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Reactions of 1,8-Nonadiyne with $Co_2(CO)_8$ and $Mo_2(C_5H_4R)_2(CO)_4$ and Crystal Structures of $[M_2L_2(CO)_4][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (M = Co, L = CO; M = Mo, L = C_5H_4R, R = H, $COCH_3$, $COOC_2H_5$)

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The treatment of 1,8-nonadiyne with $Co_2(CO)_8$ in hexane at room temperature gives a new complex $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Co_2(CO)_6]$ (**1**) followed by regioselective exchange reactions with $Na[Mo(C_5H_4R)(CO)_3]$ (R = H, $COCH_3$, $COOC_2H_5$) to afford the hetero-tetranuclear clusters $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_4R)(CO)_5]$ (**2a**, R = H; **2b**, R = $COCH_3$; **2c**, R = $COOC_2H_5$) and $[CoMo(C_5H_4R)(CO)_5][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_4R)(CO)_5]$ (**3a**, R = H; **3b**, R = $COCH_3$; **3c**, R = $COOC_2H_5$), respectively. The reaction of $Mo_2(C_5H_4R)_2(CO)_4$ with 1,8-nonadiyne produces the homo-dinuclear clusters $[HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (**4a**, R = H; **4b**, R = $COCH_3$; **4c**, R = $COOC_2H_5$) and homo-tetranuclear clusters $[Mo_2(C_5H_4R)_2(CO)_4][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (**5a**, R = H; **5b**, R = $COCH_3$; **5c**, R = $COOC_2H_5$), respectively. The clusters **4a, 4b,** and **4c** reacted with $Co_2(CO)_8$ to form the novel tetranuclear clusters $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4R)_2(CO)_4]$ (**6a**, R = H; **6b**, R = $COCH_3$; **6c**, R = $COOC_2H_5$). The structures of **5a**, **5b,** and **6a** have been determined by single-crystal X-ray diffraction, and the regioselective exchange reactions have been briefly discussed.

Introduction

The hetero-metal clusters can be formed directly in one-step[1] or in multistep addition and substitution reactions by systematic addition and incorporation of organometallic units[2,3] or by a metal exchange reaction using $Me_2AsMCp(CO)_3$, $M_2Cp_2(CO)_6$, $HMCp(CO)_3$, $ClMCp(CO)_3$, and $NaMCp(CO)_3$ as metal exchange reagents.[4,5] In these synthetic methods, the metal exchange reaction is the most simple and direct method because it exhibits advantages in both the yield and preparative process. Metal exchange in clusters was first observed in 1971 and 1972[6,7] without being explicitly recognized. However, only recently[8] did systematic studies begin to elucidate the scope and variability of this reaction. Some μ_3-XCo_2M (X = C, S, Se, Te; M = Cr, Mo, W, Fe, Ni, Ru) and C_2CoM (M = Mo, W) tetrahedral clusters were synthesized through metal exchange reaction.[4,8−10] On the other hand, the linked clusters have been receiving considerable attention in recent years because of their potential application as polymeric materials and their unusual structures and reactions.[11−13] A dimer containing two linked $Co_2(CO)_6C_2$ units has been reported previously.[14−16] Seyferth and Rubin also synthesized similar polymers containing the $Co_2(CO)_6C_2$ units.[17,18] However, no metal

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[†] State Key Laboratory for Oxo Synthesis and Selective Oxidation.

[‡] State Key Laboratory of Structure Chemistry.

(1) Khatlab, S. A.; Mark, L.; Bor, G.; Marko, B. *J. Organomet. Chem.* **1964**, *1*, 373.

(2) Steinhardt, P. C.; Gladfelter, W. L.; Harley, D.; Fox, J. R.; Geoffroy, L. *Inorg. Chem.* **1980**, *19*, 332.

(3) Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 863.

(4) Blumhofer, R.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 194. (b) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409. (c) Schach, H. T.; Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *381*, 261.

(5) Jensen, S.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1081.

(6) Hsieh, A. T.; Mays, M. J. *J. Organomet. Chem.* **1971**, *26*, 125.

(7) Knight, J.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1022.

(8) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

(9) Beurich, H.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2385.

(10) Ding, E.-R.; Yin, Y.-Q.; Sun, J. *Polyhedron* **1997**, *17*, 3067. (b) Ding, E.-R.; Liu, S.-M.; Yin, Y.-Q.; Sun, J. *Polyhedron* **1997**, *16*, 3273. (c) Ding, E.-R.; Liu, S.-M.; Zhao, Z.-Y.; Yin, Y.-Q.; Sun, J. *Polyhedron* **1997**, *14*, 2387.

(11) Karpov, M. G.; Tunik, S. P.; Denisov, V. R.; Starova, G. L.; Nikolskii, A. B.; Dolgnskin, F. M.; Yanovsky, A. I.; Sryuchkov, Yu. T. *J. Organomet. Chem.* **1995**, *485*, 219.

(12) Aime, S.; Tiripicchio, A.; Tiripicchio-Camellini, M.; Deeming, A. J. *Inorg. Chem.* **1981**, *20*, 2027. (b) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1807.

(13) Berre-Cosquer, N. L.; Kergoat, R. *J. Organomet. Chem.* **1992**, *427*, 325.

(14) Housecroft, C. E.; Johson, B. F. G.; Khan, M. S.; Lewis, J.; Raithby, P. R.; Robson, M. E.; Wilkinson, D. A.; *J. Chem. Soc., Dalton Trans.* **1992**, 3171.

(15) Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640.

(16) Onitsuku, K.; Tao, X.-Q.; Wang, W.-Q.; Otsuka, Y.; Sonogashira, K.; Adachi, T.; Yoskida, T.; *J. Organomet. Chem.* **1994**, *473*, 195.

