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X-ray Crystallographic and Variable-Temperature High-Field ^{13}C NMR Studies of $R-CCo_3(CO)_9$ and $R-CCo_3(CO)_6$(tripod) Clusters [R = CH_3, $(4-CH_3OC_6H_4)_2CH$, $(2-ClC_6H_4)(4-ClC_6H_4)CH$; tripod = 1,1,1-Tris(diphenylphosphino)methane]: Enantiomerization of a Chiral Cluster via the Inversion of a Molecular Propeller

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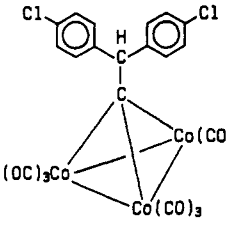
The syntheses of $(4-CH_3OC_6H_4)_2CH-CCo_3(CO)_9$ (2), $(2-ClC_6H_4)(4-ClC_6H_4)CH-CCo_3(CO)_9$ (5), and $CH_3-CCo_3(CO)_9$ from octacarbonyldicobalt and the corresponding trichloromethyl precursors are reported. The variable-temperature ^{13}CO NMR spectra of the clusters 2 and 5 are rationalized in terms of the cessation of axial–equatorial carbonyl exchange on the NMR time scale at low temperature. These three clusters react with the tridentate ligand tripod (1,1,1-tris(diphenylphosphino)methane) to yield the clusters $(4-CH_3OC_6H_4)_2CH-CCo_3(CO)_6$(tripod) (6), $(2-ClC_6H_4)(4-ClC_6H_4)CH-CCo_3(CO)_6$(tripod) (7), and $CH_3-CCo_3(CO)_6$(tripod) (8). The variable-temperature ^{13}C NMR data on these tripod clusters reveal not only that intercobalt migration of the carbonyl ligands is slowed but also that the phenyl rings of the tripod ligand exhibit two distinct fluxional processes. The first (for which $\Delta G^* \approx 8$ kcal mol^{-1}) requires only a small oscillation of each of the phenyl rings so as to racemize the clusters, which derive their chirality from the propeller-type orientation of the diphenylphosphino groups. A larger barrier ($\Delta G^* \approx 10$ kcal mol^{-1}) must be surmounted to bring about complete rotation of these phenyl rings. The structure of 8 has been confirmed by a single-crystal X-ray diffraction study. Crystals of 8 are monoclinic, of space group $P2_1/n$, with $a = 16.359$ (4) Å, $b = 13.317$ (3) Å, $c = 18.728$ (4) Å, and $V = 4076$ Å^3 for $Z = 4$.

Introduction

We have recently reported the syntheses and X-ray crystallographic characterizations of a series of carbynyltricobaltnonacarbonyl clusters in which the capping organic moiety possesses a diarylmethyl substituent, e.g. $(4-ClC_6H_4)_2CH-CCo_3(CO)_9$ (1) and $(4-CH_3OC_6H_4)_2CH-CCo_3(CO)_9$ (2).[1] These clusters were obtained via the reactions of dicobalt octacarbonyl with the appropriate trichloromethyl-containing precursors, viz. $(4-ClC_6H_4)_2CH-CCl_3$ (DDT) and $(4-CH_3OC_6H_4)_2CH-CCl_3$ (methoxychlor), the well-known pesticides. Upon recording the low-temperature ^{13}C NMR spectra of complexes 1 and 2, we were somewhat surprised to observe that the nine cobalt carbonyls were no longer undergoing rapid exchange on the NMR time scale but rather exhibited a 6:3 pattern at −120 °C. ΔG^* for this process was $\approx$9 kcal mol^{-1}. To our knowledge, the splitting of the degeneracy of a $Co(CO)_3$ fragment in such a cluster is unprecedented; all previous examples (except for $CH_3-CCo_3(CO)_8P(C_6H_{11})_3$ in which three of the carbonyls are in bridging positions)[2] exhibited sharp ^{13}C NMR singlets at all temperatures.[3] Moreover, in a particularly fine example, Aime has noted that in $Co_2(CO)_6Fe(CO)_3S$ (3) the equatorial and axial ligands of the tricarbonyliron fragment split into a 2:1 pattern at low temperature but the tricarbonylcobalt vertices yield only a sharp singlet even at −100 °C.[4]



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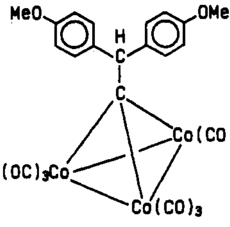

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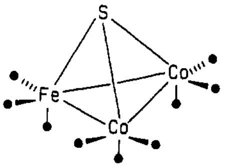

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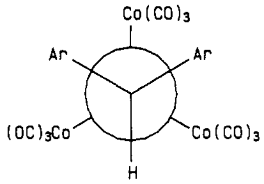
There are two viable hypotheses to account for the 6:3 ^{13}CO splitting in 1 and 2: The first would require that the capping group exhibit slowed rotation to give a staggered-ethane type conformation as in 4; this would lower the overall molecular symmetry to C_s, thus rendering two of the cobalt vertices different from the third. The second scenario would slow exchange between the three axial and six equatorial carbonyls so that, even while effective C_{3v} symmetry is maintained, the ^{13}CO NMR spectrum would reflect the difference in chemical environments. Although slow exchange between axial and equatorial carbonyls in heavy metal clusters such as those containing iridium or



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[3] Sutin, K. A.; Kolis, J. W.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A.; Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* 1987, *6*, 439 and references therein.

[4] Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* 1977, *25*, 103.

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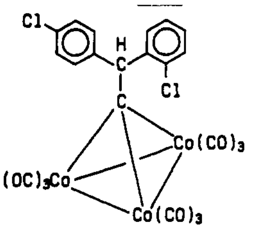
osmium has been well documented,[5] such is not commonly the case with first-row metals.

In order to investigate further this initial observation, we chose to construct some related tricobalt clusters that contained additional NMR probes by use of which we hoped to clarify the situation. To this end, we now describe the syntheses and NMR spectra of $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_9$ (**5**) (derived from *o,p'*-DDT) and of $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_6$(tripod) (**6**), $(4\text{-}CH_3OC_6H_4)_2CH\text{-}CCo_3(CO)_6$(tripod) (**7**), and $CH_3\text{-}CCo_3(CO)_6$(tripod) (**8**), where tripod is the 1,1,1-tris(diphenylphosphino)methane ligand. We also discuss the X-ray crystal structures of **7** and **8**.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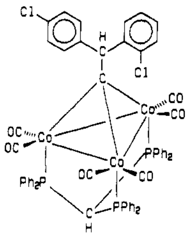
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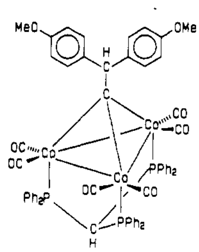
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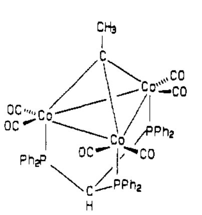
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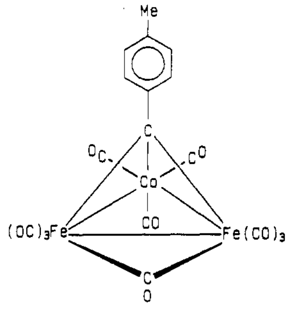
Results and Discussion

