Reactivity of $[ClCCo_3(CO)_9]$ with Metal Iron Carbonyl Clusters. Formation of Carbide and Dicarbide Mixed Metal Clusters

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The reaction of $[ClCCo_3(CO)_9]$ with $(PPh_4)_2[Fe_3(CO)_{11}]$ in CH_2Cl_2 at room temperature in the presence of thallium salt gives the brown cluster complex $(PPh_4)[Co_5Fe(C_2)(CO)_{17}]$ (**1**), on which X-ray crystal structure determination has been carried out. The anion of **1** consists of two distorted Co_3C and Co_2FeC tetrahedra linked by a C−C bond (dicarbide unit) and by a Co−Co bond. The reactivity of $[ClCCo_3(CO)_9]$ with the anions $[Fe_4C(CO)_{12}]^{2-}$ and $[Fe_5C(CO)_{14}]^{2-}$ was tested, giving $[Fe_4CoC(CO)_{14}]^{2-}$ and $[Fe_5CoC(CO)_{16}]^{2-}$, respectively, as major products. Addition of $[ClCCo_3(CO)_9]$ to a solution of $[Fe_3(CO)_9(CCO)]^{2-}$ in CH_2Cl_2, in the presence of thallium salt, generates the species $[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO)\}]^-$ (**2**). Subsequent addition of ethanol affords the hexametallic complex $(PPh_4)_2[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO_2C_2H_5)\}]$ (**3**), which reacts with $ClAuPPh_3$ in a 1:3 molar ratio, in the presence of thallium salt, to form the cluster $[\{AuPPh_3\}_3Fe_3(CO)_9(CCO_2C_2H_5)]$ (**4**). According to its X-ray crystal determination, the anion of **4** can be described as a 48-electron Fe_3 equilateral triangle capped on both sides by a μ_3-$CCO_2C_2H_5$ group and a $AuPPh_3$ fragment. Additionally, two $AuPPh_3$ units cap Fe_2Au faces.

Introduction

Although the chemistry of metal cluster carbides is well developed, clusters containing the simple diatomic C_2 ligand are rare. Thus, for cobalt, apart from the neutral $[Co_3(CO)_9C]_2$,[1] only the high-nuclearity anion species $[Co_9(C_2)(CO)_{19}]^{2-}$,[2] $[Co_{11}(C_2)(CO)_{22}]^{3-}$,[3] $[Co_{13}(C_2)(CO)_{24}]^{4-}$,[4] and $[Co_{13}(C_2)(CO)_{24}]^{3-}$ [5] are known. An example of a mixed Fe/Co dicarbidocluster, $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$,[6] has also been reported and characterized by X-ray diffraction. The main reason for the paucity of dicarbides is the lack of applicable synthetic routes. In general, dicarbides can be prepared through redox condensation of carbides with $[ClCCo_3(CO)_9]$, by pyrolytic decomposition of a carbide cluster, or by using the ketenylidene ligand (CCO) as a precursor.

The final structure results from a compromise between the tendency of the metal atoms toward closely packed arrangements and the need for suitable cavities for the allocation of the interstitial atoms. Consequently, for high nuclearity clusters, the C_2 units remain encapsulated in the middle of the polyhedron; however, for $[Co_3(CO)_9C]_2$ or $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$, the C_2 moiety is too large to be completely encapsulated and obliges the metal atoms to reorganize in a more open structure. In both cases, the bonding between the dicarbon entities and the metal atoms can be explained following the Dewar−Chatt−Duncanson model, resulting from an important forward electron donation from occupied C_2 orbitals to acceptor metallic orbitals, accompanied by a back-donation from occupied metallic orbitals into vacant C_2 π^* orbitals.[7]

To extend the research in this field, we have investigated the reaction of $[ClCCo_3(CO)_9]$, which is a carbide source, with the anions $[Fe_3(CO)_{11}]^{2-}$ and $[Fe_3(CO)_9CCO]^{2-}$. We report the unexpected synthesis and structural characterization of a new iron/cobalt dicarbide cluster and a mixed hexanuclear iron/gold ketenylidene cluster.