(17) Seyferth, D.; Withers, H. P. *Inorg. Chem.* **1983**, *22*, 2931.

(18) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 4966.

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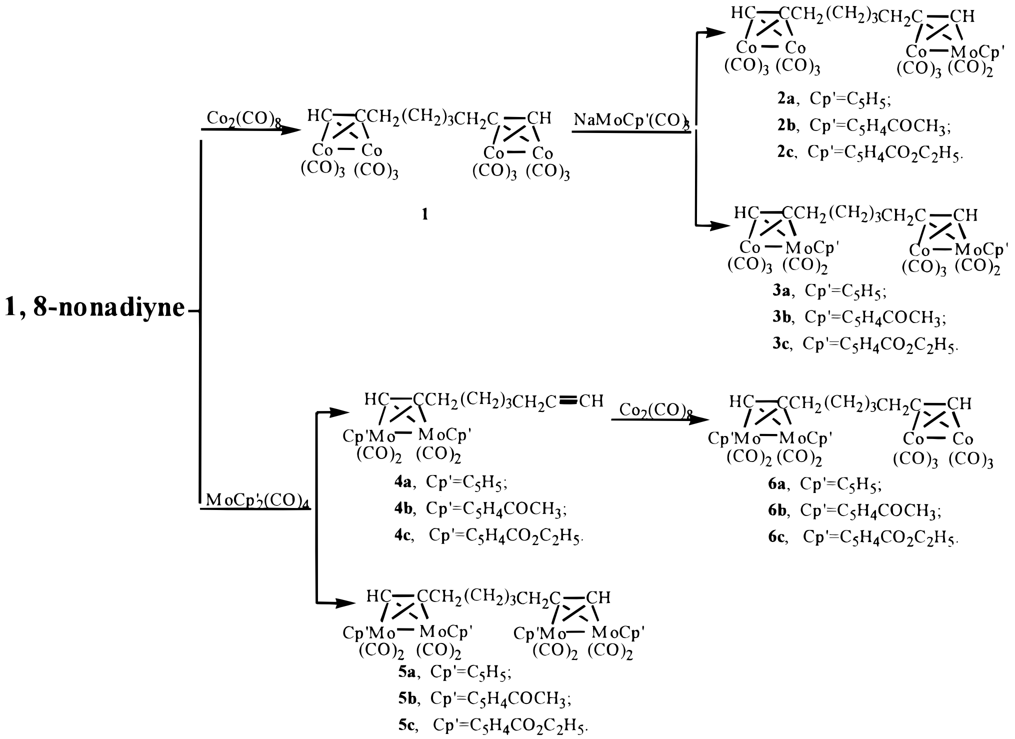
Scheme 1. Summary of the Reactions



exchange reaction of linked clusters has been reported up to now. To investigate the metal exchange reaction of linked clusters, we initiated a study of reactions of 1,8-nonadiyne with dinuclear species and the metal exchange reactions of the linked clusters by using the metal exchange reagents $Na[Mo(C_5H_4R)(CO)_3]$ (R = H, $COCH_3$, $COOC_2H_5$). Sixteen novel clusters were prepared, and the crystal structures of **5a**, **5b,** and **6a** were determined. Particularly, it is surprising that the metal exchange reaction in linked clusters appears to be regioselective, leading to a Co–Mo system coordinated to the alkyne unit.

Results and Discussion

The reactions described in this work are summarized in Scheme 1. Treatment of $Co_2(CO)_8$ in hexane with 1,8-nonadiyne in 1:2 molar ratio at room temperature affords the complex **1**. Subsequently, the exchange reagent $Na[Mo(C_5H_4R)(CO)_3]$, prepared by refluxing a THF solution of $Na(C_5H_4R)$ and $Mo(CO)_6$,[19] is reacted in situ with **1** at room temperature for 60 h to give two types of hetero-tetranuclear clusters, **2a**–**2c** and **3a**–**3c**, respectively. It is surprising that the second exchange reaction appears to be regioselective, so the complexes **3a**–**3c** contain two C_2CoMo cores without one C_2Co_2 core and one C_2Mo_2 core in contrast to complexes **6a**–**6c**. To prepare the other isomers **6a**–**6c** and further confirm the regioselectivity of the metal exchange reaction in linked clusters, through in situ reaction of the 1,8-nonadiyne with the triply bonded complex $[Mo_2(C_5H_4R)_2(CO)_4]$ (R = H, $COCH_3$, $COOC_2H_5$), prepared by refluxing a toluene solution of metal–metal single-bonded dimer $[Mo_2(C_5H_4R)_2(CO)_6]$ (R = H, $COCH_3$, $COOC_2H_5$),[20] the homo-dinuclear clusters **4a**–**4c** and homo-tetranuclear clusters **5a**–**5c** are obtained. Further reactions of **4a**–**4c** with $Co_2(CO)_8$ in THF at room temperature produce the novel tetranuclear clusters **6a**–**6c**, which are isomers of **3a**–**3c**. High yields are obtained in capping reactions, and low yields in exchange reactions. All exchange reactions require a long time at room temperature, but at high temperature (refluxing THF) the reactant decomposes and the expected products are not obtained. This case contrasts with the exchange reactions of the $RCCo_3(CO)_9$ clusters, which are accelerated by heating.[21,22]

All complexes show a large number of strong terminal carbonyl absorption bands located at 2093–1878 cm^{-1} in the IR spectra, whereas in the IR spectra of **4**–**6**, besides the terminal carbonyl absorption bands, there are absorption bands in the region 1821–1849 cm^{-1} characteristic of semibridging carbonyls. The absorption of carbonyl ligands coordinated to Co atoms occurs at higher wavenumbers than those coordinated to Mo atoms.[23,24] The ^1H NMR spectra of all clusters show the presence of hydrogen atoms in their corresponding organic groups. For the substituted cyclopentadienyl rings, the ^1H NMR spectra of **b** and **c** exhibit four asymmetric singlets in the range δ 5.99–5.28 instead of two groups of triplets (A_2B_2 type), comprising two upfield singlets assignable to the two protons at the 3,4-positions of the substituted cyclopentadienyl rings and

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[19] Macomber, D. M.; Rauck, M. D. *J. Organomet. Chem.* **1983**, *258*, 331.

