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Regioselective Metal Exchange Reactions in Linked Clusters

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Regioselective metal exchange reactions in linked clusters, $[(CO)_9Co_3(\mu_3\text{-}C)COOCH_2]_2$ (**1**) and $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**2**), were investigated. The reactions of **1** with $Na[M(CO)_3(C_5H_4R)]$ (M = Mo, W; R = H, $COCH_3$, $COOC_2H_5$) gave one-step or two-step exchange products, $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2M(CO)_8(C_5H_4R)$ (**3a**, M = Mo, R = H; **3b**, M = Mo, R = $COCH_3$; **3c**, M = Mo, R = $COOC_2H_5$; **3d**, M = W, R = H; **3e**, M = W, R = $COCH_3$; **3f**, M = W, R = $COOC_2H_5$) or $[(CO)_8(C_5H_4R)Co_2M(\mu_3\text{-}C)COOCH_2]_2$ (**4a**, M = Mo, R = H; **4b**, M = Mo, R = $COCH_3$; **4c**, M = Mo, R = $COOC_2H_5$; **4d**, M = W, R = H; **4e**, M = W, R = $COCH_3$; **4f**, M = W, R = $COOC_2H_5$). The reactions of **1** with $Na_2[p\text{-}\{M(CO)_3C_5H_4CO\}_2C_6H_4]$ (M = Mo, W) gave cyclic clusters, $CH_2OCO(\mu_3\text{-}C)Co_2M(CO)_8C_5H_4COC_6H_4COC_5H_4(CO)_8MCo_2(\mu_3\text{-}C)COOCH_2$ (**5a**, M = Mo; **5b**, M = W). Further reaction of **3e** or **4e** with $Na[Mo(CO)_3(C_5H_5)]$ gave a two-step exchange product, $(CO)_8(C_5H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)CoMoW(CO)_7(C_5H_5)(C_5H_4COCH_3)$ (**6**) or $[(CO)_7(C_5H_5)(C_5H_4COCH_3)CoMoW(\mu_3\text{-}C)COOCH_2]_2$ (**7**). The reactions of **2** with $Na[Mo(CO)_3(C_5H_4R)]$ (R = H, $COCH_3$, $COOC_2H_5$) also gave one-step or two-step exchange products, $(CO)_8(C_5H_4R)Co_2Mo(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**8a**, R = H; **8b**, R = $COCH_3$; **8c**, R = $COOC_2H_5$) or $(CO)_7(C_5H_4R)_2CoMo_2(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**9a**, R = H; **9b**, R = $COCH_3$; **9c**, R = $COOC_2H_5$). The reaction of **2** with $Na_2[p\text{-}\{Mo(CO)_3C_5H_4CO\}_2C_6H_4]$ gave a linear cluster, $p\text{-}[(CO)_6Co_2(\mu\text{-}CHC)CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8C_5H_4CO]_2C_6H_4$ (**10**). The structures of **3a** and **8a** have been determined by single-crystal X-ray diffraction.

Introduction

Constructing higher nuclearity clusters with well-defined dimensions and structures provides a rather active field of chemistry with potential applications in areas including nanotechnology, molecular recognition, and catalysis.[1] Linearly arranged supraclusters are expected to show interesting electronic properties such as quantum wires if their lengths are in the range of approximately 10 nm, and cyclic or helical supraclusters may have enzyme-like behaviors.[2] In addition, such supraclusters should have an opportunity to form a field for excellent molecular recognition, because various kinds of substituents, including functional groups, can be introduced to them.[2,3] For these reasons, a continuing effort has been directed toward developing a better methodology for systematic synthesis of supracluster compounds through molecular design.[4]

Metal exchange reaction in cluster compounds was first observed in 1971 and 1972 without being explicitly recognized.[5] However, only in the 1980s did systematic studies begin to elucidate the scope and variability of this type of reaction.[6,7] Some $(\mu_3\text{-}X)Co_2M$ (X = C, S, Se, Te; M = Cr, Mo, W, Fe, Ni, Ru) and $(\mu\text{-}C_2)CoM$ (M = Mo, W) tetrahedral clusters were synthesized through metal exchange reactions.[7−9] Additionally, by employing novel metal exchange reagents, some double tetrahedron cluster compounds were obtained.[10,11] Recently, we

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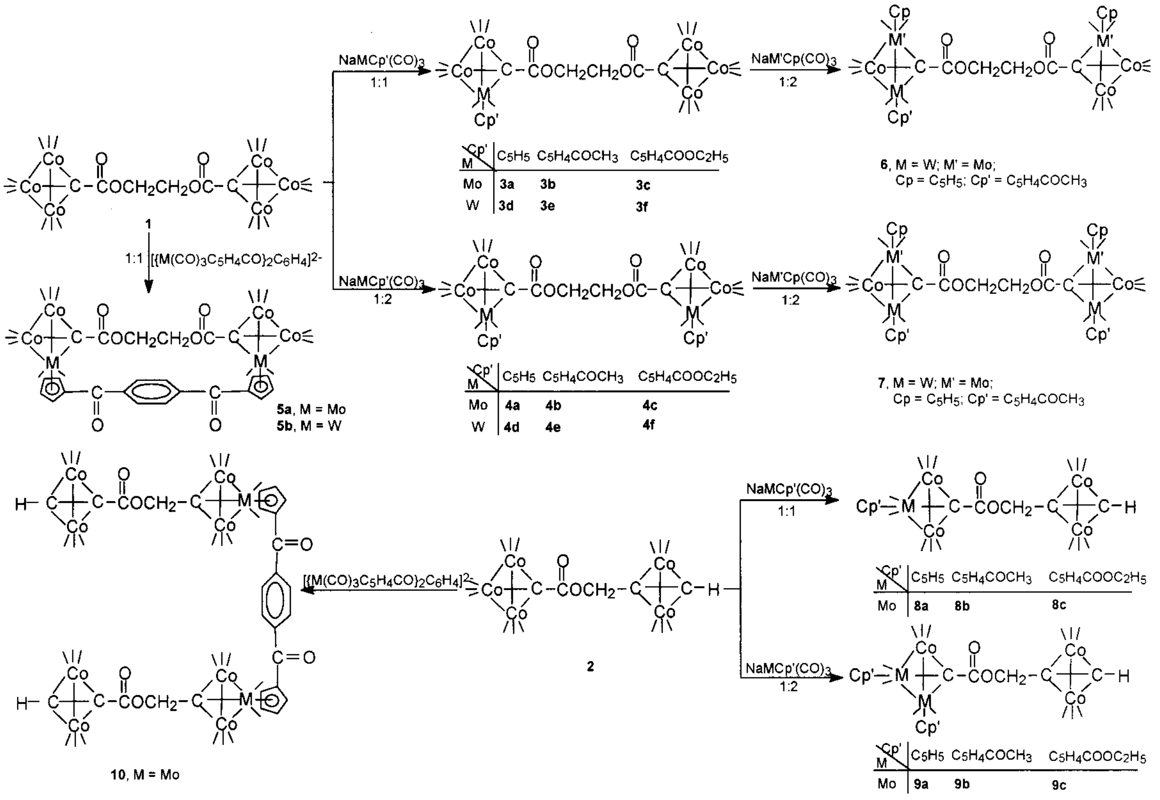
Scheme 1. Summary of the Reactions



reported the reactivity of some linked cluster compounds.[12,13] It seemed that the metal exchange reaction in linked clusters was regioselective. If this conclusion can be universally used, it might be possible to synthesize supracluster compounds in a molecular design manner by the metal exchange reactions of linked clusters.