Results and Discussion

The reaction of $[ClCCo_3(CO)_9]$ with carbonyl metal anions is, in some cases, an appropriate route to mixed carbido metal clusters. However, given that the attempts to obtain iron/cobalt species by using some iron anions[8] were not successful, we decided to investigate

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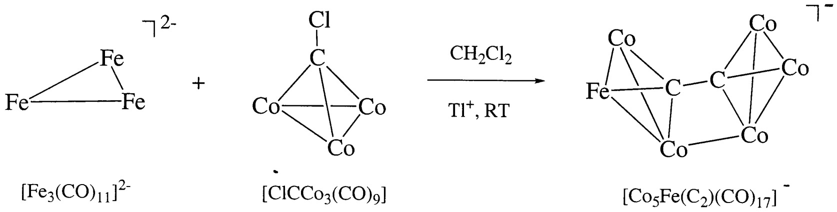
Scheme 1



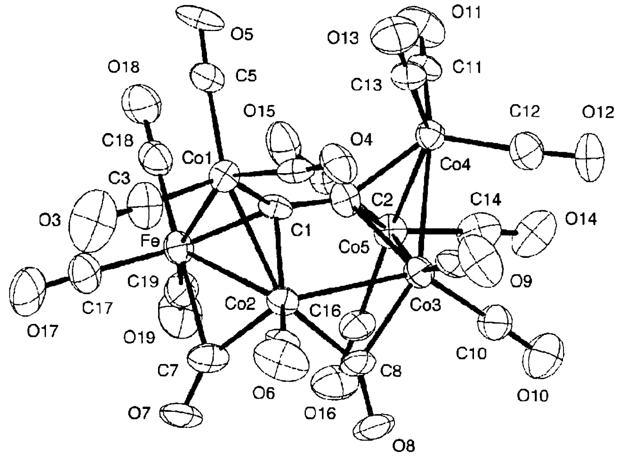


Figure 1. Molecular structure of the anionic cluster **1**. Selected bond lengths (Å) and angles (deg): Co(1)–Co(2) = 2.520(2), Co(1)–C(1) = 1.918(8), Co(1)–Fe = 2.5547(16), Co(2)–C(1) = 1.945(9), Co(2)–Fe = 2.5447(17), Fe–C(1) = 1.930(8), Co(2)–Co(3) = 2.6431(15), Co(3)–C(2) = 1.960(9), Co(3)–Co(5) = 2.4797(14), Co(4)–C(2) = 1.901(8), Co(3)–Co(4) = 2.535(2), Co(5)–C(2) = 1.940(7), Co(4)–Co(5) = 2.4804(18), C(1)–C(2) = 1.363(10), Co(2)–Co(1)–Fe = 60.19(5), C(1)–Co(2)–Co(3) = 73.6(2), Co(1)–Co(2)–Fe = 60.59(5), C(2)–Co(3)–Co(2), 67.8(2), Co(1)–Co(2)–Co(3) = 106.71(7), Co(1)–C(1)–Fe = 83.2(3), Fe–Co(2)–Co(3) = 113.80(6), Co(1)–C(1)–Co(2) = 81.4(3), Co(5)–Co(3)–Co(4) = 59.28(5), Fe–C(1)–Co(2) = 82.1(4), C(2)–C(1)–Co(1) = 137.2(6), C(2)–C(1)–Co(2) = 103.9(7).

the same reaction in the presence of Tl^+ salt to facilitate the abstraction of the chloride.

Treatment of the complex $[ClCCo_3(CO)_9]$ with $(PPh_4)_2$-$[Fe_3(CO)_{11}]$ in CH_2Cl_2 at room temperature in the presence of thallium salt gave the brown cluster complex $(PPh_4)[Co_5Fe(C_2)(CO)_{17}]$ (**1**), according to Scheme 1.

The reaction was monitored by IR spectroscopy, which showed, after a few minutes, a broad band between 2040 and 1980 cm^{-1}, accompanied by another at 1890 cm^{-1}. The latter is characteristic of the $[Co(CO)_4]^-$ anion. The formation of $[Co(CO)_4]^-$ suggests that displacement from the cobalt triangle occurs. The reaction mixture was evaporated to dryness, and the residue was extracted with ethyl ether. The solution was layered with pentane, and suitable crystals for an X-ray structure determination were obtained. The structure of the anion complex $[PPh_4][Co_5Fe(C_2)(CO)_{17}]$ (**1**) is shown in Figure 1.