[20] Adams, H.; Gill, L. J.; Morris, M. J. *Organometallics* **1996**, *15*, 4182.

[21] Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 98. (b) Blumhofer, R.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 194.

[22] Wu, H.-P.; Yin, Y.-Q.; Huang, X.-Y.; Yu, K.-B. *J. Organomet. Chem.* **1995**, *498*, 119. (b) Wu, H.-P.; Yin, Y.-Q.; Huang, X.-Y. *Polyhedron* **1995**, *14*, 2993.

[23] Wu, H.-P.; Zhao, Z.-Y.; Liu, S.-M.; Ding, E.-R.; Yin, Y.-Q. *Polyhedron* **1996**, *15*, 4117.

[24] Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1690.

Table 1. Summary of the Crystallographic Data for Compounds 5a, 5b, and 6a

	5a·CH_2Cl_2	**5b**·$2H_2O$	**6a**
formula	$C_{38}H_{34}O_8Cl_2Mo_4$	$C_{45}H_{44}O_{14}Mo_4$	$C_{29}H_{22}O_{10}Co_2Mo_2$
fw	1073.55	1192.59	840.23
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2/*c* (No. 13)	*P*2/*n* (No. 13)	*C*2/*c* (No. 5)
a, Å	16.576(4)	17.876(6)	31.103(6)
b, Å	7.602(2)	7.533(1)	7.981(1)
c, Å	17.238(3)	18.646(6)	26.945(7)
β, deg	118.63(2)	112.75(2)	107.38(2)
V, $Å^3$	1906(1)	2315(2)	6383(2)
Z	2	2	8
D_c, g cm^{-3}	1.870	1.710	1.748
radiation	Mo Kα	Mo Kα	Mo Kα
temp, K	296	296	296
F(000)	1056	1188	3312
μ, cm^{-1}	14.47	10.96	18.21
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{max}$, deg	51.9	52.0	52.0
no. of observns	3043 ($I > 2.00\sigma(I)$)	2836 ($I > 2.00\sigma(I)$)	3633 ($I > 2.00\sigma(I)$)
no. of variables	236	282	388
R	0.049	0.074	0.061
R_w	0.059	0.078	0.064
goodness of fit indicator	1.53	1.40	1.22
max shift in final cycle	0.006	0.004	0.009
lagest peak in final diff map, e $Å^{-3}$	0.91	1.47	0.63

two downfield singlets assignable to the 2,5-protons, resulting from the different deshielding effects of electron-withdrawing groups $COCH_3$ and $COOC_2H_5$ on these nuclei.[21,25] However, the protons of unsubstituted cyclopentadienyl appear as a singlet in the range δ 5.39–5.27.

From IR and ^1H NMR spectra, configurations of isomers **3a** and **6a** could be distinguished. The absorption band of semibridging carbonyl is not observed in the IR spectrum of **3a,** but it appears at 1835 cm^{-1} in the IR spectrum of **6a**. Because the semibridging carbonyl appears in the $C_2Mo_2(C_5H_5)_2(CO)_4$, $C_2W_2(C_5H_5)_2(CO)_4$, and $C_2MoW(C_5H_5)_2(CO)_4$ cores and does not appear in the $C_2CoMo(C_5H_5)(CO)_5$ core,[26-29] it could be considered that **3a** possesses two C_2CoMo cores and **6a** possesses one C_2Co_2 core and one C_2Mo_2 core, which is confirmed by single-crystal X-ray diffraction. In ^1H NMR spectrum, the two protons of the two C_2H groups of **3a** have the same chemical shift at δ 5.77. This indicates that the two protons occur in the same chemical environment. However, the two protons of the two C_2H groups of **6a** appear as two singlets at δ 6.02 and 5.96, respectively. Compared with the ^1H NMR spectra of **1**, **4a,** and **5a**, the singlet at δ 6.02 is assignable to the proton of the C_2H group coordinated to Co–Co and at δ 5.96 to the proton of the C_2H group coordinated to Mo–Mo. Similarly, four protons of the two CH_2 groups also appear as a broad singlet at δ 2.81 in **3a** and two triplets at δ 2.84 and 2.58 in **6a**. All this is consistent with the configurations of isomers **3a** and **6a**. Thus, it is confirmed that the metal exchange reaction in linked clusters appears to be regioselective.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cluster 5a

Mo(1)–Mo(2)	2.974(1)	Mo(1)–C(5)	2.112(6)
Mo(1)–C(6)	2.215(5)	Mo(2)–C(5)	2.199(5)
Mo(2)–C(6)	2.183(5)	Mo(1)–C(1)	1.944(7)
Mo(2)–C(1)	2.890(7)	C(5)–C(6)	1.353(7)
C(6)–C(7)	1.485(7)	C(7)–C(8)	1.512(8)
Mo(1)–C(av, Cp)	2.347	Mo(2)–C(av, Cp)	2.320
C(5)–Mo(1)–C(6)	36.3(2)	C(5)–Mo(1)–Mo(2)	47.6(1)
C(6)–Mo(1)–Mo(2)	47.0(1)	C(5)–Mo(2)–C(6)	36.0(2)
C(5)–Mo(2)–Mo(1)	45.2(2)	C(6)–Mo(2)–Mo(1)	47.9(1)
Mo(1)–C(5)–C(6)	76.0(3)	Mo(1)–C(5)–Mo(2)	87.2(2)
C(6)–C(5)–Mo(2)	71.4(3)	Mo(1)–C(6)–C(5)	67.7(3)
Mo(1)–C(6)–Mo(2)	85.1(2)	C(5)–C(6)–Mo(2)	72.7(3)
C(5)–C(6)–C(7)	134.9(5)	C(6)–C(7)–C(8)	113.4(5)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cluster 5b

