t, 2 H, H(3), H(4)] ppm. MS (EI, Mo^{98}), *m/z* (relative intensity): 580 [$Me_3SiC_5H_4MoCo_3(CO)_6^+$, 2.3], 524 [$Me_3SiC_5H_4MoCo_3(CO)_4^+$, 4.9], 496 [$Me_3SiC_5H_4MoCo_3(CO)_3^+$, 1.8], 468 [$Me_3SiC_5H_4MoCo_3(CO)_2^+$, 4.0], 440 [$Me_3SiC_5H_4MoCo_3(CO)^+$, 4.6], 412 ($Me_3SiC_5H_4MoCo_3^+$, 3.4), 451 [$C_5H_4MoCo_3(CO)_4^+$, 5.5], 423 [$C_5H_4MoCo_3(CO)_3^+$, 2.4], 395 [$C_5H_4MoCo_3(CO)_2^+$, 4.6], 443 [$MoCo_3(CO)_6^+$, 4.7], 415 [$MoCo_3(CO)_5^+$, 2.6], 387 [$MoCo_3(CO)_4^+$, 5.3], 359 [$MoCo_3(CO)_3^+$, 2.4], 331 [$MoCo_3(CO)_2^+$, 2.3], 275 [$MoCo_3^+$, 4.3].

2b. The workup for **2b–f** was the same as in the preparation of **2a**. To the flask described above were added 303 mg (0.5 mmol) of [$\eta^5\text{-}CH_3O_2CC_5H_4Mo(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and refluxed for 10 h. After workup a trace of $Co_4(CO)_{12}$ and 100 mg (27%) of **2b** were obtained. **2b**, as black solid: mp 112 °C dec. Anal. Calcd for $C_{18}H_7Co_3MoO_{13}$: C, 30.71; H, 1.00. Found: C, 30.58; H, 0.85. IR (KBr disk): $\nu(C{=}O)$ 1729 (s) cm^{-1}; ν(terminal $C\equiv O$) 2082 (s), 2032 (vs), 2005 (s), 1991 (s), 1959 (s); ν(bridging carbonyls) 1877 (m), 1852 (s), 1827 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.75 (s, 3 H, CO_2CH_3), 5.50 [t, 2 H, H(3), H(4)], 5.62 [t, 2 H, H(2), H(5)] ppm. MS (EI, Mo^{98}), m/z (relative intensity): 426 [$MeO_2CC_5H_4MoCo_3(CO)^+$, 1.9], 398 ($MeO_2CC_5H_4MoCo_3^+$, 2.2), 451 [$C_5H_4MoCo_3(CO)_4^+$, 1.3], 395 [$C_5H_4MoCo_3(CO)_2^+$, 0.8]. 367 [$C_5H_4MoCo_3(CO)^+$, 1.1], 415 [$MoCo_3(CO)_5^+$, 1.4], 359 [$MoCo_3(CO)_3^+$, 1.7], 331 [$MoCo_3(CO)_2^+$, 1.7], 303 [$MoCo_3(CO)^+$, 2.3], 275, ($MoCo_3^+$, 0.7].

2c. To the flask described above were added 317 mg (0.5 mmol) of [$(\eta^5\text{-}C_2H_5O_2CC_5H_4)Mo(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and refluxed for 10 h. After workup, a trace of $Co_4(CO)_{12}$ and 76 mg (20%) of **2c** were produced. **2c**, as black solid: mp 188 °C dec. Anal. Calcd for $C_{19}H_9Co_3MoO_{13}$: C, 31.78; H, 1.26. Found: C, 31.63; H, 1.13. IR (KBr disk): $\nu(C{=}O)$, 1724 (s) cm^{-1}; ν(terminal $C\equiv O$), 2080 (s), 2041 (vs), 2017 (s), 2005 (vs), 1990 (s), 1968 (s); ν(bridging carbonyls), 1879 (s), 1853 (s), 1818 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.24 (t, *J* = 7.20 Hz, 3 H, $CO_2CH_2CH_3$), 4.22 (q, *J* = 7.20 Hz, 2 H, $CO_2CH_2CH_3$), 5.47 [t, 2 H, H(3), H(4)], 5.61 [t, 2 H, H(2), H(5)] ppm. MS (EI, Mo^{98}), *m/z* (relative intensity): 580 [$EtO_2CC_5H_4MoCo_3(CO)_6^+$, 0.5], 496 [$EtO_2CC_5H_4MoCo_3(CO)_3^+$, 1.8], 468 [$EtO_2CC_5H_4MoCo_3(CO)_2^+$, 3.0], 440 [$EtO_2CC_5H_4MoCo_3(CO)^+$, 3.8], 395 [$C_5H_4MoCo_3(CO)_2^+$, 2.4], 367 [$C_5H_4MoCo_3(CO)^+$, 3.9], 339 ($C_5H_4MoCo_3^+$, 3.8), 471 [$MoCo_3(CO)_7^+$, 0.9], 387 [$MoCo_3(CO)_4^+$, 1.5], 359 [$MoCo_3(CO)_3^+$, 4.5], 331 [$MoCo_3(CO)_2^+$, 2.8], 303 [$MoCo_3(CO)^+$, 1.9], 275 ($MoCo_3^+$, 2.1).

