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High-Field NMR Study of Vertex Rotation in $(C_5H_nMe_{5-n})MCo_2(CO)_8CR$ Clusters (M = Mo, W): X-ray Crystal Structure of $(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr

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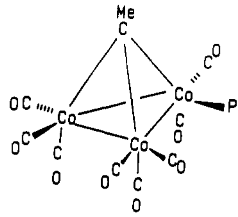
The variable-temperature ^{13}C NMR spectra of the clusters $(C_5H_nMe_{5-n})MCo_2(CO)_8CCO_2$-*i*-Pr, where n = 5, 4, and 0 and M = Mo and W, reveal the existence of two interconverting rotamers whereby the $CpM(CO)_2$ vertex is oriented either proximal or distal to the capping carbynyl group. When Cp = C_5H_5 or C_5H_4Me, this group is predominantly distal whereas for Cp = C_5Me_5 the ring is proximal and the Mo (or W) carbonyls semibridge to the cobalts. This is confirmed by an X-ray diffraction study of $(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr, which crystallizes in the monoclinic space group $P2_1/n$ with a = 9.781 (2) Å, b = 10.217 (2) Å, c = 27.225 (9) Å, β = 103.80 (2)°, V = 2642.12 Å^3, and Z = 4. Simulation of the carbonyl-exchange process reveals that the migration of CO ligands between cobalt and molybdenum has the same activation energy barrier as the interconversion of proximal and distal cyclopentadienyl rings; it is proposed that these fluxional processes are correlated. Use of a capping fragment derived from a natural product such as menthol or podocarpic acid renders the cluster chiral and allows the detection of slowed carbonyl exchange between the diastereotopic cobalt centers.

Introduction

Over the past few years, logical synthetic routes to mixed-metal clusters have been developed.[1-3] In particular, tetrahedral systems comprising three transition-metal vertices and a capping carbynyl moiety have been intensively studied and it is now possible to focus on the structural and spectroscopic parameters and also the molecular dynamics of a series of such molecules. Two general synthetic approaches are widely applicable. The first involves the production of a cluster type such as $RCCo_3(CO)_9$, which is readily available in multigram quantities[4,5] and which undergoes facile substitution of a tricarbonylcobalt vertex by an isolobal[6] fragment such as $CpMo(CO)_2$,[7] CpNi,[8] or $Ru(CO)_3^-$,[9] as in Scheme I. The second general route proceeds via the reaction of a metal–carbyne complex with a molecule containing (or capable of generating) a metal–metal triple bond.[1,10]

In small clusters the fluxionality of ligands (and even of vertices[11,12]) is well established.[13] Typically, $RCCo_3(CO)_8L$ complexes are known in which the carbonyl ligands are found only in terminal positions, as in 1, or in both terminal and bridging environments, as in 2. In these latter cases the solution infrared spectra exhibit more ν_{CO} stretching vibrations than can be assigned to a single structure.[14,15] However, on the NMR time scale, these exchange processes are so fast as to yield only an averaged ^{13}CO resonance in most cases. With the advent of very high field spectrometers, it is occasionally possible to slow such exchange processes on the NMR time scale and so establish the molecular structure. To take a particularly fine example, we note that the C_s symmetry of $H_2Os_3(CO)_9CCO$ in solution was first demonstrated by ^{13}C NMR spectroscopy, which revealed a 2:1:2:2:2 pattern for the CO's at low temperature;[16] subsequently, X-ray crystallography was used to show that the molecule adopted the same structure in the solid state.[17]



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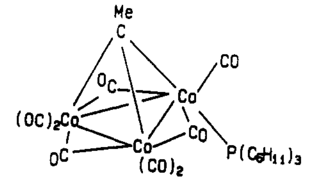

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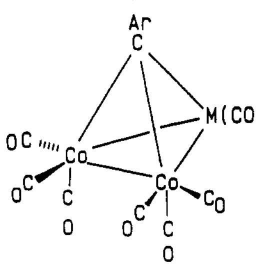
The molecules $(C_5H_5)MoCo_2(CO)_8CC_6H_5$ (3) and $(C_5H_5)WCo_2(CO)_8CC_6H_4CH_3$ (4) have been characterized X-ray crystallographically;[18,19] the structures are almost



3 M = Mo; Ar = C_6H_5
4 M = W; Ar = C_6H_4Me

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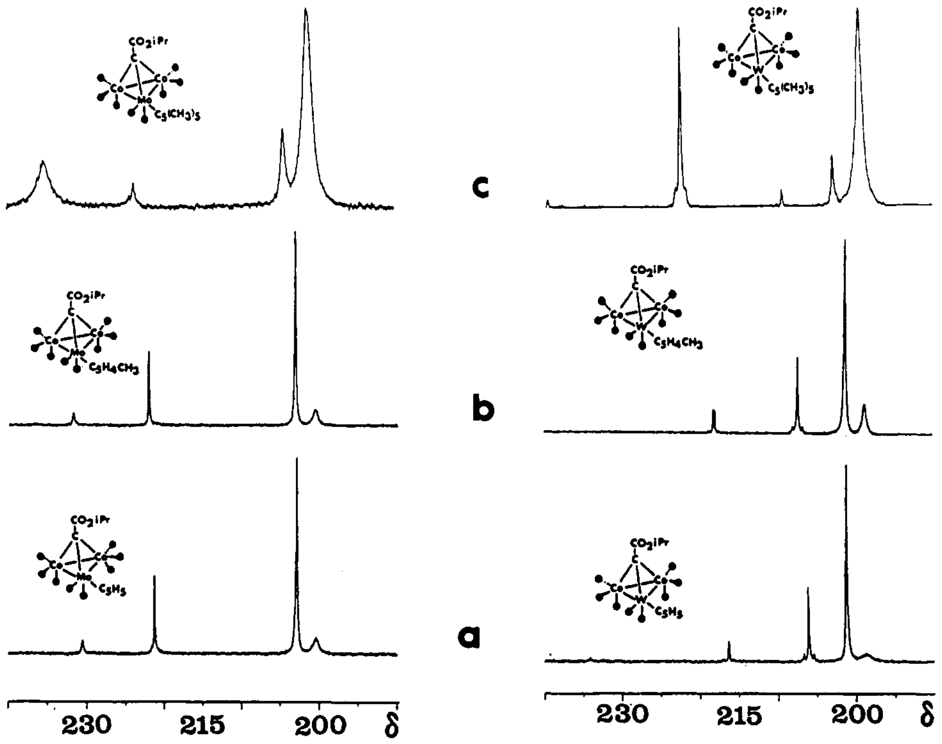
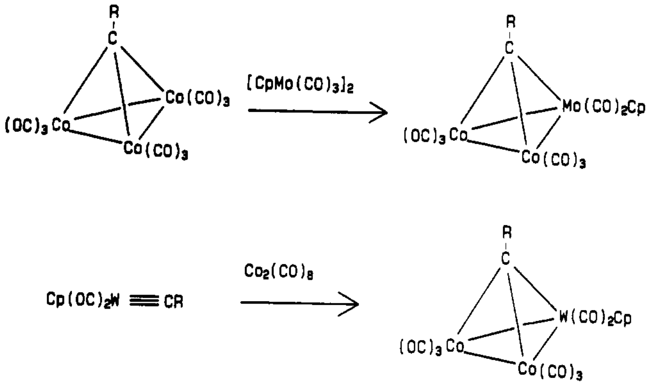
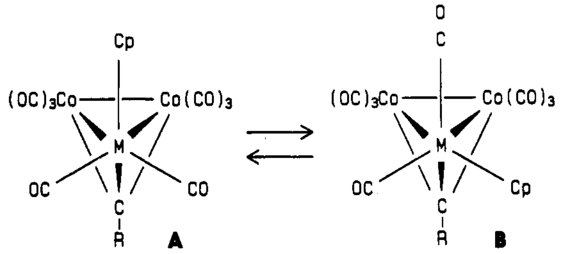


Figure 1. Low-temperature 125.7-MHz ^{13}C NMR spectra in the metal carbonyl region for (a) 5 and 8, (b) 6 and 9, and (c) 7 and 10.

