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Registry No. 1a, 87114-37-2; 1b, 87114-38-3; 1c, 87114-39-4; 1e, 86403-93-2; 2a, 87114-40-7; 2b, 87114-41-8; 2c, 87114-42-9; 2e, 58640-56-5; 3a, 87114-43-0; 3b, 87114-44-1; 3c, 87114-45-2; 3d, 87114-46-3; 3e, 86403-94-3; Mo₂(CO)₄(PEt₃)Cp₂, 87114-47-4; [Mo(CO)₃Cp]₂, 12091-64-4; W₂(CO)₅(PEt₃)Cp₂, 87114-48-5; [W-

(CO)₃Cp]₂, 12091-65-5; Na[Cr(CO)₃Cp], 12203-12-2; Na[Mo(CO)₃Cp], 12107-35-6; Na[W(CO)₃Cp], 12107-36-7; *trans*-PdCl₂(PEt₃)₂, 15642-19-0; *trans*-PdCl₂(PPh₃)₂, 28966-81-6; *trans*-PdCl₂(PhCN)₂, 15617-18-2.

Supplementary Material Available: Selected least-squares planes (Table X), anisotropic thermal parameters for 1b, 2b, and 3b (Tables XV-XVII), and observed and calculated structure factors (Table XVIII) (62 pages). Ordering information is given on any current masthead page.

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Reactions of Transition-Metal Carbonyl Anions with Group 2B Metal Acceptors and the Crystal Structure of Tetra-*n*-butylammonium Tris(dicarbonyl(η⁵-cyclopentadienyl)iron)zincate

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Complexes of the type M'(ML_n)₃⁻ were prepared from the reaction of bis(transition-metal carbonyl)-group 2B metal acceptors, M'(ML_n)₂, where M' is Zn, Cd, or Hg, with metal carbonyl anions, ML_n⁻ = FeCp(CO)₂, WCp(CO)₃, CrCp(CO)₃, and Co(CO)₄ (Cp = η⁵-C₅H₅), in dichloromethane or tetrahydrofuran. Among the crystalline complexes isolated was (n-Bu)₄N⁺Zn[FeCp(CO)₂]₃⁻, which was characterized by single-crystal X-ray structure analysis. This compound crystallizes in space group P2₁/c with Z = 4 and monoclinic unit cell dimensions a = 9.8192 (3) Å, b = 21.813 (7) Å, c = 18.650 (5) Å, and β = 106.93 (2)°. This is the first tetrametal trigonal-planar zinc complex and has an average Zn-Fe distance of 2.541 Å. A partially refined X-ray structure of Me₄N⁺Hg[Co(CO)₄]₃⁻ revealed trigonal-planar coordination about mercury. By analysis of infrared spectroscopic data, approximate formation constants were determined for the complexes. For all complexes studied, the magnitudes of these constants were in the order Cd > Zn > Hg. The relative magnitudes of the formation constants were found to depend on M', ML_n, and solvent in a systematic way. Increasing the basicity of ML_n in M'(ML_n)₂ decreases the magnitude of the complex formation for a given anion. Complex formation is decreased in solvents with high donor numbers. Evidence was also obtained for the equilibrium nature of complex formation.

Introduction

Although there has been a great deal of study of the Lewis acidity of the group 2B metals, very little is known about the structure of the acid-base complexes they form. The best studied complex, Hg[Co(CO)₄]₃⁻, was first postulated to be a radical anion, Hg[Co(CO)₄]₂⁻,¹ and later correctly identified as a tetrametallic cluster by several groups.²⁻⁴ By analysis of infrared (IR) spectra and by derivative formation, the compound was identified as an adduct between the Lewis acid Hg[Co(CO)₄]₂ and the base Co(CO)₄⁻, but the structure remained unknown.

Prior to this work there were no definitive structural studies of three-coordinate zinc or cadmium. Recently Boersma and co-workers described the structure of an internally coordinated organozinc-transition metal compound, (CH₃)₂N-(CH₂)₃ZnW(η⁵-C₅H₅)(CO)₃, which contains a nearly planar sphere including carbon, nitrogen, and tungsten.⁵ Only one structure of a complex containing a transition metal coordinated to three-coordinate mercury has been described, viz. [Ru(Cp)₂HgCl₂]₂[RuCp₂(HgCl₂)₂]₆,⁶ which contains one trigonal, one tetrahedral, and one octahedral mercury. The five-co-

ordinate complex [CoCp(CO)₂]₂HgCl₂ is trigonal bipyramidal, with very long intermolecular axial Hg-Cl interactions, so it is assigned a primary coordination number of 3.⁷

Although structural studies of complexes formed from group 2B Lewis acids and transition-metal Lewis bases are scarce, there have been several studies of these complexes. In addition to those already mentioned, the following complexes have been described: [Mo(mes)(CO)₃]₂HgCl₂,⁸ Fe(CO)₃L₂HgCl₂,⁷ Fe(CO)₅HgCl₂,⁹ and Hg[FeCp(CO)₂]₂Bu⁻.¹⁰ The complex Hg[FeCp(CO)₂]₃⁻ has been formed from the electrochemical reduction of Hg[FeCp(CO)₂]₂ at a dropping-mercury electrode and by the reaction of Hg[FeCp(CO)₂]₂ with FeCp(CO)₂⁻.¹¹ The formation of a complex from Hg[Co(CO)₄]₂ and X⁻ (X = Cl, Br)^{3,12} has also been observed. The only reported adducts containing cadmium are Cd[MoCp(CO)₃]₂I⁻, Cd[MoCp(CO)₃]₂I₂⁻,¹³ and CdCo(CO)₄Br₂.¹⁴ No adducts with metal bases have been reported for zinc besides those in our preliminary report of this work.^{11b}

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Table I. Experimental Conditions for Formation of $M'(ML_n)_3^-$ Complexes

acceptor	anion salt	reactn solvent	solvent for recrystn	% yield
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ Na ⁺	THF		a
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ K ⁺	THF	CH ₂ Cl ₂ /methanol ^b	30
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ Me ₄ N ⁺	THF/methanol	CH ₂ Cl ₂ /hexane ^b	76, e
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF		a
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ Ph ₄ As ⁺	THF/methanol		a
Hg[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Cd[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ Me ₄ N ⁺	THF/methanol	CH ₂ Cl ₂ /hexane	70
Zn[Co(CO) ₄] ₂	Co(CO) ₄ ⁻ Me ₄ N ⁺	THF	CH ₂ Cl ₂	53
Hg[Co(CO) ₄] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		a
Hg[Co(CO) ₄][WCp(CO) ₃]	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Cd[Co(CO) ₄] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		a
Zn[Co(CO) ₄] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		a
Hg[FeCp(CO) ₂][Co(CO) ₄]	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		c
Hg[CrCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		c
Cd[CrCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Zn[CrCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Hg[WCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		c
Cd[WCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Cd[WCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF		d
Cd[WCp(CO) ₃] ₂	Co(CO) ₄ ⁻ Me ₄ N ⁺	CH ₂ Cl ₂	CH ₂ Cl ₂ /methanol	15
Zn[WCp(CO) ₃] ₂	Co(CO) ₄ ⁻ (Ph ₃ P) ₂ N ⁺	CH ₂ Cl ₂		a
Cd[FeCp(CO) ₂] ₂	Co(CO) ₄ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF		c
Hg[WCp(CO) ₃] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF		c
Cd[WCp(CO) ₃] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂	CH ₂ Cl ₂ /hexane	40
Zn[WCp(CO) ₃] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF	CH ₂ Cl ₂ /toluene	67
Hg[FeCp(CO) ₂] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		c
Cd[FeCp(CO) ₂] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		a
Zn[FeCp(CO) ₂] ₂	WCp(CO) ₃ ⁻ (<i>n</i> -Bu) ₄ N ⁺	CH ₂ Cl ₂		c
Hg[FeCp(CO) ₂] ₂	FeCp(CO) ₂ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF	THF/hexane	44
Cd[FeCp(CO) ₂] ₂	FeCp(CO) ₂ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF	THF/toluene	83
Zn[FeCp(CO) ₂] ₂	FeCp(CO) ₂ ⁻ (<i>n</i> -Bu) ₄ N ⁺	THF	THF/hexane	92, e

^a This system showed evidence of complex formation by infrared spectroscopy only; see Table III. ^b Requires careful adjustment of temperature and concentration; see text. ^c Showed no complex formation in CH₂Cl₂ by IR spectroscopy. ^d Showed no complex formation in THF. When solvent is removed by TTVD and the resulting solid is dissolved in CH₂Cl₂, complex formation is observed. ^e Characterized by X-ray single-crystal analysis.