Mo(1)–Mo(2)	2.976(2)	Mo(1)–C(5)	2.19(1)
Mo(1)–C(6)	2.15(1)	Mo(2)–C(5)	2.10(1)
Mo(2)–C(6)	2.23(1)	Mo(1)–C(3)	2.92(1)
Mo(2)–C(3)	1.92(1)	C(5)–C(6)	1.36(1)
C(6)–C(7)	1.50(2)	C(7)–C(8)	1.53(2)
C(10)–C(15)	1.48(2)	C(15)–C(16)	1.51(2)
C(17)–C(22A)	1.47(3)	C(22A)-C(23A)	1.53(4)
Mo(1)–C(av, Cp)	2.31	Mo(2)–C(av, Cp)	2.33
C(5)–Mo(1)–C(6)	36.(4)	C(5)–Mo(1)–Mo(2)	44.9(3)
C(6)–Mo(1)–Mo(2)	48.3(3)	C(5)–Mo(2)–C(6)	36.4(4)
C(5)–Mo(2)–Mo(1)	47.3(3)	C(6)–Mo(2)–Mo(1)	46.9(3)
Mo(1)–C(5)–C(6)	70.3(6)	Mo(1)–C(5)–Mo(2)	87.8(4)
C(6)–C(5)–Mo(2)	76,8(7)	Mo(1)–C(6)–C(5)	73.3(7)
Mo(1)–C(6)–Mo(2)	85.7(4)	C(5)–C(6)–Mo(2)	66.8(6)
C(5)–C(6)–C(7)	137(1)	C(6)–C(7)–C(8)	113(1)

Although the crystal structure of **6a** was determined, crystals of **3a** were not obtained. This hinders further confirmation by using crystal structure, but a similar conclusion is obtained by comparing the IR and ^1H NMR spectra of **3b**, **3c** with **6b**, **6c**.

The crystal structures of **5a**, **5b,** and **6a** were determined by X-ray structural analyses. Crystallographic data are collected in Table 1 and selected bond distances and angles are listed in Tables 2, 3, and 4. Figures 1, 2, and 3 show the molecular structure of **5a**, **5b,** and **6a**, respectively.

As can be seen from Figures 1 and 2, the molecules

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(25) Wu, H.-P.; Yin, Y.-Q.; Yang, Q.-C. *Inorg. Chim. Acta* **1996**, *245*, 143.

(26) Bailey, R. J.; Chisholm, M. H.; Cotton, F. A.; Raukel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

(27) Klinger, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034. (b) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

(28) Song, L.-C.; Shen, J.-Y.; Hu, Q.-M.; Han, B.-S.; Wang, R.-J.; Wang, H.-G. *Inorg. Chim. Acta* **1994**, *219*, 93.

(29) Wu, S,-L.; Ding, E.-R.; Yin, Y.-Q.; Sun, J. *J. Organomet. Chem.* **1998**, *570*, 71.

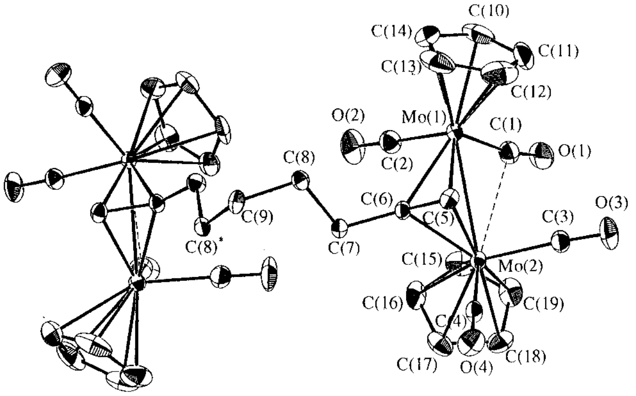

Figure 1. Molecular structure of compound **5a**.

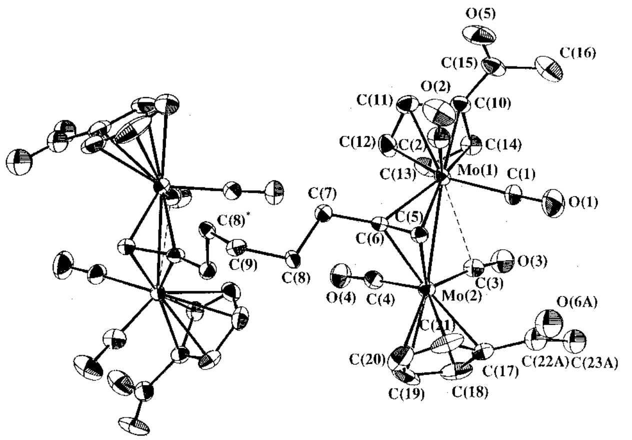

Figure 2. Molecular structure of compound **5b**.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Cluster 6a