The X-ray crystal structure of $(4\text{-}ClC_6H_4)_2CH\text{-}CCo_3(CO)_9$ (**1**) reveals that, in the solid state at least, the capping diarylmethyl fragment adopts a staggered orientation with respect to the triangle of cobalts;[1] furthermore, although the *p*-chlorophenyl rings are slightly twisted so as to remove the potential mirror plane, the overall symmetry is not greatly distorted from C_s. These structural features are also manifested in the ^{13}C NMR spectrum of **2**, which reveals at low temperature a doubling of the ortho and meta ring carbon resonances; this is readily explicable in terms of slowed rotation of the *p*-methoxyphenyl rings. That is, the edges of the aryl rings have been rendered nonequivalent. (Such a phenomenon has been previously noted in, for example, the ^{13}C NMR spectra of diarylmethyl anions[6] or their $Cr(CO)_3$ complexes.[7]) The more interesting observation, however, was the splitting of the degeneracy of the nine carbonyl ligands into a 6:3 pattern. One might interpret this result in terms of slowed rotation of the capping carbynyl group together with cessation of the intermetal carbonyl ligand migration but with continued rapid axial–equatorial interconversion at each cobalt vertex. However, we do not favor such a proposal for the following reasons. First, the closely related cluster **5** under the same circumstances would be expected to exhibit three $Co(CO)_3$ environments, since the chiral capping group lowers the molecular symmetry to C_1. The cluster **5** exhibits ^{13}CO NMR behavior identical with that of **1** and **2**; i.e., the room temperature singlet yields a clearly resolved 6:3 pattern at −120 °C. Furthermore, although it has been claimed that the observation of four aryl $^{13}C\text{-}H$ environments in $4\text{-}MeC_6H_4\text{-}CCo(CO)_3Fe_2(\mu\text{-}CO)(CO)_6$ (**9a**) can be interpreted as evidence of slowed rotation of the capping aryl moiety,[8] this phenomenon has been more prosaically explained in terms of the formation of a second isomer **9b** in which the iron–iron vector is unbridged but instead carbonyls now bridge both iron–cobalt bonds.[9] Moreover, it has been unequivocally demonstrated that it is not possible by using peak coalescence techniques to detect slowed aryl rotation in $(C_5H_5)_2Co_3(CO)_4C\text{-}Ar$ systems, even on an 11.7-T instrument at -100 °C! Finally, very recent ^{13}C NMR T_1 measurements on $C_6H_5\text{-}CCo_3(CO)_9$ have shown that the rate of phenyl spinning must be extremely fast on the time scale of NMR line-broadening experiments.[10]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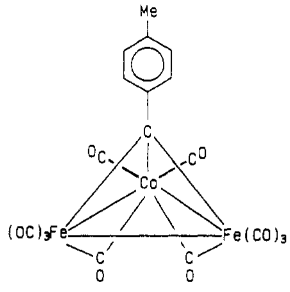
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One is therefore left with the conclusion that the 6:3 ^{13}CO NMR pattern is most readily explicable in terms of slowed axial–equatorial carbonyl exchange, an unprecedented situation in a nonacarbonyltricobalt cluster.[11] However, the separation into six equatorial and three axial ligands at low temperature raises the question as to whether the equatorial carbonyls are still undergoing intermetal migration, presumably via a merry-go-round[12] process. The fact that the ^{13}CO resonances for the chiral cluster $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_9$ (**5**) appear as a 6:3 peak pattern at −120 °C (i.e., a single peak for the six equatorial carbonyls) suggests that the merry-go-round process is still rapid at low temperature. If intermetal exchange were to stop, one would expect to observe a 3:3 splitting of these equatorial ligands, since the chiral nature of the capping fragment in **5** renders diastereotopic each pair of equatorial carbonyls at any individual cobalt vertex. (It is interesting to note that if the low-temperature ^{13}CO NMR spectra of **5** had yielded a 3:3:3 pattern, it would have been difficult to differentiate between the two scenarios outlined above: slowed rotation of the capping group together with the cessation of intermetal exchange but allowing local rotation to continue would also give rise to a 3:3:3 peak splitting.)

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[5] (a) Mann, B. E.; Pickup, B. T. *J. Chem. Soc., Dalton Trans* **1989**, 889 and references therein. (b) Sievert, R. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.

[6] Bank, S.; Sturgess, J. S.; Heyer, D.; Bushweller, C. H. *J. Am. Chem. Soc.* **1980**, *102*, 3982.

[7] Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6426.

[8] Evans, D. G.; Howard, J. A. K.; Jeffrey, J. C.; Lewis, D. B.; Lewis, G. E.; Grosse-Ophoff, M. J.; Parrot, M. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1723.

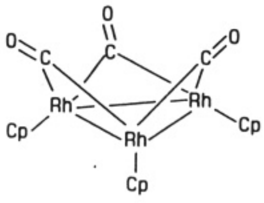
[9] Sutin, K. A.; Faggiani, R.; McGlinchey, M. J. *New J. Chem.* **1988**, *12*, 419.

[10] Wang, S. P.; Chen, A. F. T.; Richmond, M. G.; Schwartz, M. *J. Organomet. Chem.* **1989**, *371*, 81.

[11] It has been reported that the low-temperature ^{13}C NMR spectrum of the cluster $Cl\text{-}CCo_3(CO)_7[P(OEt)_3]_2$ exhibits numerous different environments. This would suggest the cessation of local tripodal rotation; however, the structure of this molecule is still a matter of conjecture: Aime, S.; Botta, M.; Gobetto, R.; Osella, D.; Milone, L. *Gazz. Chim. Ital.* **1987**, *117*, 773.

[12] (a) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083. (b) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

At this juncture we chose to attempt a modification of the elegant experiment of Shapley, who demonstrated unequivocally that the bridging carbonyl ligands in $(C_5H_5)_3Rh_3(\mu\text{-}CO)_3$ (**10**) can migrate around the metal triangle. In that case, each carbonyl exhibits a triplet attributable to coupling to two ^{103}Rh nuclei; upon warming, the ^{13}CO resonance becomes a quartet, since rapid migration allows each carbonyl carbon to interact with all three rhodium atoms.[13] In the tricobalt clusters such an approach is not viable, since although ^{59}Co is 100% abundant with $I = {}^7/_2$, the relatively large quadrupole moment precludes the detection of ^{13}C–^{59}Co coupling constants unless the cobalt nucleus resides in a highly symmetrical environment.[14] However, the incorporation of the 1,1,1-tris(diphenylphosphino)methane ligand (tripod) may alleviate some of these problems. First, replacement of each of the three axial carbonyls by phosphorus-containing ligands provides a direct probe of the molecular symmetry. Thus, in $(4\text{-}CH_3OC_6H_4)_2CH\text{–}CCo_3(CO)_6$(tripod) (**7**) slowed rotation of the capping diarylmethyl fragment would split the ^{31}P resonances into a 2:1 ratio, while in $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{–}CCo_3(CO)_6$(tripod) (**6**) all three phosphorus environments would be nonequivalent. Furthermore, if it were observable, the doublet or quartet character of the ^{13}CO resonance should tell us whether the carbonyl carbon is coupling to only one or all three ^{31}P nuclei, respectively.



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Experimentally, the ^{31}P resonances in both **6** and **7** remain as sharp singlets; furthermore, ^{31}P–^{13}CO coupling is not observed over the entire temperature range from +25 to −120 °C. Nevertheless, the variable-temperature ^{13}C data for the clusters **6**–**8** provide very valuable information that allows us to understand the molecular dynamics of these tripod-containing systems. Considering first the methoxychlor-derived cluster **7**, we see that the initial ^{13}CO singlet splits at low temperature to produce two equally intense singlets; the coalescence behavior yields a barrier $\Delta G^{\ddagger}_{195} \approx 9.1 \pm 0.5$ kcal mol^{-1}. These singlet resonances at 206.6 and 204.7 ppm are clearly attributable to terminally bonded carbonyl ligands, and the situation is quite different from the behavior manifested by $Co_4(CO)_9$(tripod) in which each phosphorus-bearing cobalt is bonded to one terminal (at 202.0 ppm) and two bridging carbonyls (at 254.6 ppm), as in **11**.[15] The chiral molecule $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{–}CCo_3(CO)_6$(tripod) (**6**) behaves in an identical manner to give a 3:3 splitting of ^{13}CO peaks at −120 °C.