In this paper we report the preparation of several complexes of the type $M'(ML_n)_3^-$, including several containing zinc. The formation of the complexes was followed by IR spectroscopy, and formation constants were determined. This allowed the factors which affect complex formation to be assessed.¹⁵

Experimental Section

All operations involving air-sensitive materials were carried out under a purified argon atmosphere. The apparatus and techniques for handling air-sensitive compounds have been described in detail elsewhere.¹⁷ Infrared spectra were recorded either on a Perkin-Elmer Model 337 spectrophotometer, calibrated with polystyrene, or, in expanded form, on a Perkin-Elmer Model 521 spectrometer calibrated with DCl using cells described previously.¹⁷ Melting points were taken in sealed, argon-filled capillaries with use of a Buchi apparatus and are corrected. Elemental analyses were carried out by F. Pascher, Bonn, Germany, and A. Bernhardt, Müllheim, Germany. Nuclear magnetic resonance spectra were obtained on a Varian A-60A instrument.

Reagents. All solvents were reagent grade and were degassed and distilled from appropriate drying agents directly into the reaction vessels.¹⁷

The following compounds were prepared by literature methods: (Ph₃P)₂NCl,¹⁸ (Ph₃P)₂N⁺Co(CO)₄⁻,¹⁸ (*n*-Bu)₄N⁺WCp(CO)₃⁻,¹⁹ (*n*-Bu)₄N⁺FeCp(CO)₂⁻,¹⁹ Et₄N⁺FeCp(CO)₂⁻,¹⁹ Hg[Co(CO)₄]₂,²⁰ Cd[Co(CO)₄]₂,²¹ Zn[Co(CO)₄]₂,²¹ Hg[CrCp(CO)₃]₂,²² Cd[CrCp(CO)₃]₂,²¹ Zn[CrCp(CO)₃]₂,²¹ Hg[WCp(CO)₃]₂,²³ Cd[WCp(CO)₃]₂,²¹

Zn[WCp(CO)₃]₂,²¹ Hg[FeCp(CO)₂]₂,²⁴ Cd[FeCp(CO)₂]₂,²¹ Zn[FeCp(CO)₂]₂,²¹ HgFeCp(CO)₂Co(CO)₄,²⁵ HgWCp(CO)₃Co(CO)₄,²⁶ Hg[Co(CO)₄](PPh₃)₂,²⁷ and [Ni(phen)]₃[Co(CO)₄]₂.²⁸

Due to the large number of compounds synthesized, only two synthesis reactions will be described in detail. The other clusters were prepared by similar procedures using the conditions listed in Table I. Physical properties of the complexes and analytical data are given in Table II.

Preparation of Me₄N⁺Hg[Co(CO)₄]₂⁻. A solution of 0.543 g (1.00 mmol) of Hg[Co(CO)₄]₂ in 15 mL of THF was stirred for 30 min with 70 g of 1/2% sodium amalgam. Filtration through a "fine" frit into a Schlenk reaction vessel (SRV) gave a clear, colorless solution, which was added to a solution of 0.219 g (2.00 mmol) of tetramethylammonium chloride in 10 mL of methanol. The mixture was stirred at room temperature for 12 h, was digested at 50 °C without stirring for 30 min, and was filtered through a "fine" frit containing Celite into a SRV to afford a clear, colorless solution. Addition of 1.086 g (2.00 mmol) of Hg[Co(CO)₄]₂ gave a dark red-brown solution. Removal of the solvent by trap-to-trap vacuum distillation (TTVD) left a crystalline red-brown solid. Methylene dichloride (25 mL) was added to give a dark red-brown solution with a small amount of undissolved off-white solid, presumably Co(CO)₄Me₄N⁺. Cooling to -10 °C dissolved the off-white solid. At -5 °C, 3 mL of hexane was added to the solution, which was then filtered through a "fine" frit into a SRV and cooled slowly from -5 to -50 °C. The brown-orange supernatant liquid was decanted, and the dark red-brown crystals were dried under vacuum to afford 1.203 g (76.5 %) of Me₄N⁺Hg[Co(CO)₄]₂⁻, mp 118–120 °C.

Preparation of (*n*-Bu)₄N⁺Zn[FeCp(CO)₂]₂⁻. A solution of 0.089 g (0.25 mmol) of [FeCp(CO)₂]₂ in 20 mL of THF was stirred for 1 1/2 h at room temperature with 70 g of 1/2% sodium amalgam (15 mmol of Na) in a SRV. The resulting cherry red solution of Na⁺-

(15) Portions of this work were taken from the Ph.D. thesis of R.B.P.¹⁶

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Table II. Analyses and Physical Properties of $M'(ML_n)_m(M''L_n)_{3-m}^-$ Complexes

complex	color	mp, ^a °C	% calcd		% found	
			C	H	C	H
[Co(CO) ₄] ₃ Hg ⁻ K ⁺	dk red-brown	dec pt >110	19.2 (Co 23.5)		18.54 (Co 22.8)	
[Co(CO) ₄] ₃ Hg ⁻ Me ₄ N ⁺	dk red-brown	118-120	24.4 (N 1.78)	1.54	24.01 (N 1.80)	1.64
[Co(CO) ₄] ₃ Cd ⁻ Me ₄ N ⁺	yellow	160-163 dec	(Co 22.4) (Hg 25.5)	1.73	(Co 22.80) (Hg 27.21)	1.56
[Co(CO) ₄] ₃ Zn ⁻ Me ₄ N ⁺	yellow	199-202 dec	27.5 (Co 25.2) (Cd 16.1)	1.86	27.85 (Co 24.93) (Cd 16.20)	2.02
[Co(CO) ₄][WCp(CO) ₃] ₂ Cd ⁻ Me ₄ N ⁺	yellow	276-277 dec	29.5 (N 2.15) (Co 27.0) (Zn 10.0)	2.17	29.48 (N 2.27) (Co 26.57) (Zn 9.65)	2.32
[WCp(CO) ₃] ₃ Cd ⁻ (<i>n</i> -Bu) ₄ N ⁺	yellow	212-215	35.5 (W 40.7)	3.80	35.68 (W 40.65)	3.84
[WCp(CO) ₃] ₃ Zn ⁻ (<i>n</i> -Bu) ₄ N ⁺	yellow	165-166	36.8 (W 42.3)	3.93	36.84 (W 41.72)	3.88
[FeCp(CO) ₂] ₃ Hg ⁻ (<i>n</i> -Bu) ₄ N ⁺	v dk purple	123-124.5	45.6 (Fe 17.2)	5.28	45.18 (Fe 19.18)	5.27
[FeCp(CO) ₂] ₃ Cd ⁻ (<i>n</i> -Bu) ₄ N ⁺	maroon	131-134	50.2 (Fe 18.9)	5.81	49.93 (Fe 19.01)	5.77
[FeCp(CO) ₂] ₃ Zn ⁻ (<i>n</i> -Bu) ₄ N ⁺	red	140-143	52.9 (Fe 19.9)	6.13	52.90 (Fe 20.55)	6.17

^a Melting points taken in argon-filled capillaries.

FeCp(CO)₂⁻ was added to 0.210 g (0.50 mmol) of Zn[FeCp(CO)₂]₂ in a SRV. Although the solution showed no color change, an infrared spectrum showed extensive complex formation: $\nu(\text{CO})$ in THF at 1972 (m, sh), ca. 1950 (w, sh), 1941 (s), 1924 (vs), 1869 (s), 1852 (m), and 1835 (m) cm⁻¹. This solution was added to 0.161 g (0.50 mmol) of tetra-*n*-butylammonium bromide in a SRV, and the mixture was stirred for 10 h at room temperature and then was filtered through a "fine" frit containing Celite into a SRV to give a clear, cherry red solution. Addition of 15 mL of hexane at 50 °C followed by slow cooling to -25 °C gave red, octahedral, slightly air-sensitive crystals. The supernatant liquid was decanted, and the crystals were dried under vacuum to afford 0.385 g (92%) of (*n*-Bu)₄N⁺Zn[FeCp(CO)₂]₃⁻, mp 140-143 °C.

Separation of Me₄N⁺Hg[Co(CO)₄]₃⁻ into Its Components by Precipitation as Hg[Co(CO)₃(PPh₃)₂]₂ and [Ni(phen)₃]²⁺[Co(CO)₄]₂⁻. Triphenylphosphine (0.786 g, 3.00 mmol) was dissolved in 30 mL of warm methanol in a previously weighed "fine" frit containing a stirring bar. Upon addition of 0.798 g (1.00 mmol) of Me₄N⁺Hg[Co(CO)₄]₃⁻, vigorous evolution of CO gas occurred through an oil bubbler attached to the frit. Evolution of gas appeared complete after a few minutes, but stirring was continued for 4 h. Filtration gave a clear, pale yellow solution for which the IR spectrum showed only absorptions due to Me₄N⁺Co(CO)₄⁻: $\nu(\text{CO})$ in THF at 1905 cm⁻¹. The bright orange residue was dried in the frit under vacuum for 4 h and weighed 0.991 g (98%). The product was identified as Hg[Co(CO)₃(PPh₃)₂]₂ by comparison of its IR spectrum with that of an authentic sample.