2d. To the flask described above were added 375 mg (0.5 mmol) of [$(\eta^5\text{-}MeC(O)C_5H_4)W(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and refluxed for 10 h. After workup, a trace amount of $Co_4(CO)_{12}$ and 95 mg (24%) of **2d** were produced. **2d**, as black solid; mp 114 °C dec. Anal. Calcd for $C_{18}H_7Co_3O_{12}W$: C, 27.86; H, 0.91. Found: C, 27.97; H, 0.84. IR (KBr disk): ν $(C{=}O)$ 1688 (s) cm^{-1}; ν (terminal $C\equiv O$) 2082 (s), 2032 (vs), 1983 (s), 1926 (s); ν (bridging carbonyls) 1885 (m), 1844 (vs), 1835 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.17 [s, 3 H, $C(O)CH_3$], 5.42 [t, 2 H, H(3), H(4)], 5.70 [t, 2 H, H(2), H(5)] ppm. MS (EI, W^{184}): *m/z* (relative intensity): 636 [$MeC(O)C_5H_4WCo_3(CO)_6^+$, 1.0], 580 [$MeC(O)C_5H_4WCo_3(CO)_4^+$, 6.0], 552 [$MeC(O)C_5H_4WCo_3(CO)_3^+$, 2.0], 524 [$MeC(O)C_5H_4WCo_3(CO)_2^+$, 2.0], 496 [$MeC(O)C_5H_4WCo_3(CO)^+$, 1.0], 537 [$C_5H_4WCo_3(CO)_4^+$, 1.0], 509 [$C_5H_4WCo_3(CO)_3^+$, 1.0], 481 [$C_5H_4WCo_3(CO)_2^+$, 1.0], 453 [$C_5H_4WCo_3(CO)^+$, 1.0], 585 [$WCo_3(CO)_8^+$, 1.0], 529 [$WCo_3(CO)_6^+$, 1.0], 501 [$WCo_3(CO)_5^+$, 1.0], 473 [$WCo_3(CO)_4^+$, 1.0], 445 [$WCo_3(CO)_3^+$, 1.0], 417 [$WCo_3(CO)_2^+$, 1.0].

2e. To the flask described above were added 391 mg (0.5 mmol) of [$(\eta^5\text{-}MeO_2CC_5H_4)W(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and refluxed for 10 h. After workup, a trace amount of $Co_4(CO)_{12}$ and 120 mg (29%) of **2e** were produced. **2e**, as black solid; mp 122 °C dec. Anal. Calcd for $C_{18}H_7Co_3O_{13}W$: C, 27.30; H, 0.89. Found: C, 27.23; H, 0.94. IR (KBr disk): $\nu(C{=}O)$ 1729 (s) cm^{-1}; ν(terminal $C\equiv O$) 2082 (s), 2032 (vs), 2004 (s), 1988 (s), 1950 (vs); ν(bridging carbonyls) 1877 (m), 1853 (s), 1827 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 3 H, CO_2CH_3), 5.50 [t, 2 H, H(3), H(4)], 5.64 [t, 2 H, H(2), H(5)] ppm. MS (EI, W^{184}); *m/z* (relative intensity): 540 [$MeO_2CC_5H_4WCo_3(CO)_2^+$, 0.2], 425 ($C_5H_4WCo_3^+$, 0.1).

