

The d-d band is only weakly structured in these complexes, but in some cases three components are distinguishable corresponding to transitions from the manifold of filled d orbitals of Figure 6 to the σ^* orbital of xy symmetry. The σ interaction between the xy and z^2 d orbitals with the ligand σ orbitals could be the same in the green and the orange complexes. Then the difference in the d-d absorption maximum for the two groups of complexes would be determined by a different amount of interaction between the yz , zx d orbitals and the ligand π orbitals. The most important interaction will be with the lowest lying empty π^* orbital which stabilizes the d_{xy} orbitals. The stabilization must be most pronounced in the complexes having an even number of ligand π orbitals only half filled, i.e., in the green complexes. We would therefore expect the d-d transitions in the green complexes to occur at a higher energy than in the orange complexes. The opposite is observed, and we interpret this as an indication of significantly different σ interactions in the two groups of complexes. This effect is not evident from the variation of bond lengths.

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Supplementary Material Available: Tables A1-A3, hydrogen atom positional and thermal parameters for structures I-III, and Tables A4-A6, listings of $10|F_o|$ and $10|F_c|$ for all three compounds (24 pages). Ordering information is given on any current masthead page.

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Coordination of Metal Carbonyl Anions to Triphenylaluminum, -gallium, and -indium and the Crystal Structure of Tetraethylammonium Triphenyl((η^5 -cyclopentadienyl)dicarbonyliron)aluminate ($Fe-Al$)¹

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Complexes of triphenylmetal acceptors, Ph_3E , where E is Al, Ga, or In, with metal carbonyl anions, $m^- = CpFe(CO)_2^-$, $CpW(CO)_3^-$, $Co(CO)_4^-$, and $Mn(CO)_5^-$, where $Cp = \eta^5-C_5H_5$, were prepared by combining the donor salt with the acceptor in dichloromethane or, in the case of $CpFe(CO)_2^-$, in tetrahydrofuran. The following crystalline complexes were isolated: $Et_4N^+Ph_3EFe(CO)_2Cp^-$ (E = Al, Ga, and In), $((n-Bu)_4N^+Ph_3E)CpW(CO)_3^-$ (E = Al and In), $(Ph_3P)_2N^+Ph_3InCo(CO)_4^-$, and $(n-Pr)_4N^+Ph_3InMn(CO)_5^-$. The title compound crystallized in space group $P2_1/c$ with $a = 10.507(3) \text{ \AA}$, $b = 15.254(4) \text{ \AA}$, $c = 18.892(4) \text{ \AA}$, and $\beta = 92.63(2)^\circ$. The complex possesses a direct Fe-Al bond of length 2.510(2) \AA between the donor and acceptor moieties. This bond, the first between iron and aluminum in an organometallic complex, appears to have predominantly single bond character. By analysis of infrared spectroscopic data (ν_{C-O}) the presence of a metal-metal bond was revealed in all complexes except that of $(n-Bu)_4N^+CpW(CO)_3^-$ with Ph_3Al in which case the oxygen atom of a carbonyl ligand is the site of Lewis basicity in a $WC\equiv OAl$ link. Dichloromethane solutions of $(n-Bu)_4N^+Ph_3GaCpW(CO)_3^-$ contain, in addition to uncomplexed $CpW(CO)_3^-$, two isomeric complexes: a metal-metal bonded species analogous to the corresponding Ph_3In complex and a C- and O-bonded adduct of the type found in the Ph_3Al complex. Complexes of Ph_3Ga and, especially, of Ph_3Al with $Co(CO)_4^-$ and $Mn(CO)_5^-$ were thermally unstable. Approximate formation constants for the complexes were estimated from IR band intensities and the relative magnitudes can be rationalized in terms of the principle of hard and soft acids and bases.

Introduction

Transition-metal carbonyl anions, m^- , have been used widely for the synthesis of numerous derivatives $m-X$ in which the

metal, M, as the site of Lewis basicity, forms a direct covalent M-X bond.^{2,3} With certain acceptors, however, the interposition of a carbonyl group generates an $MC\equiv OX$ sequence

in which the carbonyl oxygen is the site of Lewis basicity.^{4,5} Moreover, Shriver and co-workers observed an analogous bonding mode involving a bridging carbonyl ligand⁶ and subsequently studied a variety of such C- and O-bonded carbonyl complexes.⁷ The role of metal basicity in determining the structure of such coordination complexes is clearly important and metal carbonyl complexes with BH_3 ,⁸ InBr_3 ,⁹ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ¹⁰ have been described¹¹ in these terms.

Numerous coordination complexes of Ph_3E acceptors (E = B, Al, Ga, and In) with main group bases (especially nitrogen bases) have been described, but relatively few anionic complexes are known.¹² Although triaryl derivatives of the group 3 elements are weaker Lewis acids than the corresponding halides, their reactions with nucleophilic metal carbonyl anions are not complicated by displacement reactions.¹¹ In the present study, complexes of these triaryl derivatives^{13,14} are compared for a wide range of metal carbonyl anion base strengths, namely, $\text{Fe}(\text{CO})_2\text{Cp}^- \gg \text{W}(\text{CO})_3\text{Cp}^- > \text{Mn}(\text{CO})_5^- > \text{Co}(\text{CO})_4^-$.

Experimental Section

Unless stated otherwise, all operations were carried out under a purified argon atmosphere; the apparatus and techniques employed for handling air-sensitive compounds have been described in detail elsewhere.¹⁵ Infrared (IR) spectra were obtained either on a Perkin-Elmer Model 337 spectrometer, calibrated with polystyrene, or on a Model 521, calibrated with DCl, using cells previously described.¹⁵ Unless noted, all melting points were determined in sealed, argon-filled capillaries using a Büchi melting point apparatus and are corrected. Elemental analyses were carried out by the Pascher Microanalytical Laboratory, Bonn, Germany, and by A. Bernhardt, Mülheim, Germany.

Reagents. All solvents were reagent grade and were dried and degassed prior to distillation under an argon atmosphere. Tetrahydrofuran and toluene were distilled from potassium or sodium benzophenone ketyl, respectively. Hexane (mixed isomer) was distilled from potassium and benzophenone. Methylene chloride and diethyl ether were distilled from P_4O_{10} and CaH_2 , respectively.

The following compounds were prepared by literature methods: $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$,¹⁶ $(\text{Ph}_3\text{P})_2\text{NCl}$,¹⁶ Ph_3Al ,¹⁷ Ph_3Ga ,¹⁸ Ph_3In ,¹⁸ $\text{Mn}_2(\text{CO})_{10}$,¹⁹ and $\text{Hg}[\text{CpW}(\text{CO})_3]_2$.²⁰

Preparation of $(n\text{-Pr})_4\text{N}^+\text{Mn}(\text{CO})_5^-$. A solution of 1.56 g (4.00 mmol) of $\text{Mn}_2(\text{CO})_{10}$ in 30 mL of THF was stirred with 70 g of 0.5% sodium amalgam (15 mg-atoms of Na) for 1 h. The yellow solution of $\text{Na}^+\text{Mn}(\text{CO})_5^-$ was decanted into a Schlenk reaction vessel (SRV) containing 2.66 g (10 mmol) of $(n\text{-Pr})_4\text{N}^+\text{Br}^-$ (Eastman Organic Chemicals) and was stirred at room temperature for 12 h. Filtration through a "fine" frit into a SRV gave a clear, greenish yellow solution. Addition of 40 mL of toluene followed by cooling caused no solid to form. Trap-to-trap vacuum distillation (TTVD) removed 30 mL of solvent, leaving a green oil. The supernatant liquid was withdrawn, and the green oil was dried under vacuum to afford a light green, crystalline solid. Diethyl ether (25 mL) was added, followed by methanol (3 mL), to give a clear, green solution. Slow cooling to -40°C gave yellow crystals. The supernatant liquid was decanted into a SRV, and the crystals were dried under vacuum to afford 1.46 g (48%) of air-sensitive $(n\text{-Pr})_4\text{N}^+\text{Mn}(\text{CO})_5^-$. To the supernatant liquid, 10 mL of Et_2O was added, and the solution was cooled slowly to -60°C . The supernatant liquid was withdrawn from the yellow crystals which had formed, and these were dried under vacuum to afford an additional 0.34 g (11%) of product, mp $74.5\text{--}75.5^\circ\text{C}$. Anal. Calcd for $(\text{C}_3\text{H}_7)_4\text{NMn}(\text{CO})_5$: C, 53.6; H, 7.41; N, 3.68. Found: C, 52.82; H, 7.37; N, 3.75. IR, $\nu(\text{CO})$ in CH_2Cl_2 : 1899 (6), 1857 (10) cm^{-1} .

Preparation of $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$. A solution of 6.069 g (7.00 mmol) of $[\text{Cp}(\text{CO})_3\text{W}]_2\text{Hg}$ in 30 mL of THF was stirred with 70 g of 1% sodium amalgam (30 mg-atoms of Na) at room temperature for 3 h resulting in a color change from orange to cloudy yellow. Filtration through a "fine" porosity frit containing Celite gave a clear, yellow solution. Tetra-*n*-butylammonium bromide (4.51 g, 14.0 mmol, Eastman Organic Chemicals) was dried under vacuum in a SRV for 15 min and then was dissolved in 20 mL of warm THF. To this solution, the $\text{Na}^+\text{CpW}(\text{CO})_3^-$ in THF was added. The mixture was stirred for 18 h at room temperature and then was filtered through a "fine" porosity frit containing Celite to give a clear, yellow solution.