To investigate metal exchange reactions in linked clusters more extensively, we initiated a study of reactions of $[(CO)_9Co_3(\mu_3\text{-}C)COOCH_2]_2$ (**1**) or $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**2**) with $Na[M(CO)_3(C_5H_4R)]$ (M = Mo, W; R = H, $COCH_3$, $COOC_2H_5$) or $Na_2[p\text{-}\{M(CO)_3C_5H_4CO\}_2C_6H_4]$ (M = Mo, W). Twenty-three novel cluster compounds were prepared, and the crystal structures of **3a** and **8a** were determined. The results indicate that the $Co(CO)_3$ fragment in different cluster cores has a different reaction activity in a metal exchange reaction, following the series $Co_3(\mu_3\text{-}C) > Co_2W(\mu_3\text{-}C) > Co_2Mo(\mu_3\text{-}C) > CoW_2(\mu_3\text{-}C)$, $CoMo_2(\mu_3\text{-}C)$, $Co_2(\mu\text{-}C_2)$.

Results and Discussion

The reactions described in this work are summarized in Scheme 1. Compound **1** or **2** can react with metal exchange reagent $Na[M(CO)_3(C_5H_4R)]$ (M = Mo, W; R = H, $COCH_3$, $COOC_2H_5$) in THF solution at room temperature. When **1** reacts with $Na[M(CO)_3(C_5H_4R)]$ in 1:1 molecular ratio, one $Co(CO)_3$ fragment in a $Co_3(\mu_3\text{-}C)$ core is replaced by a $M(CO)_2(C_5H_4R)$ fragment to form one-step exchange products **3a**–**f**. When the molecular ratio is 1:2, two $Co(CO)_3$ fragments in two $Co_3(\mu_3\text{-}C)$ cores are replaced to form two-step exchange products **4a**–**f**. It should be noted that compounds **4a**–**f** contain two $Co_2M(\mu_3\text{-}C)$ cores rather than one $Co_3(\mu_3\text{-}C)$ core and one $CoM_2(\mu_3\text{-}C)$ core. This indicates that the second step is regioselective. The $Co(CO)_3$ fragment in a $Co_3(\mu_3\text{-}C)$ core is more active than the one in a $Co_2M(\mu_3\text{-}C)$ (M = Mo, W) core. When **3e** is treated with $Na[Mo(CO)_3(C_5H_5)]$ in 1:2 molecular ratio, a $Co(CO)_3$ fragment in the $Co_3(\mu_3\text{-}C)$ core as well as in the $Co_2W(\mu_3\text{-}C)$ core is replaced to form **6**, in which a $Co_2Mo(\mu_3\text{-}C)$ core and a $CoMoW(\mu_3\text{-}C)$ core are linked by a carbon chain. Similarly, compound **7**, which contains two $CoMoW(\mu_3\text{-}C)$ cores, can be formed by treating **4e** with $Na[Mo(CO)_3(C_5H_5)]$ in 1:2 molecular ratio. The formations of compounds **6** and **7** are also regioselective. The $Co(CO)_3$ fragment in a $Co_2W(\mu_3\text{-}C)$ core is more active than that in a $Co_2Mo(\mu_3\text{-}C)$ core. There are two different cluster cores, $Co_3(\mu_3\text{-}C)$ and $Co_2(\mu\text{-}C_2)$, in compound **2**. The reactions of **2** with $Na[Mo(CO)_3(C_5H_4R)]$ (R = H, $COCH_3$, $COOC_2H_5$) in 1:1 or 1:2 molecular ratio afford one-step exchange products **8a**–**c** or two-step exchange products **9a**–**c**. This is in accord with what has been observed in the reactions of **2** with $Na[W(CO)_3(C_5H_4R)]$ (R = H, $COCH_3$, $COC_6H_4COOCH_3$).[12] In all these exchange reactions for compound **2**, the $Co_2(\mu\text{-}C_2)$ core is retained. Our previous studies indicate that the $Co(CO)_3$ exchange in a $Co_2(\mu\text{-}C_2)$ core can also be observed at room temperature provided that the reaction time is long enough (at least 48 h).[13] This indicates that the $Co(CO)_3$ fragment in a $Co_2(\mu\text{-}C_2)$ core is far less active than that in a $Co_3(\mu_3\text{-}C)$ or $Co_2M(\mu_3\text{-}C)$ (M = Mo, W) core. From the above information, it can be concluded that

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the $Co(CO)_3$ fragment in different cluster cores has a different reaction activity in a metal exchange reaction, following the series $Co_3(\mu_3\text{-}C) > Co_2W(\mu_3\text{-}C) > Co_2Mo(\mu_3\text{-}C) > CoW_2(\mu_3\text{-}C)$, $CoMo_2(\mu_3\text{-}C)$, $Co_2(\mu\text{-}C_2)$.

Generally speaking, a metal−carbon bond is stronger than a metal−metal bond.[6,14] So, it is clear why the $Co(CO)_3$ fragment in a $Co_3(\mu_3\text{-}C)$ or $Co_2M(\mu_3\text{-}C)$ (M = Mo, W) core is more active than the one in a $Co_2(\mu\text{-}C_2)$ core in a metal exchange reaction. To substitute a $Co(CO)_3$ fragment in a $Co_2(\mu\text{-}C_2)$ core, the cleavage of two metal−carbon bonds and one metal−metal bond is required, while substituting the same fragment in a $Co_3(\mu_3\text{-}C)$ or $Co_2M(\mu_3\text{-}C)$ (M = Mo, W) core requires breaking only one metal−carbon bond and two metal−metal bonds.

Metal exchange reagents of the $[\{M(CO)_3(C_5H_4)\}_2R]^{2-}$ (M = Mo, W) type proved to be effective in the syntheses of double tetrahedron cluster compounds.[10,11,15] Additionally, just as stated above, the metal exchange reactions in linked clusters are regioselective. So, it is worthwhile to test the reactions of $[\{M(CO)_3(C_5H_4)\}_2R]^{2-}$ with linked clusters. We treated compound **1** or **2** with $Na_2[p\text{-}\{M(CO)_3C_5H_4CO\}_2C_6H_4]$ (M = Mo, W). The reactions of **1** with $Na_2[p\text{-}\{M(CO)_3C_5H_4CO\}_2C_6H_4]$ in 1:1 molecular ratio give cyclic cluster compounds, **5a** and **5b**, in which two tetrahedron cluster cores are linked by two carbon chains. The reaction of **2** with $Na_2[p\text{-}\{Mo(CO)_3C_5H_4CO\}_2C_6H_4]$ in 2:1 molecular ratio gives a linear cluster compound, **10**, in which four tetrahedron cluster cores are linked by three carbon chains. The formations of **5** and **10** indicate that the reactions of metal exchange reagents of the $[\{M(CO)_3(C_5H_4)\}_2R]^{2-}$ type with linked clusters have a potential application in the syntheses of polymeric species with metal cluster centers.