From the filtered THF solution of Me₄N⁺Co(CO)₄⁻, the solvent was removed by TTVD and the cream-colored residue was extracted by stirring with 40 mL of warm, degassed water for 2 h. Following filtration through a "medium" frit into a SRV, 25 mL of aqueous Ni(phen)₃Cl₂ solution, made from 1.25 mmol of NiCl₂·6H₂O (0.30 g) and 0.775 g (3.75 mmol) of 1,10-phenanthroline in 25 mL of distilled, degassed water, was added, resulting in immediate formation of an orange suspension.²⁹ Digestion at 50 °C for 30 min gave a flocculent orange precipitate which, when collected on a "fine" frit

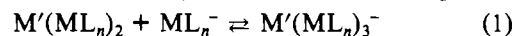
and dried under vacuum for 20 h, afforded 0.423 g (90%) of [Ni(phen)₃]²⁺[Co(CO)₄]₂⁻, the IR spectrum of which was identical with that of an authentic sample.

Calculation of Formation Constants for M'(ML_n)₃⁻ from IR Spectra. Formation constant determinations, defined as $K_f = [M'(ML_n)_3^-] / [M'(ML_n)_2][ML_n^-]$ were made at ambient temperature by means of Beer's law. Changes in concentrations of components on complex formation were made by recording the spectrum of the simple anion, followed by superimposing the spectrum of the solution of simple anion with acceptor added and noting the decrease in height of the anion peaks, or by the reverse process, whereby the spectrum of the acceptor with simple anion added was superimposed upon that of the acceptor alone. In two cases where extensive overlap of peaks occurred, it was necessary to estimate component concentration by means of molar absorptivities calculated from related species.

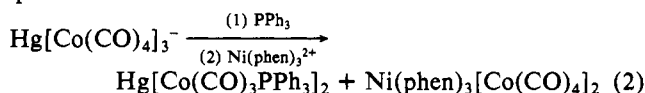
Collection of X-ray Diffraction Data. In a nitrogen-filled drybox, a red crystal of (*n*-Bu)₄N⁺Zn[FeCp(CO)₂]₃⁻, prepared as described above, was mounted on the tip of a 0.3-mm Lindemann glass capillary that was sealed into a 0.5-mm capillary under argon. The crystal was mounted on a Syntex P2₁ automated four-circle diffractometer equipped with a graphite monochromator and was centered with 15 reflections having $2\theta > 21^\circ$. Details of the crystal data, data collection, data reduction, and the structure solution and refinement are presented in Table IV. All non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were included at calculated positions for each of the last four cycles but were not refined. Selected bond distances and angles are given in Tables VII and VIII, respectively.

Results and Discussion

Preparation of Complexes. Addition of a metal carbonyl anion, ML_n⁻ to a disubstituted transition-metal derivative of a group 2B metal, M'(ML_n)₂ where M' is zinc, cadmium, or mercury, generally gives an equilibrium described by eq 1. In



favorable cases, if the formation constant of the complex, K_f , is large and if the appropriate cation is used, the tetrametal cluster anion can be isolated in crystalline form. The compositions of the isolated products were established by elemental analyses (cf. Table II) and in one case by derivatization (eq 2). The yields of these two derivatives were essentially quantitative.



- (29) Sternberg, H. W.; Wender, I.; Orchin, M. *Anal. Chem.* **1952**, *24*, 174.
 (30) Lonsdale, K.; Henry, N. F. M., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.
 (31) All crystallographic computations were done on a Prime 850 computer operated by the Department of Chemistry, Cornell University. Principal programs used: REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BDLS, block-diagonal least squares, K. Hirotsu and E. Arnold, Cornell University; MULTAN-76, direct methods and fast Fourier transform, G. Germain, P. Main, and M. Woolfson, University of York; BOND, structural parameters and errors, K. Hirotsu, Cornell University; ORTEP-II, crystallographic illustration program, C. Johnson, Oak Ridge National Laboratory, 1976.

Table III. Infrared Spectra of $M'(ML_n)_m(M''L_n)_{3-m}^-$ Complexes^a

complex	solvent	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Co}(\text{CO})_4]_3\text{Hg}^- \text{K}^+$	THF	2069 (0.5), 2039 (7.5), 1996 (1, sh), 1963 (10), 1893 (1), 1855 (0.5)
$[\text{Co}(\text{CO})_4]_3\text{Hg}^- \text{Me}_4\text{N}^+$	THF	2069 (0.5), 2039 (7.5), 1996 (1.5, sh), 1963 (10), 1887 (1)
	KBr	2071 (2.5), 2039 (8.5), 2000 (5, sh), 1960 (10), ca. 1890 (2)
	CH_2Cl_2	2071 (5.0), 2036 (8.5), 2000 (5.5), 1966 (10), 1889 (3.0)
$[\text{Co}(\text{CO})_4]_3\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2071 (0.5), 2035 (7), 2002 (1, sh), 1965 (10), 1888 (1)
$[\text{Co}(\text{CO})_4]_3\text{Cd}^- \text{Me}_4\text{N}^+$	CH_2Cl_2	2043 (6.5), 1976 (6.5, sh), 1961 (10)
$[\text{Co}(\text{CO})_4]_3\text{Zn}^- \text{Me}_4\text{N}^+$	CH_2Cl_2	2046 (5.5), 1980 (6.5, sh), 1962 (10)
$[\text{Co}(\text{CO})_4]_2[\text{WCp}(\text{CO})_3]_1\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2071 (2), 2034 (3.5), 2007 (2.5, sh), 1989 (6), 1964 (8.5), 1890 (10)
$[\text{Co}(\text{CO})_4]_2[\text{FeCp}(\text{CO})_2]_1\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2067 (4.5), 2035 (1.5), 2002 (4.5), 1988 (6), 1970 (7.5), 1947 (3.5), 1887 (10)
$[\text{Co}(\text{CO})_4][\text{CrCp}(\text{CO})_3]_2\text{Cd}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2052 (1.5), 2040 (3), 1968 (5, sh), 1947 (8.5), 1924 (10), 1890 (2.5), 1850 (6.5), 1835 (7), ca. 1770 (1)
$[\text{Co}(\text{CO})_4][\text{CrCp}(\text{CO})_3]_2\text{Zn}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2055 (0.5), 2042 (0.5), 2010 (0.5), 1982 (2.5, sh), 1965 (6.5), 1945 (2.5, sh), 1924 (2), 1887 (10), 1863 (6.5), 1770 (1)
$[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Cd}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2049 (1), 2037 (3), 1965 (6.5, sh), 1940 (8.5, sh), 1925 (10), 1890 (4), 1846 (8.5), 1828 (8.5)
$[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+{}^b$	CH_2Cl_2	2053 (0.5), 2041 (2), 1962 (8), 1940 (9.5, sh), 1929 (10), 1890 (4), 1850 (8.5, sh), 1837 (9)
$[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Zn}^-(\text{Ph}_3\text{P})_2\text{N}^+{}^b$	CH_2Cl_2	2037 (0.2), 1987 (2.5), 1967 (6.5), 1945 (2), 1925 (2), 1900 (7, sh), 1884 (10), 1860 (6.5), ca. 1830 (1)
$[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_2\text{Hg}^-(n\text{-Bu})_4\text{N}^+{}^b$	CH_2Cl_2	2070 (2.5), 2034 (2.5), 2007 (2.5), 1987 (6), 1962 (6.5), 1889 (10), ca. 1845 (7, sh)
$[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+{}^b$	CH_2Cl_2	2050 (1.5), 2038 (3.5), 1962 (10), ca. 1940 (5, sh), 1885 (2), 1850 (2), 1838 (2)
$[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_2\text{Zn}^-(n\text{-Bu})_4\text{N}^+{}^b$	CH_2Cl_2	2055 (1), 2044 (3.5), 1982 (5, sh), 1965 (10), 1887 (5.5), ca. 1850 (3, sh)
$[\text{WCp}(\text{CO})_3]_3\text{Cd}^-(n\text{-Bu})_4\text{N}^+$	THF	1960 (1, sh), 1942 (4), 1925 (9), 1886 (2), 1866 (3, sh), 1853 (9), 1835 (10), 1777 (2), 1757 (2)
	CH_2Cl_2	1959 (1), 1922 (9.5), 1884 (1), 1844 (10), 1831 (9), ca. 1765 (1)
	Nujol	ca. 1941 (4.5, sh), 1928 (7), 1913 (7), ca. 1855 (7.5, sh), 1840 (10), 1828 (8.5), 1816 (8), ca. 1805 (5, sh)
$[\text{WCp}(\text{CO})_3]_3\text{Zn}^-(n\text{-Bu})_4\text{N}^+$	THF	1972 (5), 1954 (5.5), 1930 (5), 1890 (4.5), 1867 (10), 1850 (6.5, sh), 1839 (5.5, sh), 1782 (3.5), 1764 (3.5)
	CH_2Cl_2	1990 (1.5, sh), 1969 (4), 1928 (6), 1890 (3.5), 1860 (10), 1850 (6, sh), 1832 (5), 1771 (1.5)
	Nujol	1929 (8.5), 1865 (6), 1847 (8), 1830 (10), 1790 (5.5)
$[\text{WCp}(\text{CO})_3][\text{FeCp}(\text{CO})_2]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+{}^b$	CH_2Cl_2	1970 (5), 1947 (8.5), ca. 1919 (4, sh), 1907 (10), 1887 (9), ca. 1867 (1.5, sh), ca. 1850 (1, sh), 1767 (9)
$[\text{FeCp}(\text{CO})_2]_3\text{Hg}^-(n\text{-Bu})_4\text{N}^+$	THF	1993 (1), ca. 1955 (2, sh), 1944 (3), 1916 (10), 1873 (6), ca. 1860 (3.5, sh), 1780 (2)
	Nujol	1960 (2, sh), 1938 (7), 1917 (9.5), 1911 (8.5, sh), ca. 1900 (4, sh), 1863 (7.5), 1854 (10)
$[\text{FeCp}(\text{CO})_2]_3\text{Cd}^-(n\text{-Bu})_4\text{N}^+$	THF	1935 (4), 1919 (10), 1867 (8), ca. 1854 (3.5, sh)
	Nujol	1933 (8), 1914 (10), ca. 1900 (2.5, sh), 1856 (9), 1845 (9.5), 1820 (2.5)
$[\text{FeCp}(\text{CO})_2]_3\text{Zn}^-(n\text{-Bu})_4\text{N}^+$	THF	2016 (0.5), 1994 (0.5), ca. 1960 (1.5, sh), 1938 (4.5), 1922 (10), 1867 (9), ca. 1855 (4, sh), 1783 (0.5)
	Nujol	1946 (6), 1937 (6.5), 1919 (9), ca. 1900 (3, sh), 1861 (8), 1849 (10), 1820 (3.5)