After the volume of this solution had been reduced to 36 mL by TTVD, 40 mL of toluene was added at 45°C and the solution was slowly cooled to -65°C . The supernatant liquid was decanted, and the yellow crystals were dried under vacuum to afford 7.47 g (93%) of $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$, mp $115.5\text{--}116.5^\circ\text{C}$. Anal. Calcd for $(\text{C}_4\text{H}_9)_4\text{NC}_5\text{H}_5\text{W}(\text{CO})_3$: C, 50.10; H, 7.20; N, 2.44. Found: C, 49.02; H, 7.23; N, 2.86. IR: $\nu(\text{CO})$ (in THF) 1887 (9), 1775 (10), and 1757 (9.5) cm^{-1} ; $\nu(\text{CO})$ (in CH_2Cl_2) 1887 (7.5), and 1767 (10, br) cm^{-1} ; $\nu(\text{CO})$ (in KBr) 1885 (5), 1772 (8), and 1748 (10) cm^{-1} .

Preparation of $(n\text{-Bu})_4\text{N}^+\text{CpFe}(\text{CO})_2^-$ and $\text{Et}_4\text{N}^+\text{CpFe}(\text{CO})_2^-$. A solution of 2.48 g (7.00 mmol) of $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ (Strem Chemicals, purified by vacuum sublimation) in 25 mL of THF was stirred with 70 g of 1% sodium amalgam (30 nmol of Na) at room temperature for 1 h, causing the solution to change color from dark maroon to deep orange-red. Tetra-*n*-butylammonium bromide (4.51 g, 14.0 mmol) was dried under vacuum for 15 min and then was dissolved in 20 mL of warm THF. Into this solution, the solution of $\text{Na}^+\text{CpFe}(\text{CO})_2^-$ in THF was decanted from the amalgam. After being stirred for 5 h, the mixture was filtered through a "fine" porosity frit containing Celite. Toluene (55 mL) was added at 50°C , and the clear red solution was slowly cooled to -55°C resulting in formation of rust red rectangular crystals. The supernatant liquid was decanted, and the crystals were dried under vacuum to afford 4.87 g (83%) of $(n\text{-Bu})_4\text{N}^+\text{CpFe}(\text{CO})_2^-$, mp $103\text{--}104.5^\circ\text{C}$. Anal. Calcd for $(\text{C}_4\text{H}_9)_4\text{NC}_5\text{H}_5\text{Fe}(\text{CO})_2$: C, 65.9; H, 9.86; N, 3.34. Found: C, 60.96; H, 10.21; N, 3.48. IR: $\nu(\text{CO})$ (in THF) 1865 (10) and 1770 (10) cm^{-1} (lit.²¹ $\nu(\text{CO})$ (in THF) 1865 and 1788 cm^{-1}). The solid product was very air sensitive, darkening rapidly. In a similar way, pulverized, vacuum dried tetraethylammonium bromide (2.52 g, 12 mmol) was added to $\text{Na}^+\text{CpFe}(\text{CO})_2^-$ (6.0 mmol) in THF (25 mL) and stirred for 15 h. Addition of toluene (5 mL) to the filtered, dark red solution at 60°C , followed by slow cooling to -50°C (in the presence of seed crystals formed by prior cooling to -80°C), gave brick red crystals. The product was washed with toluene (10 mL) and dried under vacuum to give 1.36 g (76%) of brownish red, crystalline $\text{Et}_4\text{N}^+\text{CpFe}(\text{CO})_2^-$, mp $111\text{--}114^\circ\text{C}$ dec. Anal. Calcd for $(\text{C}_2\text{H}_5)_4\text{NC}_5\text{H}_5\text{Fe}(\text{CO})_2$: C, 58.7; H, 8.21; N, 4.56. Found: C, 57.69; H, 8.39; N, 4.60. IR: $\nu(\text{CO})$ (in Nujol) 1871 (9), 1860 (9), 1790 (9), 1772 (10), 1760 (7.5) cm^{-1} .

$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{InCo}(\text{CO})_4^-$. Addition of 10 mL of CH_2Cl_2 to 0.334 g (0.471 mmol) of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$ and 0.163 g (0.471 mmol) of Ph_3In in a SRV gave a clear, pale yellow solution, the infrared spectrum of which showed mostly complex: $\nu(\text{CO})$ (in CH_2Cl_2) 2042 (m), ~ 1960 (m, sh), 1939 (s), and 1889 (m) cm^{-1} . Addition of 22 mL of toluene and 8 mL of CH_2Cl_2 , followed by slow cooling to -22°C , afforded colorless, needle-shaped crystals. The supernatant liquid was decanted, and the crystals were dried under vacuum, giving 0.398 g (80%) of air-stable $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{InCo}(\text{CO})_4^-$, mp $182\text{--}184^\circ\text{C}$.

$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{GaCo}(\text{CO})_4^-$. Addition of 13 mL of CH_2Cl_2 at -78°C to 0.468 g (0.66 mmol) of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$ and 0.199 g (0.66 mmol) of Ph_3Ga in a SRV gave a light yellow solution, the infrared spectrum of which at 0°C showed $\nu(\text{CO})$ 2040 (m), ~ 1958 (s, sh), 1937 (vs), and 1892 (m) cm^{-1} . Storage of the solution at 0°C for 2 h caused a color change to orange. Addition of 15 mL of hexane at room temperature gave microcrystalline cloudiness which had initially appeared as an oil. Filtration through a "fine" frit containing Celite followed by cooling to -65°C gave large, colorless crystals and a maroon supernatant liquid. The supernatant liquid was decanted and saved, and the crystals were washed at 0°C with a mixture of 10 mL of hexane and 3 mL of CH_2Cl_2 and then were dried under vacuum to afford 0.200 g (33%) of off-white, slightly air-sensitive crystals of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{GaCo}(\text{CO})_4^-$, mp $\sim 160\text{--}165^\circ\text{C}$ (Table I). A second crop of product was obtained by addition of 5 mL of hexane to the supernatant liquid, followed by cooling to -60°C . These crystals, when washed with 10 mL of hexane and dried under vacuum, weighed 0.140 g (21%) and also melted at $\sim 160\text{--}165^\circ\text{C}$.

$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{AlCo}(\text{CO})_4^-$. Addition of 19 mL of CH_2Cl_2 at -20°C to 0.690 g (0.97 mmol) of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$ and 0.251 g (0.97 mmol) of AlPh_3 in a SRV gave a clear, nearly colorless, but very thermally sensitive solution, the IR spectrum of which when taken within 2 min showed mostly complex: $\nu(\text{CO})$ at 2049 (m), 2030 (mw), 2009 (w), 1966 (s, sh), 1940 (vs), 1889 (s), and 1730 (m) cm^{-1} . Addition of 35 mL of hexane and 11 mL of CH_2Cl_2 at -15°C , followed by cooling to -65°C , gave a maroon supernatant liquid and nearly colorless, needle-shaped crystals. These were washed at -78°C with a mixture of 20 mL of hexane and 5 mL of CH_2Cl_2 and were

Table I. Analytical Data for Isolated Complexes

complex	% calcd			% found		
	C	H	N	C	H	N
(Ph ₃ P) ₂ N ⁺ Ph ₃ InCo(CO) ₄ ⁻	66.1 (Co, 5.59)	4.30		64.90 (Co, 5.18)	4.34	
(Ph ₃ P) ₂ N ⁺ Ph ₃ GaCo(CO) ₄ ⁻	69.1 (Co, 5.84)	4.50		68.02 (Co, 6.67)	4.45	
(Ph ₃ P) ₂ N ⁺ Ph ₃ AlCo(CO) ₄ ⁻	72.2 (Co, 6.00)	4.69		69.97 (Co, 5.74)	4.65	
(<i>n</i> -Pr) ₄ N ⁺ Ph ₃ InMn(CO) ₅ ⁻	57.8	5.96	1.92	55.98	5.86	2.08
(<i>n</i> -Bu) ₄ N ⁺ Ph ₃ InW(CO) ₃ Cp ⁻	54.8 (W, 19.9; In, 12.4)	6.12	1.52	55.54 (W, 19.61; In, 12.28)	6.31	1.44
(<i>n</i> -Bu) ₄ N ⁺ Ph ₃ AlOCW(CO) ₂ Cp ⁻	60.6 (W, 22.1; Al, 3.24)	6.65	1.68	58.77 (W, 22.62; Al, 3.45)	7.06	1.67
Et ₄ N ⁺ Ph ₃ InFe(CO) ₂ Cp ⁻	60.7	6.18	2.15	61.16	6.35	2.33
Et ₄ N ⁺ Ph ₃ GaFe(CO) ₂ Cp ⁻	65.2	6.63	2.30	65.32	6.76	2.35
Et ₄ N ⁺ Ph ₃ AlFe(CO) ₂ Cp ⁻	70.1	7.13	2.48	69.32	7.21	2.71

dried under vacuum to afford 0.596 g (63%) of slightly air-sensitive (Ph₃P)₂N⁺Ph₃AlCo(CO)₄⁻, mp ~140 °C dec under rapid heating to a maroon foam.

(*n*-Pr)₄N⁺Ph₃InMn(CO)₅⁻. A yellow solution of (*n*-Pr)₄N⁺Mn(CO)₅⁻ (0.225 g, 0.67 mmol) in CH₂Cl₂ (13.5 mL) was added to Ph₃In (0.232 g, 0.67 mmol) to give a very light yellow solution. Addition of 10 mL of hexane, followed by filtration through a "fine" frit and slow cooling to -55 °C, gave colorless, needle-shaped crystals which when dried under vacuum afforded 0.344 g (71%) of slightly air-sensitive (*n*-Pr)₄N⁺Ph₃InMn(CO)₅⁻, mp 150–153 °C dec.

