Complexation of Triangular Faces of Tetranuclear Clusters by the Tripod Ligands $HC(PPh_2)_3$ and $HC(AsPh_2)_3$. Molecular Structure of (π-toluene)[$HC(PPh_2)_3$]$Co_4(CO)_6$

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Received April 5, 1982

The tripod ligands $HC(PPh_2)_3$ and $HC(AsPh_2)_3$ are found to complex three metal atoms on the triangular face of tetrahedral clusters $M_4(CO)_{12}$ (M_4 = Co_4, Rh_4, Ir_4, Co_2Rh_2, $HFeCo_3$) to produce the new capped cluster species $M_4(CO)_9$(tripod). These new complexes show enhanced stability relative to the parent clusters. The molecular structure of the derivative (π-toluene)$Co_4(CO)_6$[$HC(PPh_2)_3$] shows the tripod ligand to fit well with the carbonyl-bridged triangular face of the three Co atoms, the toluene molecule being π bonded to the apical Co atom.

Introduction

Metal clusters have received much attention lately for several reasons. First, clusters have been isolated of increasing nuclearity, many of which possess fascinating and new structural forms.[1] Second, these structures bear a strong resemblance to small metal crystallites, and consequently, it is hoped that some of the catalytic properties of the latter might be reproduced by analogous molecular clusters in homogeneous solution.[2] These aspirations have yet to be realized, but model reaction chemistry has revealed a variety of polymetallic–substrate interactions unknown to mononuclear systems, which indicate that new catalytic reactions based on polymetallic complexes continue to be a feasible proposition.

Two major problems are evident for the chemist working with clusters. First, the synthesis of new clusters have been largely by happenstance, and directed strategies for their synthesis have not been widely developed.[3] Second, in reactivity and catalytic studies, clusters often undergo fragmentation, giving rise to unsaturated mononuclear species which are indeed the source of the reactivity of the complex.[4] Hence the cluster is not demonstrating polymetallic reactivity or catalysis in these cases. This fragmentation arises from the fact that metal–metal and metal–carbonyl bond energies are often comparable and hence metal–metal bond breaking is competitive with substitution processes. We would thus define a bona fide catalytic reaction of a cluster as one in which (a) the nuclearity (but not necessarily the architecture) of the cluster is maintained during the catalytic cycle and (b) more than one transition-metal center is *directly* involved in the catalytic process.

We therefore have sought by the use of suitably designed polydentate ligands to hold several metals in close proximity—ideally at a metal–metal bond distance. For the stabilization of triangular arrays of metal atoms of which most metal cluster frameworks are constructed, we have synthetized and studied a family of tripod ligands, $RC(L_1L_2L_3)$, where L_1, L_2, and L_3 are donor functions such as PR_2, AsR_2, and SR. Models show that (i) the bite angle of such a tripod ligand favors the binding of three metal atoms rather than chelation about a single metal as found for other well-known tripod ligands,[5] (ii) that the L_1–L_n distances in such a conformation is comparable (ca. 2.7 Å) to that of a metal-metal single bond, thus presenting a good fit for a triangular array of bonded metals.

In this paper, we present the synthesis of two members of this ligand family $HC(PPh_2)_3$ (1) (hereafter referred to as the *tripod* ligand) and $HC(AsPh_2)_3$ (2) and describe reactions of these ligands with some tetranuclear clusters of the type $M_4(CO)_{12}$.[6] We describe also the X-ray structure of a Co_4 cluster containing a coordinated tripod ligand. Further papers will describe reaction of the tripod ligand with other tetranuclear (e.g., $H_4Ru_4(CO)_{12}$,[7] hexanuclear (e.g., $Rh_6(CO)_{16}$), and trinuclear (e.g., $Os_3H_2(CO)_{10}$) species as well as the use of the tripod ligand for template synthesis.[8] After this work was initiated, Masters reported the reaction of an analogous ligand, $CH_3Si(P\text{-}n\text{-}Bu_2)_3$, with $Ru_3(CO)_{12}$, which indeed gave the "capped" product as shown by an X-ray structure.[9]

Results and Discussion

(a) The Tripod Ligand $HC(PPh_2)_3$ (1). The synthesis of 1 was by an unexceptional route, viz., eq 1. 1 had been

$$\begin{tikzcd} PPh_2CH_2PPh_2 \arrow[r, "\text{Li-}n\text{-Bu}", "\text{TMEDA}"'] & Ph_2PCHPPh_2^{-} + Li(TMEDA)^{+} \arrow[d, "PPh_2Cl"] \\ & HC(PPh_2)_3 \quad (\text{ca } 80\% \text{ yield}) \end{tikzcd} \tag{1}$$

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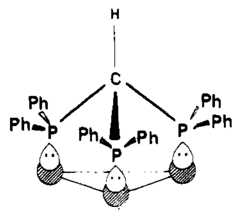

Figure 1. The tripod ligand HC(PPh$_2$)$_3$.

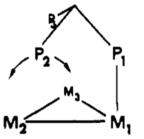

Figure 2. Stepwise substitution of the triangular array of cluster by the tripod ligand.

previously reported,[10] and we have confirmed its formulation by ^{31}P NMR (^{31}P{^{1}H} spectrum is a sharp singlet at −9.4 ppm) and mass spectral studies (parent ion at *m/e* 568). 1 is thus easily prepared and is equally easily handled (colorless crystals, only slowly oxidized in air) and has simple practical advantages in use compared with its analogues MeSi(P-*n*-Bu$_2$)$_3$[9] or HC(PMe$_2$)$_3$.[11] It can be further functionalized via deprotonation of the bridging carbon and hence also attached to polymer supports.

(b) The Tripod Ligand HC(AsPh$_2$)$_3$ (2). The synthesis above can also clearly be generalized to other tripod ligands involving different donor function L. Thus we have synthetized by a similar route the tripod ligand HC(AsPh$_2$)$_3$ (2) which has been well characterized (e.g., ^{1}H NMR and MS; see Experimental Section).

(c) Tripod Complexation of Tetranuclear Complexes. (i) Initial Considerations. Although we have represented the tripod ligand in a conformation favorable for complexation of a triangular array of metal atoms, molecular models show that other conformations of the free ligand may be more stable and that stepwise complexation to 1 could be severely impeded by steric crowding of the phenyl groups. Therefore, to test that 1 can complex three metal atoms, we chose to study its reactions with triangular faces of known clusters.

Initially we chose to study the reactivity of 1 with the known triangular cluster Ru$_3$(CO)$_{12}$. However, we (as Masters[9]) found these reactions to be more complicated than anticipated. The desired capped product Ru$_3$(CO)$_9$(tripod) could be obtained in only low yield (ca. 15%) from the 1:1 reaction mixture after chromatography.[7] At least four other products could be detected by ^{31}P NMR spectroscopy, in some of which ligand transformations had clearly occurred.[12] However, further consideration of the substitution patterns of Ru$_3$(CO)$_{12}$ offers reasons why capping is likely to be inefficient in this case. As substitution of a triangular complex by the tripod ligand presumeably proceeds stepwise, two difficulties arise. First, substitution must be axial or alternatively the axial substitution product must be reasonably accessible via equatorial to axial isomerization. The preferred substitution in Ru$_3$(CO)$_{12}$ by phosphines is equatorial.[13] Second, even if axial substitution is achieved for the first substitution of 1, the second phosphine P$_2$ can bind two sites, M$_2$ or M$_3$ (see Figure 2); the desired path (P$_2$ → M$_2$) appeared to be the least favored sterically. Of course, if such substitutions are readily reversible, such arguments are no longer valid, but it appears that trinuclear systems such as Ru$_3$(CO)$_{12}$ are not a good test of the potentialities of 1 as a ligand for a triangular array of metal atoms.