^a Concentrations of solutions 0.01–0.10 M. Largest nonsolvent peak absorbance is designated as 10. ^b Complex was not isolated. In these cases, the IR frequencies are for the mixture of components in solution.

The crystallizability of the complexes depends strongly on the cation. In many cases crystals could be obtained readily with one cation, but not at all with other cations. Most of the complexes showed air stability equal to or greater than that of the respective components, reflecting the elimination of an empty orbital on the main group metal as a site for attack by oxygen or moisture and a reduction of electron density on the metal carbonyl anion.

One compound, $\text{K}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$, demonstrated a significant temperature dependence of K_f . Cooling a mixture of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and a small amount of insoluble $\text{K}^+\text{Co}(\text{CO})_4^-$ in CH_2Cl_2 /hexane from room temperature to 0 °C caused the white $\text{K}^+\text{Co}(\text{CO})_4^-$ to dissolve. IR spectra showed only $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in solution at 30 °C, while at –5 °C, small amounts of $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ and $\text{Co}(\text{CO})_4^-$ were present, as well. Solid $\text{K}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ was isolated by a procedure that involved careful adjustment of the temperature at which saturation occurred in order to take advantage of the increased

association at lower temperature.

Equilibrium Nature of Complex Formation. Four lines of evidence pointed to the existence of an equilibrium in solutions of these complexes. First, a solution of $\text{Me}_4\text{N}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$ was treated with triphenylphosphine and the $\text{Hg}[\text{Co}(\text{CO})_4]_3^-(\text{PPh}_3)_2$ was collected and characterized. From the supernatant liquid $\text{Co}(\text{CO})_4^-$ was precipitated as $[\text{Ni}(\text{phen})_3]^{2+}[\text{Co}(\text{CO})_4]_2^-$. This demonstrated the ready dissociation of the complex. Further evidence for an equilibrium was found in the formation of $\text{Hg}[\text{Co}(\text{CO})_4]_2\text{WCp}(\text{CO})_3^-$ in two ways. Treatment of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with $(n\text{-Bu})_4\text{N}^+\text{WCp}(\text{CO})_3^-$ and treatment of $\text{HgCo}(\text{CO})_4\text{WCp}(\text{CO})_3^-$ with $(\text{Ph}_3\text{P})_2\text{N}^+(\text{Co}(\text{CO})_4)^-$ gave very similar products, as seen by their IR spectra in Table III. In particular, both showed complexed and free $\text{Co}(\text{CO})_4^-$ (1890 cm^{-1}), but neither showed free $\text{WCp}(\text{CO})_3^-$ (1890 s, and 1767 br, vs cm^{-1}). The observed formation constants were comparable. The ^1H NMR evidence is also consistent with a rapid equilibrium. The NMR spectrum of

Table IV. Experimental Conditions and Data from the X-ray Structure Analysis of $(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$

		Crystal Data			
cryst shape	irregular fragment	cell vol, Å ³	3821.5 (21)	space group	$P2_1/c$, C_{2h}^5 , No. 14 ³⁰
cryst dimens, mm	0.4 × 0.4 × 0.4	Z	4	systematic absences	0k0, $k = 2n + 1$
a, Å	9.819 (3)	ρ_{calcd} , g/cm ³	1.457		$h0l$, $l = 2n + 1$
b, Å	21.813 (7)	ρ_{obsd} , g/cm ³	1.45	formula	$\text{C}_{37}\text{H}_{51}\text{Fe}_3\text{NO}_6\text{Zn}$
c, Å	18.650 (5)	Laue symmetry	monoclinic	mol wt	838.73
β , deg	106.93 (2)				
		Data Collection and Reduction			
radiation	Mo K α	scan width, deg	1.0	criterion for observn	$3\sigma(F)$
μ , cm ⁻¹	18.3	bkg(total):scan ratio	0.5:1	total reflcns measd	5514
takeoff angle, deg	6.2	std reflcns/freq	3/50	reflcn in unique set	4214
scan type	ω	variation of I_{std} , %	<15	obsd reflcns	3916
scan speed, deg min ⁻¹	2.0-29.3	2 θ limits, deg	0.0-44.0		
		Structure Solution and Refinement ^{31,d}			
solution	direct methods	max shifts in parameters		positional 0.03;	
	and difference Fourier	in final cycle (Δ/σ)		thermal 0.2	
refinement	block-diagonal least squares	error of fit ^c		2.2	
isotropic convergence ^b	$R_1 = 0.101$; $R_2 = 0.151$	data/parameter		9.0	
anisotropic convergence ^b	$R_1 = 0.052$; $R_2 = 0.087$				

^a Measured by flotation in $\text{CCl}_4/\text{hexane}$. ^b $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. ^c Error of fit = $[\Sigma w(|F_o| - |F_c|)^2/(\text{NREF} - \text{NVAR})]^{1/2}$. ^d Corrections were made for Lorentz effects, polarization, and secondary extinction, but not for absorption or crystal decomposition (~5% decay in I of standard reflections over the period of data collection).

Table V. $M'(\text{ML}_n)_3^-$ Formation Constants in THF and in CH_2Cl_2 ^a

compd	THF	CH_2Cl_2
$\text{K}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$	5×10^3	<i>b</i>
$\text{Me}_4\text{N}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$	3×10^3	<i>b</i>
$(\text{Ph}_3\text{P})_2\text{N}^+\text{Hg}[\text{Co}(\text{CO})_4]_3^-$	<i>b</i>	4×10^3
$\text{Me}_4\text{N}^+\text{Cd}[\text{Co}(\text{CO})_4]_3^-$	<1	$>10^4$
$(n\text{-Bu})_4\text{N}^+\text{Cd}[\text{WCP}(\text{CO})_3]_3^-$	3×10^3	1×10^4
$(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{WCP}(\text{CO})_3]_3^-$	6×10	2×10^2

^a $K_f = [M'(\text{ML}_n)_3^-]/[M'(\text{ML}_n)_2][\text{ML}_n^-]$. ^b Not done.

the complex $[\text{WCP}(\text{CO})_3]_3\text{Zn}^-(n\text{-Bu})_4\text{N}^+$ showed a singlet due to Cp protons at δ 5.65 in THF at room temperature and also at -45°C . For comparison, the spectra of $[\text{WCP}(\text{CO})_3]_3(n\text{-Bu})_4\text{N}^+$ and $[\text{WCP}(\text{CO})_3]_2\text{Zn}$ showed singlets at δ 5.25 and 5.88, respectively, consistent with an increase in electron density on the $\text{WCP}(\text{CO})_3$ group in the order $[\text{WCP}(\text{CO})_3]_2\text{Zn} < [\text{WCP}(\text{CO})_3]_3\text{Zn}^- < \text{WCP}(\text{CO})_3^-$. Finally, the reversible nature of the equilibrium shown in eq 1 was demonstrated in one case by IR spectroscopic analysis of the complex formed. The IR spectrum of $\text{Hg}[\text{Co}(\text{CO})_4]_3^-\text{Me}_4\text{N}^+$ in THF showed $\nu(\text{CO})$ at 2039 and 1963 cm^{-1} for the complex anion in addition to weak bands at 2069 and 1996 cm^{-1} assigned to $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and at 1887 cm^{-1} attributed to $\text{Co}(\text{CO})_4^-\text{Me}_4\text{N}^+$. Addition of solid $\text{Co}(\text{CO})_4^-\text{Me}_4\text{N}^+$ to this solution caused the intensities of bands assigned to the complex and that assigned to $\text{Co}(\text{CO})_4^-$ to increase, while those due to $\text{Hg}[\text{Co}(\text{CO})_4]_2$ decreased.