Metal exchange reactions of simple $Co_3(\mu_3\text{-}C)$, $Co_2(\mu\text{-}C_2)$ clusters are thermal acceleration processes in THF solution.[16−18] The yields are better at higher temperatures. However, the exchange reactions described in this work could only be achieved at room temperature. Thermal reactions always gave complicated mixtures rather than the expected exchange products.

The exchange products obtained in this work are dark brown to dark green solids. Generally, they are air-stable at room temperature for several days and soluble in polar solvents such as THF and CH_2Cl_2. However, these compounds decompose completely without melting when they are heated to a higher temperature in the air or even in a nitrogen atmosphere.

The elemental analyses, IR, NMR, and MS data of these compounds are consistent with the structure formulas presented in Scheme 1. In the IR spectra, all these compounds show a group of absorption bands in the range 1900−2113 cm^{-1}. The stronger ones at higher wavenumbers should be attributed to the terminal carbonyls coordinated to cobalt atoms, while the relatively weaker ones at lower wavenumbers should be attributed to the terminal carbonyls coordinated to molybdenum or tungsten atoms.[19] For compounds **3a**−**f**, there is a mid absorption band around 2112 cm^{-1} that proved to be characteristic of the $(CO)_9Co_3(\mu_3\text{-}C)$ unit.[20] The absorption bands for the C=O groups in the substituted cyclopentadienyl rings or on the carbon chains of these compounds occur in the range 1650−1720 cm^{-1}. For most of the exchange products, there are several weak absorption bands in the range 1840−1890 cm^{-1}; these are caused by semibridging carbonyls coordinated to the Mo−Mo(W)[21] or Co−Mo(W)[22] bonds. The ^1H NMR spectra of all these compounds show the presence of protons in their corresponding organic groups. For the four protons on the $COOCH_2CH_2OCO$ chain, the chemical environments in compounds **4a**−**f**, **5a**,**b**, and **7** are identical, and the ^1H NMR spectra show a singlet. While the chemical environments of these four protons in compounds **3a**−**f** and **6** are different, the ^1H NMR spectra show a multiplet. It should be noted that the singlet of these four protons in compounds **5a** and **5b** appears upfield (δ 3.80) compared with the other compounds (δ 4.50−4.60). This is caused by the benzene ring on the other carbon chain. As we know, ^1H NMR spectra of a monosubstituted cyclopentadienyl ring in transition metal compounds vary greatly in complexity, such as a single resonance, an A_2B_2 or A_2BB' pattern, or a multiplet pattern, all depending on the nature of the substituent.[23] For the four protons on the substituted cyclopentadienyl rings of these compounds (except for **6** and **7**), two triplets are shown in the range δ 5.50−6.05. The downfield triplet should be attributed to H(2) and H(5) protons, which are close to the substituent, and the upfield one should be attributed to H(3) and H(4) protons, being remote from the substituent. This is in accord with what has been observed in the related complexes bearing monosubstituted cyclopentadienyl rings.[11,24] For compounds **6** and **7**, these four protons show a multiplet in the range δ 5.40−6.00 due to the proton−proton coupling.[25] The five protons on the unsubstituted cyclopentadienyl rings show a singlet. It should be noted that the two unsubstituted cyclopentadienyl rings in compound **6** show two 5H singlets rather than one 10H singlet. This indicates that the two unsubstituted cyclopentadienyl rings in compound **6** are located in two different cluster cores. For compounds **8a**−**c**, **9a**−**c**, and **10**, the ^1H NMR spectra show a singlet around δ 6.10, which should be attributed to the terminal proton in the $Co_2(CO)_6(\mu\text{-}CHCR)$ unit, just like

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Table 1. Summary of the Crystallographic Data for Compounds 3a and 8a

	3a	**8a**
formula	$C_{28}H_9Co_5MoO_{21}$	$C_{24}H_8Co_4MoO_{16}$
fw	997.88	883.99
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	16.618(4)	8.079(3)
b, Å	14.857(2)	8.164(4)
c, Å	16.753(4)	24.172(3)
α, deg		83.01(2)
β, deg	116.66(1)	85.15(2)
γ, deg		69.92(3)
V, Å^3	3696(1)	1485(1)
Z	4	2
D_c, g cm^{-3}	1.926	1.977
radiation	Mo Kα	Mo Kα
temp, K	293	296
$F(000)$	2088.00	860
μ, cm^{-1}	26.04	26.59
scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{max}$, deg	50.0	52.0
no. of observns	4232 ($I > 2.00\sigma(I)$)	4507 ($I > 2.00\sigma(I)$)
no. of variables	496	406
R	0.045	0.051
R_w	0.049	0.059
goodness of fit indicator	1.46	1.39
max shift in final cycle	0.06	0.002
largest peak in final diff map, e Å^{-3}	0.73	1.18

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

Mo−Co(1)	2.710(1)	Mo−Co(2)	2.667(1)
Mo−C(9)	2.074(7)	Mo−C(av, Cp)	2.31
Co(1)−Co(2)	2.494(1)	Co(1)−C(9)	1.927(7)
Co(2)−C(9)	1.916(6)	Co(3)−Co(4)	2.470(1)
Co(3)−Co(5)	2.478(2)	Co(4)−Co(5)	2.475(1)
Co(3)−C(14)	1.883(6)	Co(4)−C(14)	1.904(7)
Co(5)−C(14)	1.889(7)	C(9)−C(10)	1.482(9)
C(11)−C(12)	1.493(9)	C(13)−C(14)	1.468(9)

Co(1)−Mo−Co(2)	55.26(3)	Co(1)−Mo−C(9)	45.1(2)
Co(2)−Mo−C(9)	45.6(2)	Mo−Co(1)−Co(2)	61.49(3)
Mo−Co(1)−C(9)	49.7(2)	Co(2)−Co(1)−C(9)	49.4(2)
Mo−Co(2)−Co(1)	63.25(3)	Mo−Co(2)−C(9)	50.6(2)
Co(1)−Co(2)−C(9)	49.7(2)	Co(5)−Co(3)−C(14)	49.0(2)
Co(4)−Co(3)−Co(5)	60.03(4)	Co(4)−Co(3)−C(14)	49.7(2)
Co(3)−Co(4)−Co(5)	60.15(4)	Co(3)−Co(4)−C(14)	48.9(2)
Co(5)−Co(4)−C(14)	49.0(2)	Co(3)−Co(5)−Co(4)	59.82(4)
Co(3)−Co(5)−C(14)	48.8(2)	Co(4)−Co(5)−C(14)	49.5(2)
Co(2)−C(9)−C(10)	131.5(5)	Mo−C(9)−C(10)	135.3(5)
Co(1)−C(9)−C(10)	121.8(5)	Co(3)−C(14)−C(13)	133.4(5)
Co(4)−C(14)−C(13)	128.6(5)	Co(5)−C(14)−C(13)	130.8(5)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 8a