Mo(1)−Mo(2)	2.958(1)	Co(1)−Co(2)	2.460(2)
C(11)−C(12)	1.33(1)	C(18)−C(19)	1.29(1)
Mo(1)−C(11)	2.10(1)	Co(1)−C(19)	1.93(1)
Mo(2)−C(11)	2.18(1)	Co(2)−C(19)	1.91(1)
Mo(1)−C(12)	2.20(1)	Co(1)−C(18)	1.94(1)
Mo(2)−C(12)	2.14(1)	Co(2)−C(18)	1.95(1)
Mo(1)−C(2)	1.92(1)	Mo(2)−C(2)	2.86(1)
Mo(1)−C(av, Cpring)	2.31	Mo(2)−C(av, Cpring)	2.32
C−O(av, Mo)	1.15	C−O(av, Co)	1.14
C(11)−Mo(1)−C(12)	36.0(3)	C(19)−Co(1)−C(18)	39.0(4)
C(11)−Mo(1)−Mo(2)	47.5(3)	C(19)−Co(1)−Co(2)	49.8(4)
Mo(2)−Mo(1)−C(12)	46.3(2)	C(18)−Co(1)−Co(2)	51.1(3)
C(11)−Mo(2)−C(12)	35.8(3)	C(19)−Co(2)−C(18)	39.0(4)
C(11)−Mo(2)−Mo(1)	45.2(3)	C(19)−Co(2)−Co(1)	50.4(3)
Mo(1)−Mo(2)−C(12)	47.8(2)	C(18)−Co(2)−Co(1)	50.4(3)
Mo(1)−C(11)−Mo(2)	87.3(4)	Co(1)−C(19)−Co(2)	79.8(4)
Mo(1)−C(11)−C(12)	75.9(6)	Co(1)−C(19)−C(18)	70.8(7)
Mo(2)−C(11)−C(12)	70.5(6)	Co(2)−C(19)−C(18)	72.4(7)
Mo(1)−C(12)−Mo(2)	85.9(3)	Co(1)−C(18)−Co(2)	78.5(4)
Mo(1)−C(12)−C(11)	68.1(6)	Co(1)−C(18)−C(19)	70.2(7)
Mo(2)−C(12)−C(11)	73.7(6)	Co(2)−C(18)−C(19)	68.7(7)

inwhich the two $Mo_2(C_5H_4R)_2(CO)_4$(alkyne) units are linked by the $(CH_2)_5$ group lie on a crystallographic center of symmetry at the C(9) atom. The overall conformations of two $(CCH)Mo_2(C_5H_4R)_2(CO)_4$ moieties are quite similar to those previously described for $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu\text{-}C_2H_2)$.[26] The C_2Mo_2 core adopts a pseudo-tetrahedral geometry. All bond distances and bond angles are comparable to the corresponding values in $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu\text{-}C_2H_2)$.[26] The distances of Mo−C(Cp, ring) are not influenced by the substituted group $COCH_3$ replacing a proton in **5b**. All the C atoms in cyclopentadienyl together with C(15), C(16), and O(5) in the $COCH_3$ group and all the C atoms in other cyclopentadienyl groups together with C(22A), C(23A), and O(6A) in the other $COCH_3$ group are located in one plane. So the π-system of the substituted group $COCH_3$ is fully conjugated with the cyclopentadienyl π-system. This result is in contrast to that reported by Song et al.[30]

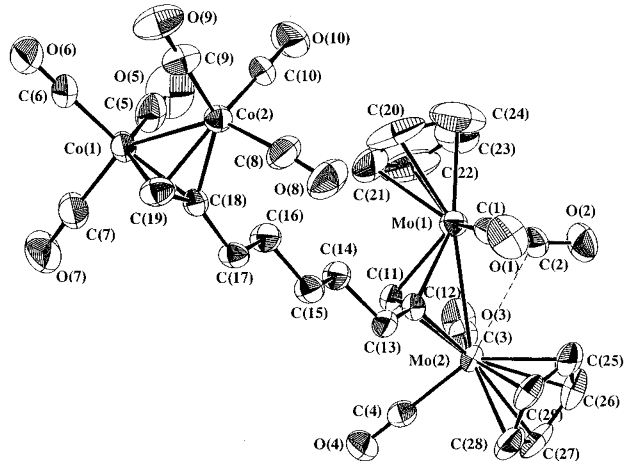

Figure 3. Molecular structure of compound **6a**.

In **6a**, a C_2Co_2 and a C_2Mo_2 core are linked by a $(CH_2)_5$ group, and all conformations of the C_2Co_2 and C_2Mo_2 core are quite similar to those previously described for compounds containing a C_2Co_2 or a C_2Mo_2 core.[14,26] The C_2Co_2 and C_2Mo_2 cores all adopt pseudo-tetrahedral conformations, and all bond distances and bond angles are in the normal range. Comparing the C_2Co_2 core with the C_2Mo_2 core, the bond distance of C(18)−C(19) is shorter than that of C(11)−C(12) and the bond distance of C−O in the C_2Co_2 core is slightly shorter than that of C−O in the C_2Mo_2 core, which is consistent with the IR spectra. It is indicated that the C_2Mo_2 core possesses a stronger ability to delocalize electron density.

Finally it is important to note that in the three molecular structures, besides the terminal carbonyls, there are semibridging carbonyls in the $C_2Mo_2(C_5H_4R)_2(CO)_4$ core.[26,27] The coexistence of both terminal and semibridging carbonyls is consistent with the IR spectra of **4**−**6** showing several strong absorption bands from 2092 to 1821 cm^{-1}.

Experimental Section

General Comments. All reactions were carried out under pure nitrogen using standard Schlenk techniques. Hexane, THF, and petroleum (60−90 °C) were dried by sodium, while CH_2Cl_2 was distilled from CaH_2. Chromatographic separations were performed on silica columns (160−200 mesh) of varying length. Thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.20 mm layer of silica.

Infrared spectra were recorded in NaCl cells on a Nicolet FT-IR 10 DX spectrometer. Spectra of compounds in the solid state were recorded as pressed KBr disks. Proton NMR spectra were recorded on a Bruker AM 300 (300 MHz) in $CDCl_3$ deuterated solvent. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). Elemental analyses were carried out on a Carlo Erba 1106 type analyzer.