Scheme I. Synthetic Routes to Mixed-Metal Clusters



Scheme II. Rotation of a $CpMo(CO)_2$ Vertex Relative to a Triangular Face

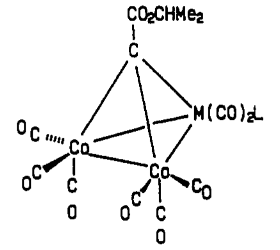


identical and show that (a) all carbonyls are terminal, (b) the cyclopentadienyl ring is positioned below the trimetallic plane (i.e., distal to the capping group), and (c) the plane of the aryl ring is parallel to the cobalt–cobalt vector. However, as was pointed out by both sets of authors, the solution infrared data exhibited too many carbonyl stretching vibrations to be assigned solely to the structure of the crystalline form. Furthermore, the observation of an infrared band at ~1875 cm^{-1} was interpreted as implying the presence of an isomer with semibridging carbonyl ligands. The comment was also made[19] that rotational isomerism attributable to different orientations of the $CpM(CO)_2$ fragment relative to the Co_2C triangular face should be considered (see Scheme II).

To clarify the conformational behavior of these molecules, we undertook a 125-MHz ^{13}C NMR study of a series of $RCCo_2(CO)_6M(CO)_2Cp$ clusters, where M = Mo or W, in which the bulk of the substituents in the cyclopentadienyl ring could be modified. As the apical substituent, we chose the isopropyl ester functionality, since its potentially diastereotopic methyl groups could be used as a probe for chiral systems such as conformation **B** in Scheme II.[20]

Results and Discussion

^{13}C NMR and Infrared Spectroscopy. In connection with our earlier studies on chiral mixed-metal clusters,[21] we had prepared $(C_5H_5)MoCo_2(CO)_8C\text{-}CO_2CHMe_2$ (5) and



5 M = Mo; L = C_5H_5
6 M = Mo; L = C_5H_4Me
7 M = Mo; L = C_5Me_5
8 M = W; L = C_5H_5
9 M = W; L = C_5H_4Me
10 M = W; L = C_5Me_5

recorded its ^{13}C NMR spectrum over the temperature

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[18] Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 863.

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range +30 to −90 °C. The metal carbonyl resonances appear as a single peak at room temperature on an 80-MHz spectrometer, but at −50 °C on a 250-MHz instrument the peak broadens and splits into a 2:6 pattern with shifts characteristic of carbonyls bonded to molybdenum and cobalt, respectively. The −90 °C ^{13}C spectrum recorded at 11.7 T (500 MHz for ^{1}H, 125 MHz for ^{13}C) is shown as trace a in Figure 1. Clearly, two isomers are present in solution. The major component has a cobalt carbonyl peak at 203 ppm and a molybdenum carbonyl resonance at 221 ppm; the integrated intensity ratio is 3:1, corresponding to $Co_2(CO)_6$ and $Mo(CO)_2$ fragments. The minor component likewise exhibits a 6:2 ratio of cobalt to molybdenum carbonyls, but now the latter resonance is found at 230 ppm—a region more typical of bridging or semibridging carbon monoxide ligands on molybdenum.[22] As shown in trace b of Figure 1, similar behavior is exhibited by the monomethylcyclopentadienyl analogue **6**, but the pattern is completely reversed for the pentamethylcyclopentadienyl complex **7**. Figure 1 also shows the 125-MHz ^{13}C NMR spectra of the corresponding tungsten clusters, and again the $(C_5H_5)WCo_2(CO)_8CR$ (**8**) and $(C_5H_4Me)WCo_2(CO)_8CR$ (**9**) molecules favor the structure with high-field tungsten carbonyls (at 208 ppm), while in the $(C_5Me_5)WCo_2(CO)_8CR$ system, **10**, the low-field (high-frequency) tungsten carbonyl peak predominates. In these latter molecules, the carbonyl resonances assigned to the $W(CO)_2$ fragment are unambiguously distinguished from those of the $Co(CO)_3$ groups not only by their characteristic chemical shifts but also by the observation of satellite peaks attributable to coupling to the ^{183}W nuclei ($I = {}^1/_2$; 14% abundant).

It is a commonly observed phenomenon that carbonyl ligands which find themselves in bridging environments exhibit a marked high-frequency shift relative to situations in which they are terminally bonded to the same metal. Typically, $Fe(^{13}CO)_3$ moieties in clusters resonate at approximately 215 ppm, but a carbonyl that bridges two Fe atoms can be deshielded by more than 30 ppm; analogous data exist for bridging carbonyls bonded to a variety of other metals.[23,24] The evidence thus suggests that, in the clusters **5**–**10**, the predominant conformation adopted by those molecules containing unsubstituted or monosubstituted cyclopentadienyl groups is one in which the carbonyl ligands bonded to molybdenum or tungsten possess only terminal carbonyls; in contrast, with the much more bulky pentamethylcyclopentadienyl group, the CO's attached to the group 6 metal apparently adopt a bridging or semibridging position in the predominant isomer.

The low-temperature ^{13}C NMR spectrum of $PhCCo_2(CO)_6Mo(CO)_2(C_5H_5)$ (**3**) is in accord with the pattern observed for all the other complexes bearing unsubstituted cyclopentadienyl rings. That is, the predominant isomer exhibits a Mo–carbonyl resonance at 223 ppm, while in the minor isomer the corresponding peak is found at 232.5 ppm. Again, the major constituent has terminal carbonyls on molybdenum in accord with the structure found X-ray crystallographically in the solid state. These arguments are buttressed by infrared data on $PhCCo_2(CO)_6Mo(CO)_2(C_5H_5)$. As previously reported by Vahrenkamp and shown again in Figure 2, the infrared spectrum in CH_2Cl_2 exhibits many ν_{CO} bands, including a weak absorbance at ~1875 cm^{-1}, which suggests the existence of a semibridging carbonyl. This feature is entirely absent when the infrared spectrum of **3** is recorded as a KBr pellet. In an entirely analogous fashion, the solution and solid-state infrared spectra of $(C_5H_4Me)WCo_2(CO)_8CCO_2$-*i*-Pr (**9**) demonstrate (see Figure 2) the existence of a small fraction of the semibridged isomer in solution but a single all-terminal structure in the solid state. The situation is quite different for the pentamethylcyclopentadienyl complexes **7** and **10**, for which the semibridging situation is favored both in solution and in the solid phase.

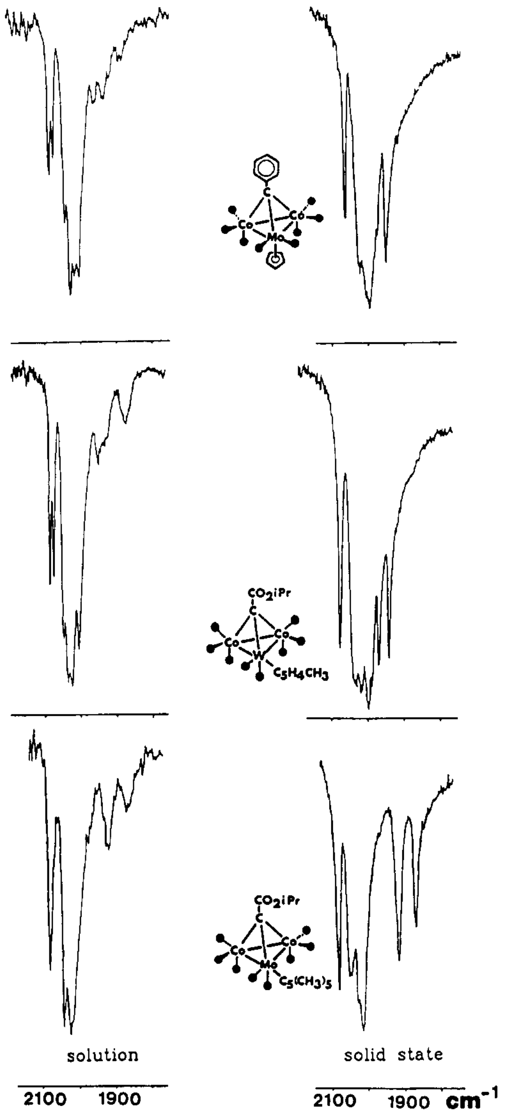

Figure 2. Sections of the infrared spectra of the clusters **3**, **9**, and **7** in solution in methylene chloride and in the solid state as KBr pellets.