Mo(1)−Co(1)	2.652(1)	Mo(1)−Co(2)	2.703(2)
Mo(1)−C(15)	2.078(5)	Mo(1)−C(av, Cp)	2.333
Co(1)−Co(2)	2.494(2)	Co(2)−C(15)	1.917(6)
Co(1)−C(15)	1.908(5)	Co(3)−Co(4)	2.463(2)
Co(4)−C(19)	1.936(9)	Co(4)−C(18)	1.948(9)
Co(3)−C(19)	1.938(7)	Co(3)−C(18)	1.942(8)
C(18)−C(19)	1.30(1)	C(15)−C(16)	1.480(8)
C(17)−C(18)	1.49(1)		

Co(1)−Mo(1)−Co(2)	55.52(4)	C(15)−Mo(1)−Co(1)	45.6(1)
C(15)−Mo(1)−Co(2)	45.0(2)	C(15)−Co(1)−Co(2)	49.5(2)
C(15)−Co(1)−Mo(1)	51.1(2)	Co(2)−Co(1)−Mo(1)	63.29(4)
Co(1)−Co(2)−Mo(1)	61.19(4)	C(15)−Co(2)−Co(1)	49.2(2)
C(15)−Co(2)−Mo(1)	50.0(2)	C(18)−Co(3)−Co(4)	50.8(3)
C(19)−Co(3)−C(18)	39.3(3)	C(19)−Co(3)−Co(4)	50.5(3)
C(19)−Co(4)−Co(3)	50.6(2)	C(19)−C(18)−C(17)	141.0(8)
C(19)−C(18)−Co(3)	70.2(5)	C(19)−C(18)−Co(4)	69.9(6)
C(17)−C(18)−Co(3)	133.6(6)	C(18)−C(19)−Co(4)	70.9(5)
C(18)−C(19)−Co(3)	70.5(5)	Co(4)−C(19)−Co(3)	78.9(3)
C(16)−C(15)−Co(1)	132.4(4)	C(16)−C(15)−Co(2)	120.6(4)
Co(1)−C(15)−Co(2)	81.4(2)	Co(1)−C(15)−Mo(1)	83.3(2)
Co(2)−C(15)−Mo(1)	85.1(2)		

their precursor compound **2**.[26] So, the $Co_2(\mu\text{-}C_2)$ core is intact during the metal exchange processes. If the $CoMo(CO)_5(C_5H_4R)(\mu\text{-CHCR})$ unit were formed, this signal should appear around δ 5.90 because of the stronger deshielding effect of the molybdenum fragment $[Mo(CO)_2(C_5H_4R)]$.[18]

It has been shown that in clusters of the $CpMCo_2(CO)_8$-CR type, where M = Mo or W and Cp bear zero, one, or five methyl substituents, there exist two interconverting rotamers whereby the $CpM(CO)_2$ vertex is oriented either proximal or distal to the capping carbonyl group. When Cp = C_5H_5 or $C_5H_4CH_3$, this group is predominantly distal, whereas for Cp = $C_5(CH_3)_5$ the ring is proximal and the Mo (or W) carbonyls semibridge to the cobalts.[22] This interesting phenomenon was also shown by the infrared spectra for some compounds in this work, as mentioned above.

The crystal structures of **3a** and **8a** were determined by X-ray structure analyses. Crystallographic data are collected in Table 1, and selected bond distances and angles are listed in Tables 2 and 3. Figures 1 and 2 show the molecular structures of **3a** and **8a**.

The molecule of compound **3a** contains $Co_3(\mu_3\text{-C})$ and $Co_2Mo(\mu_3\text{-C})$, two different cluster cores bridged by a $COOCH_2CH_2OCO$ chain. Each cobalt atom is coordinated by three terminal carbonyls, and the molybdenum atom is coordinated by two terminal carbonyls and one cyclopentadienyl ligand. In the $Co_2Mo(\mu_3\text{-C})$ tetrahedron skeleton, the average Co−Mo bond length is 2.69 Å, the average Co−C bond length is 1.92 Å, the Co(1)−Co(2) bond length is 2.494(1) Å, the C(9)−Mo bond length is 2.074(7) Å, and the average distance of the molybdenum atom to the carbon atoms on the cyclopentadienyl ring is 1.92 Å. All these values are close to the corresponding values found in the simple $Co_2Mo(\mu_3\text{-C})$ clusters.[17] In the $Co_3(\mu_3\text{-C})$ tetrahedron skeleton, the average Co−Co bond length is 2.47 Å and the average Co−C bond length is 1.89 Å. These values are also close to the corresponding values found in the simple $Co_3(\mu_3\text{-C})$ cluster.[27] The other geometrical parameters in compound **3a** are close to its precursor compound **1**.[28]

Generally, the structure of compound **8a** is similar to its precursor compound **2**.[26] In the molecule of **8a**, a $Co_2Mo(\mu_3\text{-C})$ tetrahedron skeleton is connected with a $Co_2(\mu\text{-}C_2)$ tetrahedron skeleton through a $COOCH_2$ chain. Again, each cobalt atom is coordinated by three terminal carbonyls, and the molybdenum atom is coordinated by two terminal carbonyls and one cyclopentadienyl ligand. The geometries of the $Co_2Mo(\mu_3\text{-C})$ skeleton in compound **8a** are similar to those of compound **3a**. In the $Co_2(\mu\text{-}C_2)$ skeleton, like in other related compounds,[29] the C(18)−C(19) bond length (1.30(1) Å) is much longer than a normal C≡C bond. Compound **8a** also has a similar structure feature with its counterpart $(CO)_8(C_5H_5)Co_2W(\mu_3\text{-C})COOCH_2(\mu\text{-CCH})Co_2(CO)_6$.[12]