Reaction of (*n*-Pr)₄N⁺Mn(CO)₅⁻ with Ph₃Ga. A solution of (*n*-Pr)₄N⁺Mn(CO)₅⁻ (0.391 g, 1.03 mmol) in CH₂Cl₂ (20 mL) was added to 0.309 g (1.03 mmol) of Ph₃Ga at -78 °C. The IR spectrum of the resulting colorless solution was taken quickly and had $\nu(\text{CO})$ at 2047 (m), 1960 (m, sh), 1935 (vs), and 1858 (m-w) cm⁻¹. The solution was warmed to 0 °C and hexane (11 mL) was added. Cooling to -55 °C gave colorless, needle-shaped crystals which when dried under vacuum afforded 0.314 g (45%) of air-sensitive and thermally unstable (*n*-Pr)₄N⁺Ph₃GaMn(CO)₅⁻, mp (with rapid heating) ~130–133 °C dec. The crystalline product gradually turned yellow and then orange while under argon at room temperature. An elemental analysis was not obtained due to this thermal instability.

Reaction of (*n*-Pr)₄N⁺Mn(CO)₅⁻ with Ph₃Al. To 0.34 g (1.33 mmol) of Ph₃Al at -78 °C was added a solution of 0.508 g (1.33 mmol) of (*n*-Pr)₄N⁺Mn(CO)₅⁻. The IR spectrum of the pale yellow, very thermally sensitive solution was taken rapidly and contained $\nu(\text{CO})$ at 2056 (m-w), 2024 (m-s), 1968 (m, sh), 1944 (s), 1900 (s), 1858 (s), 1696 (m), and 1684 (m) cm⁻¹. A portion of the reaction mixture was allowed to warm to room temperature for 1 h. IR: $\nu(\text{CO})$ 2124 (w), 2024 (s), 2000 (m, sh), 1972 (m), 1900 (s), and 1858 (s) cm⁻¹. Attempts to crystallize a product by addition of hexane and cooling failed.

(*n*-Bu)₄N⁺Ph₃InW(CO)₃Cp⁻. Addition of CH₂Cl₂ (13 mL) to 0.379 g (0.66 mmol) of (*n*-Bu)₄N⁺CpW(CO)₃⁻ and 0.228 g (0.66 mol) of Ph₃In gave a pale yellow solution. Addition of hexane (20 mL) followed by cooling to -35 °C gave a light yellow oil. Removal of the solvent by TTVD left a nearly white solid which was then dissolved in 50 mL of toluene at 90 °C. Slow cooling to -62 °C gave pale yellow crystals which, when dried under vacuum, afforded 0.487 g (80%) of slightly air-sensitive (*n*-Bu)₄N⁺Ph₃InW(CO)₃Cp⁻, mp 165–166 °C.

Reaction of (*n*-Bu)₄N⁺CpW(CO)₃⁻ with Ph₃Ga. A yellow solution of (*n*-Bu)₄N⁺CpW(CO)₃⁻ (0.458 g, 0.78 mmol) in CH₂Cl₂ (8 mL) was added to 0.236 g of Ph₃Ga. The IR spectrum of the resulting orange solution had $\nu(\text{CO})$ at 1971 (w), 1934 (s), 1905 (m), 1888 (w, sh), 1845 (s, sh), 1823 (s), 1800 (m, sh), 1760 (w, sh), and 1642 (m) cm⁻¹. Addition of hexane (7 mL) followed by cooling to -65 °C gave an oil.

(*n*-Bu)₄N⁺Ph₃AlOCW(CO)₂Cp⁻. Addition of CH₂Cl₂ (30 mL) to a mixture of 0.575 g (1.00 mmol) of (*n*-Bu)₄N⁺CpW(CO)₃⁻ and 0.258 g (1.00 mmol) of Ph₃Al gave a clear yellow solution. Addition of hexane (40 mL) followed by slow cooling to -60 °C gave yellow crystals. These were washed with 1:1 CH₂Cl₂-hexane (5 mL) and dried under vacuum and afforded 0.671 g (81%) of slightly air-sensitive (*n*-Bu)₄N⁺Ph₃AlOCW(CO)₂Cp⁻, mp 138–139 °C dec. This product was recrystallized from toluene (50 mL) in the temperature range +85 to -22 °C. The resulting yellow rectangular crystals had the same melting point as before.

Reaction of (*n*-Bu)₄N⁺Ph₃AlOCW(CO)₂Cp⁻ with Pyridine. To a yellow solution of (*n*-Bu)₄N⁺Ph₃AlOCW(CO)₂Cp⁻ (0.316 g, 0.380 mmol) in toluene (15 mL) at 100 °C was added pyridine (0.50 g, 0.76 mmol). Upon cooling of the solution to room temperature, an oil formed. The oil was redissolved by heating the mixture to reflux. Upon cooling of the solution to room temperature a yellow crystalline solid formed. After further cooling of the solution to -8 °C, the supernatant liquid was decanted and the crystals were dried under vacuum. The product (0.206 g, 94.5%) was identified as (*n*-Bu)₄N⁺CpW(CO)₃⁻ by melting point and mixture melting point with an authentic sample.

Et₄N⁺Ph₃InFe(CO)₂Cp⁻. Addition of 0.47 mmol (4.7 mL of a 0.10 M solution) of Et₄N⁺CpFe(CO)₂⁻ in THF to 0.162 g (0.47 mmol) of Ph₃In gave an orange-yellow solution. Cooling to -78 °C caused no change. Addition of 5 mL of hexane caused precipitation of yellow solid which redissolved when 10 mL of THF was added at 40 °C. Slow cooling to -65 °C gave orange-yellow crystals, which, when washed with 5 mL of cold toluene and dried under vacuum, afforded 0.193 g (63%) of slightly air-sensitive Et₄N⁺Ph₃InFe(CO)₂Cp⁻, mp 159.5–161 °C.

Et₄N⁺Ph₃GaFe(CO)₂Cp⁻. Addition of 0.45 mmol (4.5 mL of a 0.10 M solution) of Et₄N⁺CpFe(CO)₂⁻ in THF to 0.135 g (0.45 mmol) of Ph₃Ga gave a clear, orange-yellow solution. Addition of 5 mL of hexane caused precipitation of yellow solid which redissolved when 30 mL of THF was added at 40 °C. Slow cooling to -65 °C gave orange-yellow crystals which, when washed with 5 mL of cold toluene and dried under vacuum, afforded 0.164 g (60%) of slightly air-sensitive Et₄N⁺Ph₃GaFe(CO)₂Cp⁻, mp 173–175.5 °C dec.

Et₄N⁺Ph₃AlFe(CO)₂Cp⁻. Addition of 1.57 mmol (15.7 mL of a 0.10 M THF solution) of Et₄N⁺CpFe(CO)₂⁻ in THF to 0.405 g (1.57 mmol) of AlPh₃ in 5 mL of THF at 0 °C gave a slightly cloudy, brown-orange solution. Filtration through a "fine" frit, followed by slow cooling to -65 °C, gave acicular, ochre-yellow crystals which, when washed with 5 mL of THF at -65 °C and dried under vacuum, afforded 0.582 g (55%) of slightly air-sensitive Et₄N⁺Ph₃AlFe(CO)₂Cp⁻, mp 166–167.5 °C dec.

X-ray Structure Analysis. A yellow-brown parallelepiped of Et₄N⁺Ph₃AlFe(CO)₂Cp⁻ with approximate dimensions 0.38 × 0.25 × 0.15 mm was sealed within a thin-walled capillary under inert atmosphere. X-ray diffraction photographs revealed a monoclinic lattice with systematic absences ($l = 2n + 1$ for $h0l$, $k = 2n + 1$ for $0k0$) that uniquely determine the space group $P2_1/c$ (C_{2h}^5 , No. 14); this lattice assignment was confirmed by Delauney reduction. Lattice parameters $a = 10.507$ (3) Å, $b = 15.254$ (4) Å, $c = 18.892$ (4) Å, and $\beta = 92.63$ (2)° were obtained from least-squares refinement of 12 reflections with $2\theta \geq 30^\circ$ for Mo K α radiation which were automatically centered on a Picker FACS-I four-circle diffractometer at 20 °C. With $Z = 4$ and a formula weight of 565.52 g mol⁻¹, the calculated density is $\rho_{\text{calcd}} = 1.22$ g cm⁻³.

Diffracted intensities were measured for a total of 5784 reflections with $(\sin \theta)/\lambda \leq 0.5760$ using the diffractometer in θ - 2θ scan mode with Zr-filtered Mo K α radiation incident at a takeoff angle of 3.5°. Each scan was done at a rate of 1° of 2θ per minute and over a range of 1.2° in 2θ at minimum, plus a systematic allowance for spectral dispersion; 20-s background counts were taken at each end of the scan. Of the 4869 reflections found to be independent and not systematically absent, 4085 were regarded as objectively observed with $|F_o| \geq 1.96\sigma_F$.