Before postulating viable structures for the two isomers detectable on the NMR time scale, we must examine the evidence provided by the other NMR probes that have been built into the molecules. We note initially that the ^{13}C ring carbon resonances are split at low temperature into the same intensity ratios as are the carbonyls. We can thus associate a given set of cyclopentadienyl peaks with a particular isomer. It is also particularly significant that, although we see two sets of resonances in either the ^{1}H or ^{13}C spectra for the methyl groups of the isopropyl ester substituent, these signals are never split into diastereotopic pairs;[25] that is, the molecules adopt *achiral* conformations.

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(25) This diastereotopic character would also be detectable in the non-equivalence of the ring protons and carbons of the $C_5H_4CH_3$ ligand.

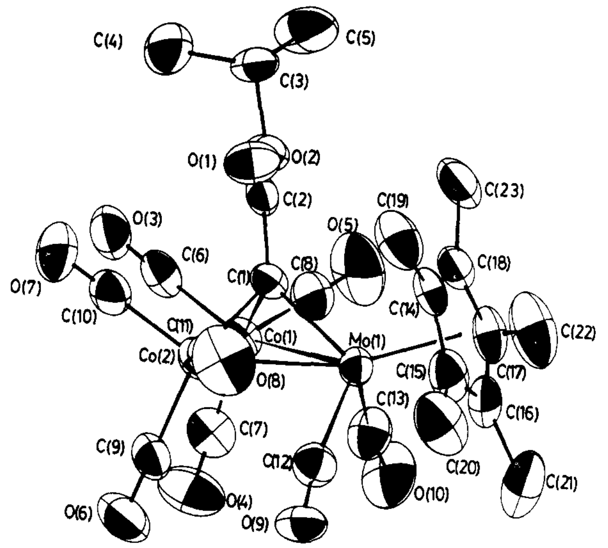
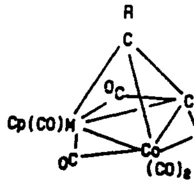


Figure 3. View of $(C_5Me_5)MoCo_2(CO)_8CCO_2$-$i$-Pr (7), showing the atom-numbering scheme.

We can therefore discount rotamers of the $CpM(CO)_2$ vertex (for example, conformer **B** in Scheme II), which place the cyclopentadienyl group in a gauche position with respect to the Co_2C triangle. [This assumption is only valid if there is no very low energy process that equilibrates enantiomeric gauche conformers. It is noteworthy that a gauche orientation for a $CpM(CO)_2$ unit has been crystallographically characterized in $(C_5H_5)W(CO)_2Fe_2(CO)_6$-$(\mu$-$CO)CC_6H_4Me$; in that case the ^{13}CO region shows only a single resonance but no low temperature data were reported.[26]] Moreover, we can also see that structures involving three bridging carbonyls, such as **11**, are not viable candidates, since the observed ratio of cobalt carbonyls to molybdenum or tungsten carbonyls is inconsistent with such a formulation. The most reasonable structures for the isomers observable by NMR spectroscopy are those that place the cyclopentadienyl rings either below (distal to the carbynyl cap) or above the trimetallic plane (proximal to the cap), as in **12** or **13**, respectively, and that preserve the mirror symmetry of the molecule.



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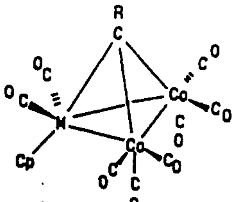

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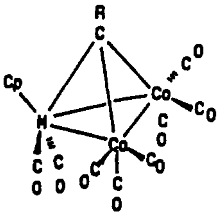

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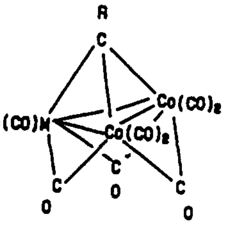

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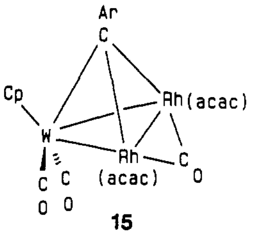
X-ray Crystallography. Crystals of $(C_5Me_5)MoCo_2$-$(CO)_8CCO_2$-i-Pr (7), grown from hexane/ether, were suitable for X-ray diffraction, and the resulting molecular structure is shown in Figure 3. The cobalt–molybdenum and cobalt–cobalt distances of 2.735 (average) and 2.515 Å in 7 are somewhat longer than the corresponding bond lengths in $(C_5H_5)MoCo_2(CO)_8CC_6H_5$ (**3**) [Mo–Co = 2.672 Å; Co–Co = 2.489 Å].[18] Concomitantly, the metal–carbyne distances in 7 are slightly shorter [Mo–C = 2.073 Å; Co–C = 1.933 Å (average)] than in 3 for which Mo–C = 2.109 Å and Co–C = 1.95 Å. The metal to Cp-ring-centroid distances are essentially identical (2.019 Å) in **3**, **4**, and **7**. The crucial differences relate to the orientation of the $Cp^*Mo(CO)_2$ moiety, which is now positioned such that the C_5Me_5 ring is proximal with respect to the carbynyl capping unit. In 3 the molybdenum–ring-centroid vector is bent down through an angle of 54.5° from the trimetallic plane; in 7 the corresponding angle is 24° in the opposite direction Moreover, the molybdenum carbonyls, which are clearly terminal and linear in 3 and 4, are semibridging in 7 with Mo–C–O angles of 169.3 and 170.5°. The distances from these molybdenum-bonded carbonyls to their neighboring cobalt atoms (Co(1)··C(8) = 2.703 Å; Co(2)··C(13) = 2.695 Å) are much shorter than the sum of their van der Waals radii (3.25 Å);[27] these bonds are, however, not as short as the semibridging carbonyls in the closo cluster $[(C_5H_5)Co]_2Fe(CO)_3(C_5H_5)Mo(CO)_2CCO_2$-$i$-Pr where the molybdenum carbonyls are only 2.57 Å from the cobalts.[28]

It is interesting to speculate on the reasons for the preferred orientation of the bulky pentamethylcyclopentadienyl ring in a site proximal to the carbynyl cap. One might suggest that the enhanced electron-donating capability of the pentamethylated ring causes a build-up of charge on the molybdenum or tungsten atom; this in turn can best be alleviated by transferring the excess electron density to the tricarbonylcobalt centers, via semibridging carbonyls. In this vein, we note that in $(C_5H_5)W(CO)_2Rh_2(acac)_2(\mu$-$CO)CC_6H_4Me$ (**15**) the cyclopentadienyl group is proximal and the semibridging tungsten carbonyls appear to be trying to compensate for the electron deficiency at the rhodium centers.[19]



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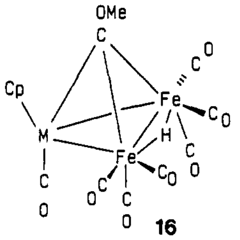

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We can now have some confidence that in solution the predominant conformers of $(C_5H_5)MCo_2(CO)_8CR$, i.e., **3**–**5** and **8**, and of $(C_5H_4Me)MCo_2(CO)_8C$-R, i.e., **6** and **9**, are of type **12** whereby the cyclopentadienyl group is oriented below the plane of the three metals and all the carbonyls are clearly terminal, as in the solid state.[29] In contrast, conformation **13** is found in both phases for the analogous C_5Me_5 clusters **7** and **10**. Nevertheless, since the room-temperature NMR spectrum shows only an averaged ^{13}CO environment, it is obviously incumbent upon the molecule to spend at least part of its time in a conformation that facilitates the transfer of carbonyl ligands from one metal vertex to another. This criterion may best be satisfied by

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[26] Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

[27] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

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[29] The room-temperature ^{13}C NMR solid-state spectrum of C_6H_5C-$Co_2Mo(CO)_8(C_5H_5)$ (3) shows signals corresponding to the phenyl and cyclopentadienyl ring carbons of the major isomer; the carbonyl signals were broadened because of chemical exchange.