The identities of metals could not be determined from diffraction data, so they are tentatively assigned positions that are compatible with the spectroscopic data. Particularly interesting are the results from FABS (−) and ES (−) mass spectrometry, which permitted detection of the molecular peak (m/z = 851) and the succesive loss of carbonyl groups. The structure consists of two distorted Co_3C and Co_2FeC tetrahedra linked by the dicarbide bond and by a Co–Co bond. This cluster closely resembles $[Fe_3Co_3(C_2)(CO)_{18}]^-$,[6] featuring two M_3 triangles oriented orthogonally to the dicarbide ligand in a slightly staggered arrangement. The metal planes in **1** are tipped toward one another (43.6°), making the distance Co(2)–Co(3) 2.643 Å. The Co_3 triangle displays eight CO terminal ligands, whereas the Co_2Fe one shows a carbonyl group bridging an Fe–Co bond. Despite this, both metal frameworks are nearly equilateral. In addition, a carbonyl group bridges the Co–Co bond between the two metallic units. The metal–metal distances are not significantly different from those reported in the literature for triangular cobalt clusters. The length of the dicarbido bond is 1.363(10) Å, equivalent to the distance found in $[Co_6(C_2)(CO)_{18}]$ (1.37 Å),[1b] $[Co_6(C_2)(CO)_{14}S]$[9] (1.37 Å), and $[Fe_3Co_3(C_2)(CO)_{18}]^-$ [6] (1.362 Å), but somewhat shorter than those distances reported for complexes containing the dicarbide group completely encapsulated: $[Rh_{12}(C_2)(CO)_{25}]$ (1.48 Å),[10] $[Co_{11}(C_2)(CO)_{22}]^{3-}$ (1.62 Å),[3] and $[Co_9(C_2)(CO)_{19}]^{2-}$ (1.39 Å).[2]

The structure can be viewed as derived from that of 96-electron species $[Co_6(C_2)(CO)_{18}]$ in which a $Co(CO)_3$ unit has been substituted for an $Fe(CO)_2^-$ fragment to afford a 94 metallic valence electron species. As a result, the PSPE electron-counting rules predict an additional metal–metal bond for **1**, which is created by tilting the triangular metallic planes. This structural situation contrasts with the parallel and nonbonded metal triangles found in $[Co_6(C_2)(CO)_{18}]$. An explanation of the structural differences between both species is obtained with the help of EH calculations. It has been shown that for $[Co_6(C_2)(CO)_{18}]$ the HOMOs are nearly degenerate and fully occupied for a count of 96 MVEs;[6] however, with two electrons fewer, the system becomes Jahn–Teller unstable and a distorted structure is expected. In fact, Shriver et al. showed that if the two Co_3 planes tilt in such a way that two metal atoms get close to each other, the HOMO/LUMO gap for the count of 94 MVEs increases, due to the destabilization of the LUMO. This is exactly what happens in the 94-MVE compound $[Fe_3Co_3(CO)_{18}(C_2)]^-$, in which a long intertriangle Fe–Co bond (2.90 Å) is formed by a tilt of ca. 18°. In our case, the higher tilt (42°) makes the intertriangle Co(2)–Co(3) bond shorter (2.6 Å), confirming the predictions.

The synthesis of **1** from $[ClCCo_3(CO)_9]$ and $[Fe_3(CO)_{11}]^{2-}$ in the presence of thallium salt can be rationalized by assuming that the first step involves Tl^+ abstraction of chloride and reduction of $[CCo_3(CO)_9]^+$ in a second step to give $[Co_6(C_2)(CO)_{18}]$, followed by the substitution of a $Co(CO)_3$ unit by an $Fe(CO)_2^-$ fragment.

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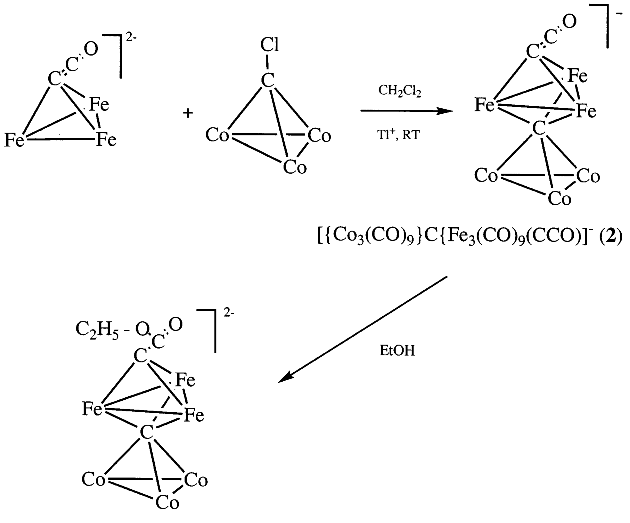
Scheme 2



$[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO)]^-$ (**2**)