Chart I. Approximate Formation Constants and Modes of Bonding for $(\text{Ph}_3\text{E})\text{m}^-$ Complexes^a

EPh_3	$(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$	$(n\text{-Pr})_2\text{N}^+\text{Mn}(\text{CO})_5^-$	$(n\text{-Bu})_4\text{N}^+\text{W}(\text{CO})_3\text{Cp}^-$	$\text{Na}^+\text{Fe}(\text{CO})_2\text{Cp}^-$ ^b
Ph_3B	$<10^{-3}$ ^c	$<10^{-3}$ ^c	$<10^{-3}$ ^c	$>10^5$ (B-Fe) ^c
Ph_3Al	(Al-Co) ^d	(Al-Mn) ^d	1×10^3 (Al-OC-W)	$>10^5$ (Al-Fe)
Ph_3Ga	1×10^3 (Ga-Co) ^e	6×10^2 (Ga-Mn) ^e	1×10^4 (Ga-W + Ga-OC-W)	$>10^5$ (Ga-Fe)
Ph_3In	6×10^2 (In-Co)	$>10^5$ (In-Mn)	5×10^3 (In-W)	$>10^5$ (In-Fe) ^f

^a Formation constants are defined as $K_F = [(\text{Ph}_3\text{E})\text{m}^-]/[(\text{Ph}_3\text{E})][\text{m}^-]$; except as noted all measurements were made in CH_2Cl_2 at room temperature. (See appendix in ref 25.) ^b THF was the solvent for this series. ^c Data from J. H. Burk, M. S. Thesis, Cornell University, 1974. ^d Thermal decomposition prevented a reliable estimate. ^e The spectrum was recorded as the complex was warming from $\sim 0^\circ\text{C}$ to ambient temperature. ^f The $(n\text{-Bu})_4\text{N}^+$ salt was used.

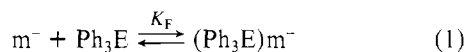
where $|F_0| = [(C - tB)/Lp]^{1/2}$ and $\sigma_F = (C + t^2B)^{1/2}/(2|F_0|Lp) + 0.02|F_0|$; C is the total count recorded during the scan, t is the ratio of the scanning time to the total time for the background B , and L and p are the Lorentz and polarization corrections, respectively. Correction of the data for absorption of X-rays was not made, as careful estimation of this factor using a linear mass absorption coefficient $\mu = 0.564 \text{ mm}^{-1}$ produced a maximum of 5% variation in diffracted intensity within the entire data set. Three standard reflections were periodically monitored with each 50 data throughout the 18-day experiment and the average standard deviation of these intensity measurements was less than 1%.

Structure Determination and Refinement. The positions of the iron and aluminum atoms were located in Patterson analyses and subsequent Fourier syntheses revealed the complete anion structure with clarity. The cation, however, was poorly resolved in the maps; after full-matrix least-squares refinement of positional and isotropic thermal parameters converged to a residual of about 0.12, it became apparent that this ion was disordered in the lattice. A two-state model was adopted for the α carbons of the ethyl groups, using site occupancies of $1/3$ and $2/3$ determined from an analysis of the electron density map. Block-diagonal refinement using anisotropic thermal parameters for the anion atoms only slightly reduced the residual and further parameterization by the introduction of calculated anion hydrogen positions, with isotropic thermal coefficients 0.5 \AA^2 larger than those of the adjacent carbon atoms, was also inadequate to deal with the complex disorder. It was clear that the disorder could not be modeled by a two-state parameterization and it was judged that more elaborate models would not yield any new significant structural information. Therefore, anisotropic temperature factors were applied to the two-state cation and all nonhydrogen atom parameters were refined until convergence. The total number of parameters thus varied was 379, including a scale factor.

The quantity minimized in the least-squares analysis was $\sum w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2$ with σ defined above. Scattering factors were those of Cromer and Mann²² and anomalous dispersion corrections applied to the iron and aluminum form factors were those of Cromer.²³ The final conventional residual was $R_1 = 0.097$ and the weighted residual, $R_2 = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$, was 0.098 with a data-to-parameter ratio of 10.8 to 1. The final difference Fourier synthesis displayed a maximum residual density of 0.46 e/\AA^3 at several places in the cation region of the cell, reflecting a more complex disorder than parameterized above. The final structural parameters are listed in Tables II, III, and IV.

Results and Discussion

Preparation of Complexes. The general method of preparation of the complexes is shown in eq 1. A triphenylmetal



Lewis acid, Ph_3E , where E is Al, Ga, or In, was combined with a metal carbonyl anion, m^- , where m is $\text{Co}(\text{CO})_4$, $\text{Mn}(\text{CO})_5$, $\text{CpW}(\text{CO})_3$, or $\text{CpFe}(\text{CO})_2$, in a weakly basic solvent. Dichloromethane was the solvent for all reactions except those involving $\text{CpFe}(\text{CO})_2^-$ with which it rapidly reacted; for this anion, tetrahydrofuran was used as the solvent. Equilibrium concentrations of the metal carbonyl anions were estimated from intensities of infrared spectra; these yielded formation constants, K_F , with estimated uncertainties of $\pm 20\%$. The values, listed in Chart I, provide an approximate measure of the relative tendencies for complex formation. The chart also summarizes the modes of bonding for each complex as deduced from the results of this study.

Table II. Fractional Coordinates for Nonhydrogen Atoms of $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$ ^a

	10^4x	10^4y	10^4z
Fe	2960.3 (9)	950.4 (6)	4508.8 (4)
Al	1910 (2)	2424 (1)	4390.6 (9)
C ₁	2063 (7)	857 (4)	5251 (3)
O ₁	1461 (5)	771 (3)	5745 (3)
C ₂	4168 (6)	1561 (4)	4922 (3)
O ₂	5005 (5)	1948 (4)	5191 (3)
C ₁ (1)	3013 (9)	-341 (5)	4106 (4)
C ₂ (1)	1923 (8)	122 (5)	3819 (4)
C ₃ (1)	2356 (8)	849 (5)	3440 (3)
C ₄ (1)	3691 (8)	850 (5)	3504 (4)
C ₅ (1)	4089 (8)	114 (6)	3912 (4)
C ₁ (2)	2023 (6)	3185 (4)	5266 (3)
C ₂ (2)	1555 (7)	4029 (5)	5194 (4)
C ₃ (2)	1621 (8)	4637 (5)	5741 (4)
C ₄ (2)	2181 (8)	4417 (5)	6386 (4)
C ₅ (2)	2648 (8)	3584 (5)	6487 (4)
C ₆ (2)	2577 (7)	2997 (4)	5933 (4)
C ₁ (3)	2817 (6)	3126 (4)	3661 (3)
C ₂ (3)	2468 (7)	3220 (5)	2947 (3)
C ₃ (3)	3142 (10)	3715 (6)	2482 (4)
C ₄ (3)	4231 (10)	4124 (6)	2709 (5)
C ₅ (3)	4653 (7)	4058 (5)	3418 (5)
C ₆ (3)	3941 (6)	3568 (5)	3867 (4)
C ₁ (4)	23 (6)	2321 (4)	4114 (3)
C ₂ (4)	-747 (6)	1622 (4)	4302 (3)
C ₃ (4)	-2062 (7)	1612 (5)	4182 (4)
C ₄ (4)	-2663 (6)	2318 (5)	3850 (4)
C ₅ (4)	-1928 (7)	3016 (5)	3640 (4)
C ₆ (4)	-617 (6)	3010 (4)	3770 (4)
N	7826 (6)	1559 (4)	1528 (3)
C ₃	7424 (14)	1655 (9)	720 (6)
C ₃ '	7458 (28)	758 (22)	1094 (17)
C _{3a}	6429 (10)	1005 (7)	458 (5)
C ₄	8446 (10)	655 (8)	1622 (6)
C ₄ '	8368 (39)	1113 (25)	2302 (16)
C _{4a}	9154 (10)	484 (7)	2352 (5)
C ₅	8696 (22)	2343 (13)	1740 (9)
C ₅ '	9017 (26)	2063 (17)	1193 (19)
C _{5a}	9509 (12)	2753 (9)	1439 (7)
C ₆	6642 (15)	1561 (8)	2032 (7)
C ₆ '	6789 (19)	2200 (21)	1740 (16)
C _{6a}	5790 (12)	2305 (10)	1959 (6)

^a Estimated standard deviations in parentheses correspond to the last significant digit.

The crystallizability of the adducts depended strongly upon the cation. The complexes usually had the same colors as their metal carbonyl anion precursors but of a lighter shade.

$\text{Et}_4\text{N}^+\text{Ph}_3\text{EFe}(\text{CO})_2\text{Cp}^-$ Complexes. The three members of this series with E as In, Ga, or Al were obtained as yellow-orange, slightly air-sensitive crystalline solids. The aluminum compound showed some thermal instability in hot THF; the dark red product of its decomposition may result from migration of the Ph_3Al group to the Cp ring analogous to the behavior of $\text{Et}_4\text{N}^+\text{Ph}_3\text{BFe}(\text{CO})_2\text{Cp}^-$.^{13,24}

Infrared spectra of all the complexes in this group, recorded from mineral oil mulls (Table V), have two $^{12}\text{C}-\text{O}$ stretching absorptions consistent with C_s local symmetry and the presence of a direct iron-to-group 3 element link (vide infra). The higher frequency absorption is assigned to the symmetric mode.