We suspected that the environment of the six equatorial carbonyl ligands in **7** had been lowered from effective C_{3v} symmetry to C_3. This could be accomplished by freezing out the orientations of the diphenylphosphino moieties in a propeller conformation. To check this hypothesis, crystals of $(4\text{-}CH_3OC_6H_4)_2CH\text{-}CCo_3(CO)_6$(tripod) (**7**) were prepared for characterization by X-ray diffraction techniques. However, in the latter stages of refinement, a disorder problem prevented the structure from being refined to an acceptable *R* value, and so we prefer not to claim accurate bond parameters. Nevertheless, as shown in Figure 1, the gross molecular structure matches that anticipated from the NMR data. The six phenyls of the tripod ligand are canted away from the vertical position by 32 ± 8° in the same direction; this lowers the symmetry of the $Co_3(CO)_6$(tripod) fragment such that it has only an (approximate) 3-fold axis. Thus, the six terminal carbonyls are separated into two sets of three, which, in principle, can be interconverted via oscillations of the phenyl rings attached to the phosphorus atoms, as shown in Scheme I and discussed in more detail below.

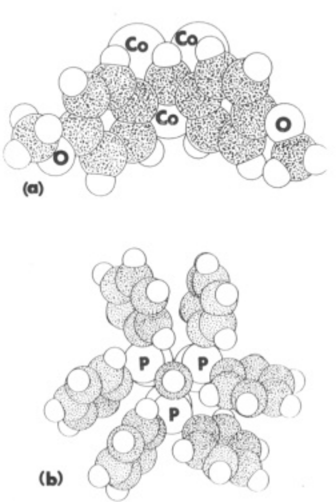
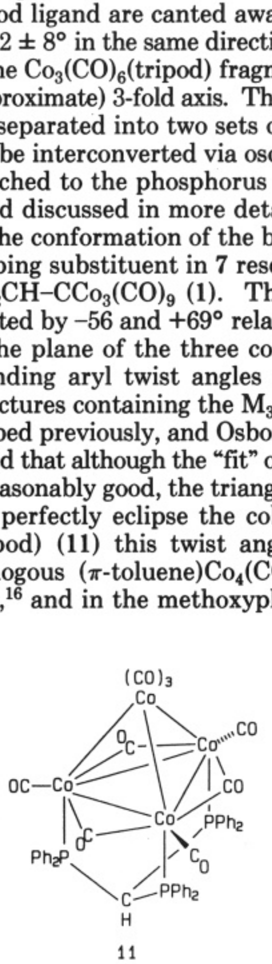


Figure 1. Space-filling models of (a) the staggered orientation of the (bis(4-methoxyphenyl)methyl)carbynyl capping group in $(4\text{-}CH_3OC_6H_4)_2CH\text{–}CCo_3(CO)_6$(tripod) (**7**) and (b) the propeller-type orientation of the phenyl rings of the tripod ligand in **7**.

The conformation of the bis(4-methoxyphenyl)methyl capping substituent in **7** resembles that seen in $(4\text{-}ClC_6H_4)_2CH\text{–}CCo_3(CO)_9$ (**1**). The methoxyphenyl rings are twisted by −56 and +69° relative to an axis perpendicular to the plane of the three cobalt atoms. In **1** the corresponding aryl twist angles are −58 and +83°.[1] Other structures containing the $M_3(CO)_6$(tripod) have been described previously, and Osborn[16] and Darensbourg[15] have noted that although the "fit" of the tripod to the metal base is reasonably good, the triangle of phosphorus atoms does not perfectly eclipse the cobalt triangle. In $Co_4(CO)_9$(tripod) (**11**) this twist angle is 3.8°,[15] in the closely analogous (π-toluene)$Co_4(CO)_6$(tripod) system **12** it is 4.3°,[16] and in the methoxyphenyl cluster **7** it is 5.9°.



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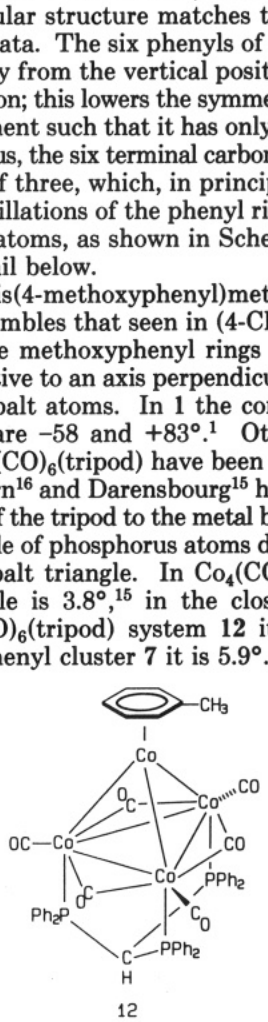

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[13] Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433.

[14] (a) Laszlo, P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 253–274. (b) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; pp 225–244.

[15] Darensbourg, D. J.; Zalewski, D. J.; Delord, T. *Organometallics* **1984**, *3*, 1210.

[16] Bahsoun, A. A.; Osborn, J. A.; Voelken, C.; Bonnet, J. J.; Lavigne, G. *Organometallics* **1982**, *1*, 1114.

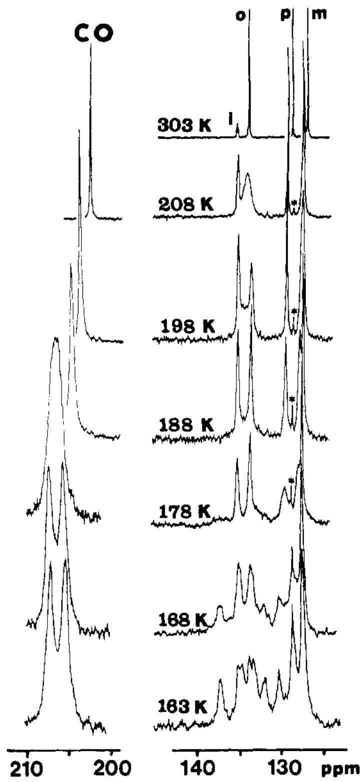


Figure 2. Sections of the 125-MHz ^{13}C variable-temperature NMR spectra of CH_3–$CCo_3(CO)_6$(tripod) (8), showing the coalescence behavior of the carbonyl peaks and of the phenyl resonances. A small impurity peak is marked with an asterisk.

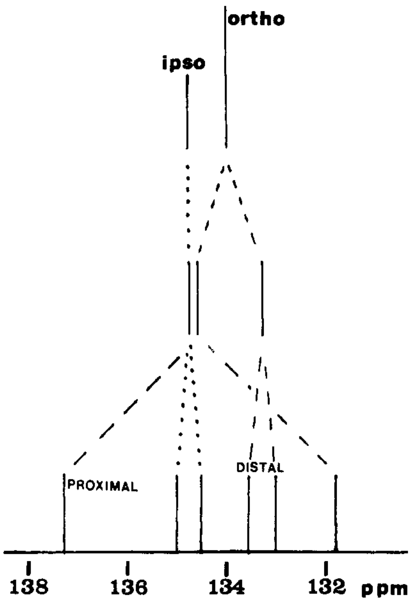
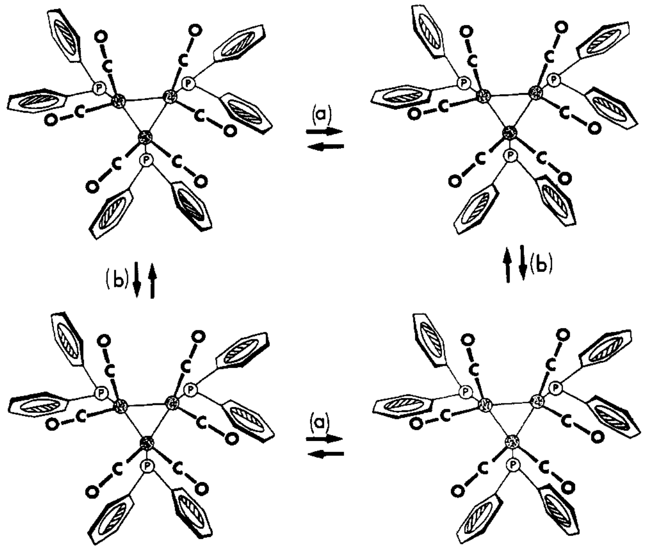


Figure 3. Schematic representation of the coalescence behavior of the ortho and ipso carbon-13 resonances of 8.