1,8-Nonadiyne was purchased from Aldrich Chemical Co., and $Co_2(CO)_8$,[31] $Na(C_5H_4R)$ (R = H, $COCH_3$, $COOC_2H_5$),[32] and $Mo_2(C_5H_4R)_2(CO)_6$[33] were prepared according to the literature.

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(30) Song, L.-C.; Shen, J.-Y.; Hu, Q.-M. *Organometallics* **1993**, *12*, 408.

Preparation of $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Co_2(CO)_6]$ (1). $Co_2(CO)_8$ (684 mg, 2 mmol) and 1,8-nonadiyne (120 mg, 1 mmol) were dissolved in hexane (30 cm^3). The solution was stirred at room temperature for 3 h. A color change from brown to red was observed, and TLC monitoring showed the disappearance of the starting material, $Co_2(CO)_8$. After addition of a small amount of silica the solvent was removed and the residue chromatographed. Elution with benzene produced red bands, and the volume of the resulting solution was reduced to ca. 10 cm^3. Crystallization at −20 °C yielded a red oil (489 mg, 69.7%): IR (νCO) 2093(s), 2049(vs), 2017(vs), 1976(vs, sh), 1940(m), 1873(w) cm^{-1}; ^1H NMR δ 6.02 (s, 2H, 2CH), 2.89 (s, br, 4H, $2CH_2$), 1.68 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{21}H_{12}O_{12}Co_4$: C, 36.44; H, 1.75. Found: C, 36.39; H, 1.80.

Preparation of $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_5)(CO)_5]$ (2a) and $[CoMo(C_5H_5)(CO)_5][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_5)(CO)_5]$ (3a). $Mo(CO)_6$ (132 mg, 0.5 mmol) was added to a solution of 89 mg (0.5 mmol) of $NaC_5H_5{\cdot}DME$ in THF (30 cm^3). The mixture was heated under reflux 20 h and cooled to room temperature. Then cluster **1** (173 mg, 0.25 mmol) was added, and the mixture was stirred at room temperature for 60 h. The solvent was removed under vacuum, the residue was extracted by a minimum amount of CH_2Cl_2, and the products were chromatographed on a silica gel column using CH_2Cl_2/petroleum ether (2:3) as eluent to give two red fractions of clusters **2a** and **3a**. Cluster **2a** was recrystallized from hexane/CH_2Cl_2 at −20 °C to give a red oil (60 mg, 31.4%, based on **1**): IR (νCO) 2092(s), 2050(vs), 2035(vs), 1994(vs), 1981(vs), 1937(s), 1886(m) cm^{-1}; ^1H NMR δ 6.02 (s, 1H, C_2H), 5.76 (s, 1H, C_2H), 5.39 (s, 5H, C_5H_5), 2.86 (s, br, 4H, $2CH_2$), 1.64 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{25}H_{16}O_{11}Co_3Mo$: C, 39.24; H, 2.11. Found: C, 39.28; H, 2.01. Cluster **3a** was recrystallized from hexane/CH_2Cl_2 at −20 °C to give red crystals (80 mg, 38.1%, based on **1**): IR (νCO) 2046(vs), 1977(vs), 1929(s), 1885(m) cm^{-1}; ^1H NMR δ 5.77 (s, 2H, $2C_2H$), 5.39 (s, 10H, $2C_5H_5$), 2.81 (s, br, 4H, $2CH_2$), 1.49 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{29}H_{22}O_{10}Co_2Mo_2$: C, 41.45; H, 2.64. Found: C, 41.36; H, 2.72.

The following complexes were similarly prepared. $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_4COCH_3)(CO)_5]$ (**2b**): a red oil (80 mg, 39.6%, based on **1**); IR (νCO) 2092(s), 2051(vs), 2004(vs, br), 1944(s), 1891(s) cm^{-1}; ($\nu C{=}O$) 1683(s) cm^{-1}; ^1H NMR δ 6.02 (s, br, 2H, $2C_2H$), 5.96−5.46 (qs, 4H, C_5H_4), 2.80 (s, br, 2H, CH_2), 2.76 (s, br, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.41 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{27}H_{19}O_{12}Co_3Mo$: C, 40.12; H, 2.37. Found: C, 40.36; H, 2.26. $[CoMo(C_5H_4COCH_3)(CO)_5][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_4COCH_3)(CO)_5]$ (**3b**): red crystals (70 mg, 30.3%, based on **1**); IR (νCO) 2066(vs), 1995(vs, br), 1937(vs), 1878(s) cm^{-1}; ($\nu C{=}O$) 1676(s) cm^{-1}; ^1H NMR δ 6.01 (s, 2H, $2C_2H$), 5.99−5.49 (qs, 8H, $2C_5H_4$), 2.86 (s, br, 4H, $2CH_2$), 2.29 (s, 6H, $2CH_3$), 1.51 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{33}H_{26}O_{12}Co_2Mo_2$: C, 42.88; H, 2.84. Found: C, 42.76; H, 2.62. $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][CoMo(C_5H_4COOC_2H_5)(CO)_5]$ (**2c**): a red oil (50 mg, 23.9%, based on **1**); IR (νCO) 2093(s), 2051(vs), 2002(vs, br), 1945(s), 1892(s) cm^{-1}; ($\nu C{=}O$) 1721(s) cm^{-1}; ^1H NMR δ 6.00 (s, br, 2H, $2C_2H$), 5.89−5.49 (qs, 4H, C_5H_4), 4.24 (q, 2H, CH_2, $J = 7.4$ Hz), 2.86 (s, br, 4H, $2CH_2$), 1.50 (m, 6H, $CH_2CH_2CH_2$), 1.29 (t, 3H, CH_3, $J = 7.4$ Hz). Anal. Calcd for $C_{28}H_{21}O_{13}Co_3Mo$: C, 40.12; H, 2.53. Found: C, 40.02; H, 2.66. $[CoMo(C_5H_4COOC_2H_5)(CO)_5][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu]$ $[CoMo(C_5H_4COOC_2H_5)(CO)_5]$ (**3c**): a red oil (40 mg, 16.3%, based on **1**); IR (νCO) 2091(s), 2065(vs), 2052(vs), 1998(vs, br), 1943(vs), 1890(s) cm^{-1}; ($\nu C{=}O$) 1720(vs) cm^{-1}; ^1H NMR δ 6.01 (s, 2H, $2C_2H$), 5.89−5.48 (qs, 8H, $2C_5H_4$), 4.24 (q, 4H, $2CH_2$, $J = 7.6$ Hz), 2.82 (s, br, 4H, $2CH_2$), 1.41 (m, 6H, $CH_2CH_2CH_2$), 1.30 (t, 6H, $2CH_3$, $J = 7.6$ Hz) Anal. Calcd for $C_{35}H_{30}O_{14}Co_2Mo_2$: C, 42.70; H, 3.07. Found: C, 42.82; H, 3.06.