Table III. Thermal Parameters for Nonhydrogen Atoms of $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$ ^a

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	$B, \text{Å}^2$
Fe	108 (1)	37.7 (4)	24.0 (3)	14.1 (6)	0.3 (4)	-0.4 (3)	3.79
Al	88 (2)	36.9 (9)	23.5 (6)	5 (1)	1.5 (8)	1.6 (6)	3.53
C ₁	150 (10)	36 (4)	29 (2)	2 (5)	-7 (4)	-3 (2)	4.45
O ₁	217 (9)	64 (3)	34 (2)	-18 (4)	34 (3)	-1 (2)	6.09
C ₂	108 (8)	53 (4)	31 (3)	25 (5)	-1 (4)	9 (3)	4.44
O ₂	115 (7)	77 (4)	54 (3)	2 (4)	-15 (3)	-7 (3)	6.45
C ₁ (1)	238 (15)	40 (4)	38 (3)	31 (6)	1 (5)	-4 (3)	5.71
C ₂ (1)	163 (12)	54 (5)	38 (3)	-6 (6)	1 (5)	-19 (3)	5.44
C ₃ (1)	194 (12)	59 (5)	23 (2)	19 (6)	-6 (4)	-5 (3)	5.25
C ₄ (1)	157 (12)	79 (6)	25 (2)	10 (7)	19 (4)	-5 (3)	5.43
C ₁ (1)	167 (13)	73 (5)	39 (3)	57 (7)	15 (5)	-11 (3)	5.60
C ₁ (2)	112 (8)	32 (3)	27 (2)	-9 (4)	6 (4)	0 (2)	3.76
C ₂ (2)	168 (11)	44 (4)	34 (3)	5 (6)	6 (4)	-4 (3)	5.21
C ₃ (2)	201 (13)	41 (4)	46 (3)	11 (6)	19 (5)	-2 (3)	5.93
C ₄ (2)	162 (12)	58 (5)	43 (3)	-40 (6)	18 (5)	-18 (3)	5.55
C ₅ (2)	187 (11)	64 (5)	28 (3)	-9 (7)	-1 (5)	-7 (3)	5.73
C ₆ (2)	147 (11)	48 (4)	30 (3)	13 (5)	-4 (4)	1 (3)	4.94
C ₁ (3)	119 (8)	32 (3)	30 (2)	9 (4)	11 (4)	4 (2)	3.98
C ₂ (3)	180 (12)	53 (5)	26 (3)	6 (6)	3 (4)	1 (3)	5.24
C ₃ (3)	277 (17)	66 (5)	30 (3)	9 (8)	31 (6)	11 (3)	6.43
C ₄ (3)	250 (16)	58 (5)	60 (4)	23 (8)	82 (7)	11 (4)	6.45
C ₅ (3)	131 (11)	65 (5)	65 (5)	0 (6)	35 (6)	14 (4)	6.41
C ₆ (3)	107 (9)	54 (4)	41 (3)	10 (5)	12 (4)	12 (3)	4.99
C ₁ (4)	83 (7)	43 (4)	26 (2)	6 (4)	1 (3)	-6 (2)	3.73
C ₂ (4)	101 (9)	55 (4)	33 (3)	5 (5)	4 (4)	7 (3)	4.70
C ₃ (4)	100 (9)	67 (5)	38 (3)	-10 (5)	10 (4)	2 (3)	5.22
C ₄ (4)	89 (8)	80 (6)	36 (3)	-6 (6)	2 (4)	-13 (3)	5.21
C ₅ (4)	109 (9)	51 (4)	43 (3)	25 (5)	-15 (4)	-7 (3)	4.91
C ₆ (4)	100 (9)	37 (4)	39 (3)	8 (5)	-6 (4)	-5 (3)	4.33
N	157 (8)	60 (4)	34 (2)	-14 (4)	-1 (3)	1 (2)	5.71
C ₃	251 (22)	76 (8)	31 (4)	12 (11)	7 (7)	14 (5)	6.82
C ₃ '	177 (42)	113 (21)	75 (13)	6 (23)	-4 (18)	-52 (14)	8.44
C _{3a}	274 (16)	92 (7)	43 (3)	20 (9)	-40 (6)	-12 (4)	8.10
C ₄	115 (13)	70 (7)	43 (4)	10 (8)	-18 (6)	-6 (5)	5.73
C ₄ '	350 (64)	117 (28)	49 (13)	-28 (34)	-30 (23)	6 (16)	10.29
C _{4a}	200 (14)	107 (8)	61 (4)	25 (8)	-43 (6)	3 (5)	8.57
C ₅	418 (42)	141 (12)	62 (7)	-152 (19)	9 (14)	-2 (7)	10.89
C ₅ '	197 (30)	77 (13)	119 (16)	-57 (16)	155 (20)	-2 (12)	6.17
C _{5a}	224 (16)	154 (10)	116 (7)	-107 (11)	6 (9)	51 (7)	10.55
C ₆	269 (24)	50 (7)	39 (5)	15 (10)	6 (8)	2 (5)	6.72
C ₆ '	32 (16)	127 (23)	78 (14)	11 (15)	18 (12)	-29 (15)	5.08
C _{6a}	254 (20)	193 (13)	65 (5)	99 (12)	-17 (8)	-6 (6)	11.36

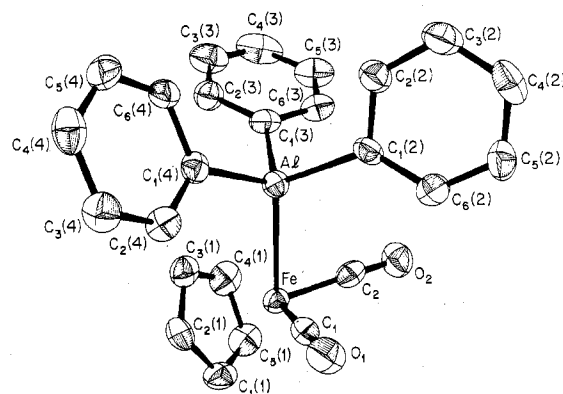
^a The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{13} + 2kl\beta_{23})]$. The isotropic equivalent of the anisotropic thermal parameters was obtained from $B = 4.0[V^2 \det(\beta_{ij})]^{1/3}$ and is in the form $\exp[-B(\sin^2 \theta)/\lambda^2]$. Estimated standard deviations in parentheses correspond to the last significant digit.

Table IV. Hydrogen Atom Parameters for $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$ ^a

	10^4x	10^4y	10^4z	$B, \text{Å}^2$
H ₁ (1)	2997	-880	4401	6.332
H ₂ (1)	1007	-45	3871	5.780
H ₃ (1)	1808	1292	3178	5.627
H ₄ (1)	4236	1282	3289	5.991
H ₅ (1)	4994	-49	4039	6.255
H ₂ (2)	1144	4202	4725	5.647
H ₃ (2)	1239	5235	5665	6.509
H ₄ (2)	2264	4851	6785	6.217
H ₅ (2)	3036	3396	6955	6.322
H ₆ (2)	2925	2395	6011	5.452
H ₁ (3)	1689	2930	2766	5.681
H ₃ (3)	2853	3795	1979	7.091
H ₄ (3)	4741	4473	2378	7.150
H ₅ (3)	5458	4361	3592	6.996
H ₆ (3)	4221	3546	4373	5.498
H ₂ (4)	-338	1091	4521	5.429
H ₃ (4)	-2576	1105	4345	5.823
H ₄ (4)	-3601	2331	3767	5.887
H ₅ (4)	-2337	3527	3388	5.575
H ₆ (4)	-109	3526	3607	4.906

^a Isotropic thermal parameters are in the form $\exp[-B(\sin^2 \theta)/\lambda^2]$. The numbering of the hydrogen atoms is the same as that of the carbon atoms to which they are bonded.

The shift to higher energy, $\Delta\nu(\text{CO})^{\text{as}}$, of the asymmetric C-O stretching vibration resulting from complex formation has been

Figure 1. A perspective view of the anion in $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$.

used²⁶ as a measure of the acceptor strength of Lewis acids for the base $\text{NCFe}(\text{CO})_2\text{Cp}$. In the present case $\Delta\nu(\text{CO})^{\text{as}}$ for complexation of $\text{Et}_4\text{N}^+\text{CpFe}(\text{CO})_2^-$ by Ph_3E was $90 \pm 2 \text{ cm}^{-1}$ when E was Al, Ga, or In but was $139 \pm 1 \text{ cm}^{-1}$ when E was boron.^{13,27} These values and NMR spectroscopic evidence¹³ strongly suggest that the transfer of charge from iron to the main group element is substantially greater for $\text{Ph}_3\text{BFe}(\text{CO})_2\text{Cp}^-$ than for the other anions.