Equilibrium concentrations of the metal carbonyl anions were estimated from changes in absorbances in IR spectra.¹⁶ These yielded formation constants, K_f , with estimated uncertainties of $\pm 30\%$. These values, listed in Tables V and VI, provide an approximate measure of relative tendencies for complex formation and are discussed below.

Factors That Affect the Extent of Complex Formation. There appear to be three factors that affect the extent of $M'(\text{ML}_n)_3^-$ complex formation. These are the main-group metal used, the choice of solvent, and the basicity of the transition metals attached to the main-group metal.

Effect of the Main-Group Metal, M' , on the Extent of Complex Formation. The first factor that influences complex formation is the particular main-group metal. It can be seen in Table VI that, for every complex observed, the extent of complex formation decreases in the order $\text{Cd} > \text{Zn} > \text{Hg}$. This is the opposite order to that observed for the average C-O stretching frequencies in $M'(\text{ML}_n)_2$, where $\nu(\text{CO})$ is in the

Table VI. $M'(\text{ML}_n)_3^-$ Formation Constants in CH_2Cl_2 ^a

ligands	Hg	Cd	Zn
$[\text{Co}(\text{CO})_4]_3$	4×10^3	$>10^4$	$>10^4$
$[\text{Co}(\text{CO})_4]_2\text{WCp}(\text{CO})_3$	9×10	$>10^4$	$>10^4$
$[\text{Co}(\text{CO})_4]_2\text{FeCp}(\text{CO})_2$	6	<i>b</i>	<i>b</i>
$\text{Co}(\text{CO})_4[\text{CrCp}(\text{CO})_3]_2$	<1	4×10^2	1×10
$\text{Co}(\text{CO})_4[\text{WCp}(\text{CO})_3]_2$	<1	5×10	3
$\text{Co}(\text{CO})_4[\text{FeCp}(\text{CO})_2]_2$	<i>b</i>	<1	<i>b</i>
$[\text{WCp}(\text{CO})_3]_3$	<1	1×10^4	2×10^2
$\text{WCp}(\text{CO})_3[\text{FeCp}(\text{CO})_2]_2$	<1	3	<1
$[\text{FeCp}(\text{CO})_2]_3$	$>10^4$ ^c	$>10^4$ ^c	$>10^4$ ^c

^a $K_f = [M'(\text{ML}_n)_3^-]/[M'(\text{ML}_n)_2][\text{ML}_n^-]$. ^b Not done.

^c THF was used due to reactivity of $\text{FeCp}(\text{CO})_2^-$ with CH_2Cl_2 .

Table VII. Selected Bond Distances (Å) of $(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ ^{a,b}

Zn-Fe1	2.536 (2)	Fe1-Cp1	1.730 (13)
Zn-Fe2	2.563 (2)	Fe2-Cp2	1.733 (12)
Zn-Fe3	2.524 (2)	Fe3-Cp3	1.734 (13)
av Zn-Fe	2.541	av Fe-Cp	1.732
Fe1-C11	1.733 (11)	av Fe-C(Cp)	2.105
Fe1-C12	1.725 (11)	C11-O11	1.152 (14)
Fe2-C21	1.708 (12)	C12-O12	1.171 (14)
Fe2-C22	1.749 (12)	C21-O21	1.165 (15)
Fe3-C31	1.722 (11)	C22-O22	1.155 (15)
Fe3-C32	1.711 (12)	C31-O31	1.176 (14)
av Fe-C	1.725	C32-O32	1.157 (15)
		av C-O	1.163

^a The standard deviation of the least significant figure of each distance is given in parentheses. ^b Cp refers to the center of the C_5H_5 ring.

order $[\text{ML}_n]_2\text{Hg} > [\text{ML}_n]_2\text{Zn} > [\text{ML}_n]_2\text{Cd}$.¹⁶ Both of these effects are indicative of lower electron density on Cd than on Zn or Hg. Lower electron density makes Cd a better Lewis acid and also lowers the average $\nu(\text{CO})$'s because more of the charge is found on the transition metals.

Solvent. The second factor that influences complex formation is the choice of solvent. It can be seen in Table V that Zn and Cd complexes are more dissociated in THF than in CH_2Cl_2 . On the other hand, the Hg complex has about the same formation constant in both solvents. This can be attributed to both Zn and Cd being considered harder acids than Hg³² and therefore having a higher affinity for the hard oxygen donor, THF.

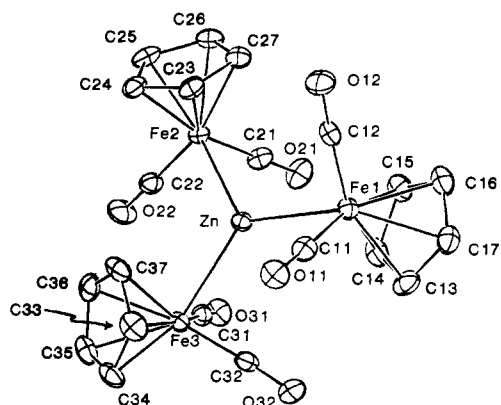
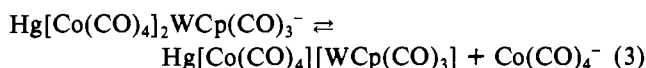


Figure 1. ORTEP drawing of the $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ anion. Hydrogen atoms have been omitted for clarity.

Effect of Transition-Metal Basicity on Complex Formation.

The third factor observed to affect complex formation is the basicity of the transition metal attached to the main-group acceptor. The basicity of the transition-metal anions can be measured as the ease of protonation of the metal, as shown in Table VII. Since complex formation is an equilibrium, the least basic anion will be in equilibrium with the complex. For example, when $(n\text{-Bu})_4\text{N}^+\text{WCp}(\text{CO})_3^-$ was added to $\text{Hg}[\text{Co}(\text{CO})_4]_2$, the equilibrium that obtains is shown in eq 3.



Therefore, the complexes in Table VII have been divided into three groups, based on the least basic transition-metal anion in each complex. In each of these groups, it is clear that the more basic the metals attached to the central metal atom are, the smaller is the formation constant. This is exactly the effect expected since an acceptor attached to basic groups is much more electron rich, and thus less acidic, than one with less basic transition metals. Conversely, increasing the basicity of the least basic transition metal involved in complex formation increases K_f . Thus, for complex formation involving $\text{Cd}[\text{FeCp}(\text{CO})_2]_2$ with $\text{Co}(\text{CO})_4^-$, $\text{WCp}(\text{CO})_3^-$, and $\text{FeCp}(\text{CO})_2^-$, the formation constants are ~ 0 , 3, and $>10^4$, respectively. The same effect was observed in an earlier work with halide ions and N donors as bases.³ In some cases, the solvent and the transition-metal anion may compete for the acid site on the main-group metal. Thus, while $\text{Cd}[\text{WCp}(\text{CO})_3]_3^-$ and $\text{Cd}[\text{Co}(\text{CO})_4]_3^-$ are both formed extensively in CH_2Cl_2 , only the tungsten compound shows complex formation in THF. This effect is due to $\text{WCp}(\text{CO})_3^-$ being a stronger base than $\text{Co}(\text{CO})_4^-$ and thus being better able to compete with THF oxygen.^{33,34}

The net effect of all these factors is that the most complex formation occurs for complexes where the group 2B metal has either three weakly basic transition-metal ligands or three very basic ones, but not for mixed complexes. In the former case, the transition metals do not put enough electron density onto the acceptor metal to alter its acidity very much. In the latter case, even though the central metal is not very acidic due to the strong donors attached to it, the anion is still basic enough to form a strong complex. The same explanation has been offered for the inability to form $\text{Hg}[\text{ML}_n]_2\text{X}^-$ complexes from $\text{Hg}[\text{ML}_n]_2$ and halide ion when ML_n is more basic than $\text{Co}(\text{CO})_4^-$.³