Preparation of $[HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_5)_2(CO)_4]$ (4a) and $[Mo_2(C_5H_5)_2(CO)_4][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_5)_2(CO)_4]$ (5a). A solution of $Mo_2(C_5H_5)_2(CO)_6$ (490 mg, 1 mmol) in toluene (30 cm^3) was refluxed for 14 h. Upon cooling to room temperature, 1,8-nonadiyne (120 mg, 1 mmol) was added, and the mixtures were stirred for another 3 h at room temperature. The solvent was removed under vacuum, and the products were chromatographed on a silica gel column using CH_2Cl_2/petroleum ether (1:1) as eluent to give two red fractions of clusters **4a** and **5a**. Cluster **4a** was recrystallized from hexane/CH_2Cl_2 at −20 °C to give red crystals (280 mg, 50.5%): IR (νCO) 1974(vs), 1917(vs), 1894(vs), 1821(vs) cm^{-1}; ($\nu C{\equiv}C{-}H$) 3297(s) cm^{-1}; ($\nu C{\equiv}C$) 2114(w) cm^{-1}; ^1H NMR δ 5.99 (s, 1H, C_2H), 5.28 (s, 10H, $2C_5H_5$), 2.57 (t, 2H, CH_2, $J = 7.6$ Hz), 2.19 (dt, 2H, CH_2, $J = 2.4$ Hz, $J = 7.6$ Hz), 1.95 (t, 1H, $C{\equiv}CH$, $J = 2.5$ Hz), 1.52 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{23}H_{22}O_4Mo_2$: C, 49.83; H, 4.00. Found: C, 49.82; H, 3.88. Cluster **5a** was recrystallized from hexane/CH_2Cl_2 at −20 °C to give red crystals **$5a{\cdot}CH_2Cl_2$** (130 mg, 24.2%, based on $Mo_2(C_5H_5)_2(CO)_6$): IR (νCO) 1989(vs), 1936(vs), 1910(vs, sh), 1896(vs), 1826(vs) cm^{-1}; ^1H NMR δ 5.97 (s, 2H, $2C_2H$), 5.29 (s, 20H, $4C_5H_5$), 2.50 (t, 4H, $2CH_2$, $J = 7.7$ Hz), 1.35 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{38}H_{34}O_8Cl_2Mo_4$: C, 42.52; H, 3.19. Found: C, 42.42; H, 3.20.

The following complexes were similarly prepared. $[HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COCH_3)_2(CO)_4]$ (**4b**): a red oil (200 mg, 31.3%); IR (νCO) 1993(vs), 1915(vs), 1844(vs) cm^{-1}; ($\nu C{=}O$) 1675(s) cm^{-1}; ($\nu C{\equiv}C{-}H$) 3305(s) cm^{-1}; ($\nu C{\equiv}C$) 2116(w) cm^{-1}; ^1H NMR δ 6.04 (s, 1H, C_2H), 5.82−5.34 (qs, 8H, $2C_5H_4$), 2.61 (t, 2H, CH_2, $J = 7.5$ Hz), 2.30 (s, 6H, $2CH_3$), 2.20 (dt, 2H, CH_2, $J = 2.6$ Hz, $J = 7.6$ Hz), 1.98 (t, 1H, $C{\equiv}CH$, $J = 2.6$ Hz), 1.46 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{27}H_{26}O_6Mo_2$: C, 50.80; H, 4.11. Found: C, 50.66; H, 4.02. $[Mo_2(C_5H_4COCH_3)_2(CO)_4][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COCH_3)_2(CO)_4]$ (**5b**): Recrystallization from hexane/CH_2Cl_2 at −20 °C to give red crystals **$5b{\cdot}2H_2O$** (110 mg, 19.0%, based on $Mo_2(C_5H_4COCH_3)_2(CO)_6$); IR ($\nu$CO) 1992(vs), 1914(vs), 1844(vs) cm^{-1}; ($\upsilon C{=}O$) 1674(s) cm^{-1}; ^1H NMR δ 6.03 (s, 2H, $2C_2H$), 5.84−5.37 (qs, 16H, $4C_5H_4$), 2.59 (t, 4H, $2CH_2$, $J = 7.6$ Hz), 2.31 (s, 12H, $4CH_3$), 1.39 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{45}H_{44}O_{14}Mo_4$: C, 45.32; H, 3.72. Found: C, 45.38; H, 3.62. $[HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COOC_2H_5)_2(CO)_4]$ (**4c**): a red oil (230 mg, 32.4%); IR (νCO) 1996(vs), 1915(vs), 1848(vs) cm^{-1}; ($\nu C{=}O$) 1716(vs) cm^{-1}; ($\nu C{\equiv}C{-}H$) 3306(s) cm^{-1}; ($\nu C{\equiv}C$) 2117(w) cm^{-1}; ^1H NMR δ 6.09 (s, 1H, C_2H), 5.89−5.29 (qs, 8H, $2C_5H_4$), 4.21 (q, 4H, $2CH_2$, $J = 7.2$ Hz), 2.62 (t, 2H, CH_2, $J = 7.6$ Hz), 2.19 (dt, 2H, CH_2, $J = 2.6$ Hz, $J = 7.6$ Hz), 1.96 (t, 1H, $C{\equiv}CH$, $J = 2.6$ Hz), 1.49 (m, 6H, $CH_2CH_2CH_2$), 1.28 (t, 6H, $2CH_3$, $J = 7.2$ Hz). Anal. Calcd for $C_{29}H_{30}O_8Mo_2$: C, 49.87; H, 4.33. Found: C, 50.04; H, 4.36. $[Mo_2(C_5H_4COOC_2H_5)_2(CO)_4][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COOC_2H_5)_2(CO)_4]$ (**5c**): a red oil (100 mg, 15.7%, based on $Mo_2(C_5H_4COOC_2H_5)_2(CO)_6$); IR ($\nu$CO) 1995(vs), 1915(vs), 1847(vs) cm^{-1}; ($\nu C{=}O$) 1716(vs) cm^{-1}; ^1H NMR δ 6.07 (s, 2H, $2C_2H$), 5.89−5.30 (qs, 16H, $4C_5H_4$), 4.22 (q, 8H, $4CH_2$, $J = 7.1$ Hz),2.63 (t, 4H, $2CH_2$, $J = 7.6$ Hz), 1.33 (m, 6H, $CH_2CH_2CH_2$), 1.29 (t, 12H, $4CH_3$, $J = 7.1$ Hz). Anal. Calcd for $C_{49}H_{48}O_{16}Mo_4$: C, 46.10; H, 3.79. Found: C, 46.26; H, 3.88