Crystal Structure of $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$. The perspective view of the anion presented in Figure 1 illustrates that

Table V. Infrared Spectra of Complexes^a

complex	solvent	$\nu(\text{CO})$, ^b cm^{-1}
$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{InCo}(\text{CO})_4^-$	CH_2Cl_2	2042 (3), ~1960 (5, sh), 1939 (10), 1889 (3) ^d
	Nujol	2045 (5), 1968 (6.5), 1942 (8.5), 1925 (10)
$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{GaCo}(\text{CO})_4^-$	CH_2Cl_2	2040 (3), ~1958 (5.5, sh), 1937 (10), 1892 (4.5) ^d
	Nujol	2042 (4), 1966 (6.5), 1941 (8), 1927 (10), 1890 (1.5)
$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{AlCo}(\text{CO})_4^-$	CH_2Cl_2	2049 (2), 2030 (1.5), 2009 (0.5, sh), ~1966 (4, sh), 1940 (10), 1889 (5), ^d 1730 (2)
	Nujol	2050 (3.5), 1971 (6.5), 1944 (9), 1927 (10), 1890 (2.5, sh)
$(n\text{-Pr})_2\text{N}^+\text{Ph}_3\text{InMn}(\text{CO})_5^-$	CH_2Cl_2	2051 (2.5), ~1960 (4, sh), 1942 (10), 1935 (10)
	Nujol	2049 (4), 1963 (5.5), 1949 (10), 1927 (9), 1907 (2), 1895 (1.5), ~1858 (0.5, sh)
$(n\text{-Pr})_2\text{N}^+\text{Ph}_3\text{GaMn}(\text{CO})_5^-$	CH_2Cl_2	2047 (2.5), 2015 (0.5), ~1960 (2.5, sh), 1935 (10), 1858 (1.5)
	Nujol	2044 (4.5), 2015 (0.5), 1955 (7), 1938 (10), 1922 (9.5), ~1895 (2, sh), ~1860 (1, sh)
$(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{AlMn}(\text{CO})_5^-$ ^c	CH_2Cl_2	2056 (0.5), 2024 (3), ~1968 (1.5, sh), 1944 (4.5), 1900 (5.5), ^d 1858 (5.5), ^d 1696 (1.5), ^e 1684 (1.5) ^e
	Nujol	1933 (7.5), 1883 (1), ^d 1839 (7), 1819 (10), 1764 (1) ^d
$(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{InW}(\text{CO})_3\text{Cp}^-$	CH_2Cl_2	1931 (10), 1840 (7), 1820 (7.5)
	Nujol	1971 (1), 1934 (9), 1905 (3), ~1888 (2, sh), ^d 1845 (8), 1823 (10), ~1800 (5, sh), 1755 (0.5, sh), ^d 1642 (3.5)
$(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{GaW}(\text{CO})_3\text{Cp}^-$ ^c	CH_2Cl_2	1968 (1.5), 1934 (5.5), 1903 (4), 1890 (2.5, sh), 1845 (5.5), 1818 (10), ~1800 (7, sh), 1755 (1, sh), 1633 (4.5), 1605 (3, sh)
	toluene	1922 (7.5), 1885 (2.5), ^d 1825 (10), 1765 (2.5), ^d 1600 (7.5)
$(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{AlOCW}(\text{CO})_2\text{Cp}^-$	CH_2Cl_2	1920 (8), 1905 (1.5), 1890 (0.5), 1833 (10), 1803 (1), ~1775 (0.5, sh), 1600 (8), 1578 (2.5), 1562 (1)
	Nujol	1937 (10), ~1917 (1, sh), 1871 (10), 1843 (1.5)
$\text{Et}_4\text{N}^+\text{Ph}_3\text{InFe}(\text{CO})_2\text{Cp}^-$	Nujol	1938 (10), 1915 (1), 1871 (10), 1844 (1)
$\text{Et}_4\text{N}^+\text{Ph}_3\text{GaFe}(\text{CO})_2\text{Cp}^-$	Nujol	2012 (0.2), ^e 1960 (0.3), ^e 1940 (8), ~1920 (1, sh), 1871 (10), 1843 (1.5)

^a Solution concentrations are in the range 0.01–0.1 M. ^b Relative absorbance values are given in parentheses. ^c This complex was not isolated as a solid; the spectrum is that of the reaction mixture. ^d This band is assigned to ν^- . ^e The intensity of this band, relative to those of the strong bands, varied from sample to sample. The band is assigned to a product of spurious oxidation or hydrolysis.

Table VI. Selected Anion Distances (Å) and Angles (deg) for $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$ ^a

Fe–Al	2.510 (2)	Al–C ₁ (3)	2.018 (6)
Fe–C ₁	1.732 (7)	Al–C ₁ (4)	2.033 (6)
Fe–C ₂	1.731 (8)	C ₁ –O ₁	1.159 (7)
Al–C ₁ (2)	2.019 (6)	C ₂ –O ₂	1.157 (7)
Al–Fe–C ₁	83.8 (2)	O ₂ –C ₂ –Fe	177.6 (8)
Al–Fe–C ₂	82.4 (2)	Fe–Al–C ₁ (2)	115.7 (2)
Al–Fe–CG	117.3 (2)	Fe–Al–C ₁ (3)	108.4 (2)
C ₁ –Fe–C ₂	95.4 (3)	Fe–Al–C ₁ (4)	111.9 (2)
C ₁ –Fe–CG	131.5 (9)	C ₁ (2)–Al–C ₁ (3)	104.0 (3)
C ₂ –Fe–CG	128.5 (9)	C ₁ (2)–Al–C ₁ (4)	105.9 (2)
O ₁ –C ₁ –Fe	178.2 (10)	C ₁ (3)–Al–C ₁ (4)	110.5 (3)

^a CG refers to the center of gravity of the cyclopentadienyl ring. Estimated standard deviations in parentheses correspond to the last significant digit.

this ion is composed of two organometallic species connected by a metal–metal bond. The Fe–Al bond length, 2.510 (2) Å, is given in Table VI, which contains details of the geometry about the heavy atoms. This distance lies within the range of iron–aluminum bonds, 2.3–2.8 Å, found in binary alloys such as FeAl_3 ,²⁸ where the average Fe–Al distance is 2.55 Å. No structural report of an iron–aluminum bond in an organometallic compound could be found in the literature, but there are examples of bonds between aluminum and other transition metals, although not with four-coordinate Al atoms that form only one metal–metal bond. The Al–Mo distance has been determined in the transition-metal cluster compounds $\text{C}_{25}\text{H}_{35}\text{Al}_3\text{Mo}_2$ ²⁹ and $\text{C}_{26}\text{H}_{34}\text{Al}_4\text{Mo}_2$ ²⁹ to be 2.654 (4) Å; two values were reported in $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{MoH}]_2\text{Al}_3(\text{CH}_3)_5$,³⁰ 2.659 (5) and 2.974 (6) Å. The Al–Ti distance in $[(\text{C}_5\text{H}_5)_2\text{TiAl}(\text{C}_2\text{H}_5)_2]_2$ ³¹ was found to be 2.79 (1) Å.

Crystal structures of several other $\text{XFe}(\text{CO})_2\text{Cp}$ compounds have been reported and these bond lengths provide useful comparisons. For nonmetallic elements such as X = S, Cl, and I, the respective distances are 2.201 (6),³² 2.30 (1),³³ and 2.588 (2) Å;³⁴ for X = Sb, the bond length is 2.539 (3) Å.³⁵ Other structures with elements from group 4A have been reported; for X = Ge, Sn, and Pb, the corresponding bond lengths are 2.357 (4),³⁶ 2.536 (3),³⁷ and 2.71 Å.³⁸

The structure of $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}^{37}$ is of particular interest; differing only in the replacement of Sn for Al, this uncharged molecule adopts a geometry nearly identical with that of the anion. It was noted that the Fe–Sn distance is shorter than expected for a formal single bond between these metals and it was suggested that the bond possessed some d character. In the present structure, however, the iron–aluminum distance is well approximated by calculations using accepted atomic radii. The best agreement is obtained when the d^{2sp^3} octahedral radius³⁹ of 1.23 Å is used for iron; this value produces a bond length of 2.49 Å using the accepted covalent radius of 1.26 Å for Al. If single-bond metallic radii⁴⁰ are used for both metals (1.17 Å for Fe, 1.25 Å for Al), the predicted distance is 2.42 Å, which corresponds to a bond order of $\sim 3/4$ using Pauling's equation⁴¹ for bond orders less than unity. Thus there appears to be no basis for concluding that there is any multiple bond character in the Fe–Al bond.

Despite this difference in the character of metal–metal bond, detailed comparison of the present structure with that of the tin analogue reveals many striking similarities. The Fe–Al anion does exhibit a slightly shorter CO bond length (1.158 (5) vs. 1.18 (1) Å) and a somewhat more acute metal–metal–carbonyl angle (83.1 (1) vs. 86.8°) but the iron carbonyl distances and CO–Fe–CO angles agree. The bond angles about the aluminum atom show small distortions from ideal tetrahedral values, with the phenyl groups inclined away from the metal–metal bond. The average Fe–Al–phenyl angle is 112.0 (1)° with the average phenyl–Al–phenyl angle reduced to 106.5 (1)°; the tin analogue displays similar deviations with corresponding average angles of 114 and 105°, respectively. The average angle subtended at the iron atom by the centroid of the cyclopentadienyl ring and the carbonyls is slightly larger (130.0 (6) vs. 127°) in the anion and the ring–metal–metal angle is correspondingly decreased (117.3 (2) vs. 122°). In both studies, the average iron–carbon and carbon–carbon bond lengths for the cyclopentadienyl ring agree (Al 2.097 (3) and 1.409 (5) Å; Sn 2.10 and 1.40 Å).

The only other report in the structural literature of a triphenylaluminum moiety is that of the so-called "triphenylaluminum dimer", $[(\text{C}_6\text{H}_5)_3\text{Al}]_2$,⁴² although this compound

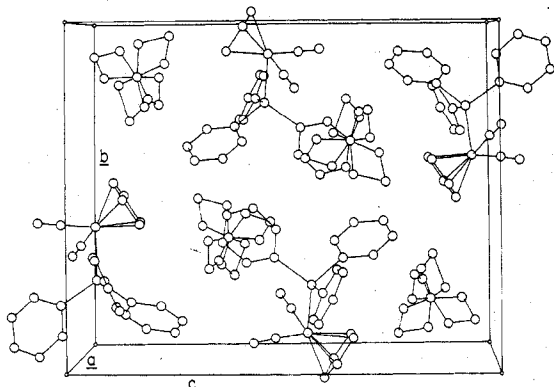


Figure 2. Packing of $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$ as viewed down the a axis. The two-state modeling of the Et_4N^+ cation is indicated.

actually possesses only two terminal phenyls per metal, with two rings bridging the metal-metal bond. The average Al-C bond length for the terminal rings is 1.958 (3) Å and the average C-C distance is 1.386 (2) Å; the corresponding values from this study are 2.023 (3) and 1.385 (2) Å. Although the distortions in bond lengths in the phenyl rings do not possess an obvious pattern, the internal angle at each bridgehead carbon is significantly reduced (114.3 (3)° average) from the sp^2 optimum of 120°, while the angles adjacent to it on the ring open somewhat (123.6 (3)° average); the other angles in the rings appear normal (119.5 (2)° average). The orientation of the rings is staggered, with the average angle between ring plane normals being about 66°; this value for the tin analogue is about 73°.