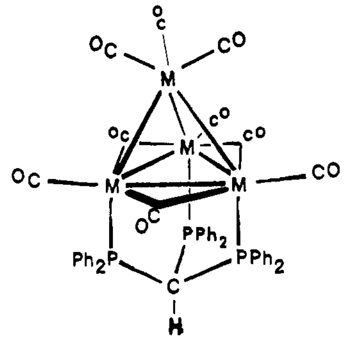

Figure 3. C_{3v} structure proposed for the M$_4$(CO)$_9$(tripod) cluster.

Tetrahedral (and octahedral) clusters, which possess a threefold axis passing *through* the point of the first substitution, do not impose such strict stereochemical problems to substitution. Consequently we have tested the tripod ligands for their capping properties on such systems.

(ii) Synthesis and the Proposed Structure of M$_4$(CO)$_9$(tripod). The reaction of 1 molar equiv of the ligand tripod with M$_4$(CO)$_{12}$ clusters in the refluxed hydrocarbon (M$_4$ = Co$_4$, HFeCo$_3$, Ir$_4$) or at room temperature (toluene–hexane) (M$_4$ = Rh$_4$, Co$_2$Rh$_2$) yields good yields of the desired products (50–80%). We have not investigated as yet the minor products.

Spectroscopic data lead us to propose the structure proposed in Figure 3. Hence all capped products show terminal and bridging carbonyl frequencies in the infrared spectrum which have been shifted to lower frequencies (ca. 80–100 cm^{-1}) in comparison with those of the parent cluster. The simplicity of the spectrum along with the large shift of the bridging carbonyls indicates that the phosphine is bound to the bridged face in a high-symmetry C_{3v} structure. This is confirmed by NMR studies below.

(iii) ^{31}P and ^{13}C NMR Studies of M$_4$(CO)$_9$(tripod) (M = Co, Rh, Ir). In all cases a single resonance for ^{31}P{^{1}H} was observed. The Rh$_4$ compound showed a complex but symmetrical doublet spectrum for an AA′A″XX′X″Y system, which can be approximately analyzed as a lightly coupled double doublet of triplets with $^1J_{\text{Rh-P}} \simeq 130$ Hz, $^2J_{\text{Rh-P}} \simeq 7$ Hz (apical Rh), and either $^2J_{\text{Rh-P}}$ (basal Rh) or $^3J_{\text{P-P}} \simeq 14$ Hz or 0.

The ^{13}C NMR spectra were also studied for the ^{13}CO-enriched (ca. 35%) complex Rh$_4$(CO)$_9$[HC(PPh$_2$)$_3$]. An approximately 1:1:1 pattern is observed at 242, 190.2, and 186.4 ppm downfield from Me$_4$Si (see Figure 4). The triplet resonance at 242 ppm results from the bridging carbonyls ($^1J_{\text{Rh-C}} = 35$ Hz) and the doublet at 190.2 ppm from the terminal carbonyl groups in the basal plane ($^1J_{\text{Rh-C}} = 75$ Hz). The apical carbonyls appear as a doublet of overlapping quartets resulting from coupling to the nearest ^{103}Rh nucleus ($^1J_{\text{C-Rh}} = 65$ Hz) and further long-range coupling to the three phosphorus nuclei with $^3J_{\text{C-P}}(\text{av}) = 24$ Hz. In order to gain further evidence in support of the latter long-range coupling, the ^{13}C NMR spectra, studied for ^{13}CO-enriched (ca. 45%) complex Rh$_4$(CO)$_9$[HC(AsPh$_2$)$_3$], show an 1:1:1 pattern at 242.8, 189.5, and 186.6 ppm; the doublet of triplet resonances at 242.8 ppm results from the bridging carbonyls ($^1J_{\text{Rh-C}} =$ 30 Hz and $^2J_{\text{Rh-Rh-C}} = 10$ Hz) and the doublet at 189.5 ppm from the terminal carbonyls groups in the basal plane ($^1J_{\text{Rh-C}} = 76$ Hz). The apical carbonyls appear as a doublet

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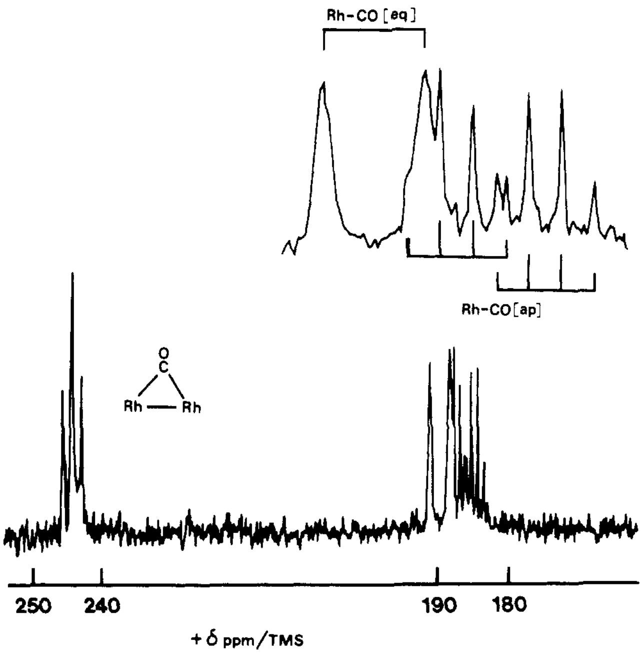

Figure 4. ^{13}C NMR spectra of the CO region for $Rh_4(CO)_9[HC(PPh_2)_3]$.

centered at 186.6 ppm ($^1J_{Rh-C}$ = 63 Hz). Furthermore, the ^{13}C NMR spectrum[7] of the isoelectronic complex $H_4Ru_4(CO)_9[HC(PPh_2)_3]$ shows the apical carbonyl resonances to arise as quartet ($^3J_{C-Ru-Ru-P}$ = 4 Hz). These spectroscopic features imply that rapid intramolecular exchange of apical carbonyl groups occur about the C_3 axis. We note however that in the tripod complex all other exchange processes involving CO ligands are now sufficiently slow, not to be observed even at +70 °C. Furthermore, the parent cluster $Rh_4(CO)_{12}$ shows a limiting spectrum only at −65 °C[14] containing four resonances with a relative intensity ratio of 1:1:1:1, in which the apical CO resonances arise as a doublet with any further long-range coupling ($^2J_{C-Rh(ap)-Rh(eq)}$ = 0). Shapley[15] in a detailed study of $Ir_4(CO)_{12-n}(PR_3)_n$ complexes showed that intramolecular carbonyl scrambling processes were slowed by increasing phosphine substitution. We show in an analogous system, $H_4Ru_4(CO)_9$(tripod), that the tripod ligand impedes the merry-go-round carbonyl processes[16] because of steric interactions with the phenyl groups. However, there appears to be an inversion in behavior when $Rh_4(CO)_9$(tripod) and $Ir_4(CO)_{11}(PPh_2Me)$ are compared. In the former, all carbonyl scrambling processes are slowed except, apparently, the rapid intramolecular exchange of apical carbonyl groups around the C_3 axis, whereas the reverse was true with the Ir_4 system. However, the unknown process at high temperature observed by Shapley may involve a simple pseudo C_3 rotational mechanism. Finally, the reaction of ^{13}CO with $Rh_4(CO)_9$(tripod) is found to give rise to statistical incorporation of all carbonyl sites, indicating that intramolecular exchange does occur slowly but occurs at a rate faster than the intermolecular exchange of ^{13}CO.