Crystal Structure of $(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$. The molecular structure of the anion $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ is shown in Figure 1. The cation is not unusual in any respect and so

is omitted. The geometry around zinc is trigonal planar with the zinc atom 0.024 Å from the plane of the three iron atoms and with all angles $120 \pm 3^\circ$. The structure of $\text{Hg}[\text{Co}(\text{CO})_4]_3^-\text{Me}_4\text{N}^+$ also shows trigonal-planar geometry around mercury.³⁵

The recently reported structure of a three-coordinate zinc complex, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{ZnW}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$, showed some deviation from planarity, which was attributed to weak intramolecular coordination to a carbonyl oxygen.⁵ Complexes containing mercury bonded to three main-group elements fall into two categories: the T-shaped complexes and the trigonal-planar complexes. The T-shaped mercury complexes involve linear coordination of mercury with a third, weak interaction approximately at right angles to the other two.³⁶⁻³⁹ Because the third interaction is so weak, these complexes are probably best considered to have primary coordination numbers of 2. The second class of three-coordinate mercury complexes are those with approximately equal bond lengths to three ligands. These are invariably trigonal planar. Those that have been structurally characterized at this time are $\{\text{Hg}[\text{Si}(\text{CH}_3)_2\text{Ph}]_3\}_2\text{Mg}_4(\text{OMe})_6(\text{DME})_2^{2+}$,⁴⁰ $\text{Hg}(\text{TePh})_3^-$,⁴¹ $\text{Hg}(\text{SCN})_2(\text{AsPh}_3)$,⁴² $\text{HgI}_3^-(n\text{-Bu})_4\text{N}^+$,⁴³ $\text{HgBr}_3^-\text{Me}_4\text{N}^+$,⁴⁴ and $\text{HgCl}_3^-\text{Et}_4\text{N}^+$.⁴⁵

The Zn-Fe distances in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ are unusual in two respects. First, there is a large range of distances, 2.524 (1)–2.563 (1) Å, which is surprising because the $\text{FeCp}(\text{CO})_2$ units should be equivalent. This effect has been observed in the trichloromercurate(II) anion, HgCl_3^- , where the Hg-Cl distances range from 2.426 (3) to 2.444 (3) Å.⁴⁵ The crystal structures of the corresponding triiodomercurate⁴⁴ and triodommercurate⁴³ anions show some differences in distances, but these differences are not statistically significant ($>3\sigma$). Structures of the type MX_4^{2-} are related to the MX_3^- structures by the addition of another anion and frequently show a similar variation in M-X distances. In HgI_4^{2-} , the distances vary from 2.68 (2) to 2.80 (2) Å⁴⁶ and $\text{Hg}(\text{SCN})_4^{2-}$ has Hg-S distances from 2.491 (3) to 2.575 (3) Å.⁴⁷ No explanation has been offered for this phenomenon.

The average Zn-Fe distance of 2.541 Å is quite long when compared with those of other complexes. In the tetramer

(35) $\text{Hg}[\text{Co}(\text{CO})_4]_3^-\text{Me}_4\text{N}^+$ crystallizes in space group $P2_1/a$ (a nonstandard setting of $P2_1/c$, C_{2h}^2 , No. 14³⁰) with $a = 14.268$ (3) Å, $b = 14.460$ (3) Å, $c = 19.213$ (4) Å, $\beta = 96.80$ (1) $^\circ$, and $Z = 8$. The structure was solved by direct methods and Fourier syntheses and refined by block-diagonal least squares to a final residual of $R = 0.100$ for 4383 observed reflections. The experimental and computational procedures used were similar to those employed in the $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-(n\text{-Bu})_4\text{N}^+$ determination. For the two unique molecules in the unit cell, the mercury atom is displaced by 0.017 and 0.024 Å from the plane of the three cobalt atoms. The Co-Hg-Co angles are all within the range 117.0–124.8 $^\circ$. The average Hg-Co distance is 2.687 Å, which can be compared with 2.499 Å for both $\text{Hg}[\text{Co}(\text{CO})_4]_2^{59}$ and $\text{Hg}[\text{Co}(\text{CO})_3^-(\text{PEt}_3)]_2$,^{69,72} consistent with the explanation given in the text for long Zn-Fe distances in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-(n\text{-Bu})_4\text{N}^+$. In the case of $\text{Hg}[\text{Co}(\text{CO})_4]_3^-$, there are no significant differences between the Hg-Co distances. All other parameters are similar to those of $\text{Hg}[\text{Co}(\text{CO})_4]_2$.

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Table VIII. Selected Bond Angles (deg) of $(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$, ^{a, b}

Fe1-Zn-Fe2	120.7 (1)	C11-Fe1-C12	91.7 (5)
Fe1-Zn-Fe3	122.1 (1)	C21-Fe2-C22	91.0 (6)
Fe2-Zn-Fe3	117.1 (1)	C31-Fe3-C32	91.0 (6)
av Fe-Zn-Fe	120.0	av C-Fe-C	91.2
Zn-Fe1-C11	81.7 (4)	C11-Fe1-Cp1	133.1 (6)
Zn-Fe1-C12	94.5 (4)	C12-Fe1-Cp1	128.0 (5)
Zn-Fe2-C21	76.8 (4)	C21-Fe2-Cp2	132.7 (5)
Zn-Fe2-C22	92.4 (4)	C22-Fe2-Cp2	129.9 (6)
Zn-Fe3-C31	80.2 (3)	C31-Fe3-Cp3	135.4 (6)
Zn-Fe3-C32	89.1 (3)	C32-Fe3-Cp3	128.6 (6)
av Zn-Fe-C	85.8	av C-Fe-Cp	131.3
Zn-Fe1-Cp1	113.9 (5)	Fe1-C11-O11	177.0 (10)
Zn-Fe2-Cp2	117.2 (4)	Fe1-C12-O12	175.1 (11)
Zn-Fe3-Cp3	115.3 (4)	Fe2-C21-O21	176.4 (12)
av Zn-Fe-Cp	115.5	Fe2-C22-O22	174.4 (10)
		Fe3-C31-O31	177.3 (10)
		Fe3-C32-O32	177.2 (9)
		av Fe-C-O	176.2

^a The standard deviation of the least significant figure is given in parentheses. ^b Cp refers to the center of the C_5H_5 ring.

$[\text{CH}_3\text{OZnFeCp}(\text{CO})_2]_4$, the average Zn-Fe distance is 2.350 Å.⁴⁸ A distance of 2.317 Å has been found for $\text{Zn}[\text{Fe}(\text{CO})_4]_2^{2-}$.⁴⁹ The Zn-Fe distance in $[(\text{bpy})\text{ZnFe}(\text{CO})_4]_2$ is 2.558 Å.⁵⁰ There are several possible reasons that the Zn-Fe bonds in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ are at the longer end of this range. First, it has been observed that there is a correlation between the number of $\text{FeCp}(\text{CO})_2$ moieties attached to a central atom, Y, and the average Fe-Y distance. For example, the Fe-Y distances are 2.539 and 2.440 Å for $[\text{FeCp}(\text{CO})_2]_3\text{SbCl}^+$ and $[\text{FeCp}(\text{CO})_2]_2\text{SbCl}_2^+$,^{51,52} 2.280, 2.201, and 2.109 Å for $[\text{FeCp}(\text{CO})_2]_2\text{SO}_2$, $\text{FeCp}(\text{CO})_2\text{SO}_2\text{C}_6\text{F}_5$, and $\text{FeCp}(\text{CO})_2\text{SO}_2^+$,^{53,54} 2.492 and 2.466 Å for $[\text{FeCp}(\text{CO})_2]_2\text{SnCl}_2$ and $\text{FeCp}(\text{CO})_2\text{SnCl}_3$,^{55,56} and 2.280 and 2.264 Å for $[\text{FeCp}(\text{CO})_2]_2\text{SiCl}_4\text{Si}_2\text{C}_3\text{H}_6$ and $\text{FeCp}(\text{CO})_2\text{SiCl}_3\text{Si}_2\text{C}_3\text{H}_6$, respectively.⁵⁷ An increase in Hg-Co bond distances is seen when $\text{FeCp}(\text{CO})_2\text{HgCo}(\text{CO})_4$ is compared to $\text{Hg}[\text{Co}(\text{CO})_4]_2$. The Hg-Co distances are 2.573 and 2.499 Å, respectively.^{58,59} At least part of the increase in bond length is probably due to the increase in electron density on Y by the very basic $\text{FeCp}(\text{CO})_2$ group. This effect has ample precedent as seen in the following bond lengths: 2.520 and 2.484 Å for Fe-Fe distances in $[\text{FeCp}(\text{CO})]_4$ and $[\text{FeCp}(\text{CO})]_4^+$,^{60,61} 2.693 and 2.651 Å for Fe-S distances in $[\text{Fe}(\text{NO})\text{S}]_4^-$ and $[\text{Fe}(\text{NO})\text{S}]_4$,⁶²

and 2.313 and 2.179 Å for Fe-Cl distances in FeCl_4^{2-} and FeCl_4^- , respectively.⁵¹