$[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO_2C_2H_5)\}]^-$ (**3**)

In fact, the homonuclear cobalt cluster is obtained by refluxing $[ClCo_3(CO)_9]]$ in toluene.[1a] On the other hand, Shriver detected easy interchange of iron and cobalt units during the synthesis of $[Fe_3Co_3(C_2)(CO)_{18}]^-$.[6]

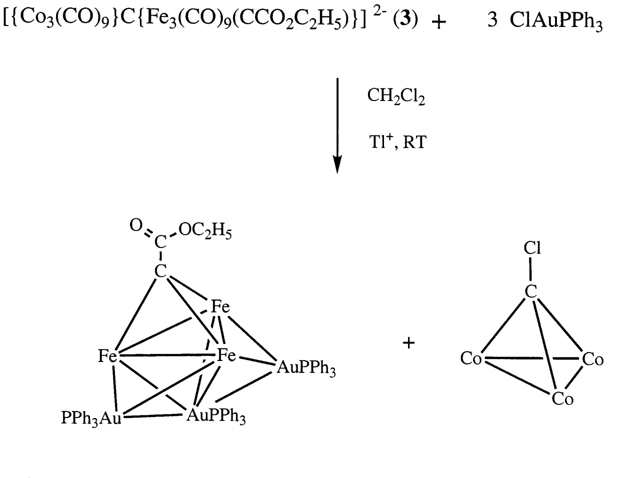
These results suggested that a systematic study of the reactivity of $[ClCCo_3(CO)_9]$ with other iron carbonyl anions might provide a fruitful area of research. Thus, we reacted the anions $[Fe_4C(CO)_{12}]^{2-}$ and $[Fe_5C(CO)_{14}]^{2-}$ with the tricobalt cluster and were able to isolate from the reaction solutions the compounds $[PPh_4]_2[Fe_4CoC(CO)_{14}]$ and $[PPh_4]_2[Fe_5CoC(CO)_{16}]$, as major products resulting from condensation processes. Both of these compounds had been described earlier,[11] and their nature was elucidated by their IR spectra and ES(−) mass spectroscopy. Consequently, the strategy shown here permits the addition of one or more cobalt fragments to the starting iron anions. Moreover, despite the fact that the resulting products were known, the synthetic procedure seems to open a new way in the building of high-nuclearity mixed Fe−Co metal clusters.

It is evident from our results that the starting $[Fe_3(CO)_{11}]^{2-}$ cluster decomposes in the course of the formation of **1**. Probably, the anions $[Fe_4C(CO)_{12}]^{2-}$ and $[Fe_5C(CO)_{14}]^{2-}$ similarly undergo partial fragmentation. To avoid the cleavage of the iron−iron bonds, we envisaged using an iron cluster having a μ_3 ligand group anchored to three metals. The ketenylidene derivative $[Fe_3(CO)_9(CCO)]^{2-}$ was chosen for this because of its interest as a precursor to dicarbido cluster complexes.

The addition of $[ClCCo_3(CO)_9]$ to a solution of $[Fe_3(CO)_9(CCO)]^{2-}$ in CH_2Cl_2, in the presence of thallium salt, generates the compound $[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO)\}]^-$ (**2**) (Scheme 2).

The reaction was monitored by IR spectroscopy, and the intermediate **2** was detected. It presented bands at 2053(m), 2017(vs), 2000(msh), 1971(msh), 1869(vw), and 1845(vw) cm^{-1} due to the CO ligands, along with one at 1654 cm^{-1} that was assigned to the CO of the ketenyl group. Unfortunately, all attempts to isolate this complex were unsuccessful and decomposition products were observed in all cases.

Scheme 3



$[\{AuPPh_3\}_3Fe_3(CO)_9(CCO_2C_2H_5)]$ (**4**)

Addition of ethanol to the reaction solution yielded the hexametallic complex $(PPh_4)_2[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO_2C_2H_5)\}]$ (**3**) and minor quantities of $[Fe_3(CO)_{10}CH]^-$. **3** was formed by the nucleophilic attack of the ethoxy on the C_β atom of the ketenyl group. The ^1H NMR of **3** showed the characteristic peaks of the ethoxy group at $\delta(CH_2CH_3) = 4.26$(q) and 1.31(t) ppm ($J_{H-H} = 7.1$ Hz). The ^{13}C NMR presents, in addition to signals due to the ethoxy group (60.1 and 14.8 ppm), those corresponding to the CO ligands: a sharp peak at 213.4 ppm, attributable to carbonyl groups bonded to iron metals, and a broad signal, due to coupling with cobalt quadrupole, centered at 219.2 ppm, and belonging to ligands attached to the triangle formed by the cobalt atoms. The FAB(−) mass spectrum showed a peak corresponding to the species $[M - 5(CO)]^-$, confirming the nature of **3**. All attempts to grow single crystals of **3** were unsuccessful.