Scheme I. Two Fluxional Mechanisms Available to the Phenyl Rings of the tripod Ligand[a]



[a] (a) Enantiomerization of the cluster via oscillation through ±30° so as to render equivalent the two types of proximal (distal) edges ($\Delta G^{\ddagger} \approx 8$ kcal mol^{-1}) and (b) complete rotation of the phenyl rings through 180° so as to interconvert proximal and distal environments ($\Delta G^{\ddagger} \approx 10$ kcal mol^{-1}).

The observation of the propeller conformation adopted by the diphenylphosphino units in 7 prompted us to measure the barrier to phenyl rotation in such a system. In principle, this could be accomplished by following the ^{13}C NMR coalescence behavior of the ortho and meta ring carbon nuclei of the $(C_6H_5)_2P$ units. However, the overlap of these diphenylphosphino resonances with those of the diarylmethyl capping groups in 6 and 7 precluded such a study, and so instead we synthesized CH_3–$CCo_3(CO)_6$(tripod) (8), in which the phenyl ring peaks were no longer obscured.

As was the case for 6 and 7, the room-temperature ^{13}CO singlet resonance in 8 underwent decoalescence at low temperature to give two equally intense peaks. The Gutowsky–Holm approximation yields an activation energy barrier $\Delta G^{\ddagger}_{173} = 7.9 \pm 0.4$ kcal mol^{-1}. Moreover, as shown in Figure 2, the ortho and meta and ipso carbons of the diphenylphosphino rings also exhibit fluxional behavior. In particular, the clear separation of the ortho ring carbon peaks at −110 °C allows these fluxional processes to be understood in some detail. The initial ortho singlet at 134.1 ppm broadens upon cooling and then splits into two peaks yielding a $\Delta G^{\ddagger}_{213}$ value of approximately 9.9 ± 0.4 kcal mol^{-1}. As shown schematically in Figure 3, these peaks subsequently underwent further decoalescence to give a closely spaced pair of peaks (at 133.5 and 133.1 ppm) and also a more widely separated pair (at 131.7 and 137.0); the $\Delta G^{\ddagger}_{183}$ value for this process is approximately 8.0 ± 0.5 kcal mol^{-1}. Concomitantly, the ipso carbons at 135.5 ppm (which are readily recognized by their low intensity and by their coupling to the ^{31}P nuclei) also split at low temperature as do the meta carbons.

This fluxional behavior can be rationalized in terms of the two processes depicted in Scheme I. The higher activation energy is presumably a measure of the barrier to phenyl rotation through π radians and so distinguishes the phenyl ring edges that are *distal* to the tricobalt plane from those that are *proximally* oriented. The second (i.e., the lower energy) process must break the molecular symmetry from C_{3v} to C_3. That is, the 10 kcal mol^{-1} process slows phenyl rotation (and thus differentiates between the edges of any given ring) but leaves these aryl groups free to oscillate about the three vertical mirror planes. The 8 kcal mol^{-1} barrier slows the enantiomerization process (i.e., the interconversion of the propellers) and consequently splits the six phenyl rings into two sets of three. We assign the *closely spaced* pair of ortho carbon resonances to those ring edges that are distal with respect to the array of cobalt carbonyl ligands. This leaves the *widely spaced* pair of ortho carbon resonances at 168 K as those positioned *proximal* to the cobalt plane; their relatively large chemical shift difference presumably is a consequence of the diamagnetic anisotropy of the carbonyl ligands.[17] This pic-

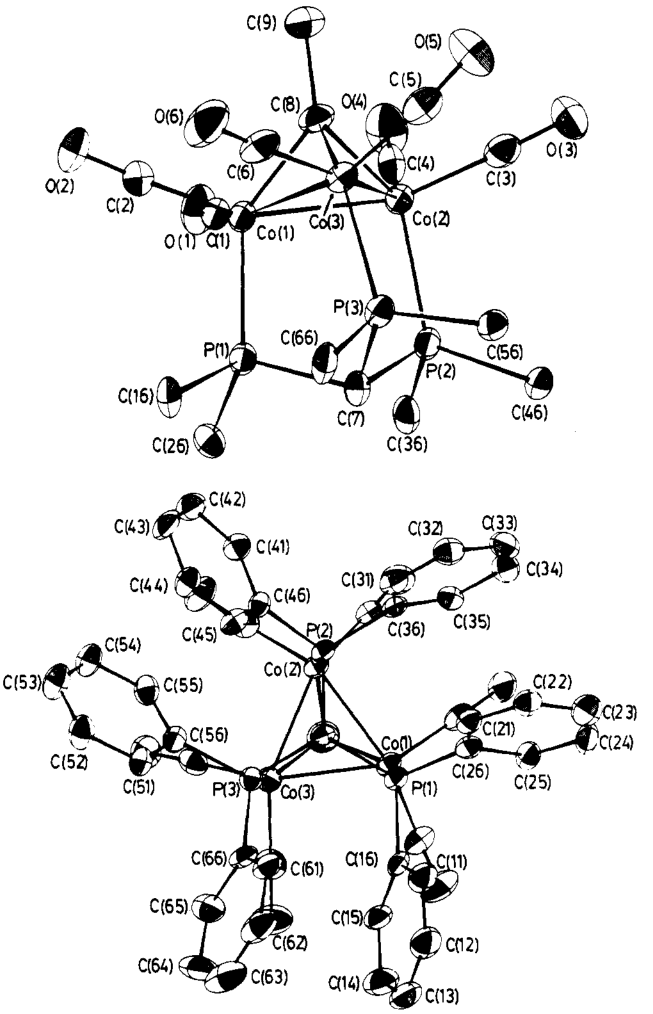


Figure 4. Two views of the structure of CH_3–$CCo_3(CO)_6$(tripod) (8), showing (a, top) the coordination of tripod (phenyl rings omitted for clarity) to the triangle of cobalts, each of which bears two terminally bonded carbonyl ligands, and (b, bottom) the propeller-like orientation of the phenyl rings of the tripod ligand. Note also the twist of the phosphorus triangle relative to the trimetallic base of the cluster.

ture is consonant with the observed barrier to carbonyl exchange, since the ΔG^{*} values for the CO ligands and for ring oscillation overlap within the experimental error limits. However, we cannot claim that these two fluxional process are necessarily correlated. It could simply be that the barrier to intermetal migration of the carbonyls is greater than 8 kcal mol^{-1}, but we can only detect that the CO ligands are no longer moving when the tripod propellers are interconverting slowly on the NMR time scale.