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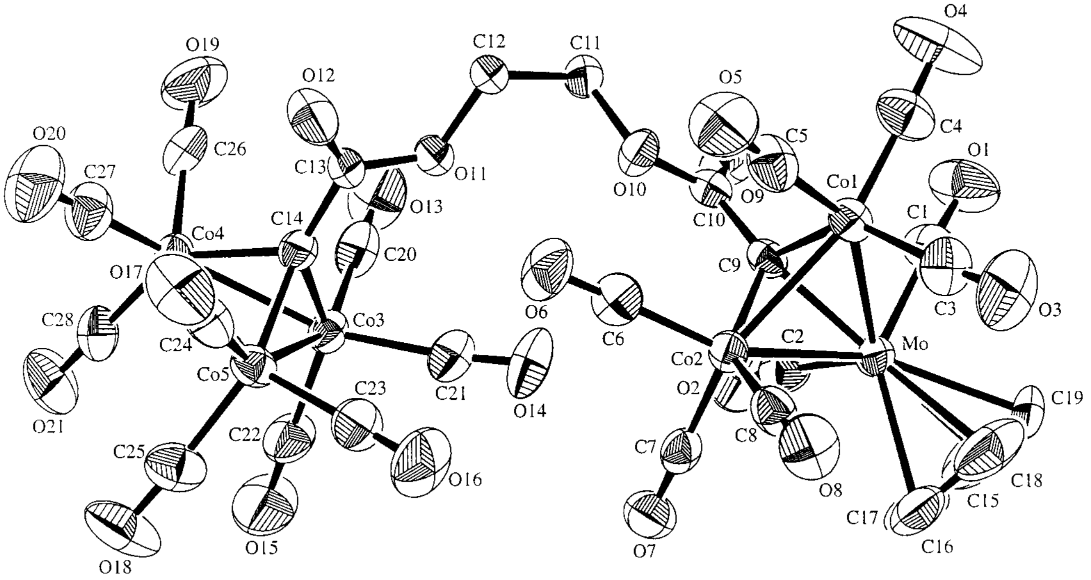

Figure 1. Molecular structure of compound **3a**.

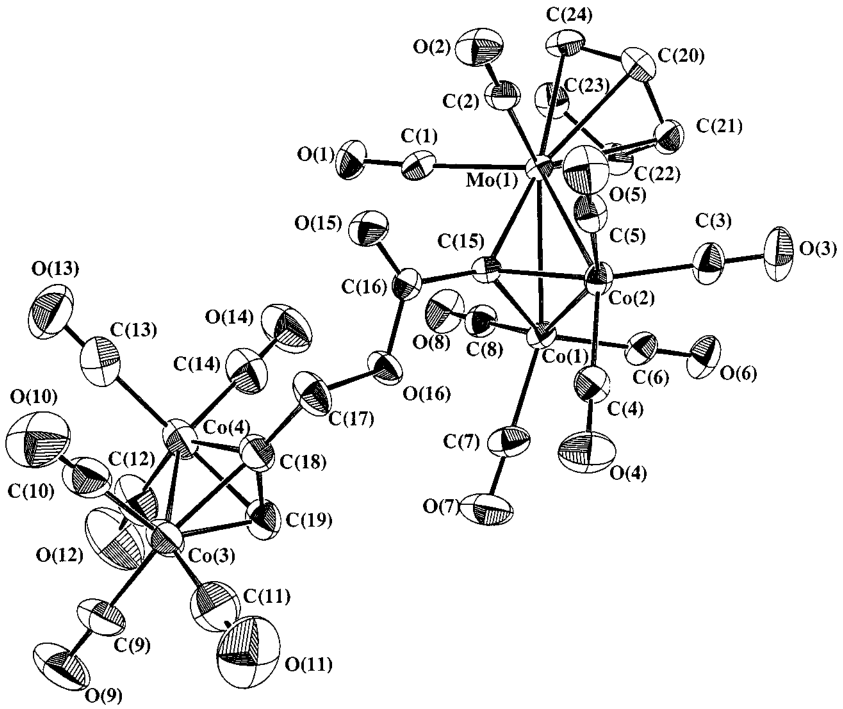

Figure 2. Molecular structure of compound **8a**.

Experimental Section

General Comments. All reactions were carried out under pure nitrogen using standard Schlenk techniques. All solvents were dried and deoxygenated according to standard procedures[30] before use. Chromatographic separations and purification were performed on 160−200 mesh silica gel.

Infrared spectra were recorded as pressed KBr disks on a Nicolet FT-IR 10 DX spectrophotometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer in $CDCl_3$-deuterated solvent at ambient temperature. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). Elemental analyses and FAB MS determination were performed on a Carlo Erba 1106 type analyzer and Finnigan MAT 8430, respectively.

$[(CO)_9Co_3(\mu_3\text{-}C)COOCH_2]_2$ (**1**),[28] $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**2**),[26] $NaM(CO)_3C_5H_4R$ (M = Mo, W; R = H, $COCH_3$, $COOC_2H_5$), and $Na_2[p\text{-}\{M(CO)_3C_5H_4CO\}_2C_6H_4]$ (M = Mo, W)[31] were prepared according to the literature methods or slight modifications thereof.

Preparation of 3a−f and 4a−f. $NaMo(CO)_3(C_5H_5)$ (80 mg, 0.3 mmol) and **1** (299 mg, 0.3 mmol) were dissolved in THF (30 cm^3). The solution was stirred at room temperature for 15 h. Then the solvent was removed under reduced pressure, and the residue was chromatographed. Elution with CH_2Cl_2/petroleum ether (2:1) produced (i) starting material **1** (53 mg) and (ii) dark brown solid $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8(C_5H_5)$ (**3a**) (124 mg, 38.6%, based on **1**): IR (νCO) 2112(m), 2065(vs), 2028(vs), 2004(m, sh), 1940(m), 1899(m) cm^{-1}; (νC=O) 1671(m) cm^{-1}; ^{1}H NMR δ 4.57−4.59 (m, 4H,

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[30] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

[31] Ding, E. R.; Yin, Y. Q.; Sun, J. *J. Organomet. Chem.* **1998**, *559*, 157.

2CH$_2$), 5.44 (s, 5H, C_5H_5). Anal. Calcd for $C_{28}H_9Co_5MoO_{21}$: C, 31.34; H, 0.84. Found: C, 31.51; H, 0.92.

$NaMo(CO)_3(C_5H_5)$ (80 mg, 0.3 mmol) and **1** (150 mg, 0.15 mmol) were dissolved in THF (30 cm^3). The other manipulation was similar to that described above. Elution with CH_2Cl_2/ether (40:1) produced a dark brown solid, $[(CO)_8(C_5H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2]_2$ (**4a**) (83 mg, 48.3%, based on **1**): IR (νCO) 2079(s), 2024(vs), 2000(vs), 1951(m), 1890(w) cm^{-1}; (νC=O) 1670(m) cm^{-1}; ^{1}H NMR δ 4.55 (s, 4H, 2CH$_2$), 5.45 (s, 10H, 2C$_5$H$_5$). Anal. Calcd for $C_{32}H_{14}Co_4Mo_2O_{20}$: C, 33.51; H, 1.22. Found: C, 33.40; H, 1.15.