Another factor that contributes to the observed bond lengthening in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ is the increase in bond distance with increased coordination number for group 2B complexes. In related systems, the average Hg-Co distances are 2.58 and 2.504 Å for $\text{Hg}[\text{CoCp}(\text{CO})_2]_2\text{Cl}_2$ and $\text{Hg}[\text{CoCp}(\text{CO})_2]_2\text{Cl}^+$; the Hg-Cl distances are 2.46 and 2.348 Å.⁶³ In the case of halides and isothiocyanate ligands, it is observed in every case that the average Hg-X distances decrease in the order $\text{HgX}_4^{2-} > \text{HgX}_3^- > \text{HgX}_2$.^{43-47,64-67} From the preceding discussion, it seems reasonable that the Zn-Fe bond length would increase from 2.350 Å in $[\text{CH}_3\text{OZnFeCp}(\text{CO})_2]_4$ with a neutral Zn and only one $\text{FeCp}(\text{CO})_2$ unit to 2.541 Å in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ with anionic zinc and three $\text{FeCp}(\text{CO})_2$ moieties.

A second interesting feature of the $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ structure involves the Zn-Fe-C(CO) angles. From Table VIII, it can be seen that each iron is bonded to one carbonyl with a Zn-Fe-C(CO) angle of $\sim 80^\circ$ and one of $\sim 90^\circ$ (average 85.8°). Since it had been reported that this angle for most $\text{FeCp}(\text{CO})_2$ complexes is very close to 90° , as expected for pseudooctahedral coordination, and since $[\text{CH}_3\text{OZnFeCp}(\text{CO})_2]_4$ also has a small average Zn-Fe-C(CO) angle (81.7°), an extensive literature search was done for compounds containing the $\text{FeCp}(\text{CO})_2$ group bonded to a main-group element, Y. The results are presented in Table IX. It can be seen that, in general, the angle increases going from left to right in the periodic table and from bottom to top, paralleling the electronegativity of Y. Thus, the fairly small angle observed for $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ is in accord with past structures. The large range of angles ($76.8\text{--}94.5^\circ$) in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ is unusual, but not unprecedented. In $[\text{FeCp}(\text{CO})_2]_2\text{Sn}(\eta^1\text{-Cp})_2$, the range is $83.3\text{--}92.3^\circ$,⁶⁸ and in $(\text{FeCp}(\text{CO})_2\text{AsOAs})_2\text{OFeCp}(\text{CO})^+$, the range is $87.2\text{--}94.5^\circ$.⁶⁹ In many of the structures listed in Table IX, the range of angles is $>4^\circ$. The range in $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ (17.7°) is the largest found for any compound listed in Table IX, and the angle of 76.8° is the smallest found. In spite of this, there is no evidence for any bridging character in these carbonyls. The average Fe-C-O angle of 176.3° agrees well with those of most of the other complexes reported, and none of the Fe-C-O angles in this complex deviate by more than 2σ from the average. In addition, the Zn-C distance is 2.80 ± 0.06 Å for the three carbonyls with the smallest Zn-Fe-C(CO) angle. This can be compared with 2.502 Å in $\text{Zn}[\text{Fe}(\text{CO})_4]_2^{2-}$, where the authors stated that there is little or no CO-Zn interaction and supported this with theoretical calculations.⁴⁹ There is no clear explanation for either the general trend in Zn-Fe-C(CO) angles or the large range of angle observed in this and other complexes.

The Fe-C(CO) distance also displays a slight trend for the Y- $\text{FeCp}(\text{CO})_2$ complexes reported with the bond length increasing toward the right of the periodic table, consistent with the 1.725 Å for $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ compared to 1.758 Å (average) for all complexes. The Fe-C(Cp) distances showed no apparent trend and the 2.105 Å for $\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ agrees very well with the 2.098 Å average for the compounds that were included in Table IX. The C(CO)-Fe-C(CO) angle

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Table IX. Structural Parameters for Crystal Structures Containing the FeCp(CO)₂ Moiety Bonded to a Main-Group Element^a

Key:					
Element, Y	C	N	O	F	
(No. of Structures)	(22) ^d	(3) ^e	(5) ^f		
Avg. Y-Fe-C(CO) Angle (°)	90.4	93.6	94.4		
Avg. Fe-Y Distance (Å)	1.996	1.923	1.975		
Apparent Fe radius ^b	1.23	1.22	1.31		
	<u>Al</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Cl</u>
	(1) ^g	(4) ^h	(5) ⁱ	(6) ^j	(2) ^k
	83.1	86.4	92.3	92.5	92.6
	2.510	2.312	2.245	2.240	2.301
	1.08	1.14	1.15	1.20	1.31
	<u>Zn</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	<u>Br</u>
	(2) ^l	(2) ^m	(2) ⁿ		
	83.5	87.4	90.3		
	2.445	2.364	2.384		
	1.07	1.14	1.17		
	<u>Cd</u>	<u>In</u>	<u>Sn</u>	<u>Te</u>	<u>I</u>
			(13) ^o		(1) ^q
			88.9		92.3
			2.522		2.588
			1.12		1.31
	<u>Hg</u>	<u>Tl</u>	<u>Pb</u>	<u>Po</u>	<u>At</u>
	(1) ^r		(1) ^s		
	-		83.8		
	2.49		2.708		
	1.05		1.17		

^a Structures containing bridging carbonyls or substituted Cp rings were not included. There is also one transition-metal cluster, (CO)₄Mn-FeCp(CO)₂,^c which has an average Mn-Fe-C(CO) angle of 85.7° and an Fe-Mn distance of 2.843 Å. ^b Obtained by subtracting the covalent radius of Y⁷¹ from the average Fe-Y distance. ^c Hansen, P. J.; Jacobson, R. A. *J. Organomet. Chem.* 1966, 6, 389. ^d Clark, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1974, 2027. ^e Goddard, R.; Howard, J.; Woodward, P. *Ibid.* 1974, 2025. ^f Andrianov, V. G.; Struchkov, Yu. T.; Zlotina, I. B.; Khomutov, M. A. *Koord. Khim.* 1979, 5, 1872. ^g Gress, M. E.; Jacobson, R. A. *Inorg. Chem.* 1973, 12, 1746. ^h Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* 1979, 112, 218. ⁱ Laing, M.; Kruger, G.; DuPreez, A. L. *J. Organomet. Chem.* 1974, 82, C40. ^j Slovokhotov, Yu. L.; Yanovsky, A. I.; Andrianov, V. G.; Struchkov, Yu. T. *Ibid.* 1980, 184, C57. ^k Rybin, L. V.; Petrovskaya, E. A.; Batsanov, A. 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Table X. Fractional Coordinates for $(n\text{-Bu})_4\text{N}^+\text{Zn}[\text{FeCp}(\text{CO})_2]_3^-$ ^a