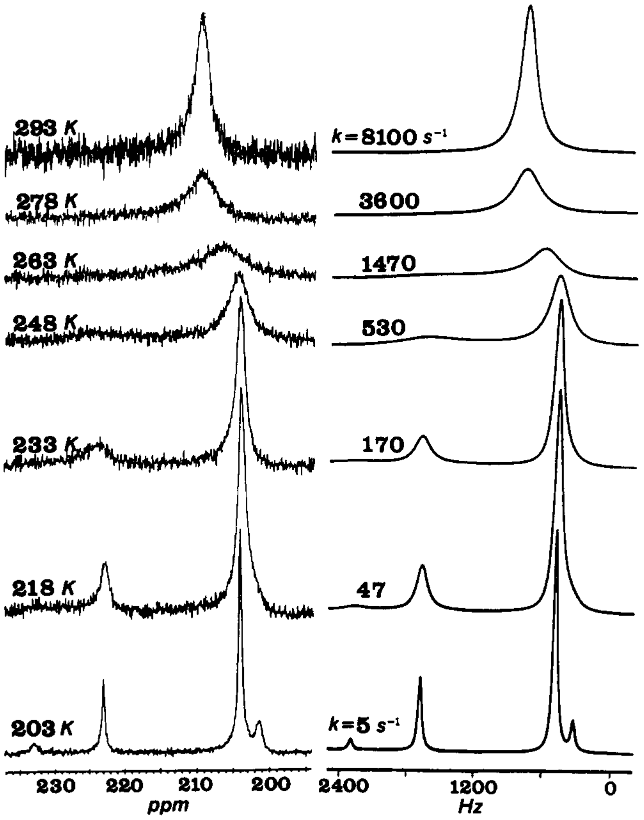
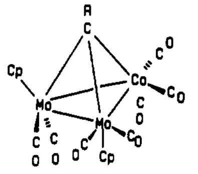


Figure 4. Experimental and simulated 62.86-MHz ^{13}C variable-temperature NMR spectra of 6 in the metal carbonyl region.

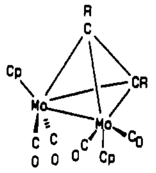
a conformation such as 14, which could be attained from 13 with only minor adjustments. Fluxionality of axial ligands has been invoked in $RCCo_3(CO)_7$(diphos) and related molecules[21,30] in which the diphos ligand occupies two equatorial sites and so blocks the conventional merry-go-round.[13] Moreover, Farrugia has shown that in $Fe_2M(\mu$-$H)(\mu_3$-$COCH_3)(CO)_7(\eta$-$C_5H_5)$ (16), where M = Co or Rh, the single carbonyl bound to cobalt or rhodium is axially positioned and can undergo exchange with the carbonyls on the iron atoms.[31,32] (In some ways this process resembles the intermetallic carbonyl migration in $(C_5H_5)_3Rh_3(CO)_3$ reported some years ago by Shapley.[33]) We have already reported[21] that the barriers to intermetallic carbonyl scrambling in tetrahedral $CpMCo_2(CO)_8CR$ systems are of the order of 9–10 kcal mol^{-1} and such values fit in well with the barriers to rotation of the $(C_5H_{5-n}Me_n)Mo$ vertices in $(RC{\equiv}CR)Cp_2M_2(CO)_4$ clusters;[34-36] it is interesting to speculate whether these two fluxional processes are interdependent. Since the CO ligands can only be transferred from metal to metal when they can adopt a bridging or semibridging bonding mode, it seems not unreasonable to postulate that the ability of the carbonyl ligands to migrate over the triangle of metals is controlled by the ease of rotation of the $CpM(CO)_2$ vertex.

To investigate the viability of the hypothesis that the intermetallic migration of carbonyls is controlled by the barrier to $CpM(CO)_2$ vertex rotation, we recorded the variable-temperature ^{13}C spectra of $(C_5H_4Me)MoCo_2(CO)_8CCO_2CHMe_2$ (6), and Figure 4 shows the behavior of the metal carbonyl resonances over the range 203–293 K. It is clear that rotation of the $CpMo(CO)_2$ vertex must interconvert the Mo–CO peaks at δ 231.8 and 222.2 as well as the Co–CO resonances at δ 204.1 and 200.9. Moreover, if the migration of carbonyl ligands between molybdenum and cobalt centers can only occur when the molybdenum vertex adopts a particular conformation (for example, a gauche rotamer), then the rate constant for intermetallic carbonyl exchange cannot exceed the rate of vertex rotation. Thus, the simulated spectra shown in Figure 4 were obtained by using the same rate constant for proximal–distal interconversion as for intermetallic carbonyl migration at any given temperature; gratifyingly, the agreement is excellent. An Arrhenius plot of these data yield an activation energy barrier of 8.8 ± 0.3 kcal mol^{-1}. We are therefore drawn to the conclusion that these two fluxional processes are indeed correlated. Currently, we are carrying out EHMO investigations on the energetic requirements of this and other related migration mechanisms, and the results will be the topic of a future report.[37]

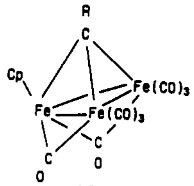
In searching the X-ray crystallographic literature for precedents in which $CpM(CO)_2$ vertices are positioned differently from the situation found in $CpMoCo_2(CO)_8CR$ and its W analogue, we noted an interesting report from Vahrenkamp's laboratory in which the two $CpMo(CO)_2$ vertices in $Cp_2Mo_2Co(CO)_7CCO_2Me$ (17) have very different orientations.[38] In this latter molecule, the cyclopentadienyl rings are found such that one is above and the other is below the $CoMo_2$ plane. Of course, the two rings can be seen to be avoiding mutually unfavorable steric interactions, but there is a more subtle message here. Several years ago, Cotton and co-workers showed that in $(HC{\equiv}CH)Cp_2Mo_2(CO)_4$ (18) the cyclopentadienyl rings are oriented in precisely this manner; furthermore, one of the carbonyls adopts a semibridging position while the other three are terminally bonded.[34] In fact, the Vahrenkamp molecule, 17, represents a direct isolobal replacement of a CH unit in 18 by a $Co(CO)_3$ fragment. One can easily visualize that replacement of either one of the $CpMo(CO)_2$ vertices in 17 by an isolobal $Co(CO)_3$ moiety leads directly to a rotamer of 5.



17



18



19

To extend the isolobal concept to an even more closely analogous system, we note that Farrugia[39] has characterized the cluster $CpFe_3(CO)_8COMe$ (19), in which the cyclopentadienyl ring is proximal to the capping methoxycarbynyl fragment and the two carbonyls attached to the unique iron atom lie below the Fe_3 plane and are in bridging positions. Now, replacement of the $CpFe(CO)_2$ vertex by $Cp^*Mo(CO)_2$, together with substitution of the $Fe(CO)_3$ fragments by $Co(CO)_3$ units, effectively gives 7. It is necessary merely to make the bridging carbonyls semibridging so that, formally at least, the effective atomic

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[31] Aichison, A. A.; Farrugia, L. J. *Organometallics* **1986**, *5*, 1103.