(iv) $Co_2Rh_2(CO)_9$(tripod) and $HFeCo_2(CO)_9$(tripod). In both these complexes, two isomers are possible since there are two types of triangular face available. The ^{31}P NMR of $HFeCo_3(CO)_9$(tripod) shows a broad singlet at 44.5 ppm, indicating a C_{3v} structure with the tripod ligand binding to a Co_3 face. For $Co_2Rh_2(CO)_9$(tripod) the ^{31}P NMR shows three resonance regions of relative intensity 1:1:1. The broad resonance at 33 ppm is assigned to P nucleus bound to a Co atom; the two doublets centered at 29 and 25.2 ppm result from a AA′XX′ spectrum of two phosphorus atoms bound to two chemically equivalent rhodium atoms ($^1J_{Rh-P}$ = 137 Hz and either $^3J_{P-P}$ or $^2J_{Rh-P}$ = 18.4 Hz or 0). Hence the tripod ligand has selected the Rh_2Co over the Co_2Rh face. Since, in general, substitution on Rh_4 is easier than on Co_4 clusters, kinetic selection is operating although we have not noted the formation of the other isomers in solution over long periods.

The ^{13}C NMR data confirm this assignment. ^{13}CO-enriched $Co_2Rh_2(CO)_9$(tripod) shows a ^{13}C carbonyl spectrum with terminal carbonyl resonances at 205.2 and 203.6 ppm (broad) assigned to three Co–CO (apical) and one Co–CO (radial) resonance, a double doublet centered at 189.2 ppm assigned to two terminal Rh–CO (radial) resonances ($^1J_{Rh-C}$ = 72 Hz; $^2J_{Rh-C}$ = 16 Hz), and bridging carbonyl resonances at 246.3 ppm (dt) resulting from two carbonyls bridging between Co and Rh ($^1J_{Rh-C}$ = 20 Hz) and 234.2 ppm (tt) ascribed to a CO bridging two Rh atoms ($^1J_{Rh-C}$ = 43 Hz). Thus again intramolecular rearrangements of the carbonyl groups is slow, although ^{13}CO incorporation experiments (as for Rh_4 described above) indicate such an exchange to be relatively rapid on a chemical time scale.

(v) Some Stability Tests on $M_4(CO)_9$(tripod) Complexes. We have briefly studied the reactivity of these constrained clusters to test whether they are more resistant to fragmentation than the parent complexes, a property of potential use if cluster catalysis is to be observed.

$M_4(CO)_9$(tripod) (M = Co, Rh) shows no appreciable decomposition in toluene at 100 °C under CO (30 bar) over an 18-h period. Under comparable conditions the parent carbonyls (or their phosphine-substituted derivatives) are unstable. Thus $Co_4(CO)_{12}$ yields $Co_2(CO)_8$ (35–105 °C (27–110 bar of CO),[17] and $Rh_4(CO)_{10}(PPh_3)_2$ gives dimeric products (50 °C (10–80 bar of CO)).[18]

$Co_4(CO)_9$(tripod) can be refluxed in toluene to produce the apically substituted derivative (π-toluene)$Co_4(CO)_6$(tripod) in high yield with no special precautions whereas under similar conditions the direct substitution of $Co_4(CO)_{12}$ with arenes undergoes extensive decomposition owing to the limited thermal stability of the product.[19] The X-ray structure of (π-toluene)$Co_4(CO)_6$(tripod) is described below. Substitution of the apical site of $Co_4(CO)_9$(tripod) by PMe_3 produces the complex $Co_4(CO)_8(PMe_3)$(tripod) in high yield.

We note also that the Rh_4 and Ir_4 clusters can be reversibly protonated without decomposition, and details will be described elsewhere.

(vi) The X-ray Structure of (π-toluene)$Co_4(CO)_6[HC(PPh_3)_3]$. The only previously reported structure involving a capped triangular face of metal atoms was that of $Ru_3(CO)_9(CH_3Si(P\text{-}n\text{-}Bu_2)_3)$.[9] The X-ray structure of (π-toluene)$Co_4(CO)_6[HC(PPh_2)_3]$ is presented in Figure 5. The structure, as anticipated, consists of a tetrahedral metal framework, with the tripod ligand capping one face (Co(1)Co(2)Co(3)) with the toluene molecule π bonding to the apical cobalt atom Co(4). Selected bond distances and bond angles are found in Tables IV and V.

The "fit" of the tripod ligand on the Co_3 triangular face is reasonably good as is illustrated by the near orthogo-

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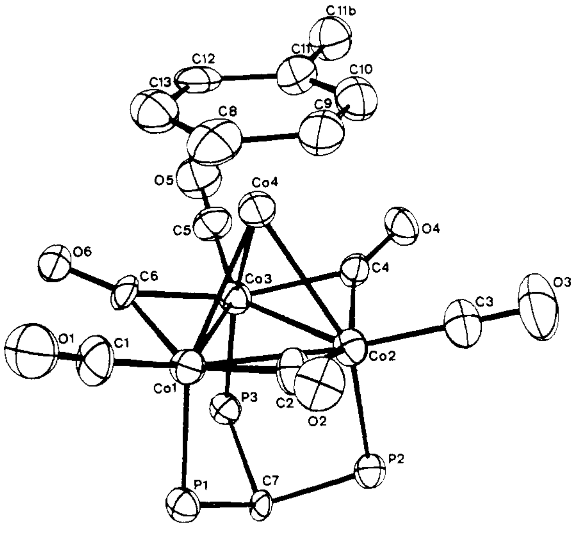

Figure 5. X-ray structure of (π-toluene)$Co_4(CO)_6[HC(PPh_2)_3]$. Geometry and labeling of the complex; phenyl rings on the tripod ligand have been omitted for clarity.

nality of the Co–P vectors to the plane of the Co_3 triangular face (mean P(*n*)–Co(*n*)–Co(*m*) angle = 96.8°). Other details are not exceptional, the complex showing strong similarities to the parent $Co_4(CO)_{12}$ structure.[20] Hence the six metal–metal bonds have a mean value of 2.459 Å compared with the 2.489-Å value for the parent cluster. No chemical conclusions can be drawn from these small differences as the previous values could have been influenced by crystal disorder.[20] The distribution of the six basal carbonyl ligands is also closely related to that found in $Co_4(CO)_{12}$, but we note that significant differences between terminal and bridging carbonyls are evident: mean values of Co–C and C–O bond lengths for terminal carbonyls are 1.75 and 1.14 Å, respectively, whereas the corresponding values for bridging carbonyls are 1.91 and 1.18 Å. These values are also close to those found[21] for the (π-arene)$Co_4(CO)_9$ complexes (arene = xylene, benzene). We note however, a slightly shorter distance is observed (1.57 Å) between the apical cobalt and the centroid of the toluene ligand than that found for the (π-arene)$Co_4(CO)_9$ complexes (1.62 Å).