Figure 2 details the packing of the molecules in the unit cell as viewed down the lattice a axis. It appears that the molecular packing is primarily driven by the bulkiness of the quasi-spherical triphenyl units which are arranged in slightly puckered hexagonal sheets perpendicular to the lattice c^* axis. The stacking approximates simple hexagonal packing with the distance between anion layers comparable to the distances between anions within the sheets.

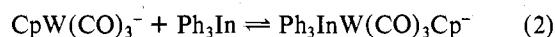
The cation correlations are less obvious; the intercalated layers are more irregular and the hexagonal arrangement more disordered. In simple hexagonal packing there are four-coordinate square-planar and six-coordinate trigonal prism interlayer sites. The cations occupy positions intermediate between these sites and alternate layers shift between two equivalent orientations. One might describe the packing as ABAC, where A refers to anion sheets and B and C refer to the two types of cation layers. In structures of spheres with equal radii, this arrangement is called doubly hexagonal closest packing.

In this packing arrangement there is a sharply delimited size range for the cation. It is noteworthy that it was not possible to crystallize either the Na^+ or $(n\text{-Bu})_4\text{N}^+$ derivatives of the $\text{Ph}_3\text{MFe}(\text{CO})_2\text{Cp}^-$ complexes; only the Et_4N^+ salts were obtained as solids.²⁵ Furthermore, when the boron analogue of this anion was synthesized, the Na^+ , $(n\text{-Pr})_4\text{N}^+$, and $(n\text{-Bu})_4\text{N}^+$ salts could only be recovered as oils, while the Et_4N^+ derivative was easily recovered in crystalline form.⁴³ These observations reflect the close interrelationships between ion size and crystallizability in these systems.

$(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{EW}(\text{CO})_3\text{Cp}^-$ Complexes. The In and Al members of this group, obtained as yellow crystalline solids, had good air and thermal stability in the solid state. The triphenylgallium complex was somewhat thermally unstable in solution and could not be isolated in crystalline form.

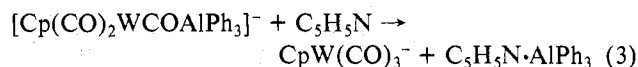
The presence of an indium-tungsten bond in $[\text{Ph}_3\text{InW}(\text{CO})_3\text{Cp}]^-$ is strongly indicated by its IR spectra. The solid-state spectrum (Table V) contains three C-O stretching absorptions which correspond closely to the three strongest

absorptions observed in the spectrum from a dichloromethane solution. The latter also contains two weak absorptions attributable to $\text{CpW}(\text{CO})_3^-$ in an equilibrium situation (eq 2)

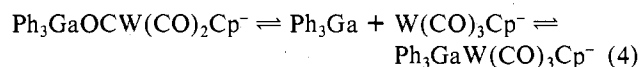


which could be established from either direction. The average $\nu(\text{CO})$ for $\text{Ph}_3\text{InW}(\text{CO})_3\text{Cp}^-$ is $\sim 56 \text{ cm}^{-1}$ higher than that of $\text{W}(\text{CO})_3\text{Cp}^-$, suggesting modest reduction of negative charge on tungsten as a result of complex formation. Because all the absorptions of the complex are higher in energy than the corresponding absorptions of $\text{CpW}(\text{CO})_3^-$ (see Experimental Section), O coordination of a carbonyl is discounted (vide infra) and the tungsten atom is considered to be the site of Lewis basicity.¹⁴ For a structure with C_s symmetry three IR-active modes are expected ($2 A_1 + A''$); they appear in a pattern comparable to that of $\text{Ph}_3\text{SnW}(\text{CO})_3\text{Cp}^{44}$ ($\nu(\text{CO})$ at 1995, 1923, and 1894 cm^{-1} in CH_2Cl_2),²⁵ a complex that almost certainly contains a tin-to-tungsten bond.

In contrast, an entirely different structure for $\text{Ph}_3\text{AlW}(\text{CO})_3\text{Cp}^-$ is indicated by its IR spectra which contain two strong bands in the terminal C-O stretching region and one of comparable intensity at 1600 cm^{-1} . These absorptions were present in the spectra of the solid and of a CH_2Cl_2 solution (Table V); the latter also contained weak bands from dissociated $\text{CpW}(\text{CO})_3^-$ with intensities comparable to those observed for the indium complex. The lowering of $\nu(\text{CO})$ by O coordination is now well documented for several types of metal carbonyls.^{7,11} Accordingly, the 1600 cm^{-1} absorption is assigned to a carbonyl ligand of the $\text{CpW}(\text{CO})_3$ moiety which is coordinated to aluminum via its oxygen end as found in $[\text{Cp}(\text{CO})_2\text{WCOAl}(\text{C}_4\text{H}_8\text{O})_3]$ by single-crystal X-ray analysis.⁴ Spectra of this and similar Al(III) complexes have several medium-to-strong absorptions in the 1550–1650- cm^{-1} region.²⁵ The two remaining carbonyls of $\text{Ph}_3\text{AlW}(\text{CO})_3\text{Cp}^-$ account for the two higher frequency bands. Chemical evidence for the adduct nature of the complex comes from the observation that 95% of the $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$ was recovered upon treatment with a slight excess of pyridine (eq 3).



The IR spectrum of a CH_2Cl_2 solution of equimolar quantities of Ph_3Ga and $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$ shows five well-resolved C-O bands (Table V), a barely resolved shoulder at 1800 cm^{-1} , and two weak absorptions identical with those of $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$. The bands at 1934, 1845, and 1823 cm^{-1} are assigned to $\text{Ph}_3\text{GaW}(\text{CO})_3\text{Cp}^-$ having a gallium-tungsten bond analogous to the triphenylindium complex. The other three (1905, 1800, and 1642 cm^{-1}) are assigned to a C- and O-bonded adduct analogous to the triphenylaluminum complex. The higher frequency of the C- and O-bonded carbonyl and a correspondingly lower set of "terminal" C-O frequencies suggest that the oxygen-gallium interaction is substantially weaker than the oxygen-aluminum one in $\text{Ph}_3\text{AlW}(\text{CO})_3\text{Cp}^-$. This probably contributes to produce the equilibria (eq 4) that describe linkage isomerism of the



metal-metal bonded and the C- and O-bonded species. Comparison of band intensities with those of the indium and aluminum analogues indicates that the two isomers are present in approximately equal concentrations.

$(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{ECo}(\text{CO})_4^-$ Complexes. With the tetracarbonylcobaltate anion, crystalline adducts could only be obtained with $(\text{Ph}_3\text{P})_2\text{N}^+$. The Ph_3In adduct did not exhibit

noticeable air or thermal sensitivity in the solid state. The adducts with Ph_3Ga and especially with Ph_3Al were thermally sensitive in solution and were obtained from CH_2Cl_2 -hexane solution kept at all times below 0°C . As in previous cases, the triphenylindium complex has an IR spectrum directly comparable to that of the analogous triphenyltin derivative, $\text{Ph}_3\text{SnCo}(\text{CO})_4$, except for a shift of $\sim 60\text{ cm}^{-1}$ to lower energy. In addition to the three bands readily assigned to the $2\text{ A}_1 + \text{E}$ modes of the $\text{Co}(\text{CO})_4$ group with C_{3v} symmetry, a band at 1889 cm^{-1} indicated partial dissociation of the In-Co bond to $\text{Co}(\text{CO})_4$.⁴⁵ In the solid-state spectrum, the E mode (1939 cm^{-1}) is split, possibly by lower site symmetry in the crystal.

A nearly identical spectrum was obtained for $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{GaCo}(\text{CO})_4^-$ except for the appearance of a band of moderate intensity at 1890 cm^{-1} , which suggests some dissociation may occur even in the mineral oil medium. In CH_2Cl_2 solution dissociation of $\text{Ph}_3\text{GaCo}(\text{CO})_4^-$ was found to be more extensive than that of the indium analogue under the same conditions. The IR spectrum of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{AlCo}(\text{CO})_4^-$ in the solid state is very similar to those of the gallium and indium analogues and strongly suggests the presence of a Co-Al bond. No evidence for coordination by carbonyl oxygen was obtained. Thermal instability of the complex in CH_2Cl_2 solution has limited the conclusions which can be drawn from spectra thereof.⁴⁶

$(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{EMn}(\text{CO})_5^-$ Complexes. The colorless, crystalline adducts of $(n\text{-Pr})_4\text{N}^+\text{Mn}(\text{CO})_5^-$ with the Ph_3E acceptors showed greater thermal instability and air sensitivity than did those of $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$. In CH_2Cl_2 solution $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{GaMn}(\text{CO})_5^-$ had to be kept below 0°C ; even the solid discolored at room temperature. The aluminum derivative, $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{AlMn}(\text{CO})_5^-$, could not be obtained as a pure solid even when all manipulations were carried out below -20°C .