Crystals of CH_3–$CCo_3(CO)_6$(tripod) (8) suitable for X-ray diffraction were obtained, and the resulting molecular structure is depicted in Figure 4. In contrast to 7, which had a disorder problem, the methyl cluster 8 yielded a good data set, which refined in a satisfactory manner. The general structural features are in accord with those of related molecules. The cobalt–cobalt distances in 8 average 2.484 Å, slightly longer than the average values of 2.457 and 2.447 Å in $Co_4(CO)_9$(tripod) (11) and (π-toluene)-$Co_4(CO)_6$(tripod) (12), respectively. Likewise, the Co–P distances (average 2.243 Å) are somewhat longer than in 11 (2.206 Å) and 12 (2.188 Å). As seen already for 7, 11, and 12, the Co(1), Co(2), Co(3) triangle is not perfectly eclipsed by the P(1), P(2), P(3) triangle; in 8 this twist angle is 6.8°. Apparently, the increased cobalt–cobalt bond lengths in R–$CCo_3(CO)_9$ and related systems compared to the basal–basal distances in the tetracobalt clusters 11 and 12 make the "fit" of the tridentate ligand a less good match. Consequently, it seems necessary not only to stretch the cobalt–phosphorus linkages but also to increase the twist of the triangle of phosphorus atoms relative to the cluster base from ≈4 to ≈7°. From the present perspective, the critical observation is that the phenyl rings of the tripod ligand are indeed twisted in a conrotatory manner by approximately 30° from the vertical mirror planes. It is this propeller-like symmetry of the tripod ligand that renders diastereotopic the pairs of carbonyls on the cobalt vertices.

We note that in the $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH$–$CCo_3(CO)_6$(tripod) cluster 6 the cessation of intercobalt migration should split the degeneracy of each pair of carbonyls. Indeed, the inherent chirality of each individual molecule of 6, in conjunction with the asymmetry introduced by the direction of twist of the tripod ligand, should yield a *diastereomeric* rather than an *enantiomeric* mixture. One might thus expect to see not merely a 3:3 splitting of the carbonyl environments but instead two sets of equally intense peaks. Since 6 exhibits only a single 3:3 peak pattern, we must conclude that the major contribution to the chemical shift difference between the carbonyls is their orientation relative to the diphenylphosphino moiety rather than their proximity to a chiral center. Thus, a definitive answer to the problem of slowed $Co(CO)_3$ versus carbynyl group rotation in R–$CCo_3(CO)_9$ clusters would perhaps require a chiral cap in which the three substituents were very different in character. Nevertheless, the single ^{31}P NMR resonance in the tripod systems even at low temperature establishes that carbynyl group rotation is still rapid in these clusters.

To conclude, the use of very bulky capping groups at the carbynyl-carbon position in R–$CCo_3(CO)_9$ clusters raises the barrier to axial–equatorial carbonyl exchange into the regime whereby it is detectable by using NMR line-broadening techniques. Rotation of the capping group cannot be slowed on the time scale of NMR line-broadening experiments. In R–$CCo_3(CO)_6$(tripod) complexes the phenyl rings of the phosphine ligand exhibit two fluxional processes. The cessation of complete rotation of these phenyl groups through 180° renders the edges of the rings inequivalent and has an activation energy barrier of approximately 10 kcal mol^{-1}. The second process, which involves small (≈±30°) oscillations of the rings, has a barrier of ≈8 kcal mol^{-1}. This lower energy process, which interconverts tripod propeller conformations, also leads to racemization of the clusters.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[18] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded by using Bruker AM 500 and WM 250 spectrometers. ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane, while ^{31}P chemical shifts were referenced to 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using KBr solution cells. Mass spectra were obtained with a double-focusing VG ZAB-E mass spectrometer under positive ion fast atom bombardment (FAB+) conditions. 3-Nitrobenzyl alcohol was used as the matrix, and xenon was the bombarding species (8 keV). Microanalytical data are from Guelph Chemical Lab-

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$(4\text{-}CH_3OC_6H_4)_2CH\text{-}CCo_3(CO)_9$ (2) and $CH_3\text{-}CCo_3(CO)_9$ were prepared according to published procedures.[1,19]

$(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_9$ (5). A solution of $Co_2(CO)_8$ (1.74 g, 5.09 mmole) and *o,p'*-DDT (1.00 g, 2.84 mmol) in THF (35 cm^3) was stirred at reflux under an atmosphere of N_2 for 3 h. The solution was allowed to cool to room temperature and filtered (under N_2 pressure) to remove any insoluble species. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (eluent, ether/petroleum ether, 15:85). The first band, an oily purple material, was recrystallized from hexane to give **5** as purple crystals (0.815 g, 1.20 mmol, 48.4%). ^1H NMR (acetone-d_6): δ 7.75 (m, 8 H, phenyl *H*'s) and 6.82 (s, 1 H, Ar-C*H*-Ar). ^{13}C NMR (CH_2Cl_2) (25 °C): δ 199.6 (*C*O's); δ 143.9, 142.5, 133.4, 130.2, 130.0, 129.8, 129.0, 128.7, 127.1 (phenyl carbons); δ 70.7 (Ar-CH-Ar). ^{13}C NMR (carbonyl region) ($CH_2Cl_2/CFCl_3$) (−120 °C): δ 202.6 (3, axial CO's) and 198.3 (6, equatorial CO's). IR (CH_2Cl_2): ν_{CO} at 2100 (m), 2050 (vs), 2040 (vs), and 2020 (s) cm^{-1}. Mass spectrum (FAB+): *m/z* (%) 648 (14), $C_{22}H_9O_8Cl_2Co_3$, $(M - CO)^+$; 620 (20), $(M - 2CO)^+$; 592 (16), $(M - 3CO)^+$; 564 (100), $(M - 4CO)^+$; 536 (44), $(M - 5CO)^+$; 508 (8), $(M - 6CO)^+$; 480 (9), $(M - 7CO)^+$; 452 (24), $(M - 8CO)^+$; 424 (55), $(M - 9CO)^+$; 389 (8), $(M - 9CO - Cl)^+$. Anal. Calcd for $C_{23}H_9O_9Cl_2Co_3$: C, 40.80; H, 1.34. Found: C, 40.63; H, 1.54.

$(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_6$(tripod) (6). A solution of $(2\text{-}ClC_6H_4)(4\text{-}ClC_6H_4)CH\text{-}CCo_3(CO)_9$ (5) (0.60 g, 0.89 mmol) and $(Ph_2P)_3CH$ (0.506 g, 0.90 mmol) in toluene (50 cm^3) was stirred under an atmosphere of N_2 at 70 °C for 24 h and then at 85 °C for a further 48 h. After the solution was cooled to room temperature and the toluene was evaporated, the residue was filtered through silica gel (eluent CH_2Cl_2) to give a crude product. Recrystallization from CCl_4, followed by flash chromatographic purification on silica gel (eluent ether/petroleum ether, 40:60), yielded **6** as a red solid (0.079 g, 0.068 mmol, 7.6%). ^{31}P NMR (CH_2Cl_2): (−30 °C) δ 44.9; (−110 °C) δ 45.0. ^{13}C NMR (carbonyl region) ($CH_2Cl_2/CFCl_2$): (25 °C) δ 205.8 (6 CO's); (−120 °C) δ 206.6 (3 CO's), 204.6 (3 CO's). IR (CH_2Cl_2): ν_{CO} at 2020 (m), 2000 (vs), and 1965 (sh) cm^{-1}. Mass spectrum (FAB+): *m/z* (%) 1160 (6), $C_{57}H_{40}O_6Cl_2P_3Co_3$, $(M)^+$; 1048 (8), $(M - 4CO)^+$; 1020 (100), $(M - 5CO)^+$; 992 (25), $(M - 6CO)^+$. Anal. Calcd for $C_{57}H_{40}O_6Cl_2P_3Co_3$: C, 58.94; H, 3.47; P, 8.00. Found: C, 58.66; H, 3.60; P, 7.71.