Because of the negative charge, the nucleophilic character of **3** was examined in order to form a mixed transition metal cluster. Thus, we reacted **3** with $ClAuPPh_3$, in a 1:3 molar ratio and in the presence of thallium salt. The reaction was monitored by IR spectroscopy, and after 4 h no bands of the starting compounds were present. The spectrum showed characteristic bands of $[ClCCo_3(CO)_9]$ along with new bands at 2026(m), 1997(vs), and 1981(m,sh) cm^{-1} in the carbonyl stretching region. After workup of the solution, the cluster $[\{AuPPh_3\}_3Fe_3(CO)_9(CCO_2C_2H_5)]$ (**4**) was isolated in moderate yields (Scheme 3).

Details of spectroscopic data of this compound are given in the Experimental Section. ^{31}P NMR showed a unique signal at 52.0 ppm at room temperature, indicating fluxional behavior. The spectrum could not be frozen, even after cooling to −50 °C. This fluxional process has been reported for other M_3Au_3 clusters, like $[\{AuPPh_3\}_3Ru_3(CO)_9(\mu_3\text{-}CO_2Me)]$, which displays a similar metal sekeleton.[12] The FAB mass spectrum did not show the molecular peak, but fragments due to the loss of $AuPPh_3$, Ph, CO, and $CO_2C_2H_5$ were observed.

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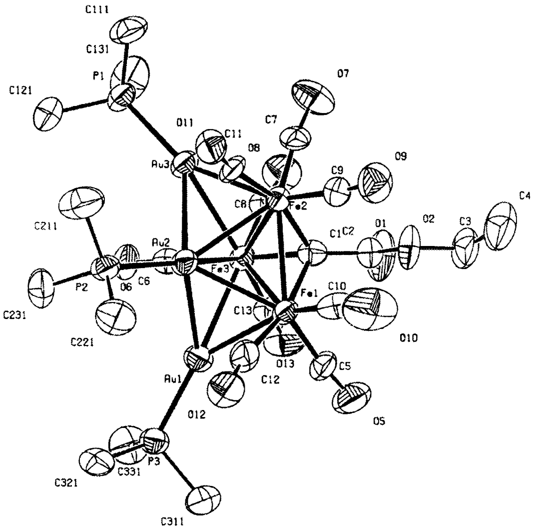

Figure 2. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Au(1)−Fe(1) = 2.7174(12), Au(1)−Au(2) = 2.9157(6), Au(1)−Fe(3) = 2.7236(11), Au(2)−Au(3) = 2.8829(4), Au(2)−Fe(1) = 2.6916(10), Fe(1)−Fe(2) = 2.6985(16), Au(2)−Fe(2) = 2.7093(10), Fe(1)−Fe(3) = 2.7164(14), Au(2)−Fe(3) = 2.8953(11), Fe(2)−Fe(3) = 2.7169(18), Au(3)−Fe(2) = 2.6956(10), Fe(1)−C(1) = 1.940(7), Au(3)−Fe(3) = 2.7650(12), Fe(2)−C(1) = 1.916(9), Fe(3)−C(1) = 1.945(8), Fe(2)−Au(3)−Fe(3) = 59.66(4), Fe(1)−Au(2)−Fe(3) = 58.04(3), Au(3)−Fe(2)−Fe(3) = 61.44(3), Fe(3)−Au(2)−Au(1) = 55.90(3), Au(2)−Fe(1)−Fe(3) = 64.74(3), Au(2)−Fe(1)−Au(1) = 65.24(3), Fe(2)−Fe(3)−Au(2) = 57.63(3).

Crystals of **4** suitable for X-ray structure determination were grown from an ether/CH_2Cl_2 solution layered with hexane. The molecular structure of **4** is shown in Figure 2. **4** can be described as a 48-electron Fe_3 equilateral triangle capped on both sides by a μ_3-$CCO_2C_2H_5$ group and a $AuPPh_3$ fragment. Moreover, two $AuPPh_3$ units capped Fe_2Au faces. This structure is close to those described for $[Au_3Ru_3(CO)_9(PPh)_3)_3(\mu_3\text{-}CO_2Me)]$,[12] $[Au_3Ru_4(CO)_{12}(PPh_3)_3(\mu_3\text{-}H)]$,[13] and $[Au_3CoRu_3(CO)_{12}(PPh_3)_3]$[14] clusters. Without doubt, the final geometry strongly results from the aurophilicity of gold atoms.