Experimental Section

Materials and Methods. All experiments were performed either in Schlenk-type glassware under prepure nitrogen or argon or in a argon-filled glovebox, except when stated. Oxygen and peroxide free solvents were obtained by conventional distillation under nitrogen in presence of the appropriate reagent, e.g., sodium benzophenone.

Bis(diphenylphosphine)methane, chlorodiphenylphosphine, bis(diphenylarsino)methane, chlorodiphenylarsine, *n*-butyllithium, and $Ir_4(CO)_{12}$ were purchased from Strem Chemicals Inc. and used as obtained. ^{13}CO (90%) was obtained from the "Service des Molécules Marquées" C.E.A. (France).

The compounds $Co_4(CO)_{12}$,[19a] $Co_2Rh_2(CO)_{12}$,[22] $HFeCo_3(CO)_{12}$,[23] $Rh_4(CO)_{12}$,[24] and $Ir_4(CO)_{11}H^-$ [25] were prepared by litterature methods.

NMR spectra were recorded on a Brüker WH 90 (^{31}P) and Varian XL-100 (^{13}C) or a Brüker SY-200 (^{13}C, ^1H) instruments. Chemical shifts are relative to $(CH_3)_4Si$ (^1H, ^{13}C) or H_3PO_4 (^{31}P). Data are presented as proton decoupled with downfield chemicals shifts as positive. Infrared spectra were obtained as Nujol nulls or in solution (0.01-mm KCl cells) by using a Perkin-Elmer 597 spectrophotometer.

Elemental analyses were performed by the Service Central d'Analyse of the C.N.R.S.

Synthesis of the Tripod Ligands. (a) 1,1,1-Tris(diphenylphosphino)methane, $HC(PPh_2)_3$. A 7.6-mL sample of tetramethylethylenediamine (TMEDA) (50 mmol) in 15 mL of toluene was added dropwise under nitrogen to a 250-mL round-bottomed flask containing 35 mL of a 1.5 M hexane solution of *n*-BuLi (ca. 50 mmol), yielding an orange-red solution of *n*-BuLi(TMEDA). A 19.2-g (50-mmol) sample of $(Ph_2P)_2CH_2$ was added as a powder in several fractions to the above solution which was stirred vigorously during the addition (1 h at 25 °C). The salt $(Ph_2P)_2CH^-{\cdot}Li(TMEDA)^+$ precipitated as pale yellow crystals, which were filtered off and washed with degassed hexane (2 × 50 mL) and dried in vacuo.

A 25-g (ca. 50-mmol) sample of the $(Ph_2P_2)CH^-{\cdot}Li(TMEDA)^+$ salt dissolved in 80 mL of tetrahydrofuran (THF), in a 250-mL flask, was treated with PPh_2Cl (12 mL, ca. 64 mmol) diluted in THF (15 mL) in a dropwise fashion under nitrogen for 1 h. The mixture was stirred for a further 3 h. The resultant pale yellow solution was evaporated to dryness, yielding a pale yellow solid. This solid was treated with toluene (200 mL) and the resultant solution filtered through a glass sintered frit. The clear yellow filtrate was concentrated in vacuo to ca. half the volume (or until precipitation starts to occur) and left standing for several hours during which time the product $HC(PPh_2)_3$ deposits as colorless crystals. These were filtered off, washed with 10 mL of cold toluene (washings added to the filtrate) and several times with hexane (50 mL), and dried in vacuo. Workup of the filtrate in a similar fashion produced a further crop of crystals: overall yield ca. 21 g of $HC(PPh_2)_3$ (ca. 75%); ^1H NMR (CD_2Cl_2) 4.25 (CH, 1 H, s), 7.1–7.4 ppm (aromatic protons, 30 H, m); ^{31}P NMR −9.4 ($C_6D_5CD_3$), −8.2 ppm (CD_2Cl_2) (relative to H_3PO_4); mass spectrum, molecular ion at *m/e* 568; IR (cm^{-1} in Nujol) 3065 (w), 3050 (mw), 3020 (w), 1580 (w), 1565 (w), 1475 (m), 1430 (s), 1090 (mw, br), 1025 (mw), 1000 (w), 775 (w), 740 (sh, s), 738 (vs), 695 (s), 600 (m), 520 (m), 498 (mw), 484 (m). Anal. Calcd for $C_{37}H_{31}P_3$ (mol wt 568): C, 78.15; H, 5.46; P, 16.35. Found: C, 77.80; H, 5.50; P, 16.20.

(b) 1,1,1-Tris(diphenylarsino)methane, $HC(AsPh_2)_3$. The ligand was obtained as described above the $HC(PPh_2)_3$, employing 3.52 g of $Ph_2AsCH_2AsPh_2$ (ca. 7.5 mmol) added as a powder to an orange solution of *n*-BuLi(TMEDA) (ca. 7.5 mmol), and the final mixture stirred vigorously for several hours. The pale yellowish salt $Ph_2AsCHAsPh_2^-{\cdot}Li(TMEDA)^+$ isolated was washed several times with hexane and dried in vacuo. A THF solution of $Ph_2AsCHAsPh_2^-$ was then treated with Ph_2AsCl (1.80 mL, ca. 2.85 g, 10 mmol) for several hours. Workup of the mother solution in a similar fashion as stated in a produced the white crystals of $HC(AsPh_2)_3$: yield ca. 3.40 g, 60%; ^1H NMR (CD_2Cl_2) 3.7 (CH, 1 H, s), 7–7.4 ppm (aromatic protons, 30 H, m); mass spectrum, molecular ion at *m/e* 700; IR (cm^{-1}) 3060 (w), 3045 (w), 3020 (w), 1578 (w), 1567 (vw, sh), 1478 (m), 1430 (s), 1070 (mw, br), 1020 (mw), 995 (w), 770 (w), 735 (vs), 692 (vs), 528 (w), 475 (m), 460 (m). Anal. Calcd for $C_{37}H_{31}As_3$ (700): C, 63.45; H 4.45. Found: C, 63.70; H, 4.35.

Preparation of the Tetranuclear Tripod Clusters. (a) $Co_4(CO)_9[HC(PPh_2)_3]$. A 250-ml of sample of methylcyclohexane containing 1.035 g (1.82 mmol) of $HC(PPh_2)_3$ was added dropwise (during ca. 45 min) under nitrogen to a refluxing solution of $Co_4(CO)_{12}$ (1.015 g, 1.77 mmol) dissolved in hexane (150 mL). The refluxing was continued for a further hour and the solution allowed to cool to room temperature. Deep green crystals precipitated and were filtered, washed twice with hexane (50 mL), and dried in vacuo (yield ca. 1.40 g, 75%). Recrystallization could be carried out in benzene, dichloromethane, or THF on addition of hexane: IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2050 (s), 2000 (s), 1975 (sh), 1780 (m); ^{31}P NMR ($C_6D_5CD_3$) +44.4 ppm (br s). Anal. Calcd for $C_{46}H_{31}O_9P_3Co_4$ (mol wt 1056): C, 52.30; H, 2.95; P, 8.80. Found: C, 51.35; H, 3.05; P, 8.05.