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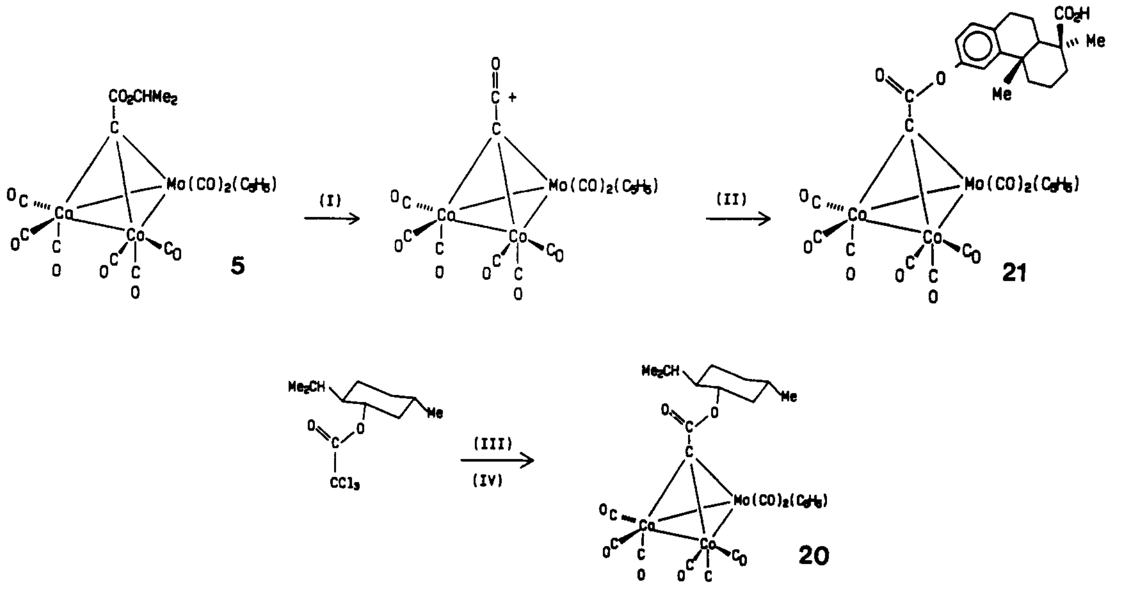
[39] Aichison, A. A.; Farrugia, L. J. *Organometallics* **1987**, *6*, 819.

Scheme III. Synthetic Routes to the Chiral Clusters 20 and 21



(I) $HPF_6/(EtCO)_2O$ (II) podocarpic acid (III) $Co_2(CO)_8$ (IV) $Cp_2Mo_2(CO)_6$

number rule is satisfied for both the $MoCo_2$ and Fe_3 clusters. Even more dramatic are Stone's carborane analogues PPh_4^+ $[(\eta^5\text{-}C_2B_9H_9Me_2)W(CO)_2Co_2(CO)_6CPh]^-$ and $(\eta^5\text{-}C_2B_9H_9Me_2)W(CO)_2Ir(PEt_3)_2CC_6H_4Me$, in which the initially proximal borane cage is locked in the distal orientation after oxidative addition by a B–H bond to the neighboring iridium center.[40,41]

It is interesting to note that in the anion $(C_5H_5)MoCo_2(\mu\text{-}PPh_2)(CO)_6CC_6H_4Me$ conformer 13 is adopted in the solid state.[42] Moreover, it has been reported that the ^{13}C NMR spectrum of a tungsten complex analogous to 10, viz., $(C_5Me_5)WCo_2(CO)_8CC_6H_4Me$, shows the presence of two rotamers at low temperature, but no structural details were advanced.[23]

Chiral Clusters. The fluxional processes discussed above involve either rotation of a $CpM(CO)_2$ vertex or the intermetallic migration of carbonyls between molybdenum (or tungsten) and cobalt vertices. However, the mirror symmetry of clusters of the type 12 and 13 precludes the detection of slowed carbonyl exchange between $Co(CO)_3$ moieties;[43] that is, such a fluxional process is hidden because the cobalt environments are equivalent. To break this symmetry, it is necessary to incorporate a chiral substituent and thus render diastereotopic the two $Co(CO)_3$ sites. We have previously reported[44-48] the syntheses of a series of such clusters in which the capping carbynyl group bears a chiral substituent derived from a natural product such as a steroid or a terpene. Scheme III shows the synthetic routes to the clusters $(C_5H_5)MoCo_2(CO)_8CR^*$ (20, 21), in which the chiral units are derived from menthol and from podocarpic acid (a naturally occurring diterpene, readily available from the New Zealand rimu tree[49]), respectively. These clusters are now not only inherently

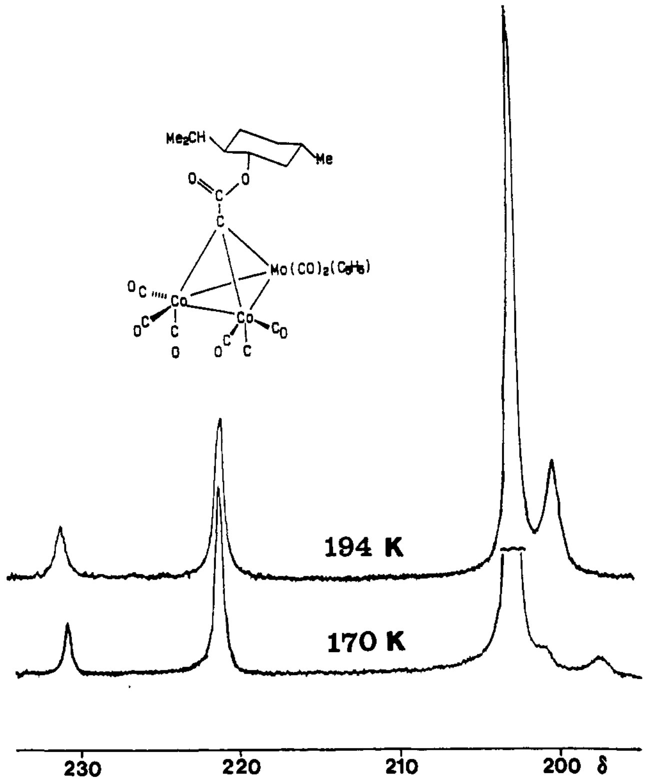


Figure 5. Variable-temperature 125.7-MHz ^{13}C NMR spectra in the metal carbonyl region for 20.

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(40) Baumann, F.-E.; Howard, J. A. K.; Musgrove, R. J.; Sherwood, P.; Sonte, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1891.

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(43) In all of these clusters local rotation of each $Co(CO)_3$ group is assumed to be fast on the NMR time scale; this process, which interconverts axial and equatorial carbonyl environments, can only be slowed when the capping carbynyl group is very bulky: D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1991**, *10*, 1383.

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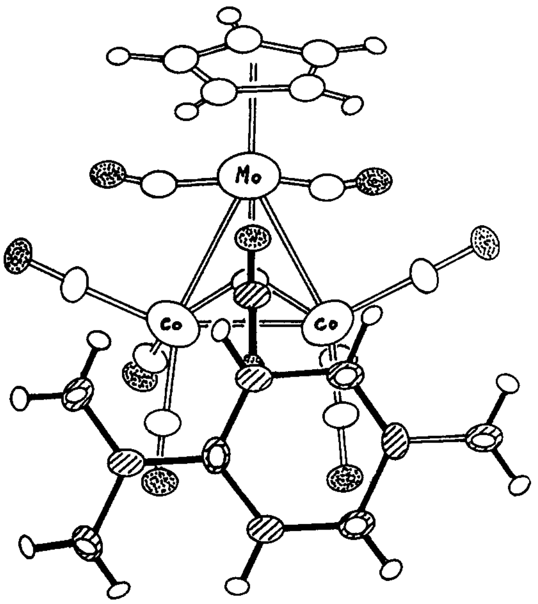

Figure 6. CHEMX model of the cluster **20** in which the C_5H_5 ligand is proximal to the capping group and the bulky menthol substituent lies over the cobalt–cobalt vector.

chiral but also bear relatively bulky ester substituents.