$(4\text{-}CH_3OC_6H_4)_2CH\text{-}CCo_3(CO)_6$(tripod) (7). A solution of $(4\text{-}CH_3OC_6H_4)_2CH\text{-}CCo_3(CO)_9$ (2) (0.486 g, 0.73 mmol) and $(PPh_2)_3CH$ (0.417 g, 0.73 mmol) in toluene (100 cm^3) was stirred at 70 °C under an atmosphere of N_2 for 14 h. After, the solvent was removed, flash chromatograpphic purification of the residue (initial eluent ether/hexane, 30:70; final eluent ether/hexane, 50:50) yielded a red-brown solid. The impurities were removed by dissolving this solid in a minimum amount of CCl_4 and filtering the slurry through glass wool to give **7** (0.035 g, 0.030 mmol, 4.1%) as red crystals. ^{31}P NMR (CH_2Cl_2): (25 °C) δ 45.5; (−100 °C) δ 45.1. ^{13}C NMR (carbonyl region) ($CH_2Cl_2/CFCl_3$): (−65 °C) δ 206.0 (CO's); (−110 °C) δ 206.6 (3 CO's) and 204.7 (3 CO's). IR (CH_2Cl_2): ν_{CO} at 2010 (m), 1990 (vs), and 1960 (sh) cm^{-1}. Mass spectrum (FAB+): *m/z* (%) 1152 (10), $C_{59}H_{46}O_8P_3Co_3$, $(M)^+$; 1124 (8), $(M - CO)^+$; 1097 (22), $(M + H - 2CO)^+$; 1068 (12), $(M - 3CO)^+$; 1041 (32), $(M + H - 4CO)^+$; 1013 (44), $(M + H - 5CO)^+$; 1012 (68), $(M - 5CO)^+$; 984 (100), $(M - 6CO)^+$. Anal. Calcd for $C_{59}H_{46}O_8P_3Co_3$: C, 61.48; H, 4.02; P, 8.06. Found: C, 61.70; H, 4.09; P, 8.23.

$CH_3\text{-}CCo_3(CO)_6$(tripod) (8). A solution of $CH_3\text{-}CCo_3(CO)_9$(0.950 g, 2.08 mmol) and $(Ph_2P)_3CH$ (1.03 g, 1.81 mmol) in toluene (60 cm^3) was stirred under an atmosphere of N_2 at 70 °C for 12 h. After the solvent was evaporated, the residue was purified by flash chromatography on silica gel (eluent ether/petroleum ether, 40:60) to yield **8** as red crystals (0.216 g, 0.23 mmol, 12.7%). ^{31}P NMR (CH_2Cl_2) (25 °C): δ 46.2. ^1H NMR (acetone-d_6): δ 7.4 (m, 12 H), 6.8 (m, 18 H), 4.05 (q, 1 H), 2.7 (s, 3 H). ^{13}C NMR (THF): δ (25 °C) δ 206.1 (*C*O's); δ 135.5 (ipso C's); δ 134.1 (ortho C's); δ 129.0 (para C's); δ 127.3 (meta C's); δ 47.6 (CH_3); (−110 °C) δ 207.4 (3 CO's); δ 205.7 (3 CO's); δ 137.0, 131.7 (proximal ortho C's); δ 134.8, 134.4 (ipso C's); δ 133.5, 133.1 (distal ortho C's); δ 130.0, 128.4, 127.2 (meta and para C's). IR (CH_2Cl_2): ν_{CO} at 2020 (s), 2000 (vs), and 1960 (sh) cm^{-1}. Mass spectrum (FAB+): *m/z* (%) 941 (10), $C_{45}H_{35}O_6P_3Co_3$, $(M + H)^+$; 912 (5), $(M - CO)^+$; 884 (7), $(M - 2CO)^+$; 856 (74), $(M - CO)^+$; 825 (54), $(M - 4CO)^+$; 800 (35), $(M - 5CO)^+$; 772 (100), $(M - 6CO)^+$. Anal. Calcd for $C_{45}H_{34}O_6P_3Co_3$: C, 57.47; H, 3.64; P, 9.88. Found: C, 57.66; H, 3.43; P, 9.51.

Table I. Crystal Data for $CH_3C\text{-}Co_3(CO)_6$(tripod) (8)

formula	$C_{45}H_{34}O_6P_3Co_3$
fw	940.48
system	monoclinic
systematic absences	$h0l$, $h + l = 2n$; $0k0$, $k = 2n$
space group	$P2_1/n$ (No. 14)
a, Å	16.359 (4)
b, Å	13.317 (3)
c, Å	18.728 (4)
β, deg	92.24 (2)
V, $Å^3$	4076 (2)
Z	4
temp, °C	−80.0
D_c, g cm^{-3}	1.53
D_m, g cm^{-3}	1.48
$F(000)$	1917.27 (1912)
μ(Mo Kα), cm^{-1}	14.19
final R_1, R_2[a,d]	0.0682, 0.0728
weighting scheme	$w = (\sigma^2F + 0.002217F^2)^{-1}$
error in observn of unit wt[b]	1.2222
highest peak, e $Å^{-3}$; location	0.92; 0.0249, 0.0896, 0.2386[c]
lowest peak, e $Å^{-3}$	−1.11

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)$. [b] $S = (\sum w(|F_o| - |F_c|)^2/(m - n))$; m = no. of reflections, n = no. of variables. [c] 1.33 Å from Co(1). [d] R_1 and R_2 for 3884 reflections with $I > 2.5\sigma(I)$ are 0.0527 and 0.0566, respectively.

Determination of the Structure of $CH_3\text{-}CCo_3(CO)_6$(tripod) (8). Crystals of $[(HC(Ph_2P)_3Co_3(CO)_6CCH_3]$ (8) were grown from CH_2Cl_2/pentane. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Reddish/purple prismatic crystals were examined under a polarizing microscope for homogeneity. A well-formed crystal, 0.3 × 0.3 × 0.4 mm, was selected and mounted on the tip of a glass fiber with use of epoxy cement. Unit cell parameters were obtained at −80 °C from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range ($18.1° < 2\theta < 25.8°$) recorded on a Nicolet P3 diffractometer with use of graphite-monochromated Mo Kα radiation (λ = 0.71069 Å at 22 °C). Intensity data were also recorded on a Nicolet P3 diffractometer at −80 °C with use of ω scans, for 5871 reflections in the quadrant ($h,k,\pm l$) with $2\theta \leq 45°$. The method of selection of scan rates and initial data treatment have been described.[20,21] Corrections for Lorentz–polarization effects were applied to all reflections. Two standard reflections (4,4,8 (2.1%) and -6,4,8 (1.85%)) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (296) were excluded, and 459 symmetry-equivalent data were then averaged (R_{int} = 0.0147) to give 5116 unique reflections. A summary of crystal data is given in Table I.

The coordinates of the cobalt atoms were found from a three-dimensional Patterson synthesis with use of the program SHELXS-86.[22] Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms and confirmed the positional assignments for the heavy atoms. After refinement the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08 $Å^2$). Further refinement using