(b) $Rh_4(CO)_9[HC(PPh_2)_3]$. 1,1,1-Tris(diphenylphosphino)methane, $HC(PPh_2)_3$ (0.430 g, 0.75 mmol), in toluene (30 mL) was added dropwise for 30 min at 25 °C to a rapidly stirred solution

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Table I. Crystal Data

compd	$Co_4(CO)_6[(P(C_6H_5)_2)_3CH](\pi\text{-toluene})$
mol wt	1063.63
a	22.43 (2) Å
b	13.13 (2) Å
c	18.72 (3) Å
β	106.724 (9)°
V	5282 Å^3
ρ (calcd)	1.338 g/cm^3
Z	4
μ	14.17 cm^{-1}
radiation, Mo Kα	λ = 0.710 73 Å from graphite monochromator
takeoff angle	2.9°
θ limits	1.5–16°
scan mode	*ω*-2*θ*
reflctns collected	6052
unique data used	4045
std reflctns[a]	400, 004, 040
final *R* value	0.09
final R_w value	0.11

[a] An intensity decrease of ca. 50% was observed and corrected. This could be related to decomposition of the crystal in the X-ray beam.

of $Rh_4(CO)_{12}$ (0.525 g, 0.70 mmol) in hexane (85 mL). Stirring was continued for 5–6 h. The solution deepened from red to dark red, and the deep red-purple crystals of $Rh_4(CO)_9HC(PPh_2)_3$ precipitated. The product was separated by filtering off the clear orange supernatant solution, washed once with 5 mL of toluene and then twice with hexane (50 mL), and dried in vacuo (yield 0.69 g, 80%). Recrystallization was achieved from THF–hexane or CH_2Cl_2–hexane: IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2060 (s), 2010 (vs), 1990 (sh), 1840 (w, sh), 1803 (m); ^{13}C NMR (CD_2Cl_2, relative intensity ratio 1:1:1) 242 (t, $\overline{\mathrm{Rh{-}CO{-}Rh}}$, $^1J_{Rh-C}$ = 35 Hz), 190.2 (d, Rh–CO (rad), $^1J_{Rh-C}$ = 75 Hz), 187.7 and 185.1 ppm (2 overlapping q, Rh–CO(ap), $^1J_{Rh-C}$ = 65.4 Hz, $^3J_{P-C}$ = 24 Hz); ^{31}P NMR (CD_2Cl_2) 18.0 (m), 14.4 ppm (m, $^1J_{Rh-P}$ = 133 Hz). Anal. Calcd for $C_{46}H_{31}O_9P_3Rh_4$ (mol wt 1232): C, 44.80; H, 2.50; P, 7.55. Found: C, 45.70; H, 2.90; P, 7.40.

(c) $Rh_4(CO)_9[HC(AsPh_2)_3]$. The complex was obtained as described above for $Rh_4(CO)_9[HC(PPh_2)_3]$, employing 0.300 g of $Rh_4(CO)_{12}$ (0.40 mmol) in 45 mL of hexane and 0.320 g of $HC(AsPh_2)_3$ (0.44 mmol) in 15 mL of toluene. The crude purple product was washed with pentane and recrystallized from the THF–hexane mixture, yielding deep purple crystals of $Rh_4(CO)_9[HC(AsPh_2)_3]$: yield 70%; IR (cm^{-1} in Ch_2Cl_2) ν_{CO} 2065 (m), 2055 (sh, m), 2015 (s), 1990 (ms), 1848 (w), 1805 (m); ^{13}C NMR (CD_2Cl_2, relative intensity ratio 1:1:1) 242.8 (dt, $\overline{\mathrm{Rh{-}CO{-}Rh}}$, $^1J_{Rh-CO-Rh}$ = 30 Hz, $^2J_{Rh-Rh-C}$ = 10 Hz), 189.5 (d, Rh–CO(rad), $^1J_{Rh-C}$ = 76 Hz), 186.6 ppm (d, Rh–CO(ap), $^1J_{Rh-C}$ = 63 Hz). Anal. Calcd for $C_{46}H_{31}O_9As_3Rh_4$ (mol wt 1364): C, 40.50; H, 2.30; As, 16.50. Found: C, 41.30; H, 2.60; As, 15.90.

(d) $Ir_4(CO)_9[HC(PPh_2)_3]$. Method 1. A 0.572 g of $Ir_4(CO)_{12}$ (0.52 mmol) and 0.354 g of $HC(PPh_2)_3$ (0.62 mmol) in dry toluene (75 mL) were heated under reflux until all the $Ir_4(CO)_{12}$ was dissolved, and the solution darkened from yellow to red (ca. 10 h). The resultant red solution was cooled and filtered to eliminate any unreacted starting materials, and the filtrate was concentrated to one-third volume. Addition of hexane precipitated the crude product which was filtered off and dried in vacuo. Purification was made by column chromatography on silica gel using dichloromethane as eluant. One band was eluted. The red eluate was concentrated to low volume and excess hexane carefully added. The mixture settled overnight at 25 °C and then was cooled at −28 °C for several days. The yellow crystals of $Ir_4(CO)_9HC(PPh_2)_3$ formed and were filtered off and dried in vacuo.

Method 2. $Ir_4(CO)_{12}$ (0.34 g, 0.030 mmol) and K_2CO_3 (0.18 g, 1.30 mmol) were stirred vigorously in methanol (35 mL) under an atmosphere of CO until all $Ir_4(CO)_{12}$ dissolved to yield a deep yellow-orange solution of $Ir_4(CO)_{11}H^-$. A solution of $HC(PPh_2)_3$ (0.196 g, 0.345 mmol) in toluene (15 mL) was added dropwise during ca. 0.5 h, while the solution was refluxed under an atmosphere of CO. Heating (66–68 °C) under CO was maintained for 12 h until the solution became red-orange. When the mixture was cooled, yellow-orange crystals precipitated and were filtered off and dried in vacuo. The resulting filtrate was concentrated to small volume, yielding a second crop of the crude product. Purification was achieved by recrystallization from CH_2Cl_2–MeOH mixture (1:2 ratio): yield 0.24 g, 50%; IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2060 (m), 2010 (s), 1970 (w), 1950 (w), 1785 (vw); ^{31}P NMR (CD_2Cl_2) −39.1 ppm (s, $\Delta\nu_{1/2}$ = 3 Hz). Anal. Calcd for $C_{46}H_{31}O_9P_3Ir_4$ (mol wt 1588.8): C, 34.75; H, 1.95; P, 5.85. Found: C, 35.40; H, 2.20; P, 5.40.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $Co_4(CO)_6[HC(PPh_2)_3][\pi\text{-}C_7H_8]$[a]