The C(1)−C(2) vector is perpendicular to the Fe(1)-Fe(2)Fe(3) plane. This contrasts with the structure of the $[Fe_2Co(CO)_9(CCO)]^-$, in which the ketenylidene ligand is tilted toward the metal plane. All carbonyl ligands are terminal, and the Fe−C−O angle for C6, C11, and C12, around 170°, indicates that a weak Au−CO interaction exists. The Fe(2)−Au(2) and Fe(1)−Au(2) bond lengths (2.70 and 2.69 Å, respectively) are significantly shorter than the Fe(3)−Au(2) distance (2.89 Å), and the dihedral angle lying between the planes Fe(1)Fe(2)Fe(3) and Fe(1)Fe(2)Au(2) is 111.1°. This value is lower than that observed for the butterfly angle in $[Fe_3Au(CO)_{11}PPh_3]^-$ [15] (120.1°). The distances Fe−Fe are longer than those found in the close $[Fe_3(CO)_9(CCO)]^{2-}$ because of the capping of the gold units, as observed in the related Au/Fe clusters containing Fe_4, Fe_5, or Fe_6 units.[16] The Au−Au distances around 2.9 Å compare very well with those reported in the literature.

In conclusion, the reaction of $[ClCCo_3(CO)_9]$ with $[Fe_3(CO)_9CCO]^{2-}$ in CH_2Cl_2 in the presence of thallium salt, followed by the addition of $ClAuPPh_3$, generates the hexanuclear Fe_3Au_3 polyhedron. This synthetic proposal is interesting since high-nuclearity Fe/Au clusters are not obtained through the reaction of iron carbonyl anions with an excess of gold derivatives in contrast with the behavior of the Ru and Os compounds.

Experimental Section

All manipulations were performed under an atmosphere of prepurified N_2 with standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Infrared spectra were measured on an FT-IR 520 Nicolet spectrophotometer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on Bruker DRX 250 and Varian XL-500 spectrometers (δ (TMS) = 0.0 ppm and δ (85% H_3PO_4) = 0.0 ppm). FABMS and ESMS were recorded in a Fisons VG Quattro spectrometer. Compounds $ClAuPPh_3$,[17] $[ClCCo_3(CO)_9]$,[18] $(PPh_4)_2[Fe_3(CO)_{11}]$,[19] $(PPh_4)_2[Fe_3(CO)_9(CCO)]$,[20] $(PPh_4)_2[Fe_4C(CO)_{12}]$,[21] and $(NEt_4)_2[Fe_5C(CO)_{14}]$[22] were synthesized as previously described. All reactions were monitored by IR spectroscopy.

Synthesis of $(PPh_4)[Co_5Fe(C)_2(CO)_{17}]$ (1). Solid $[ClCCo_3(CO)_9]$ (0.64 g, 1.3 mmol) and $TlBF_4$ (0.30 g, 1.3 mmol) were added to a solution of $(PPh_4)_2[Fe_3(CO)_{11}]$ (1.5 g, 1.3 mmol) in CH_2Cl_2 (40 mL) at room temperature. After 2 h, an excess of $(PPh_4)_2[Fe_3(CO)_{11}]$ (25%) was added. When all $[ClCCo_3(CO)_9]$ was completely reacted (2 h), the solution was filtered and concentrated to dryness. The residue was extracted with ethyl ether (40 mL), and the solution was layered with pentane (15 mL) and cooled for 48 h (−30 °C). Brown needles of compound **1** were obtained. Yield: 0.23 g (28%). IR (CH_2Cl_2, cm^{-1}) ν(CO): 2080(vw), 2040(s,sh), 2033(vs), 2020(s), 1987(m), 1952(m). IR (KBr, cm^{-1}) ν(CO): 2081(w), 2029(vs), 2014(s), 1997(vs), 1974(s), 1945(vs), 1935(vs), 1913(m,sh), 1884(m), 1839(m), 1789(m). ^{13}C NMR (298 K, CD_2Cl_2, δ(ppm)): 211 (br, *C*O), ESMS (M^-): *m/z* calcd 851; found 851. Anal. Calcd: C, 43.40; H, 1.69. Found: C, 43.90; H, 1.78.