The establishment of the rotameric structures of these clusters allows the unambiguous assignment of a given $Co(CO)_3$ resonance to a molecule in which the cyclopentadienyl ring is positioned either distal or proximal to the cap. Figure 5 shows the variable-temperature ^{13}C NMR spectra of **20** in the cobalt carbonyl region.

It is readily apparent that at the lowest accessible temperature the $Co(CO)_3$ resonances *of the minor isomer only* are split into two equally intense peaks. The Gutowsky–Holm approximation yields a ΔG^*_{180} value of ≈8.6 ± 0.5 kcal mol^{-1}. The podocarpate complex **21** behaves similarly in that the minor $Co(CO)_3$ peaks broaden out but do not yield a fully resolved limiting spectrum; apparently ΔG^* is somewhat lower than for **20**. These observations must mean that carbonyl exchange between the two cobalt centers has been slowed on the NMR time scale and the diastereotopic nature of these vertices is now evident. Since we know that in this rotamer the cyclopentadienyl unit is oriented proximally to the carbynyl cap, one might conclude that the bulky menthol (or slightly less bulky podocarpate) fragment is constrained to lie over the cobalt–cobalt bond, as depicted in the CHEMX model[50] shown in Figure 6. In the predominant isomers of **20** or **21**, where the cyclopentadienyl ring is distal and the chiral capping unit is free to rotate, the cobalt vertices are, of course, still diastereotopic but their chemical shift differences may be smaller than they are in the minor rotamer where the chiral group is held closer to these metals.

In summary, therefore, it has been shown that the fluxional behavior of clusters of the $CpMCo_2(CO)_8CR$ type, where M = Mo or W and Cp bears zero, one, or five methyl substituents, can be rationalized in terms of restricted rotation of the $CpM(CO)_2$ vertex so as to give isomers in which the cyclopentadienyl ring lies either proximal or distal with respect to the carbynyl capping group. In either case, the Cp ring is bisected by a molecular mirror plane, thus rendering the $Co(CO)_3$ vertices equivalent unless the capping group is made chiral in which case slowed exchange of CO's between cobalts is observable.

Table I. Crystal Data for $(C_5Me_5)MoCo_2(CO)_8CO_2$-*i*-Pr (7)

mol formula	$C_{23}H_{22}O_{10}Co_2Mo$
fw	672.22
cryst system	monoclinic
space group	$P2_1/n$, No. 14
a, Å	9.781 (2)
b, Å	10.217 (2)
c, Å	27.225 (9)
β, deg	103.80 (2)
V, Å^3	2642.12
Z	4
ρ_{calcd}, g cm^{-3}	1.689
F(000)	1281.64
diffractometer	Nicolet P3
temp, °C	22 (295 K)
radiation (λ, Å)	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	18.02
std reflcns	2,0,0; 0,0,−4
data collcd	$h,k,\pm l$
2θ range, deg	0–45
no. of tot. data	4110
no. of unique data	3454
R_{int}[a]	0.0068
no. of obsd data ($I > 3\sigma(I)$)	2267
final shift/error, max(av)	0.009 (0.002)
no. of variables	326
final R_1, R_2[b]	0.0355, 0.0389
error in obsvn of unit wt[c]	0.8696
secondary extinction, *x*[d]	0.00028
weighting scheme	$w = (\sigma^2(F) + 0.001753F^2)^{-1}$
highest peak, e Å^{-3}	0.32
lowest valley, e Å^{-3}	−0.33

[a] $R_{int} = (\sum(N\sum(w(\langle F\rangle - F)^2))/\sum(N-1)\sum wF_o^2)^{1/2}$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = (\sum w(|F_o| - |F_c|^2)/\sum wF_o^2)^{1/2}$. [c] $S = (\sum w(|F_o| - |F_c|)^2/(m-n))^{1/2}$; *m* = no. of reflections, *n* = no. of variables. [d] $F^* = F(1 - 0.0001xF^2/\sin\theta)$.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[51] ^{13}C NMR spectra were recorded on ^{13}CO-enriched samples at 125.7 MHz by using a Bruker AM 500 spectrometer equipped with a 5-mm dual frequency $^1H/^{13}C$ probe. All spectra were measured in methylene-d_2 chloride, and chemical shifts are reported relative to tetramethylsilane. Where necessary, peaks attributable to the minor isomer are marked with an asterisk. Solid-state ^{13}C spectra were obtained at 25.18 MHz on a Bruker MSL100 instrument operating at 2.35 T. Infrared data were obtained on a Nicolet 7199 FTIR spectrometer using either NaCl solution cells or KBr pellets. Analytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada.

$Co_3(CO)_9CCO_2$-*i*-Pr was prepared according to the literature method,[21] and ^{13}CO enrichment was carried out as previously described.[21]

$(C_5H_5)MoCo_2(CO)_8CCO_2$-*i*-Pr (5) was prepared according to the method of Mlekuz et al.[28] ^{13}C NMR: δ 247.0 (apical C), 207.9 (all CO's), 177.7 (ester CO), 92.3 (C_5H_5 ring), 69.3 (*C*HMe$_2$), 22.1 (CH*Me*$_2$); at 193 K, δ 230.5*, 221.2 (Mo–CO's), 202.8, 200.2* (Co–CO's), 94.0*, 90.1 (C_5H_5 rings).

$(C_5H_4Me)MoCo_2(CO)_8CCO_2$-*i*-Pr (6). A solution of $Co_3(CO)_9CCO_2$-*i*-Pr (0.30 g, 0.56 mmol) and $[(C_5H_4Me)Mo(CO)_3]_2$ (0.15 g, 0.29 mmol) were heated under reflux in 20 mL of THF during 8 h. Progress of the reaction was followed by TLC on Kieselgel (eluent ether/petroleum ether 15/85); the desired product **6** gave a green spot at R_f = 0.47. Chromatography on silica gel (100/200 mesh) yielded dark green crystals of **6** (0.080 g, 0.13 mmol; 23%), mp 92 °C. IR ((CH_2Cl_2): ν_{CO} 2087 (m), 2076 (m), 2050 (s), 2028 (s), 2006 (s), 1961 (w), 1938 (m), 1666 cm^{-1} (ester). IR (KBr): ν_{CO} 2074 (m), 2018 (s), 2001 (s), 1974 (m), 1952 (m), 1920 (m), 1661 cm^{-1} (ester). ^{13}C NMR: δ 247.2 (apical C), 208.3 (all CO's), 184.5 (ester CO), 106.5 (Cp ring *C*-Me), 91.3, 89.5

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(50) CHEM-X, developed and distributed by Chemical Design Ltd., Oxford, U.K.

(51) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.

Table II. Positional Parameters (×10^4) and U_{eq} (Å^2 × 10^4) for $(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr (7) with Standard Errors in Parentheses