atom	*x*	*y*	*z*	*B*(11)[b]	*B*(22)	*B*(33)	*B*(12)	*B*(13)	*B*(23)
Co(1)	0.7227 (1)	0.0191 (2)	0.1136 (1)	1.89 (6)	6.1 (2)	2.60 (9)	0.13 (9)	0.83 (6)	0.0 (1)
Co(2)	0.7899 (1)	−0.1082 (2)	0.0817 (1)	2.06 (7)	5.6 (2)	2.93 (9)	0.26 (9)	1.01 (6)	0.3 (1)
Co(3)	0.8248 (1)	0.0694 (2)	0.1029 (1)	1.83 (6)	5.7 (2)	2.92 (9)	0.19 (9)	0.79 (6)	0.1 (1)
Co (4)	0.8196 (1)	−0.0352 (2)	0.2091 (1)	2.42 (7)	6.3 (2)	2.62 (9)	0.42 (10)	0.88 (6)	0.3 (1)
P(1)	0.6686 (2)	0.0484 (4)	−0.0029 (3)	1.6 (1)	5.9 (4)	3.0 (2)	0.2 (2)	0.9 (1)	0.1 (2)
P(2)	0.7578 (2)	−0.0957 (3)	−0.0400 (2)	2.0 (1)	5.4 (4)	2.8 (2)	0.2 (2)	0.9 (1)	−0.2 (2)
P(3)	0.7910 (2)	0.1241 (4)	−0.0112 (2)	1.8 (1)	5.5 (4)	2.8 (2)	0.1 (2)	0.8 (1)	0.3 (2)
C(1)	0.6712 (9)	0.045 (2)	0.166 (1)	2.8 (6)	9 (2)	4.0 (8)	0.8 (9)	2.2 (6)	−0.5 (10)
O(1)	0.6402 (6)	0.059 (1)	0.2036 (8)	3.2 (4)	17 (2)	4.8 (6)	1.0 (7)	2.1 (4)	−0.4 (8)
C(2)	0.7190 (8)	−0.124 (1)	0.1209 (10)	2.8 (6)	4 (1)	3.5 (8)	0.5 (7)	1.7 (5)	0.6 (8)
O(2)	0.6908 (6)	−0.1915 (10)	0.1382 (7)	3.2 (4)	7 (1)	4.1 (6)	−0.9 (6)	2.0 (4)	0.8 (6)
C(3)	0.8123 (9)	−0.238 (2)	0.095 (1)	3.3 (7)	6 (2)	4.7 (9)	1.1 (9)	1.6 (6)	0 (1)
O(3)	0.8260 (8)	−0.321 (1)	0.1052 (9)	7.0 (7)	7 (1)	7.1 (8)	3.1 (8)	3.2 (6)	2.0 (9)
C(4)	0.8713 (8)	−0.053 (1)	0.1010 (9)	1.8 (5)	5 (1)	3.1 (7)	0.0 (7)	0.8 (5)	−0.8 (8)
O(4)	0.9236 (6)	−0.0806 (9)	0.1128 (6)	1.9 (4)	8 (1)	4.4 (5)	1.3 (5)	1.1 (4)	0.2 (6)
C(5)	0.8900 (9)	0.146 (2)	0.139 (1)	2.3 (5)	8 (2)	3.8 (8)	−1.0 (8)	0.6 (5)	−0.8 (10)
O(5)	0.9330 (7)	0.195 (1)	0.1650 (8)	3.1 (5)	10 (1)	6.4 (8)	−0.9 (7)	1.0 (5)	−0.4 (8)
C(6)	0.7723 (8)	0.137 (2)	0.1505 (9)	2.0 (5)	7 (2)	2.7 (7)	0.3 (7)	1.0 (5)	−2.2 (9)
O(6)	0.7694 (5)	0.2113 (10)	0.1844 (7)	2.4 (4)	7 (1)	3.7 (5)	0.3 (5)	0.8 (3)	−1.5 (6)
C(7)	0.7230 (6)	0.037 (1)	−0.0627 (8)	1.2 (4)	5 (1)	2.8 (6)	0.1 (6)	1.1 (4)	−1.3 (7)
C(8)	0.7867 (10)	−0.075 (2)	0.299 (1)	4.2 (7)	10 (2)	2.9 (8)	0 (1)	1.6 (6)	1 (1)
C(9)	0.8157 (10)	0.023 (2)	0.313 (1)	3.0 (7)	11 (2)	3.4 (8)	1 (1)	1.2 (6)	1 (1)
C(10)	0.8777 (10)	0.039 (2)	0.3061 (9)	3.0 (6)	11 (2)	1.7 (7)	1.0 (9)	−0.3 (5)	0.5 (9)
C(11)	0.9121 (10)	−0.046 (2)	0.287 (1)	3.4 (7)	8 (2)	3.2 (8)	0.7 (10)	0.8 (6)	0 (1)
C(12)	0.884 (1)	−0.142 (2)	0.277 (1)	3.6 (7)	8 (2)	3.3 (8)	1.4 (10)	1.4 (6)	1.3 (10)
C(13)	0.822 (1)	−0.159 (2)	0.283 (1)	4.7 (8)	8 (2)	2.9 (8)	1 (1)	1.0 (7)	0.6 (10)
C(11)B	0.9794 (9)	−0.029 (2)	0.286 (1)	6.2 (5)	8 (2)				

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(B(11)H^2 + B(22)k^2 + B(33)l^2 + 2B(12)hk + 2B(13)hl + 2B(23)kl)]$. The quantities given in the table are the thermal coefficients × 10^3. [b] Or *B* (Å^2).

Table IV. Selected Interatomic Distances (Å) with Esd's in Parentheses

Metal-Metal Bonds			
Co(1)-Co(2)	2.438 (3)	Co(1)-Co(4)	2.490 (3)
Co(1)-Co(3)	2.446 (3)	Co(2)-Co(4)	2.479 (3)
Co(2)-Co(3)	2.456 (3)	Co(3)-Co(4)	2.448 (3)
Metal-Phosphorus Bonds			
Co(1)-P(1)	2.202 (5)	Co(3)-P(3)	2.174 (5)
Co(2)-P(2)	2.188 (5)		
Metal-Carbon Bonds			
Co(1)-C(1)	1.75 (2)	Co(2)-C(4)	1.90 (2)
Co(1)-C(2)	1.89 (2)	Co(3)-C(4)	1.93 (2)
Co(1)-C(6)	1.92 (2)	Co(3)-C(5)	1.74 (2)
Co(2)-C(2)	1.94 (2)	Co(3)-C(6)	1.89 (2)
Co(2)-C(3)	1.77 (2)		
Carbon-Carbon Bonds (π-Toluene Ligand)			
C(8)-C(9)	1.44 (3)	C(11)-C(12)	1.40 (3)
C(9)-C(10)	1.44 (2)	C(12)-C(13)	1.45 (3)
C(10)-C(11)	1.46 (3)	C(13)-C(8)	1.44 (3)
C(11)-C(11b)	1.53 (2)		
Carbon-Oxygen Bonds			
C(1)-O(1)	1.13 (2)	C(4)-O(4)	1.18 (2)
C(2)-O(2)	1.19 (2)	C(5)-O(5)	1.14 (2)
C(3)-O(3)	1.14 (2)	C(6)-O(6)	1.17 (2)
Metal-Carbon (π-Toluene Ligand)			
Co(4)-C(8)	2.09 (2)	Co(4)-C(11)	2.17 (2)
Co(4)-C(9)	2.11 (2)	Co(4)-C(12)	2.14 (2)
Co(4)-C(10)	2.14 (2)	Co(4)-C(13)	2.13 (2)
Phosphorus-Carbon Bonds			
P(1)-C(7)	1.89 (1)	P(2)-C(32)	1.85 (1)
P(1)-C(14)	1.84 (1)	P(3)-C(7)	1.93 (1)
P(1)-C(20)	1.86 (1)	P(3)-C(38)	1.85 (1)
P(2)-C(7)	1.90 (1)	P(3)-C(44)	1.84 (1)
P(2)-C(26)	1.84 (1)		