Preparation of $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_5)_2(CO)_4]$ (6a). The cluster **4a** (110 mg, 0.2 mmol) was treated with $Co_2(CO)_8$ (70 mg, 0.2 mmol) in THF (20 cm^3) at room temperature. After being stirred for 3 h, the solvent was removed in reduced pressure and the residue purified by chromatography on silica gel using CH_2Cl_2/petroleum ether (1:5) as an eluent. Recrystallization from hexane/CH_2Cl_2 at −20 °C gave red crystals (105 mg, 62.5%): IR (νCO) 2092(s), 2050(s), 2019(vs), 1984(vs), 1902(vs), 1835(s) cm^{-1}; ^1H NMR δ 6.02 (s, 1H, C_2H), 5.96 (s, 1H, C_2H), 5.27 (s, 10H, $2C_5H_5$), 2.84 (t, 2H, CH_2, $J = 7.4$ Hz), 2.58 (t, 2H, CH_2, $J = 7.3$ Hz), 1.47

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(31) King, R. B. *Organometallic Syntheses, Vol. 1, Transition-Metal Compound*; Academic Press: New York, 1965; p 98.

(32) Seyferth, D.; Hollgren, J. E.; Huang, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.

(33) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239.

(m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{29}H_{22}O_{10}Co_2Mo_2$: C, 41.45; H, 2.64. Found: C, 41.50; H, 2.68.

The following complexes were similarly prepared. $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COCH_3)_2(CO)_4]$ (**6b**): red crystals (120, 64.9%); IR (νCO) 2091(vs), 2046(vs), 2033(vs), 2009(vs), 1991(vs), 1901(vs), 1839(s) cm^{-1}; ($\nu C{=}O$) 1678 cm^{-1}; ^1H NMR δ 6.03 (s, 1H, C_2H), 6.02 (s, 1H, C_2H), 5.83−5.33 (qs, 8H, $2C_5H_4$), 2.85 (t, 2H, CH_2, $J = 7.1$ Hz), 2.62 (t, 2H, CH_2, $J = 7.2$ Hz), 2.29 (s, 6H, $2CH_3$), 1.48 (m, 6H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{33}H_{26}O_{12}Co_2Mo_2$: C, 42.88; H, 2.84. Found: C, 43.02; H, 2.92. $[Co_2(CO)_6][\mu\text{-}HC_2(CH_2)_5C_2H\text{-}\mu][Mo_2(C_5H_4COOC_2H_5)_2(CO)_4]$ (**6c**): a red oil (140, 71.1%); IR (νCO) 2092(s), 2050(vs), 2019(vs), 2000(vs), 1918(vs), 1849(s) cm^{-1}; ($\nu C{=}O$) 1717 cm^{-1}; ^1H NMR δ 6.06 (s, 1H, C_2H), 6.02 (s, 1H, C_2H), 5.88−5.28 (qs, 8H, $2C_5H_4$), 4.21 (q, 4H, $2CH_2$, $J = 7.4$ Hz), 2.84 (t, 2H, CH_2, $J = 7.2$ Hz), 2.60 (t, 2H, CH_2, $J = 7.4$ Hz), 1.47 (m, 6H, $CH_2CH_2CH_2$), 1.28 (t, 6H, $2CH_3$, $J = 7.4$ Hz). Anal. Calcd for $C_{35}H_{30}O_{14}Co_2Mo_2$: C, 42.70; H, 3.07. Found: C, 42.54; H, 3.17.

Crystal Structure Determination of 5a, 5b, and 6a. Suitable crystals of the compounds were mounted on glass fibers and placed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Data were collected by the $\omega - 2\theta$ scan technique. The structures were solved by a direct phase determination method (MULTAN 82). The final refinement was accomplished by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a micro-VAX II computer using the TEXSAN program system.

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Supporting Information Available: Crystal data for **5a**, **5b**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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