atom	x	y	z	U_{eq}[a]
Mo(1)	4544.2 (6)	2029.3 (6)	652.6 (2)	40
Co(1)	4176.6 (10)	4071.9 (9)	984.6 (4)	43
Co(2)	5779.6 (10)	2246.9 (9)	857.3 (4)	44
C(1)	3820 (6)	2222 (6)	880 (2)	41
C(2)	2715 (6)	1630 (6)	485 (2)	41
C(3)	435 (8)	2011 (8)	−98 (3)	58
C(4)	749 (10)	2509 (11)	−575 (3)	86
C(5)	−856 (9)	2570 (13)	2 (4)	121
O(1)	2752 (6)	552 (5)	301 (2)	70
O(2)	1592 (5)	2435 (5)	326 (2)	54
C(6)	3653 (8)	4512 (6)	333 (3)	54
O(3)	3300 (6)	4798 (6)	−84 (2)	73
C(7)	5457 (9)	5351 (8)	1235 (3)	61
O(4)	6250 (6)	6144 (6)	1384 (3)	98
C(8)	2597 (9)	4594 (8)	1145 (3)	61
O(5)	1580 (6)	4905 (8)	1247 (3)	106
C(9)	7396 (9)	3180 (8)	1054 (3)	54
O(6)	8393 (6)	3768 (6)	1178 (2)	83
C(10)	5456 (8)	2273 (8)	174 (3)	58
O(7)	5253 (6)	2294 (6)	−254 (2)	84
C(11)	6386 (9)	603 (9)	933 (3)	66
O(8)	6785 (8)	−436 (6)	1002 (3)	99
C(12)	6619 (9)	1899 (6)	1869 (3)	58
O(9)	7789 (6)	1741 (6)	2053 (2)	75
C(13)	4747 (9)	3743 (8)	1995 (3)	64
O(10)	4856 (8)	4631 (6)	2261 (2)	95
C(14)	3568 (8)	−107 (6)	1694 (3)	51
C(15)	4698 (9)	118 (8)	2134 (3)	63
C(16)	4312 (10)	1167 (9)	2411 (3)	65
C(17)	2956 (9)	1597 (8)	2151 (3)	61
C(18)	2497 (6)	828 (6)	1713 (3)	50
C(19)	3504 (10)	−1217 (8)	1331 (4)	76
C(20)	5967 (10)	−761 (9)	2300 (4)	92
C(21)	5108 (13)	1638 (12)	2936 (4)	116
C(22)	2028 (12)	2576 (11)	2335 (4)	101
C(23)	1044 (8)	850 (9)	1368 (3)	74

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2(\cos\beta)_{13})$.

(Cp ring *C*H's), 69.4 (*C*HMe$_2$), 22.1 (CH*Me*$_2$), 14.1 (Cp *Me*); at 183 K, δ 231.8*, 222.2 (Mo–CO's), 203.1, 200.6* (Co–CO's), 106.5, 91.4, 89.5, 106.5*, 95.1*, 92.5* (C_5H_4Me rings). Anal. Calcd for $C_{19}H_{14}Co_2MoO_{10}$: C, 37.04; H, 2.29. Found: C, 37.07; H, 2.04.

$(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr (7) was prepared according to the method of Sutin et al.[21] ^{13}C NMR: δ 248.8 (apical C), 209.9 (all CO's), 178.5 (ester CO), 106.1 (C_5Me_5 ring), 69.0 (*C*HMe$_2$), 22.1 (CH*Me*$_2$), 10.2 (C$_5$*Me*$_5$ ring); at 193 K, δ 235.0, 223.5* (Mo–CO's), 204.1*, 200.9 (Co–CO's), 105.3, 104.8* (C_5Me_5 rings), 12.0, 10.2 (C$_5$*Me*$_5$ rings).

$(C_5H_5)WCo_2(CO)_8CCO_2$-*i*-Pr (8). Analogously to the preparation of 6, $Co_3(CO)_9CCO_2$-*i*-Pr (1.64 g, 3.04 mmol) and $[(C_5H_5)W(CO)_3]_2$ (2.10 g, 3.04 mmol) were heated under reflux in 100 mL of THF during 43 h to give brown crystals of 8 (0.055 g, 0.08 mmol; 3%), mp 99 °C. IR ((CH_2Cl_2): ν_{CO} 2087 (m), 2077 (m), 2040 (s), 2025 (s), 2006 (s), 1956 (w), 1933 (w), 1879 (w), 1668 cm^{-1} (ester). IR (KBr): ν_{CO} 2076 (m), 2019 (s), 1998 (s), 1970 (m), 1947 (m), 1921 (w), 1661 cm^{-1} (ester). ^{13}C NMR: δ 202.6 (all CO's), 90.5 (C_5H_5 ring), 69.3 (*C*HMe$_2$), 22.1 (CH*Me*$_2$); at 193 K, δ 216.3*, 206.0 [$J(^{183}W-^{13}C)$ = 165 Hz] (W–CO's), 201.0, 198.6* (Co–CO's). Anal. Calcd for $C_{18}H_{12}Co_2WO_{10}$: C, 31.33; H, 1.75. Found: C, 31.42; H, 1.93.

$(C_5H_4Me)WCo_2(CO)_8CCO_2$-*i*-Pr (9). Analogously to the preparation of 8, $Co_3(CO)_9CCO_2$-*i*-Pr (1.00 g, 1.85 mmol) and $[(C_5H_4Me)W(CO)_3]_2$ (1.30 g, 1.87 mmol) were heated under reflux in 150 mL of THF during 24 h to give brown crystals of 9 (0.101 g, 0.14 mmol; 8%). IR ((CH_2Cl_2): ν_{CO} 2086 (m), 2076 (m), 2048 (s), 2024 (s), 2005 (s), 1953 (w), 1931 (m), 1875 (w), 1662 cm^{-1} (ester). IR (KBr): ν_{CO} 2076 (m), 2031 (s), 1997 (s), 1970 (m), 1941 (m), 1661 cm^{-1} (ester). ^{13}C NMR: δ 202.9 (all CO's), 185.0 (ester CO), 106.5 (Cp ring *C*-Me), 91.6, 90.9 (Cp ring *C*H's), 69.2 (*C*HMe$_2$), 22.1 (CH*Me*$_2$), 13.8 (Cp *Me*); at 193 K, δ 218.1*, 207.3 [$J(^{183}W-^{13}C)$ = 164 Hz] (W–CO's), 201.2, 198.7* (Co–CO's), 105.8, 90.7, 89.3, 105.8*, 94.5*, 92.5* (C_5H_4Me rings). Anal. Calcd for $C_{19}H_{14}Co_2WO_{10}$: C, 32.41; H, 2.00. Found: C, 32.36; H, 2.23.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr (7) with Estimated Standard Deviations in Parentheses

(a) Distances Involving the Dicobalt–Molybdenum–Carbon Tetrahedron			
Co(1)–Co(2)	2.515 (1)	Co(1)–Mo(1)	2.737 (1)
Co(2)–Mo(1)	2.732 (1)	Co(1)–C(1)	1.940 (7)
Co(2)–C(1)	1.927 (7)	Mo(1)–C(1)	2.073 (6)
Co(1)–C(6)	1.787 (9)	Co(1)–C(7)	1.824 (9)
Co(1)–C(8)	1.796 (9)	Co(2)–C(9)	1.815 (9)
Co(2)–C(10)	1.804 (9)	Co(2)–C(11)	1.77 (1)
Mo(1)–C(12)	1.979 (9)	Mo(1)–C(13)	1.969 (9)
Mo(1)–C(14)	2.387 (7)	Mo(1)–C(15)	2.343 (8)
Mo(1)–C(16)	2.306 (8)	Mo(1)–C(17)	2.344 (8)
Mo(1)–C(18)	2.384 (7)		
(b) Carbon–Oxygen Distances			
C(2)–O(1)	1.207 (8)	C(2)–O(2)	1.360 (8)
O(2)–C(3)	1.463 (8)	C(6)–O(3)	1.140 (9)
C(7)–O(4)	1.131 (9)	C(8)–O(5)	1.125 (9)
C(9)–O(6)	1.127 (9)	C(10)–O(7)	1.138 (9)
C(11)–O(8)	1.138 (9)	C(12)–O(9)	1.147 (9)
C(13)–O(10)	1.160 (9)		
(c) Carbon–Carbon Distances			
C(1)–C(2)	1.459 (9)	C(3)–C(4)	1.494 (12)
C(3)–C(5)	1.464 (12)	C(14)–C(15)	1.436 (11)
C(15)–C(16)	1.413 (12)	C(16)–C(17)	1.411 (12)
C(17)–C(18)	1.404 (11)	C(18)–C(14)	1.433 (10)
C(14)–C(19)	1.501 (11)	C(15)–C(20)–	1.512 (12)
C(16)–C(21)	1.523 (13)	C(17)–C(22)	1.507 (12)
C(18)–C(23)	1.521 (11)		
(d) Angles in the Tetrahedral Skeleton			
Co(1)–Co(2)–Mo(1)	62.7 (0)	Co(2)–Mo(1)–Co(1)	54.8 (0)
Mo(1)–Co(1)–Co(2)	62.5 (0)	Co(1)–Co(2)–C(1)	49.6 (2)
Co(2)–Mo(1)–C(1)	44.7 (2)	Mo(1)–Co(1)–C(1)	49.1 (2)
Co(1)–Mo(1)–C(1)	45.0 (2)	Co(2)–Co(1)–C(1)	49.2 (2)
Mo(1)–Co(2)–C(1)	49.2 (2)	Co(1)–C(1)–Co(2)	81.1 (3)
Co(2)–C(1)–Mo(1)	86.1 (3)	Mo(1)–C(1)–Co(1)	85.9 (3)
(e) Angles External to the Tetrahedral Skeleton			
C(2)–C(1)–O(1)	126.2 (5)	C(2)–C(1)–Co(2)	124.0 (5)
C(2)–C(1)–Mo(1)	136.0 (5)	Co(1)–C(6)–O(3)	178.7 (8)
Co(1)–C9&)–O(4)	178.9 (9)	Co(1)–C(8)–O(5)	178.6 (8)
Co(2)–C(9)–O(6)	178.7 (8)	Co(2)–C(10)–O(7)	179.3 (8)
Co(2)–C(11)–O(8)	178.5 (9)	Mo(1)–C(12)–O(9)	170.1 (7)
Mo(1)–C(13)–O(10)	169.1 (8)		
(f) Angles in the Cyclopentadienyl Ring			
C(14)–C(15)–C(16)	121.5 (9)	C(15)–C(16)–C(17)	120.1 (9)
C(16)–C(17)–C(18)	120.2 (9)	C(17)–C(18)–C(14)	118.1 (9)
C(18)–C(14)–C(15)	123.1 (10)		