The following compounds were similarly prepared. $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8(C_5H_4COCH_3)$ (**3b**): a dark brown solid (54 mg, 16.2%, based on **1**); IR (νCO) 2113(m), 2094(vs, sh), 2038(vs), 1938(s), 1888(m) cm^{-1}; (νC=O) 1681(br m) cm^{-1}; ^{1}H NMR δ 2.35 (s, 3H, CH$_3$), 4.58−4.60 (m, 4H, 2CH$_2$), 5.53 (t, 2H, H(3) and H(4), $J = 2.3$ Hz), 6.00 (t, 2H, H(2) and H(5), $J = 2.3$ Hz). Anal. Calcd for $C_{30}H_{11}Co_5MoO_{22}$: C, 32.32; H, 0.99. Found: C, 32.21; H, 0.90. $[(CO)_8(C_5H_4COCH_3)Co_2Mo(\mu_3\text{-}C)COOCH_2]_2$ (**4b**): a dark brown solid (89 mg, 48.2%, based on **1**); IR (νCO) 2094(s), 2033(vs), 1940(m), 1889(m) cm^{-1}; (νC=O) 1682(m), 1671(m) cm^{-1}; ^{1}H NMR δ 2.35 (s, 6H, 2CH$_3$), 4.59 (s, 4H, 2CH$_2$), 5.54 (t, 4H, 2H(3) and 2H(4), $J = 2.2$ Hz), 5.95 (t, 4H, 2H(2) and 2H(5), $J = 2.2$ Hz). Anal. Calcd for $C_{36}H_{18}Co_4Mo_2O_{22}$: C, 35.12; H, 1.46. Found: C, 35.22; H, 1.39. $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8(C_5H_4COOC_2H_5)$ (**3c**): a dark brown solid (120 mg, 35.0%, based on **1**); IR (νCO) 2112(m), 2095(m), 2063(s), 1974(m), 1945(m), 1900(w) cm^{-1}; (νC=O) 1720(m), 1670(m) cm^{-1}; ^{1}H NMR δ 1.31 (t, 3H, CH$_3$, $J = 7.2$ Hz), 4.27 (q, 2H, C*H*$_2$CH$_3$, $J = 7.2$ Hz), 4.57−4.59 (m, 4H, 2CH$_2$), 5.51 (t, 2H, H(3) and H(4), $J = 2.3$ Hz), 5.96 (t, 2H, H(2) and H(5), $J = 2.3$ Hz). Anal. Calcd for $C_{31}H_{13}Co_5MoO_{23}$: C, 32.52; H, 1.14. Found: C, 32.44; H, 1.13. $[(CO)_8(C_5H_4COOC_2H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2]_2$ (**4c**): a dark brown solid (60 mg, 31.0%, based on **1**); IR (νCO) 2093(s), 2083(s), 2033(s), 2012(s), 1944(m), 1897(w) cm^{-1}; (νC=O) 1723(m), 1672(m) cm^{-1}; ^{1}H NMR δ 1.31 (t, 6H, 2CH$_3$, $J = 7.4$ Hz), 4.27 (q, 4H, 2C*H*$_2$CH$_3$, $J = 7.4$ Hz), 4.57 (s, 4H, 2CH$_2$), 5.51 (t, 4H, 2H(3) and 2H(4), $J = 2.5$ Hz), 5.96 (t, 4H, 2H(2) and 2H(5), $J = 2.5$ Hz). Anal. Calcd for $C_{38}H_{22}Co_4Mo_2O_{24}$: C, 35.35; H, 1.71. Found: C, 35.61; H, 1.90. $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2W(CO)_8(C_5H_5)$ (**3d**): a dark brown solid (45 mg, 12.9%, based on **1**); IR (νCO) 2113(m), 2055(vs), 2031(vs), 2002(vs, sh), 1967(m), 1943(m), 1886(w) cm^{-1}; (νC=O) 1675(m) cm^{-1}; ^{1}H NMR δ 4.55−4.57 (m, 4H, 2CH$_2$), 5.51 (s, 5H, C$_5$H$_5$). Anal. Calcd for $C_{28}H_9Co_5O_{21}W$: C, 28.97; H, 0.78. Found: C, 29.01; H, 0.94. $[(CO)_8(C_5H_5)Co_2W(\mu_3\text{-}C)COOCH_2]_2$ (**4d**): a dark brown solid (32 mg, 16.0%, based on **1**); IR (νCO) 2079(s), 2021(vs), 1998(vs), 1943(s), 1882(m) cm^{-1}; (νC=O) 1668(m) cm^{-1}; ^{1}H NMR δ 4.53 (s, 4H, 2CH$_2$), 5.52 (s, 10H, 2C$_5$H$_5$). Anal. Calcd for $C_{32}H_{14}Co_4O_{20}W_2$: C, 29.05; H, 1.06. Found: C, 28.91; H, 1.06. $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2W(CO)_8(C_5H_4COCH_3)$ (**3e**): a dark brown solid (88 mg, 24.4%, based on **1**); IR (νCO) 2112(m), 2094(vs, sh), 2030(vs), 1941(s), 1888(s) cm^{-1}; (νC=O) 1684(br m) cm^{-1}; ^{1}H NMR δ 2.34 (s, 3H, CH$_3$), 4.57−4.59 (m, 4H, 2CH$_2$), 5.63 (t, 2H, H(3) and H(4), $J = 2.2$ Hz), 5.98 (t, 2H, H(2) and H(5), $J = 2.2$ Hz). Anal. Calcd for $C_{30}H_{11}Co_5O_{22}W$: C, 29.95; H, 0.92. Found: C, 30.01; H, 1.04. $[(CO)_8(C_5H_4COCH_3)Co_2W(\mu_3\text{-}C)COOCH_2]_2$ (**4e**): a dark brown solid (76 mg, 36.2%, based on **1**); IR (νCO) 2091(s), 2027(vs), 1986(s), 1936(m), 1893(m) cm^{-1}; (νC=O) 1689(m), 1669(m) cm^{-1}; ^{1}H NMR δ 2.35 (s, 6H, 2CH$_3$), 4.56 (s, 4H, 2CH$_2$), 5.64 (t, 4H, 2H(3) and 2H(4), $J = 2.3$ Hz), 5.98 (t, 4H, 2H(2) and 2H(5), $J = 2.3$ Hz). Anal. Calcd for $C_{36}H_{18}Co_4O_{22}W_2$: C, 30.73; H, 1.28. Found: C, 30.94; H, 1.33. $(CO)_9Co_3(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)Co_2W(CO)_8(C_5H_4COOC_2H_5)$ (**3f**): a dark brown solid (110 mg, 29.8%, based on **1**); IR (νCO) 2112(m), 2094(m), 2063(s), 2035(s), 2002(s), 1981(m), 1967(m), 1943(m), 1890(w) cm^{-1}; (νC=O) 1722(m), 1669(m) cm^{-1}; ^{1}H NMR δ 1.30 (t, 3H, CH$_3$, $J = 7.3$ Hz), 4.28 (q, 2H, C*H*$_2$CH$_3$, $J = 7.3$ Hz), 4.57−4.59 (m, 4H, 2CH$_2$), 5.60 (t, 2H, H(3) and H(4), $J = 2.5$ Hz), 5.97 (t, 2H, H(2) and H(5), $J = 2.5$ Hz). Anal. Calcd for $C_{31}H_{13}Co_5O_{23}W$: C, 30.19; H, 1.06. Found: C, 30.43; H, 1.17. $[(CO)_8(C_5H_4COOC_2H_5)Co_2W(\mu_3\text{-}C)COOCH_2]_2$ (**4f**): a dark brown solid (51 mg, 23.1%, based on **1**); IR (νCO) 2091(s), 2059(s), 2030(s), 1999(s), 1979(m), 1964(m), 1938(m), 1886(m) cm^{-1}; (νC=O) 1720(m), 1661(m) cm^{-1}; ^{1}H NMR δ 1.31 (t, 6H, 2CH$_3$, $J = 7.1$ Hz), 4.27 (q, 4H, 2C*H*$_2$CH$_3$, $J = 7.1$ Hz), 4.55 (s, 4H, 2CH$_2$), 5.58 (t, 4H, 2H(3) and 2H(4), $J = 2.1$ Hz), 5.95 (t, 4H, 2H(2) and 2H(5), $J = 2.1$ Hz). Anal. Calcd for $C_{38}H_{22}Co_4O_{24}W_2$: C, 31.11; H, 1.50. Found: C, 31.23; H, 1.47.