2f. Method i. To the flask described above were added 405 mg (0.5 mmol) of [$EtO_2CC_5H_4W(CO)_3]_2$, 265 mg (0.775 mmol) of $Co_2(CO)_8$, and 50 mL of toluene. The mixture was stirred and refluxed for 10 h. After workup, a trace amount of $Co_4(CO)_{12}$ and 132 mg (32%) of **2f** were produced. **2f**, as black solid: mp 128 °C dec. Anal. Calcd for $C_{19}H_9Co_3O_{13}W$: C, 28.32; H, 1.12. Found: C, 28.37; H, 1.05. IR (KBr disk): $\nu(C{=}O)$ 1729 (s) cm^{-1}; ν(terminal $C\equiv O$) 2082 (s), 2041 (s), 2000 (vs), 1959 (s); ν(bridging carbonyls) 1885 (m), 1852 (s), 1819 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, *J* = 8.0 Hz, 3 H, $CO_2CH_2CH_3$), 4.23 (q, *J* = 8.0 Hz, 2 H, $CO_2CH_2CH_3$), 5.51 [t, 2 H, H(3), H(4)], 5.65 [t, 2H, H(2), H(5)] ppm. MS (EI, W^{184}), *m/z* (relative intensity): 638 [$EtO_2CC_5H_4WCo_3(CO)_5^+$, 0.5], 610 [$EtO_2CC_5H_4WCo_3(CO)_4^+$, 0.5], 582 [$EtO_2CC_5H_4WCo_3(CO)_3^+$, 0.4], 554 [$EtO_2CC_5H_4WCo_3(CO)_2^+$, 1.0], 526 [$EtO_2CC_5H_4WCo_3(CO)^+$, 0.6], 498 ($EtO_2CC_5H_4WCo_3^+$, 0.3), 481 [$C_5H_4WCo_3(CO)_2^+$, 0.2], 453 [$C_5H_4WCo_3(CO)^+$, 0.2], 425 ($C_5H_4WCo_3^+$, 0.4), 417 [$WCo_3(CO)_2^+$, 0.2], 389 [$WCo_3(CO)^+$, 0.1], 361 [$WCo_3^+$, 0.5].

2f. Method ii. To the flask described above were added 405 mg (0.5 mmol) of [$EtO_2CC_5H_4W(CO)_3]_2$, 223 mg (0.39 mmol) of $Co_4(CO)_{12}$, and 50 mL of toluene. After the mixture had been refluxed for 8 h, solvent was removed at reduced pressure and the residue extracted fully with CH_2Cl_2. Extracts were filtered and the filtrate was concentrated to an appropriate volume for TLC separation (1:1 petroleum ether/CH_2Cl_2 as eluent). Five bands were developed in the order brown [$Co_4(CO)_{12}$], green (unidentified), purple (unidentified), red brown and red (starting material [$EtO_2CC_5H_4W(CO)_3]_2$). From the fourth red brown band 60 mg (14%) of **2f** was obtained, which was identified by comparison of its IR and ^{1}H NMR spectra with those of the authentic sample.

Crystallography of 2e. A solution of **2e** in 50% (v/v) petroleum ether/CH_2Cl_2 was slowly evaporated at room temperature to give deep-red transparent crystals suitable for X-ray diffraction analysis. The crystal with approximate dimensions of 0.2 × 0.2 × 0.2 mm^3 was mounted on a glass fiber in an arbitrary orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 4045 independent reflections was collected in the range $2° \le \theta \le 25°$ by the ω–2θ scan technique at room temperature, of which 3441 reflections with $I \ge 3\sigma(I)$ were considered to be observed. The corrections for Lp factors and empirical absorption were applied to the intensity data.

The crystal is triclinic space group $P\bar{1}$, with a = 8.679 (2) Å, b = 9.473 (3) Å, c = 13.817 (4) Å, α = 78.31 (3)°, β = 82.81 (3)°, γ = 85.44 (3)°, V = 1101.9 (7) Å^3, M_r = 791.90 g/mol, Z = 2, D_x = 2.39 g/cm^3, μ = 76.00 cm^{-1}, and $F(000)$ = 748.

The structure was solved by a direct phase determination method (MULTAN 82). The tungsten atom and three cobalt atoms were located from an E map. The coordinates of the remaining non-hydrogen atoms were found in successive difference Fourier syntheses. The hydrogen atoms were not included in the refinements and the calculations of the structure factors. The final refinement by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged with unweighted and weighted R factors of 0.046 and 0.052. The highest peak on the final difference Fourier map had a height of 0.98 e/Å^3.

All calculations were performed on a PDP11/44 computer using the SDP-PLUS program system.

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Supplementary Material Available: Tables of elemental analysis, IR, ^{1}H NMR, and MS data for **2a–f** and **3a–e** and fractional coordinates, thermal parameters, and bond distances and angles for **3d** (8 pages). Ordering information is given on any current masthead page.

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