Pentacarbonylmanganese complexes with an axial substituent should display three IR-active C-O stretching modes.⁴⁷ In cases where the actual symmetry is less than C_{4v} , as in $\text{Ph}_3\text{SnMn}(\text{CO})_5$, the IR-forbidden B_1 mode has been observed along with the expected bands at $2093\text{ (A}_1)$ and 2002 cm^{-1} (degenerate A_1 and E).⁴⁸ The similarity of the IR spectrum of $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{InMn}(\text{CO})_5^-$ to that of the tin analogue leaves little doubt that the structure is comparable and contains an indium-manganese bond. In the present case, the B_1 mode appears at 1960 and at 1963 cm^{-1} for spectra in CH_2Cl_2 solution and in a mineral oil mull, respectively.

The IR spectrum (and presumably the structure) of $\text{Ph}_3\text{GaMn}(\text{CO})_5^-$ in the solid state is comparable to that of $\text{Ph}_3\text{InMn}(\text{CO})_5^-$. In cold CH_2Cl_2 solution, however, the B_1 mode was not resolved and a band due to uncomplexed $\text{Mn}(\text{CO})_5^-$ (at 1858 cm^{-1}) appeared, indicating partial dissociation of the Ga-Mn bond.

As noted above, thermal instability of $\text{Ph}_3\text{AlMn}(\text{CO})_5^-$ in dichloromethane solution prevented its isolation as a pure solid. Infrared spectra of a cold CH_2Cl_2 solution of the components contained strong bands due to $\text{Mn}(\text{CO})_5^-$ and at least two unidentified species, the relative proportions of which changed rapidly. The lowest $\nu(\text{CO})$, observed at $\sim 1700\text{ cm}^{-1}$, may be due to a carbonyl oxygen-aluminum interaction or a bridging carbonyl.

Conclusions

Spectroscopic and X-ray crystallographic evidence indicates that metal-metal bond formation predominates in the donor-acceptor interactions of the $(\text{Ph}_3\text{E})\text{m}^-$ complexes. In the case of the iron-aluminum complex, the Fe-Al link was shown to possess predominantly single bond character. The general trends can conveniently be rationalized through the principle of hard and soft acids and bases.⁴⁹ Because of its low oxidation state, the metal atom in each anion can be considered to be

functioning as a soft base. Although differences undoubtedly exist, in the absence of discriminating evidence, it will be assumed that all of the metal sites are of comparable softness. Further, it will be assumed that the base strengths of the metal sites are approximately proportional to their nucleophilicities, namely, in the order $\text{Fe}(\text{CO})_2\text{Cp}^- \gg \text{W}(\text{CO})_3\text{Cp}^- > \text{Mn}(\text{CO})_5^- > \text{Co}(\text{CO})_4^-$.⁵⁰

For neutral metal carbonyls, Shriver and Alich⁷ characterized the carbonyl oxygen as a hard, weak base with a base strength inversely related to the average $\nu(\text{CO})$. In the ionic complexes, the carbonyl oxygens will be assumed to be of comparable hardness with base strengths (determined from the average $\nu(\text{CO})$ in THF) in the order $\text{W}(\text{CO})_3\text{Cp}^- \geq \text{Fe}(\text{CO})_2\text{Cp}^- \gg \text{Mn}(\text{CO})_5^- \geq \text{Co}(\text{CO})_4^-$.

In the neutral complexes, the Lewis acids can be expected to be quite soft compared to more ionic species such as $\text{Al}(\text{THF})_3^{3+}$ in $(\text{THF})_3\text{Al}[\text{OCW}(\text{CO})_2\text{Cp}]_3$,⁵ and the softness will decrease in the order $\text{Ph}_3\text{In} > \text{Ph}_3\text{Ga} > \text{Ph}_3\text{Al} > \text{Ph}_3\text{B}$. The acid strength will be assumed to parallel the relative electron pair acceptor strengths, assigned by Strohmeier and Nützel,⁵¹ viz., $\text{B} \ll \text{Al} > \text{Ga} > \text{In}$.

As would be expected, the highest values of the formation constants, K_F , were observed for the strongest base, $\text{Fe}(\text{CO})_2\text{Cp}^-$; indeed, this anion was the only one to form an adduct with Ph_3B , clearly the weakest and the hardest of the Lewis acids. A significant exception to the general trend of increasing K_F values with increasing base strength of the metal anions was noted in that no bands due to $\text{Mn}(\text{CO})_5^-$ appeared in the IR spectrum of a solution of $\text{Ph}_3\text{InMn}(\text{CO})_5^-$ in CH_2Cl_2 . Since Ph_3In is the softest of the Lewis acids, this enhanced stability could reflect particularly favorable soft-soft factors in the bonding of one of the weakest acid-base pairs. This argument requires a delicate balance of factors since the K_F values seem to be normal for adduct formation of Ph_3In with the cobalt and tungsten anions; the base strengths of these anions are, respectively, slightly lower and higher than that of $\text{Mn}(\text{CO})_5^-$, and all of the metal sites are judged to be of equal softness. Moreover, specific solvent interactions are implied by the fact that, in acetonitrile, ionization of other pentacarbonylmanganese derivatives of indium(III) has been reported.⁵²

Despite the relative hardness of the carbonyl oxygen as a basic site for the soft Lewis acids studied, bonding through the oxygen is observed for $\text{CpW}(\text{CO})_3^-$ with Ph_3Al and Ph_3Ga . All other metal anions exhibit only metal-metal bonding, but $\text{CpW}(\text{CO})_3^-$, with the highest carbonyl oxygen base strength, shows an interesting trend with decreasing softness of the Lewis acids (Chart I). With indium, the softest acid site, only a metal-metal bond is formed; for gallium, both Ga-W and Ga-OC-W links are formed with approximately equal probability; the aluminum complex appears to exist only in the Al-OC-W form; and finally, with Ph_3B , the hardest and weakest of the acids, no complex is formed at all. This suggests that the base strength of the carbonyl oxygen is at least comparable to that of the metal site in $\text{CpW}(\text{CO})_3^-$. With increasing hardness of the Lewis acid, bonding through the oxygen becomes more and more competitive. In the adjacent iron series, only metal-metal bonding is observed because of the dominant role of the nucleophilic iron atom in $\text{CpFe}(\text{CO})_2^-$. Similarly, even though the base strength of the manganese atom in $\text{Mn}(\text{CO})_5^-$ is somewhat less than that of the tungsten atom, only metal-metal bonding is found in this series because the base strength of the carbonyl oxygen is far too low in this anion to sustain an E-OC-Mn bond.

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Registry No. $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{InCo}(\text{CO})_4^-$, 68908-27-0; $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{GaCo}(\text{CO})_4^-$, 68908-29-2; $(\text{Ph}_3\text{P})_2\text{N}^+\text{Ph}_3\text{AlCo}(\text{CO})_4^-$, 68908-31-6; $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{InMn}(\text{CO})_5^-$, 68900-42-5; $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{GaMn}(\text{CO})_5^-$, 68900-40-3; $(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{InW}(\text{CO})_3\text{Cp}^-$, 68900-38-9; $(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{AlOCW}(\text{CO})_2\text{Cp}^-$, 31781-46-1; $\text{Et}_4\text{N}^+\text{Ph}_3\text{InFe}(\text{CO})_2\text{Cp}^-$, 68900-36-7; $\text{Et}_4\text{N}^+\text{Ph}_3\text{GaFe}(\text{CO})_2\text{Cp}^-$, 68900-34-5; $\text{Et}_4\text{N}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$, 64799-18-4; $\text{Na}^+\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}^-$, 68900-32-3; $\text{Na}^+\text{Ph}_3\text{GaFe}(\text{CO})_2\text{Cp}^-$, 68900-31-2; $(n\text{-Pr})_4\text{N}^+\text{Ph}_3\text{AlMn}(\text{CO})_5^-$, 68900-30-1; $(n\text{-Bu})_4\text{N}^+\text{Ph}_3\text{GaW}(\text{CO})_3\text{Cp}^-$, 68900-28-7; $(n\text{-Pr})_4\text{N}^+\text{Mn}(\text{CO})_5^-$, 68900-26-5; $(n\text{-Bu})_4\text{N}^+\text{CpW}(\text{CO})_3^-$, 68914-56-7; $(n\text{-Bu})_4\text{N}^+\text{CpFe}(\text{CO})_2^-$, 65836-70-6; $\text{Et}_4\text{N}^+\text{CpFe}(\text{CO})_2^-$, 57812-16-5; $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$, 53433-12-8; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $[\text{Cp}(\text{CO})_3\text{W}]_2\text{Hg}$, 12289-72-4; $[\text{Cp}(\text{CO})_2\text{Fe}]_2$, 12154-95-9; Ph_3In , 3958-47-2; Ph_3Ga , 1088-02-4; AlPh_3 , 841-76-9.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, cyclopentadienyl and phenyl ring bond distances and angles, deviations of atoms from planes in the anion, and bond distances and angles in the cation (23 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) The work described in this paper was abstracted from the following Cornell University theses: R. B. Petersen, Ph.D. Thesis, 1973; M. E. Leonowicz, Ph.D. Thesis, 1976. (b) Abbreviations used in this paper are the following: m, metal carbonyl group; Cp, η^5 -cyclopentadienyl; Ph, phenyl; Et, ethyl; n-Pr, n-propyl; n-Bu, n-butyl; $(\text{Ph}_3\text{P})_2\text{N}^+$, bis(triphenylphosphine)iminium; THF, tetrahydrofuran; SRV, Schlenk reaction vessel; TVVD, trap-to-trap vacuum distillation.
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