Preparation of 6 and 7. $NaMo(CO)_3(C_5H_5)$ (80 mg, 0.3 mmol) and **3e** (180 mg, 0.15 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2/ether (25:1) produced a dark green solid, $(CO)_8(C_5H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2CH_2OCO(\mu_3\text{-}C)CoMoW(CO)_7(C_5H_5)(C_5H_4COCH_3)$ (**6**) (91 mg, 44.9%, based on **3e**): IR (νCO) 2093(m), 2079(m), 2011(vs), 1919(m), 1847(m) cm^{-1}; (νC=O) 1667(br m) cm^{-1}; ^{1}H NMR δ 2.31 (s, 3H, CH$_3$), 4.49−4.55 (m, 4H, 2CH$_2$), 5.31 (s, 5H, C$_5$H$_5$), 5.45 (s, 5H, C$_5$H$_5$), 5.54−5.99 (m, 4H, C$_5$H$_4$). Anal. Calcd for $C_{38}H_{21}Co_3Mo_2O_{20}W$: C, 33.78; H, 1.56. Found: C, 33.91; H, 1.87.

$NaMo(CO)_3(C_5H_5)$ (40 mg, 0.15 mmol) and **4e** (105 mg, 0.075 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2/ether (10:1) produced a yellow green solid, $[(CO)_7(C_5H_5)(C_5H_4COCH_3)CoMoW(\mu_3\text{-}C)COOCH_2]_2$ (**7**) (32 mg, 27.5%, based on **4e**): IR (νCO) 2090(m), 2086(m), 2050(s), 2013(vs), 1988(vs), 1921(s), 1849(m) cm^{-1}; (νC=O) 1684(m), 1667(m) cm^{-1}; ^{1}H NMR δ 2.31 (s, 6H, 2CH$_3$), 4.54 (s, 4H, 2CH$_2$), 5.30 (s, 10H, 2C$_5$H$_5$), 5.41−5.98 (m, 8H, 2C$_5$H$_4$). Anal. Calcd for $C_{44}H_{28}Co_2Mo_2O_{20}W_2$: C, 33.98; H, 1.80. Found: C, 34.11; H, 2.01.

Preparation of 5a,b. $Na_2[p\text{-}\{Mo(CO)_3C_5H_4CO\}_2C_6H_4]$ (133 mg, 0.2 mmol) and **1** (200 mg, 0.2 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2/ether (25:1) produced a brown solid, $CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8C_5H_4COC_6H_4COC_5H_4(CO)_8MoCo_2(\mu_3\text{-}C)COOCH_2$ (**5a**) (97 mg, 38.0%, based on **1**): IR (νCO) 2094(s), 2055(s), 2034(s), 1942(m), 1897(m) cm^{-1}; (νC=O) 1671(m), 1652(m) cm^{-1}; ^{1}H NMR δ 3.76 (s, 4H, 2CH$_2$), 5.75 (t, 4H, 2H(3) and 2H(4), $J = 2.2$ Hz), 6.03 (t, 4H, 2H(2) and 2H(5), $J = 2.2$ Hz), 7.91 (s, 4H, C$_6$H$_4$); ^{13}C NMR δ 243.1 (Co$_2$MoC); 200.5 (br terminal CO); 188.1, 180.1 (C=O); 140.9, 129.3 (C$_6$H$_4$); 103.8, 97.7, 95.7, 94.2 (C$_5$H$_4$); 61.4 (CH$_2$). Anal. Calcd for $C_{40}H_{16}Co_4Mo_2O_{22}$: C, 37.62; H, 1.25. Found: C, 37.79; H, 1.28.

Similarly, $CH_2OCO(\mu_3\text{-}C)Co_2W(CO)_8C_5H_4COC_6H_4COC_5H_4(CO)_8WCo_2(\mu_3\text{-}C)COOCH_2$ (**5b**) (89 mg, 30.8%, based on **1**) was obtained: IR (νCO) 2092(s), 2052(s), 2032(s), 1936(m), 1889(m) cm^{-1}; (νC=O) 1666(br m) cm^{-1}; ^{1}H NMR δ 3.83 (s, 4H, 2CH$_2$), 5.85 (t, 4H, 2H(3) and 2H(4), $J = 2.3$ Hz), 6.04 (t, 4H, 2H(2) and 2H(5), $J = 2.3$ Hz), 7.93 (s, 4H, C$_6$H$_4$); ^{13}C NMR δ 235.8 (Co$_2$WC); 198.2 (br terminal CO); 187.3, 182.9 (C=O); 140.7, 129.2 (C$_6$H$_4$); 101.5, 94.7 (C$_5$H$_4$); 61.6 (CH$_2$). Anal. Calcd for $C_{40}H_{16}Co_4O_{22}W_2$: C, 33.06; H, 1.10. Found: C, 33.17; H, 1.19. FAB MS: 1452 (M$^+$), 1284 (M$^+$ − 6CO), 1256 (M$^+$ − 7CO), 1228 (M$^+$ − 8CO), 1200 (M$^+$ − 9CO), 1172 (M$^+$ − 10CO), 1144 (M$^+$ − 11CO), 1116 (M$^+$ − 12CO), 1088 (M$^+$ − 13CO), 1060 (M$^+$ − 14CO), 1032 (M$^+$ − 15CO), 1004 (M$^+$ − 16CO).

Preparation of 8a−c and 9a−c. $NaMo(CO)_3(C_5H_5)$ (59 mg, 0.22 mmol) and **2** (178 mg, 0.22 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2/petroleum ether (5:2) produced a brown solid, $(CO)_8(C_5H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**8a**) (81 mg, 41.6%, based on **2**): IR (νCO) 2100(m), 2081(m), 2057(s), 2029(s), 2019(s), 1993(s), 1968(m), 1957(m) cm^{-1}; (νC=O) 1666(m) cm^{-1}; ^{1}H NMR δ 5.45 (s, 5H,

C_5H_5), 5.50 (s, 2H, CH_2), 6.10 (s, 1H, CH). Anal. Calcd for $C_{24}H_8Co_4MoO_{16}$: C, 32.58; H, 0.90. Found: C, 32.44; H, 0.91.