Synthesis of $(PPh_4)_2[\{Co_3(CO)_9\}C\{Fe_3(CO)_9(CCO_2C_2H_5)\}]$ (3). Solid $[ClCCo_3(CO)_9]$ (0.15 g, 0.31 mmol) and $TlBF_4$ (0.07 g, 0.31 mmol) were added to a solution of $(PPh_4)_2[Fe_3(CO)_9CCO]$ (0.35 g, 0.31 mmol) in CH_2Cl_2 (20 mL) at −12 °C. After 3 h of stirring, the mixture was filtered and the solvent evaporated to dryness in vacuo. The product was extracted with 20 mL of diethyl ether and filtered, and the resulting solution was evaporated to dryness. The product was treated with 10 mL of ethanol, layered with 3 mL of hexane, and cooled overnight (−30 °C). Brown needles of compound **3** were obtained. Yield: 0.27 g (57%). IR (CH_2Cl_2, cm^{-1}) ν(CO): 2053(m), 2010(vs) 1986(s), 1963(m), 1905(m, sh), 1843(w), 1830(w). IR (KBr, cm^{-1}) ν(CO): 2053(m), 2007(vs) 1983(s), 1955(s), 1919(m), 1901(m), 1826(m). ^1H NMR (298 K, CD_2Cl_2, δ(ppm)): 4.26 (q, CH_2), 1.31 (t, CH_3, ^3J(H−H) = 7.1 Hz). ^{13}C

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Table 1. Crystal Data and Structure Refinement for Compounds (PPh_4)[1] and 4

	(PPh_4)[**1**]	**4**
empirical formula	$C_{43}H_{22}Co_5FeO_{17}P$	$C_{71}H_{60}Au_3Fe_3O_{12}P_3$
fw	1192.08	1956.55
temp (K)	293 (2)	293(2)
wavelength (Å)	0.71069	
cryst syst	monoclinic	
space group	$P2_1/c$	
unit cell dimens	$a = 9.7070(10)$ Å $b = 31.3350(10)$ Å $c = 15.2050(10)$ Å $\alpha = 90°$ $\beta = 96.7480(10)°$ $\gamma = 90°$	$a = 13.826(1)$ Å $b = 22.962(1)$ Å $c = 21.907(1)$ Å $\beta = 97.199(1)°$
V (Å^3)	4592.8(6)	6900.0(7)
Z	4	4
density (calcd) (g/cm^3)	1.724	1.883
abs coeff (mm^{-1})	2.178	7.098
F(000)	2368	3768
cryst size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range for data collection (deg)	2.48−28.89	2.53−31.63
index ranges	$0 = h = 13$, $0 = k = 41$, $-9 = l = 9$	$-19 = h = 15$, $0 = k = 30$, $0 = l = 30$
no. of reflns collected	10 650	19 000
no. of indep reflns	4940 [R(int) = 0.0446]	9411 [R(int) = 0.0407]
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/ params	4940/0/608	9411/235/782
goodness of fit on F^2	1.052	1.064
final R indices [$I > 2\sigma(I)$]	R1 = 0.0524, wR2 = 0.1311	R1 = 0.0373, wR2 = 0.0951
R indices (all data)	R1 = 0.1160, wR2 = 0.1525	R1 = 0.0666, wR2 = 0.1030
largest diff peak and hole (e/Å^3)	0.435 and −0.408	0.851 and −0.802

NMR (298 K, CD_2Cl_2, δ(ppm)): 60.1 (CH_2), 14.8 (CH_3), 213.4 (CO), 219.2 (br,CO). ESMS (M − 5 CO)$^-$: m/z calcd 806; found 806. Anal. Calcd: C, 52.50; H, 2.79. Found: C, 52.59; H, 2.82.