$(C_5Me_5)WCo_2(CO)_8CCO_2$-*i*-Pr (10). Analogously to the preparation of 8, $Co_3(CO)_9CCO_2$-*i*-Pr (1.17 g, 2.17 mmol) and $[(C_5Me_5)W(CO)_2]_2$ (0.83 g, 1.10 mmol) were heated under reflux in 35 mL of THF during 24 h to give dark green crystals of **10** (0.055 g, 0.07 mmol; 3%), mp 173 °C. IR ((CH_2Cl_2): ν_{CO} 2081 (s), 2044 (s), 2023 (s), 1915 (m), 1856 (w), 1656 cm^{-1} (ester). IR (KBr): ν_{CO} 2080 (s), 2042 (s), 2009 (s), 1905 (m), 1858 (m), 1665 cm^{-1} (ester). ^{13}C NMR: δ 239.7 (apical C), 205.4 (all CO's), 182.2 (ester CO), 104.1 (C_5Me_5 ring), 69.0 (*C*HMe$_2$), 22.0 (CH*Me*$_2$), 10.1 (C$_5$*Me*$_5$ ring); at 193 K, δ 222.3, 209.3* [$J(^{183}W-^{13}C)$ = 165 Hz] (W–CO's), 202.7*, 199.2 (Co–CO's), 105.3, 104.8* (C_5Me_5 rings), 12.0, 10.2 (C$_5$*Me*$_5$ rings). Anal. Calcd for $C_{23}H_{22}Co_2WO_{10}$: C, 36.34; H, 2.92. Found: C, 36.10; H, 3.02.

$(C_5H_5)MoCo_2(CO)_8CPh$ (3) was prepared analogously to the method used for 5 to yield the compound previously synthesized by Beurich and Vahrenkamp.[18] ^{13}C NMR: δ 251.0 (apical C), 208 (all CO's), 160.7 (ipso-*C* in phenyl ring), 128.2, 127.6 (ortho- and meta-*C*H's), 126.5 (para-*C*H), 92.5 (C_5H_5 ring); at 193 K, δ 232.2*, 222.7 (Mo–CO's), 203.2, 201.0* (Co–CO's), 94.0*, 90.1 (C_5H_5 rings). ^{13}C solid-state NMR: δ 224 (broad, CO's undergoing exchange), 159 (ipso-*C*, 128 (*C*H's in phenyl ring), 90.1 (C_5H_5 ring).

$(C_5H_5)MoCo_2(CO)_8CCO_2$-menthyl (20) was prepared according to the method of Blumhofer and Vahrenkamp.[52] ^{13}C

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(52) Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 683.

NMR: at 194 K, δ 230.8*, 221.3 (Mo–CO's), 202.8, 200.2* (Co–CO's); at 170 K, δ 202.8, 201.0*, 197.6* (Co–CO's).

$(C_5H_5)MoCo_2(CO)_8CCO_2$-podocarpate (21). The isopropyl ester **5** (0.545 g, 0.91 mmol) was stirred with 8.6 mL of propionic anhydride in a two-necked 100-mL flask. To this flask was added 0.21 mL of a 65% aqueous solution of HPF_6. After 5 min, the resulting black crystals were filtered out under nitrogen and rinsed twice with 2.5-mL aliquots of CH_2Cl_2 to yield $[(C_5H_5)MoCo_2(CO)_8C{=}C{=}O]^+[PF_6]^-$ (0.436 g, 0.619 mmol; 68%), as described previously.[53] This salt was placed in a flask with podocarpic acid (0.197 g, 0.72 mmol) in 10 mL of methylene chloride. This slurry was then solubilized by the addition of 3 mL of ether. Immediately the contents of the flask dissolved and turned green. The product **21** was separated by chromatography on silica gel, but traces of the podocarpic acid remained. The ^{13}C NMR spectrum at ambient temperature exhibited a single carbonyl peak at 208.6 ppm. The ^{13}C NMR spectrum at 188 K exhibited δ 229.5*, 220.1 (Mo CO's), 201.8, and 199.5* (Co CO's). At 170 K, the δ 199.5 resonance broadens to give two poorly resolved peaks of equal intensity.

X-ray Crystallography of $(C_5Me_5)MoCo_2(CO)_8CCO_2$-*i*-Pr (7). Recrystallization of **7** from 85/15 hexane/ether afforded dark purple air-stable crystals. A single crystal (0.30 × 0.25 × 0.20 mm^3) suitable for X-ray diffraction was selected. Precession photographs revealed that the crystal was monoclinic, and accurate cell parameters were determined from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $21.5° < 2\theta < 29.6°$. Measurements were made on a Nicolet P3 diffractometer with use of graphite-monochromated Mo Kα radiation (λ = 0.71069 at 22 °C). Data collection over $h,k,\pm l$ resulted in 3454 unique reflections and 2267 observed reflections with $I > 3\sigma(I)$. Corrections for Lorentz and polarization effects and for absorption (ψ scans) were applied to all reflections.

Solution of the Structure. Considering only observed data, heavy-atom positions were found by direct methods (SHELXS-86).[54] Subsequent Fourier difference maps revealed the positions of all remaining atoms excluding the hydrogens, which were placed at calculated positions (SHELX-76).[55] Anisotropic refinements of all non-hydrogen atoms by full-matrix least-squares methods resulted in final R_1 and R_2 values of 0.0355 and 0.0389, respectively. Scattering curves from ref 56 and anomalous dispersion corrections from ref 57 were applied to the curves for cobalt and molybdenum during refinement of the structure. All calculations were performed on a VAX 8650 computer. Programs XTAL[58] for data reduction, TAPER[59] for absorption correction, SHELX-86[54] for structure solution, SHELX-76[55] for structure refinement, MOLGEOM[60] for molecular geometry, and SNOOPI[61] for drawing diagrams were used. Atomic positional parameters, temperature factors, and selected bond lengths and angles appear in Tables I–III.

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Supplementary Material Available: Tables of crystal data, hydrogen positional parameters, and anisotropic thermal parameters (5 pages); a table of structure factors (21 pages). Ordering information is given on any current masthead page.

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