$NaMo(CO)_3(C_5H_5)$ (108 mg, 0.44 mmol) and **2** (178 mg, 0.22 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2 produced a brown solid, $(CO)_7(C_5H_5)_2CoMo_2(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**9a**) (36 mg, 17.1%, based on **2**); IR (νCO) 2099(s), 2087(vs), 2043(vs), 2009(s), 1993(s), 1940(s), 1863(s) cm^{-1}; (νC═O) 1665(m) cm^{-1}; ^{1}H NMR δ 5.40 (s, 10H, $2C_5H_5$), 5.51 (s, 2H, CH_2), 6.11 (s, 1H, CH). Anal. Calcd for $C_{28}H_{13}Co_3Mo_2O_{15}$: C, 35.07; H, 1.36. Found: C, 35.19; H, 1.41.

The following compounds were similarly prepared. $(CO)_8(C_5H_4COCH_3)Co_2Mo(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**8b**): a brown solid (77 mg, 37.8%, based on **2**); IR (νCO) 2100(m), 2089(s), 2068(s), 2029(vs), 1996(s), 1964(m), 1938(m) cm^{-1}; (νC═O) 1698(m), 1658(m) cm^{-1}; ^{1}H NMR δ 2.35 (s, 3H, CH_3), 5.53 (s, 2H, CH_2), 5.67 (t, 2H, H(3) and H(4), $J = 2.5$ Hz), 5.96 (t, 2H, H(2) and H(5), $J = 2.5$ Hz), 6.11 (s, 1H, CH). Anal. Calcd for $C_{26}H_{10}Co_4MoO_{17}$: C, 33.69; H, 1.08. Found: C, 33.53; H, 0.93. $(CO)_7(C_5H_4COCH_3)_2CoMo_2(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**9b**): a brown solid (62 mg, 27.0%, based on **2**); IR (νCO) 2097(s), 2071(vs), 2033(vs), 1961(s), 1953(m), 1933(m), 1857(m) cm^{-1}; (νC═O) 1680(br m) cm^{-1}; ^{1}H NMR δ 2.34 (s, 6H, $2CH_3$), 5.53 (s, 2H, CH_2), 5.68 (t, 4H, 2H(3) and 2H(4), $J = 2.4$ Hz), 5.99 (t, 4H, 2H(2) and 2H(5), $J = 2.4$ Hz), 6.11 (s, 1H, CH). Anal. Calcd for $C_{32}H_{17}Co_3Mo_2O_{17}$: C, 36.85; H, 1.63. Found: C, 37.00; H, 1.69. $(CO)_8(C_5H_4COOC_2H_5)Co_2Mo(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**8c**): a brown solid (37 mg, 17.6%, based on **2**); IR (νCO) 2097(s), 2083(s), 2057(vs), 2030(vs), 1946(m), 1899(m) cm^{-1}; (νC═O) 1726(m), 1674(m) cm^{-1}; ^{1}H NMR δ 1.33 (t, 3H, CH_3, $J = 7.3$ Hz), 4.27 (q, 2H, CH_2CH_3, $J = 7.3$ Hz), 5.52 (s, 2H, CH_2), 5.62 (t, 2H, H(3) and H(4), $J = 2.3$ Hz), 5.96 (t, 2H, H(2) and H(5), $J = 2.3$ Hz), 6.11 (s, 1H, CH). Anal. Calcd for $C_{27}H_{12}Co_4MoO_{18}$: C, 33.89; H, 1.26. Found: C, 33.97; H, 1.31. $(CO)_7(C_5H_4COOC_2H_5)_2CoMo_2(\mu_3\text{-}C)COOCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (**9c**): a brown solid (35 mg, 14.4%, based on **2**); IR (νCO) 2099(s), 2079(vs), 2064(vs), 2037(s), 1940(m), 1891(m) cm^{-1}; (νC═O) 1724(m), 1682(m) cm^{-1}; ^{1}H NMR δ 1.33 (t, 6H, $2CH_3$, $J = 7.5$ Hz), 4.28 (q, 4H, $2CH_2CH_3$, $J = 7.5$ Hz), 5.53 (s, 2H, CH_2), 5.64 (t, 4H, 2H(3) and 2H(4), $J = 2.3$ Hz), 5.99 (t, 4H, 2H(2) and 2H(5), $J = 2.3$ Hz), 6.11 (s, 1H, CH). Anal. Calcd for $C_{34}H_{21}Co_3Mo_2O_{19}$: C, 37.02; H, 1.91. Found: C, 37.09; H, 1.98.

Preparation of 10. $Na_2[p\text{-}\{Mo(CO)_3C_5H_4CO\}_2C_6H_4]$ (113 mg, 0.17 mmol) and **2** (265 mg, 0.33 mmol) were dissolved in THF (30 cm^3). The rest of the manipulation was similar to that described above. Elution with CH_2Cl_2 produced a brown solid, $p\text{-}[(CO)_6Co_2(\mu\text{-}CHC)CH_2OCO(\mu_3\text{-}C)Co_2Mo(CO)_8C_5H_4CO]_2C_6H_4$ (**10**) (79 mg, 25.4%, based on **2**): IR (νCO) 2098(s), 2083(s), 2058(vs), 2027(vs), 1944(m), 1895(m) cm^{-1}; (νC═O) 1661(br m) cm^{-1}; ^{1}H NMR δ 5.48 (s, 4H, $2CH_2$), 5.64 (t, 4H, 2H(3) and 2H(4), $J = 2.5$ Hz), 6.04 (t, 4H, 2H(2) and 2H(5), $J = 2.5$ Hz), 6.09 (s, 2H, 2CH), 7.87 (s, 4H, C_6H_4); ^{13}C NMR δ 244.3 (Co_2MoC); 207.0, 206.6, 206.0, 205.5, 203.3, 199.0 (terminal CO); 188.7, 179.4 (C═O); 140.7, 128.4 (C_6H_4); 99.2, 98.0, 93.5 (C_5H_4); 87.7, 73.4 (Co_2C_2); 67.0 (CH_2). Anal. Calcd for $C_{56}H_{18}Co_8Mo_2O_{34}$: C, 35.41; H, 0.95. Found: C, 35.66; H, 0.95.

X-ray Structure Determination of 3a and 8a. X-ray quality crystals were grown for **3a** and **8a** from a hexane/CH_2Cl_2 (1:1) solution at −20 °C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71069$ Å) on a Rigaku AFC7R (for **3a**) or an Enraf-Nonius CAD4 (for **8a**) diffractometer equipped with a graphite monochromator. The structure of **3a** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure of **8a** was solved by Patterson methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were also included but not refined. All calculations were performed using the TEXSAN program system.

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Supporting Information Available: Full lists of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, least-squares planes and atomic deviations therefrom, and unit cell and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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