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Table II. Positional Parameters (×10^4) and U_{eq} (Å^2 × 10^4) for CH$_3$–CCo$_3$(CO)$_6$(tripod) (8) with Standard Errors in Parentheses

atom	x	y	z	U_{eq}[a]
Co(1)	324.8 (4)	894.7 (5)	1581.0 (4)	240
Co(2)	-437.5 (4)	157.6 (5)	2674.6 (3)	237
Co(3)	758.8 (4)	1272.6 (5)	2935.6 (4)	251
P(1)	-373.6 (8)	2334.9 (9)	1563.7 (7)	233
P(2)	-1420.8 (8)	1339.2 (9)	2621.3 (7)	227
P(3)	16.6 (8)	2629.2 (9)	3116.8 (7)	237
C(1)	-132 (3)	68 (4)	1046 (3)	293
O(1)	-412 (3)	-488 (3)	642 (2)	423
C(2)	1230 (4)	1102 (4)	1193 (3)	347
O(2)	1802 (3)	1165 (4)	882 (2)	517
C(3)	-507 (3)	-348 (4)	3538 (3)	313
O(3)	-566 (3)	-724 (3)	4084 (2)	468
C(4)	-757 (3)	-961 (4)	2241 (3)	304
O(4)	-872 (3)	-1747 (3)	2001 (2)	492
C(5)	1055 (3)	811 (4)	3789 (3)	323
O(5)	1295 (3)	461 (3)	4321 (2)	493
C(6)	1716 (4)	1773 (4)	2732 (3)	344
O(6)	2357 (3)	2077 (4)	2605 (3)	546
C(7)	-899 (3)	2563 (4)	2426 (3)	219
C(8)	681 (3)	24 (4)	2440 (3)	281
C(9)	1229 (4)	-860 (4)	2461 (3)	371
C(11)	-208 (4)	4332 (4)	1053 (3)	400
C(12)	232 (5)	5177 (5)	881 (3)	506
C(13)	1074 (5)	5211 (5)	986 (3)	501
C(14)	1481 (4)	4358 (5)	1285 (4)	477
C(15)	1045 (4)	3514 (4)	1456 (3)	351
C(16)	189 (3)	3491 (4)	1349 (3)	279
C(21)	-1894 (3)	2978 (4)	894 (3)	277
C(22)	-2441 (4)	3060 (4)	304 (3)	327
C(23)	-2261 (4)	2599 (5)	-336 (3)	422
C(24)	-1527 (4)	2087 (5)	-397 (3)	404
C(25)	-991 (4)	1989 (4)	194 (3)	313
C(26)	-1168 (3)	2430 (4)	846 (3)	269
C(31)	-2989 (3)	1784 (4)	2005 (3)	280
C(32)	-3609 (3)	1717 (4)	1482 (3)	353
C(33)	-3514 (4)	1087 (4)	901 (3)	382
C(34)	-2822 (4)	510 (4)	847 (3)	338
C(35)	-2206 (3)	570 (4)	1375 (3)	284
C(36)	-2272 (3)	1216 (4)	1949 (3)	268
C(41)	-2311 (3)	746 (4)	3774 (3)	305
C(42)	-2811 (4)	854 (5)	4351 (3)	375
C(43)	-3036 (4)	1803 (5)	4572 (3)	385
C(44)	-2768 (4)	2645 (4)	4215 (3)	330
C(45)	-2269 (3)	2528 (4)	3632 (3)	319
C(46)	-2037 (3)	1585 (4)	3407 (3)	243
C(51)	-538 (3)	3704 (4)	4323 (3)	289
C(52)	-811 (4)	3779 (4)	5023 (3)	393
C(53)	-964 (4)	2935 (5)	5407 (3)	413
C(54)	-826 (4)	1991 (4)	5116 (3)	364
C(55)	-542 (3)	1917 (4)	4432 (3)	326
C(56)	-418 (3)	2764 (4)	4018 (3)	267
C(61)	-46 (4)	4708 (4)	2739 (3)	389
C(62)	302 (5)	5659 (5)	2691 (4)	545
C(63)	1091 (6)	5802 (5)	2941 (4)	653
C(64)	1535 (5)	5022 (6)	3256 (4)	693
C(65)	1191 (4)	4063 (5)	3287 (3)	432
C(66)	406 (4)	3896 (4)	3023 (3)	294

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

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for CH$_3$C–Co$_3$(CO)$_6$(tripod) (8) with Estimated Standard Deviations in Parentheses

(A) Co–Co, Co–P, and Co–C(methylidyne) Distances			
Co(1)–Co(2)	2.483 (1)	Co(1)–P(1)	2.239 (1)
Co(2)–Co(3)	2.490 (1)	Co(2)–P(2)	2.250 (1)
Co(3)–Co(1)	2.480 (1)	Co(3)–P(3)	2.241 (2)
Co(1)–C(8)	1.907 (5)	Co(2)–C(8)	1.908 (5)
Co(3)–C(8)	1.906 (5)		
(B) Co–CO and C–O Distances and Angles			
Co(1)–C(1)	1.765 (5)	C(1)–O(1)	1.142 (7)
Co(1)–C(2)	1.792 (6)	C(2)–O(2)	1.125 (8)
Co(2)–C(3)	1.761 (6)	C(3)–O(3)	1.145 (7)
Co(2)–C(4)	1.767 (6)	C(4)–O(4)	1.152 (7)
Co(3)–C(5)	1.762 (6)	C(5)–O(5)	1.155 (7)
Co(3)–C(6)	1.758 (6)	C(6)–O(6)	1.156 (7)
Co(1)–C(1)–O(1)	178.1 (5)	Co(1)–C(2)–O(2)	175.4 (5)
Co(2)–C(3)–O(3)	176.3 (5)	Co(2)–C(4)–O(4)	170.7 (5)
Co(3)–C(5)–O(5)	174.5 (5)	Co(3)–C(6)–O(6)	178.0 (5)
(C) Angles at Cobalt			
C(8)–Co(1)–Co(2)	49.4 (2)	C(8)–Co(1)–Co(3)	49.4 (2)
C(8)–Co(2)–Co(1)	49.4 (2)	C(8)–Co(2)–Co(3)	49.2 (2)
C(8)–Co(3)–Co(1)	49.5 (2)	C(8)–Co(3)–Co(2)	49.3 (2)
Co(1)–Co(2)–Co(3)	59.8 (1)	C(8)–Co(1)–P(1)	137.2 (2)
Co(2)–Co(3)–Co(1)	59.9 (1)	C(8)–Co(2)–P(2)	138.2 (2)
Co(3)–Co(1)–Co(2)	60.2 (1)	C(8)–Co(3)–P(3)	138.6 (2)
P(1)–Co(1)–Co(2)	98.2 (1)	P(1)–Co(1)–Co(3)	92.6 (1)
P(2)–Co(2)–Co(3)	98.4 (1)	P(2)–Co(2)–Co(1)	94.0 (1)
P(3)–Co(3)–Co(1)	99.5 (1)	P(3)–Co(3)–Co(2)	93.7 (1)
C(8)–Co(1)–C(1)	103.4 (2)	C(8)–Co(1)–C(2)	103.8 (2)
C(8)–Co(2)–C(3)	105.9 (2)	C(8)–Co(2)–C(4)	94.9 (2)
C(8)–Co(3)–C(5)	98.5 (2)	C(8)–Co(3)–C(6)	105.5 (2)
C(1)–Co(1)–Co(2)	92.7 (2)	C(1)–Co(1)–Co(3)	149.7 (2)
C(2)–Co(1)–Co(2)	153.2 (2)	C(2)–Co(1)–Co(3)	103.9 (2)
C(3)–Co(2)–Co(1)	153.2 (2)	C(3)–Co(2)–Co(3)	97.2 (2)
C(4)–Co(2)–Co(1)	97.9 (2)	C(4)–Co(2)–Co(3)	144.1 (2)
C(5)–Co(3)–Co(1)	147.9 (2)	C(5)–Co(3)–Co(2)	99.0 (2)
C(6)–Co(3)–Co(1)	95.5 (2)	C(6)–Co(3)–Co(2)	152.1 (2)
C(1)–Co(1)–P(1)	105.5 (2)	C(2)–Co(1)–P(1)	104.3 (2)
C(3)–Co(2)–P(2)	103.7 (2)	C(4)–Co(2)–P(2)	111.8 (2)
C(5)–Co(3)–P(3)	106.4 (2)	C(6)–Co(3)–P(3)	104.0 (2)
C(2)–Co(1)–C(1)	95.1 (3)	C(4)–Co(2)–C(3)	94.1 (3)
C(6)–Co(3)–C(5)	96.5 (3)		

full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached 0.001. Correction for secondary extinction was made by the method in SHELX-76.[23] Final R_1 = 0.0682 and R_2 = 0.0728 for 5116 reflections. Throughout the refinement, scattering curves were taken from ref 24 and anomalous dispersion corrections from ref 25 were applied to the curve for cobalt. All calculations were performed on a VAX 8650 computer. Programs used were as follows: XTAL,[26] data reduction; SHELXS-86,[21] structure solution; SHELX-76,[23] structure refinement; MOLGEOM,[27] molecular geometry; SNOOPI,[28] diagrams. Final atomic positional parameters are given in Table II; selected bond lengths and bond angles are given in Table III.