atom	x	y	z
Zn	0.9339 (1)	0.4683 (1)	0.2262 (1)
Fe1	1.1585 (2)	0.4837 (1)	0.1874 (1)
C11	1.0760 (12)	0.4304 (5)	0.1202 (7)
O11	1.0260 (9)	0.3932 (4)	0.0760 (4)
C12	1.2532 (11)	0.4272 (5)	0.2457 (6)
O12	1.3219 (9)	0.3879 (4)	0.2812 (5)
C13	1.1263 (14)	0.5624 (5)	0.1208 (7)
C14	1.0890 (12)	0.5740 (5)	0.1869 (8)
C15	1.2160 (13)	0.5659 (6)	0.2489 (7)
C16	1.3225 (13)	0.5491 (6)	0.2175 (8)
C17	1.2697 (13)	0.5477 (5)	0.1396 (7)
Fe2	0.9460 (2)	0.4581 (1)	0.3649 (1)
C21	0.9803 (13)	0.5341 (5)	0.3560 (6)
O21	1.0010 (10)	0.5865 (4)	0.3533 (5)
C22	0.7637 (12)	0.4732 (6)	0.3467 (6)
O22	0.6471 (8)	0.4858 (5)	0.3400 (5)
C23	1.0611 (13)	0.3777 (5)	0.3568 (6)
C24	0.9494 (14)	0.3645 (5)	0.3891 (7)
C25	0.9740 (14)	0.3980 (6)	0.4565 (7)
C26	1.1015 (13)	0.4329 (5)	0.4665 (6)
C27	1.1533 (12)	0.4206 (5)	0.4051 (6)
Fe3	0.6901 (2)	0.4654 (1)	0.1320 (1)
C31	0.6747 (11)	0.5316 (5)	0.1793 (6)
O31	0.6656 (9)	0.5781 (3)	0.2095 (5)
C32	0.7561 (11)	0.5058 (6)	0.0709 (6)
O32	0.7954 (9)	0.5335 (4)	0.0277 (5)
C33	0.6840 (14)	0.3785 (6)	0.0839 (8)
C34	0.5502 (13)	0.4045 (6)	0.0556 (7)
C35	0.4978 (12)	0.4166 (5)	0.1141 (8)
C36	0.5930 (14)	0.3985 (5)	0.1802 (7)
C37	0.7121 (13)	0.3733 (5)	0.1632 (8)
N	0.3276 (9)	0.2204 (4)	0.1410 (5)
C41	0.3730 (12)	0.1595 (5)	0.1134 (6)
C42	0.4876 (14)	0.1623 (6)	0.0760 (8)
C43	0.5154 (15)	0.0984 (7)	0.0508 (8)
C44	0.6188 (19)	0.0959 (9)	0.0067 (10)
C46	0.2031 (11)	0.2046 (5)	0.1690 (6)
C47	0.1398 (13)	0.2573 (5)	0.2020 (7)
C48	-0.0011 (15)	0.2366 (6)	0.2165 (9)
C49	-0.1273 (15)	0.2268 (7)	0.1459 (11)
C51	0.4488 (11)	0.2489 (5)	0.2017 (6)
C52	0.5077 (12)	0.2119 (5)	0.2721 (7)
C53	0.6190 (15)	0.2494 (7)	0.3299 (8)
C54	0.6805 (16)	0.2190 (7)	0.4034 (8)
C56	0.2883 (12)	0.2671 (5)	0.0773 (6)
C57	0.1649 (13)	0.2493 (5)	0.0104 (7)
C58	0.1482 (16)	0.2965 (6)	-0.0525 (7)
C59	0.2709 (17)	0.2958 (8)	-0.0877 (8)

^a The standard deviation of the least significant figure is given in parentheses.

also showed no apparent trend and the 91.2° observed is somewhat less than the 94.3° average. The structure contains no nonbonded contacts shorter than 3.2 Å.

In spite of the large amount of work done with complexes of the type $M'[\text{ML}_n]_m\text{X}_{3-m}^-$,^{2-14,43-45,60,70} this is the first ex-

ample of a trigonal zinc or cadmium complex and also the first definitive structure of the type $M'(\text{ML}_n)_3^-$. Taken together with the spectroscopic evidence presented here and elsewhere,²⁻⁴ this structure strongly supports trigonal-planar structures for all the members of the $M'(\text{ML}_n)_3^-$ family.

Summary and Conclusions. Tetrametallic clusters of the type $M'(\text{ML}_n)_3^-$ where M' is a group 2B metal and ML_n is a transition-metal anion can be formed by the addition of ML_n^- to $M'(\text{ML}_n)_2$. The formation of this cluster is an equilibrium process with the choice of M' , ML_n , and solvent all affecting complex formation in a systematic way. The X-ray crystal structure of one member of this class of compounds, $(n\text{-Bu})_4\text{N}^+[\text{FeCp}(\text{CO})_2]_3\text{Zn}^-$, shows them to have trigonal-planar geometry around the central metal.

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Registry No. $[\text{Co}(\text{CO})_4]_3\text{Hg}^-\text{K}^+$, 87183-28-6; $[\text{Co}(\text{CO})_4]_3\text{Hg}^-\text{Me}_4\text{N}^+$, 26123-17-1; $[\text{Co}(\text{CO})_4]_3\text{Cd}^-\text{Me}_4\text{N}^+$, 87183-30-0; $[\text{Co}(\text{CO})_4]_3\text{Zn}^-\text{Me}_4\text{N}^+$, 87183-32-2; $[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Cd}^-\text{Me}_4\text{N}^+$, 87183-34-4; $[\text{WCp}(\text{CO})_3]_3\text{Cd}^-(n\text{-Bu})_4\text{N}^+$, 87183-36-6; $[\text{WCp}(\text{CO})_3]_3\text{Zn}^-(n\text{-Bu})_4\text{N}^+$, 87183-38-8; $[\text{FeCp}(\text{CO})_2]_3\text{Hg}^-(n\text{-Bu})_4\text{N}^+$, 11078-16-3; $[\text{FeCp}(\text{CO})_2]_3\text{Cd}^-(n\text{-Bu})_4\text{N}^+$, 87183-40-2; $[\text{FeCp}(\text{CO})_2]_3\text{Zn}^-(n\text{-Bu})_4\text{N}^+$, 87183-42-4; $[\text{Co}(\text{CO})_4]_3\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-43-5; $[\text{Co}(\text{CO})_4]_3[\text{WCp}(\text{CO})_3]\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-45-7; $[\text{Co}(\text{CO})_4][\text{FeCp}(\text{CO})_2]\text{Hg}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-49-1; $[\text{Co}(\text{CO})_4][\text{CrCp}(\text{CO})_3]_2\text{Zn}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-51-5; $[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Cd}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-52-6; $[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+$, 87189-79-5; $[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]_2\text{Zn}^-(\text{Ph}_3\text{P})_2\text{N}^+$, 87183-54-8; $[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_3\text{Hg}^-(n\text{-Bu})_4\text{N}^+$, 87183-56-0; $[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+$, 87183-58-2; $[\text{WCp}(\text{CO})_3][\text{Co}(\text{CO})_4]_2\text{Zn}^-(n\text{-Bu})_4\text{N}^+$, 87183-60-6; $[\text{WCp}(\text{CO})_3][\text{FeCp}(\text{CO})_2]_2\text{Cd}^-(n\text{-Bu})_4\text{N}^+$, 87189-81-9; $\text{Hg}[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]$, 20243-34-9; $[\text{Ni}(\text{phen})_3]^{2+}[\text{Co}(\text{CO})_4]_2^-$, 87183-61-7; $\text{Hg}[\text{Co}(\text{CO})_4]_2$, 13964-88-0; $\text{Cd}[\text{Co}(\text{CO})_4]_2$, 16986-00-8; $\text{Zn}[\text{Co}(\text{CO})_4]_2$, 16985-99-2; $\text{Hg}[\text{Co}(\text{CO})_4][\text{WCp}(\text{CO})_3]$, 87183-62-8; $\text{Hg}[\text{FeCp}(\text{CO})_2][\text{Co}(\text{CO})_4]$, 60364-19-4; $\text{Hg}[\text{CrCp}(\text{CO})_3]_2$, 12194-11-5; $\text{Cd}[\text{CrCp}(\text{CO})_3]_2$, 55518-02-0; $\text{Zn}[\text{CrCp}(\text{CO})_3]_2$, 55493-74-8; $\text{Hg}[\text{WCp}(\text{CO})_3]_2$, 12289-72-4; $\text{Cd}[\text{WCp}(\text{CO})_3]_2$, 33042-10-3; $\text{Zn}[\text{WCp}(\text{CO})_3]_2$, 63139-55-9; $\text{Cd}[\text{FeCp}(\text{CO})_2]_2$, 87183-63-9; $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$, 35885-95-1; $\text{Zn}[\text{FeCp}(\text{CO})_2]_2$, 82246-68-2; $\text{Co}(\text{CO})_4^-\text{Na}^+$, 14878-28-5; $\text{Co}(\text{CO})_4^-\text{K}^+$, 14878-26-3; $\text{Co}(\text{CO})_4^-\text{Me}_4\text{N}^+$, 87183-64-0; $\text{Co}(\text{CO})_4^-(n\text{-Bu})_4\text{N}^+$, 77170-19-5; $\text{Co}(\text{CO})_4^-\text{Ph}_4\text{As}^+$, 23807-55-8; $\text{Co}(\text{CO})_4^-(\text{Ph}_3\text{P})_2\text{N}^+$, 53433-12-8; $\text{WCp}(\text{CO})_3^-(n\text{-Bu})_4\text{N}^+$, 68914-56-7; $\text{FeCp}(\text{CO})_2^-(n\text{-Bu})_4\text{N}^+$, 65836-70-6; $[\text{FeCp}(\text{CO})_2]_2$, 12154-95-9; $\text{Na}^+\text{FeCp}(\text{CO})_2^-$, 12152-20-4; $\text{Ni}(\text{phen})_3\text{Cl}_2$, 14356-44-6.

Supplementary Material Available: Table XI (thermal parameters), Table XII (calculated H atom positions), and Table XIII (structure factor amplitudes) (31 pages). Ordering information is given on any current masthead page.

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