(e) $Co_2Rh_2(CO)_9[HC(PPh_2)_3]$. The complex was obtained as described above for $Rh_4(CO)_9[HC(PPh_2)_3]$, employing 0.17 g of $Co_2Rh_2(CO)_{12}$ (0.25 mmol) in 50 mL of hexane and 0.16 g of $HC(PPh_2)_3$ in 20 mL of toluene. Recrystallization of the crude product was made from the CH_2Cl_2–hexane mixture, yielding deep violet crystals of $Co_2Rh_2(CO)_9[HC(PPh_2)_3]$: yield 70–80%; IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2040 (s), 2005 (vs), 1985 (sh), 1845 (w), 1805 (mw), 1785 (mw); ^{31}P NMR (CD_2Cl_2, three signals, 1:1:1) 33.0 (br s), 29.0 (d), 25.2 ppm (d, $^1J_{Rh-P}$ = 137 Hz, $^3J_{P-P}$ = 18.4 Hz); ^{13}C NMR (CD_2Cl_2, relative intensity ratio 2:1:3:1:2) 246.3 (br d, $\overline{\text{Co–CO–Rh}}$, J_{Rh-C} = 20 Hz), 234.2 (t, $\overline{\text{Rh–CO–Rh}}$, J_{Rh-C} = 43 Hz), 205.2 (br s, Co–CO(ap)), 203.6 (br s, Co–CO(rad)), 189.2 ppm (dd, Rh–CO(rad), $^1J_{Rh-C}$ = 72 Hz, $^2J_{Rh-C}$ = 16 Hz). Anal. Calcd for $C_{46}H_{31}O_9P_3Co_2Rh_2$ (mol wt 1144): C, 48.25; H, 2.70; P, 8.10. Found: C, 47.20; H, 2.80; P, 7.90.

(f) $HFeCo_3(CO)_9[HC(PPh_2)_3]$. This complex was prepared conveniently as in method above for $Co_4(CO)_9[HC(PPh_2)_3]$, employing 0.21 g of $HFeCo_3(CO)_{12}$ (0.37 mmol) and 0.21 g of $HC(PPh_2)_3$ (0.37 mmol) and refluxed in hexane–methylcyclohexane for 2 h. The crude deep violet blackish product which precipitated upon cooling was recrystallized from THF–hexane mixture (yield 0.28 g, ca. 70%): IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2045 (m), 2035 (m), 2010 (vs), 1970 (sh), 1930 (mw), 1810 (m), 1780 (m). ^{31}P NMR ($C_6D_5CD_3$) +44.5 ppm (br s). Anal. Calcd for $C_{46}H_{32}O_9P_3Co_3Fe$ (mol wt 1054): C, 52.40; H, 3.05; P, 8.80. Found: C, 50.45; H, 3.60; P, 8.10.

Synthesis of $M_4(CO)_9$(tripod) Enriched in ^{13}CO (M_4 = Rh_4, Co_2Rh_2). The enriched $M_4(CO)_9$(tripod) complexes (about 35% in ^{13}CO) were obtained either by direct exchange reactions of the complex with ^{13}CO (90%) trapped from a stock flask fitted to an uptake line or by the reaction of tripod with previously enriched parent cluster (M_4 = Rh_4). ^{13}C spectra of enriched samples compared with natural abundance spectra revealed no detectable preferential substitution of the carbonyl groups in the $M_4(CO)_9$(tripod) exchange reactions (M_4 = Rh_4, Co_2Rh_2), whereas the exchange reaction of ^{13}CO with $Ir_4(CO)_9[HC(PPh_2)_3]$ shows that the apical Ir is the only detectable site of exchange.

Synthesis of Derivatives of $Co_4(CO)_9HC(PPh_2)_3$. (a) (π-C_7H_8)$Co_4(CO)_6[HC(PPh_2)_3]$. $Co_4(CO)_9$(tripod) (0.304 g, 0.288 mmol) was refluxed in 100 mL of toluene for 6 h during which time the green solution darkened to deep brown. The solvent was evaporated in vacuo to dryness, yielding the deep brown π-toluene derivative. Recrystallization from benzene–hexane (1:1) yields crystals of (π-C_7H_8)$Co_4(CO)_6$(tripod)·C_6H_6 which were suitable for X-ray analysis (yield 0.27 g, ca. 90%): IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1970 (sh), 1955 (s), 1740 (m); ^{31}P NMR (C_7D_8) +19.2 ppm (br s); ^{1}H NMR (CD_2Cl_2) 7.5–6.7 (m, aromatic H), 6.05 (m, C_6H_5), 2.61 ppm (s, CH_3). Anal. Calcd for $C_{56}H_{45}O_6P_3Co_4$ (mol wt 1142): C, 58.85; H, 3.90. Found: C, 59.15; H, 3.90.

(b) $Co_4(CO)_8(PMe_3)[HC(PPh_2)_3]$. The complex $Co_4(CO)_9$(tripod) (0.106 g, ca. 0.1 mmol) and PMe_3 (0.3 mL, ca. 2.76 mmol) in dioxan (100 mL) were heated at 100 °C for 3 h. Almost pure brown derivative was obtained by evaporation in vacuo of the solvent. Purification was achieved by recrystallization from CH_2Cl_2–hexane: yield 90%; IR (cm^{-1} in CH_2Cl_2) ν_{CO} 2010 (s), 1970 (v, s), 1950 (s, sh), 1760 (m), 1740 (m). Anal. Calcd: for $C_{48}H_{40}O_8P_4Co_4$ (mol wt 1104): C, 52.20; H, 3.60; P, 11.20. Found: C, 52.00; H, 4.20; P, 11.70.

X-ray Structure Determination of (π-C_7H_8)$Co_4(CO)_6[HC(PPh_2)_3]$. Data Collection. Preliminary Laue and precession photographs revealed that crystals of (π-C_7H_8)$Co_4(CO)_6[HC(PPh_2)_3]$ belong to the monoclinic system and show systematic extinctions ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with space group $P2_1/c$. The crystal selected for intensity measurements was sealed in a Lindeman capillary under dry nitrogen. Data collection was made at 21 °C on a Enraf-Nonius CAD4 diffractometer. The setting angles of 25 automatically centered reflections chosen from diverse regions of reciprocal space with 24° < 2θ(Mo) < 26° were refined by least-squares procedures and used to calculate the cell constants. These cell constants and other pertinent crystal data are presented in Table I. A total of 6671 reflections were recorded out to 2θ(Mo) < 32°. A regular intensity decrease up to 50% of the initial level was observed and corrected with the use of three standard reflections periodically measured every 2 h. This could be assigned to decomposition of the crystal in the X-ray beam. Intensities were also corrected