Determination of the Structure of (4-CH$_3$OC$_6$H$_4$)$_2$CH–CCo$_3$(CO)$_6$(tripod) (7). Crystals of 7 were grown from CH$_2$Cl$_2$/hexane, and data were collected on a Nicolet P3 diffractometer. The molecular crystallizes in the space group $P2_1/c$, and the unit cell dimensions were determined to be a = 13.834 Å, b = 29.224 Å, and c = 16.816 Å, β = 112.34°. A disorder problem did not allow the R value to be reduced below ≈30%. Nevertheless, all the heavy atoms were found and the structure appears as Figure 1. Bond length data: Co(1)–Co(2) = 2.49 Å, Co(1)–Co(3) = 2.48 Å, Co(2)–Co(3) = 2.51 Å, Co(1)–C(1) = 1.91 Å, Co(2)–C(1) = 1.92 Å and Co(3)–C(1) = 1.89 Å.

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Supplementary Material Available: Tables of cyrstallographic details, least-squares planes, hydrogen positional parameters, bond lengths and bond angles involving hydrogen atoms, and anisotropic thermal parameters (13 pages); a table of structure factors (31 pages). Ordering information is given on any current masthead page.

Tetranuclear Butterfly Cluster Derivatives of SMe_2. Preparation and Structures of $Ru_4(CO)_{13}(SMe_2)$, $H_2Ru_4(CO)_{12}(SMe_2)$, and $HRu_3Co(CO)_{12}(SMe_2)$

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The carbonyl clusters $Ru_4(CO)_{13}(SMe_3)$ (**1**), $H_2Ru_4(CO)_{12}(SMe_2)$ (**2**), and $HRu_3Co(CO)_{12}(SMe_2)$ (**3**) have been obtained in reactions between dimethyl sulfide and tri- or tetranuclear metal carbonyl clusters. These compounds have been characterized by X-ray diffraction studies. **1** crystallizes in space group $P2_1/n$ with $a = 9.406$ (3) Å, $b = 15.393$ (6) Å, $c = 15.812$ (6) Å, $\beta = 92.23$ (3)°, and $Z = 4$; **2**, in space group $P2_1$ with $a = 8.18$ (1) Å, $b = 15.86$ (2) Å, $c = 9.55$ (1) Å, $\beta = 114.6$ (1)°, and $Z = 2$; **3**, in space group $P2_1/n$ with $a = 9.349$ (4) Å, $b = 16.259$ (7) Å, $c = 14.469$ (6) Å, $\beta = 92.04$ (3)°, and $Z = 4$. The compounds are butterfly clusters, in which the four-electron SMe_2 ligand bridges the wing-tip positions. In **1** and **3** one of the carbonyls bridges the hinge of the butterfly; otherwise the compounds contain only terminal carbonyls. The hydrides occupy a wing and the hinge Ru–Ru bond in **2** and a wing Ru–Co bond in **3**. In **3** the cobalt atom is in a hinge position. The chalcogenide derivatives of tetranuclear Ru–Co–Rh cluster compounds show a structural trend depending on the metal composition. Terminal coordination (Co_4, $RuCo_3$, and $RuCo_2Rh$), butterfly structures (Ru_4 and Ru_3Co), or dimerization of clusters ($RuRh_3$) is found.

Introduction

During the last 10 years much attention has been focused on the synthesis and characterization of butterfly clusters. The relationships between tetranuclear clusters and the butterfly clusters have become better understood. The M_4 butterfly skeleton appears to be structurally versatile, and the geometry is determined by the steric and electronic character of the ligands.[1] The reactivity of the metal core and the ligands attached to it has been explored, and the potential applications of butterfly clusters as chemisorption models or as direct catalysts have drawn attention.[2,3]

We have previously studied the substitution reactions of tetrahedral valence isoelectronic mixed-metal clusters $H_xRu_xCo_yRh_z(CO)_{12}$ ($x, y, z = 0$–4, $x + y + z = 4$) with phosphine or XR_2 (X = S, Se, Te, R = alkyl, aryl) ligands.[4-7] These studies revealed the versatility of XR_2 ligands. In $HRuCo_3(CO)_{12}$, $HRuCo_2Rh(CO)_{12}$,[8] or $Co_4(CO)_{12}$,[9] these ligands substitute carbonyls as terminal two-electron donors. With $HRuRh_3(CO)_{12}$, dialkyl chalcogen ligands act as four-electron donors, forming unusual dimeric structures $[HRuRh_3(CO)_9]_2[XMe_2]_3$.

In this work we have found that when the ruthenium content of the cluster is increased, butterfly formation becomes the most favorable reaction type. SMe_2 acts as a four-electron donor and causes a Ru–Ru bond breaking.

Results and Discussion

$Ru_4(CO)_{13}(SMe_2)$ (**1**) was prepared in the reaction between $Ru_3(CO)_{12}$ and SMe_2. Refluxing in tetrahydrofuran solvent produces **1** in 30% yield in a few hours—in dichloromethane the reaction does not occur in reasonable times.

Table I. Atomic Coordinates (×10⁴) for $Ru_4(CO)_{13}(SMe_2)$ (1)

atom	*x*	*y*	*z*
Ru(1)	1732 (1)	1887 (1)	6780 (1)
Ru(2)	−210 (1)	1297 (1)	7968 (1)
Ru(3)	551 (1)	3058 (1)	7978 (1)
Ru(4)	−1967 (1)	2549 (1)	7075 (1)
S(1)	−351 (1)	2276 (1)	5987 (1)
O(1)	2250 (6)	209 (3)	5821 (3)
O(2)	4040 (5)	1496 (3)	8134 (3)
O(3)	3785 (5)	2946 (3)	5733 (3)
O(4)	−1355 (6)	−61 (3)	6726 (3)
O(5)	1863 (6)	−61 (3)	8704 (4)
O(6)	−2487 (5)	890 (3)	9240 (3)
O(7)	−490 (7)	4145 (4)	9450 (4)
O(8)	3618 (5)	3702 (3)	7978 (3)
O(9)	−371 (6)	4605 (3)	6892 (3)
O(10)	−4146 (5)	1203 (3)	6511 (3)
O(11)	−3236 (5)	2897 (3)	8773 (3)
O(12)	−3615 (5)	4053 (3)	6227 (3)
O(13)	1468 (5)	2024 (3)	9570 (3)
C(1)	2040 (6)	828 (4)	6183 (4)
C(2)	3146 (6)	1637 (4)	7634 (3)
C(3)	2986 (6)	2581 (4)	6126 (4)
C(4)	−943 (6)	485 (4)	7164 (3)
C(5)	1131 (6)	451 (4)	8415 (4)
C(6)	−1649 (6)	1075 (4)	8774 (3)
C(7)	−154 (7)	3740 (4)	8907 (4)
C(8)	2481 (7)	3436 (4)	7971 (3)
C(9)	−145 (8)	3948 (4)	7214 (4)
C(10)	−3328 (6)	1700 (4)	6717 (4)
C(11)	−2720 (6)	2760 (4)	8145 (3)
C(12)	−2988 (6)	3493 (4)	6520 (4)
C(13)	966 (6)	2151 (3)	8906 (3)
C(21)	−950 (6)	1485 (4)	5202 (3)
C(22)	−121 (6)	3180 (4)	5280 (3)

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