Synthesis of [{$AuPPh_3$}$_3Fe_3(CO)_9(CCO_2C_2H_5)$] (4). Solid $ClAuPPh_3$ (0.15 g, 0.30 mmol) and $TlBF_4$ (0.07 g, 0.30 mmol) were added to a solution of **3** (0.15 g, 0.09 mmol) in CH_2Cl_2 (15 mL) at room temperature. The solution was stirred for 4 h, and 10 mL of diethyl ether was added. The mixture was filtered, and the solution was evaporated to dryness. The residue was extracted with a mixture of CH_2Cl_2 and diethyl ether in a ratio of 1:10 (15 mL) and layered with hexane (1.5 mL). When the mixture stood at −30 °C for 48 h, brown crystals of **4** were formed. Yield: 0.05 g (30%). IR (CH_2Cl_2, cm^{-1}) ν(CO): 2054(w), 2026(m), 1997(vs), 1981(m), 1912(m). IR (KBr, cm^{-1}) ν(CO): 2025(m), 1995(vs), 1980(s), 1950(w), 1912(m). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2, δ(ppm)): 52.0 (s, PPh_3). ^1H NMR (298 K, CD_2Cl_2, δ(ppm)): 7.9−6.9 (m, Ph), 4.3 (br, CH_2), 1.23 (br, CH_3). ^{13}C NMR (195 K, CD_2Cl_2, δ(ppm)): 220.4 (br, CO), 216.0 (br, CO), 134−128 (m, Ph), 60.1 (s, CH_2), 14.6 (s, CH_3). ESMS (M − $AuPPh_3$)$^-$: m/z calcd 1391; found 1391. Anal. Calcd: C, 42.75; H, 2.68. Found: C, 42.85; H, 2.70.

Reaction of $(PPh_4)_2[Fe_4C(CO)_{12}]$ with $[ClCCo_3(CO)_9]$. Synthesis of $(PPh_4)[Fe_4CoC(CO)_{14}]$. Solid $[ClCCo_3(CO)_9]$ (0.15 g, 0.31 mmol) and $TlBF_4$ (0.09 g, 0.31 mmol) were added to a solution of $(PPh_4)_2[Fe_4C(CO)_{12}]$ (0.40 g, 0.31 mmol) in CH_2Cl_2 (30 mL) at −12 °C. After 4 days, 40 mL of diethyl ether was added and the mixture was filtered off. The solution was concentrated to dryness, and the solid was washed with 40 mL of hexane to eliminate the $[ClCCo_3(CO)_9]$ present. The residue was extracted with 20 mL of CH_2Cl_2 and filtered, and the resulting solution was layered with 10 mL of hexane and cooled overnight at −30 °C, giving $Tl_2[Fe_4C(CO)_{12}]$ (0.1 g). The solution was filtered and layered with 10 mL of hexane. After cooling overnight at −30 °C, brown crystals of $(PPh_4)[Fe_4CoC(CO)_{14}]$ were obtained. Yield: 0.12 g (36%). ESMS (M$^-$): m/z calcd 687; found 687. IR (CH_2Cl_2, cm^{-1}) ν(CO): 2055(w), 2006(vs), 1991(s, sh), 1973(m, sh), 1944(m).

Reaction of $(NEt_4)_2[Fe_5C(CO)_{14}]$ with $[ClCCo_3(CO)_9]$. Synthesis of $(NEt_4)[Fe_5CoC(CO)_{16}]$. To a solution of $(NEt_4)_2[Fe_5C(CO)_{14}]$ (0.44 g, 0.46 mmol) in thf (30 mL) at room temperature were added solid $[ClCCo_3(CO)_9]$ (0.22 g, 0.46 mmol) and TlBF4 (0.13 g, 0.46 mmol). After stirring the mixture for 4 days 45 mL of diethyl ether was added. The solution was filtered and concentrated to dryness. The residue was washed in hexane (40 mL) and extracted with 15 mL of CH_2Cl_2. The solution obtained was layered with 10 mL of hexane and cooled for 8 h at −30 °C. The Tl^+ salts were filtered off, and to the resulting solution was added 5 mL of hexane and the mixture was cooled for 48 h. Black crsytals of $(NEt_4)[Fe_5CoC(CO)_{16}]$ were obtained. Yield: 0.15 g (37%). IR (CH_2Cl_2, cm^{-1}) ν(CO): 2013(s), 2006(vs), 1989(s). ESMS (M$^-$): m/z calcd 799; found 799.

X-ray Structure Determination of 1 and 4. Brown block crystals of compounds **1** and **4** were selected and mounted on a Mar345 diffractometer with a image plate detector. Crystallographic and experimental details of both compounds are summarized in Table 1. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner.

The structures were solved by direct methods, using the SHELXS computer program, and refined by the full-matrix least-squares method with the SHELX97 computer program.[24] The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0774P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f', and f'' were taken from International Tables of X-Ray Crystallography.[25] All H atoms were computed and refined with an overall isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the atom to which they are linked using a riding model.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for compounds (PPh_4)[**1**] and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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