Table V. Selected Bond Angles (Deg), with Esd's in Parentheses

Co(2)-Co(1)-Co(3)	60.39 (9)	Co(1)-Co(2)-Co(4)	60.84 (9)	Co(2)-Co(3)-Co(4)	60.72 (9)
Co(2)-Co(1)-Co(4)	60.39 (9)	Co(3)-Co(2)-Co(4)	59.47 (9)	Co(1)-Co(4)-Co(2)	58.76 (9)
Co(3)-Co(1)-Co(4)	59.45 (9)	Co(1)-Co(3)-Co(2)	59.64 (9)	Co(2)-Co(4)-Co(3)	59.81 (9)
Co(1)-Co(2)-Co(3)	59.97 (9)	Co(1)-Co(3)-Co(4)	61.16 (9)	Co(3)-Co(4)-Co(1)	59.38 (9)
P(1)-Co(1)-Co(2)	94.6 (1)	P(2)-Co(2)-Co(1)	99.3 (1)	P(3)-Co(3)-Co(1)	95.7 (1)
P(1)-Co(1)-Co(3)	97.7 (1)	P(2)-Co(2)-Co(3)	95.2 (1)	P(3)-Co(3)-Co(2)	98.6 (1)
C(1)-Co(1)-C(2)	95.7 (8)	C(3)-Co(2)-C(4)	96.8 (8)	C(5)-Co(3)-C(6)	96.4 (8)
C(2)-Co(2)-C(3)	94.3 (8)	C(4)-Co(3)-C(5)	95.1 (8)	C(6)-Co(1)-C(1)	93.0 (8)
P(1)-C(7)-P(2)	103.6 (8)	P(2)-C(7)-P(3)	102.6 (7)	P(1)-C(7)-P(3)	101.9 (7)
C(1)-Co(1)-Co(4)	103.4 (6)	C(3)-Co(2)-Co(4)	104.3 (7)	C(5)-Co(3)-Co(4)	103.6 (6)
C(2)-Co(1)-Co(4)	73.1 (6)	C(4)-Co(2)-Co(4)	72.1 (5)	C(6)-Co(3)-Co(4)	72.5 (6)
C(2)-Co(2)-Co(4)	72.5 (5)	C(4)-Co(3)-Co(4)	72.4 (5)	C(6)-Co(1)-Co(4)	71.1 (5)
C(1)-Co(1)-P(1)	104.9 (6)	C(3)-Co(2)-P(2)	102.5 (7)	C(5)-Co(3)-P(3)	102.2 (6)
C(2)-Co(1)-P(1)	102.8 (5)	C(4)-Co(2)-P(2)	100.4 (5)	C(6)-Co(3)-P(3)	102.7 (6)
C(2)-Co(2)-P(2)	109.9 (5)	C(4)-Co(3)-P(3)	107.2 (5)	C(6)-Co(1)-P(1)	108.3 (5)

for Lorentz and polarization effects and reduced to structure factor amplitudes, using a *p* value of 0.03.[26] Only those 4045 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations.

Solution and Refinement of the Structure. Atomic scattering factors were taken from Cromer and Waber's tabulation[27] for all atoms except hydrogen, for which the values of Steward et al. were used.[28] Anomalous dispersion terms[29] for Co and P atoms were included in F_c.

The direct method approach,[30] based on 650 normalized structure factors, yielded the correct positions of the Co and P atoms. All other atoms were located through the usual combination of structure factors calculations and difference Fourier syntheses. After location of the molecular $(\pi\text{-}C_7H_8)Co_4(CO)_6(HC(PPh_2)_3$ complex, a Fourier difference map revealed the presence of a free benzene molecule in the lattice. This additional molecule was included in the model. The six phenyl rings of the tripod ligand and the benzene molecule were entered as rigid groups, including hydrogen atoms in idealized positions (D_{6h} symmetry; C–C = 1.39 and C–H = 0.95 Å). Anisotropic thermal parameters were used for 27 atoms.

Full-matrix least-squares refinement of such a model led to R_wF = 0.09 and R_{wF} = 0.11 for the 4045 reflections. These relatively high values have to be related to the significant decomposition of the crystal in the X-ray beam.

Complete listing of positional and thermal parameters are given in Table II, and selected interatomic distances and bond angles are given in Tables IV and V.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique (E.R.A. 721) and A.T.P. No. 4095 (Catalyse Homogène). Partial support from GRECO (CO) is also gratefully acknowledged.

Registry No. 1, 28926-65-0; **2**, 82198-75-2; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_9$(tripod), 82264-79-7; $Co_4(CO)_{12}$, 17786-31-1; $HFeCo_3(CO)_{12}$, 21750-96-9; $Ir_4(CO)_{12}$, 18827-81-1; $Rh_4(CO)_{12}$, 19584-30-6; $Co_2Rh_2(CO)_{12}$, 50696-78-1; $Co_4(CO)_9$(tripod), 75801-99-9; $Rh_4(CO)_9$(tripod), 75790-10-2; $Ir_4(CO)_9$(tripod), 82246-60-4; $Rh_4(CO)_9[HC(AsPh_2)_3]$, 82246-61-5; $H_4Ru_4(CO)_9$(tripod), 82246-62-6; $Co_2Rh_2(CO)_9$(tripod), 75790-08-8; $HFeCo_3(CO)_9$(tripod), 75790-06-6; $(\pi\text{-}C_7H_8)CO_4(CO)_6$(tripod), 82264-80-0; $Co_4(CO)_8(PMe_3)$(tripod), 82264-81-1; Co, 7440-48-4; Ru, 7440-18-8; Ir, 7439-88-5; Fe, 7439-89-6; Rh, 7440-16-6.

Supplementary Material Available: Complete listing of observed and calculated structure factors and Table III, derived parameters for the rigid-group atoms of $Co_4(CO)_6[HC(PPh_2)_3](\pi\text{-}C_7H_8)$ (21 pages). Ordering information is given on any current masthead page.

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Reaction of $HCo(CO)_4$ and CO with Styrene. Mechanism of (α-Phenylpropionyl)- and (β-Phenylpropionyl)cobalt Tetracarbonyl Formation

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Received March 26, 1982

Cobalt tetracarbonyl hydride and styrene react in the presence of carbon monoxide to form ethylbenzene and (α-phenylpropionyl)cobalt tetracarbonyl; both reactions are first order in $HCo(CO)_4$ and PhCH═CH$_2$ and independent of CO and $Co_2(CO)_8$ concentration. The kinetic data suggest a common radical pair intermediate for both reactions. (α-Phenylpropionyl)cobalt tetracarbonyl is not the final product of the reaction: it slowly decomposes into ethylbenzene, CO, and $Co_2(CO)_8$ and partly isomerizes into (β-phenylpropionyl)cobalt tetracarbonyl. Accordingly, among these acyl complexes the branched-chain isomer is the kineticly controlled product and the straight-chain isomer the thermodynamicly controlled product.

Introduction

The reaction between $HCo(CO)_4$ and olefin is regarded as a component of the hydroformylation catalytic cycle in the presence of cobalt carbonyls, and because of the industrial significance of hydroformylation, it has been repeatedly studied.[1] The main products of this stoichiometric reaction are aldehydes (at low olefin/$HCo(CO)_4$ ratios) or acylcobalt tetracarbonyls, $RCOCo(CO)_4$ (at high olefin/$HCo(CO)_4$ ratios in the presence of CO). Saturated hydrocarbons are formed as byproducts.

Recent kinetic studies[2] suggested that with aliphatic α-olefins an alkylcobalt tricarbonyl is the common intermediate of hydrocarbon and acylcobalt tetracarbonyl formation and that the carbonylation/hydrogenation ratio is determined by the relative reactivities of this species toward CO and $HCo(CO)_4$. Furthermore it was found that CO inhibits and $Co_2(CO)_8$ catalyzes these reactions. Presumably the role of $Co_2(CO)_8$ is to generate radical species and thereby to facilitate the substitution of a CO ligand by an olefin in $HCo(CO)_4$.

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