Contribution from the Department of Chemistry,
William Marsh Rice University, Houston, Texas 77001

Reduction of the Group 2B Tetracarbonylferrates in Lewis Bases. Synthesis, Characterization, and Structural Features of the $(Na\{THF\}_2)^+{}_2[M'(Fe(CO)_4)_2]^{2-}$ (M′ = Zn, Cd, and Hg) Series

BARRIE A. SOSINSKY,*[1] ROBERT G. SHONG, BRIAN J. FITZGERALD, NATHAN NOREM,
and CAROL O'ROURKE

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In the presence of Lewis bases $[M'Fe(CO)_4]_x$ complexes (I; M′ = Zn, Cd, and Hg) undergo mild stepwise reduction to give first the kinetically stable $[M'(Fe(CO)_4)_2]^{2-}$ (II) and subsequently $[Fe_2(CO)_8]^{2-}$ (III). The mechanism for base reduction is considered in terms of competing base reactions. The solid-state structures of $(Na\{THF\}_2)^+{}_2[M'(Fe(CO)_4)_2]^{2-}$ (IIa–c; M′ = Zn, Cd, and Hg, respectively) have been determined and are directly related to their solution-state infrared spectra with distortions in the dianions retained in both states. The results of our structure determination on $(Na\{THF\}_2)^+{}_2$-$[Zn(Fe(CO)_4)_2]^{2-}$ have been described in a previous communication. Crystals of the Hg analogue form in the same space group, and C_{2h} site symmetry is also imposed on the complex anion. Cell dimensions for IIc are $a = 12.39$ (3) Å, $b = 8.54$ (1) Å, $c = 16.01$ (1) Å, $\beta = 105.5$ (2)°, and $V = 1636$ Å^3. The geometry about the Fe atoms is that of a $Fe(CO)_4$ tetrahedron with the Fe–Hg bond capping one face. Bonds between carbonyl oxygen atoms of the anion and the $Na(THF)_2^+$ cations result in an extended oligomeric structure in the solid state. ^{57}Fe Mössbauer spectra recorded on $[M'(Fe(CO)_4)_2]^{2-}$ gave the following parameters: M′ = Zn, $\delta = 0.416$, $\Delta = 1.429$ mm s^{-1}; M′ = Cd, $\delta = 0.232$ and 1.192, $\Delta = 1.112$ and 0.808 mm s^{-1}, respectively (relative to SNP). IIb has two magnetically distinct iron atoms. IIa does not undergo facile reaction toward mercury and is sluggishly reactive toward $NiCl_2$, yielding III. Reaction of IIa with $HgCl_2$ yields the transmetalated product $[Fe(CO)_4(HgCl)_2]$, whereas reaction of IIa with Hg_2Cl_2 yields only III with small amounts of IIa and IIc.

Introduction

There has been considerable recent interest in the synthesis and chemical properties of polynuclear complexes containing heterobimetallic metal–metal bonds.[2] Much of this interest is related to the unique catalytic properties that a complex having a polar bonding interaction between metal centers might offer. Of particular relevance in this regard is the use of reduced heterogeneous catalysts incorporating a variety of transition-metal ions on a ZnO support in CO reduction processes.[3] Chromium oxide on ZnO is used in commercial methanol synthesis.[4] Molecular systems may be used to provide specific information on unique modes of bonding and substrate activation since they are amenable to precise characterization using a variety of structure determination methods.

Mixed-metal bimetallic complexes have been found to undergo mild reduction in the presence of Lewis bases {B}. In previous work, $[Fe(CO)_4(SnR_2)]_2$ in the form of $[Fe(CO)_4(SnR_2\{B\})]$ was reduced to the dianion[5] $[Fe(CO)_4(SnR_2)]^{2-}$, which our studies indicate is monomeric and very nearly isoelectronic to the base adduct.[6] In this paper we report that $[M'Fe(CO)_4]_x$ complexes (M′ = Zn (Ia), Cd (Ib), and Hg (Ic)) undergo stepwise reduction in base solution to give first $[M'(Fe(CO)_4)_2]^{2-}$ (M′ = Zn (IIa), Cd (IIb), and Hg (IIc)) and then $[Fe_2(CO)_8]^{2-}$. Figure 1 shows the structures of II and their counterions, and Figure 2 their spectra. We have discussed the implications of the Mössbauer spectra of these complexes in the general context of five-coordinate tetracarbonylferrates elsewhere.[7] Our synthesis of II represents a significant improvement over a previous report.[8] Herein, we will discuss further the nature of the base reduction and the factors that influence the stability of the various mixed-metal species.

The general bonding patterns of bimetallics are suggestive of promotional effects, and their elucidation should be instructive in understanding organometallic reaction mechanisms and the nature of the changes in electronic configuration that accompany them. Complexes II illustrate a series where the group 2B–iron bond description varies from near-ionic-distorted T_d $d^{10-\delta}$–$Fe^{2-(+\delta)}$ ((IIa) to near-covalent d^8–Fe^0 (IIb,c). Ionicity in the group 2B–iron bond changes both the electronic and the nuclear properties of the iron atom. Careful description of the factors influencing M″–M bond polarity is useful in determining favored geometries and electronic configurations and may ultimately explain organometallic reaction pathways.

Experimental Section

All complexes were handled under rigorous air-free conditions with use of standard techniques.[9] Solvents were dried and deoxygenated thoroughly prior to use. Infrared spectra were recorded on a Beckman IR 4230 spectrophotometer in the form indicated with polystyrene as reference. The ^{13}C NMR spectra were measured on a JEOL FX-90 Q. Iron-57 Mössbauer measurements were performed on an apparatus described previously[6] using sodium nitroprusside dehydrate as standard but converted to an iron metal standard. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY 11377. Solution conductivities were obtained in acetonitrile on a Yellow Springs Institute Model 31 conductivity bridge.

The compounds PPN^+Cl^-,[10] $[Zn(NH_3)_3Fe(CO)_4]$,[11] $[CdFe(CO)_4]$,[12] $[(HgCl)_2Fe(CO)_4]$,[13] and $[HgFe(CO)_4]$[14] were prepared by literature

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(3) (a) Krylov, O. V. "Catalysis by Non-Metals"; Academic Press: New York, 1970. (b) Gay, R. R.; Nodine, M. H.; Henrich, V. E.; Zieger, H. J.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 6752 and references contained therein.

(4) (a) Imperial Chemical Industries Ltd., methanol catalyst. (b) Mehta, D. D.; Ross, D. E. *Hydrocarbon Process.* **1970**, 183.

(5) Recent work has shown that $[Fe(CO)_4SnR_2]^{2-}$ contains one unpaired electron as assessed by the Evans method. Sodium analyses show one sodium per ion. This suggests these species may be better characterized as a radical anion. Crystals of R = Ph are now in hand, and a structure is being determined by Professor C. G. Pierpont at the University of Colorado.

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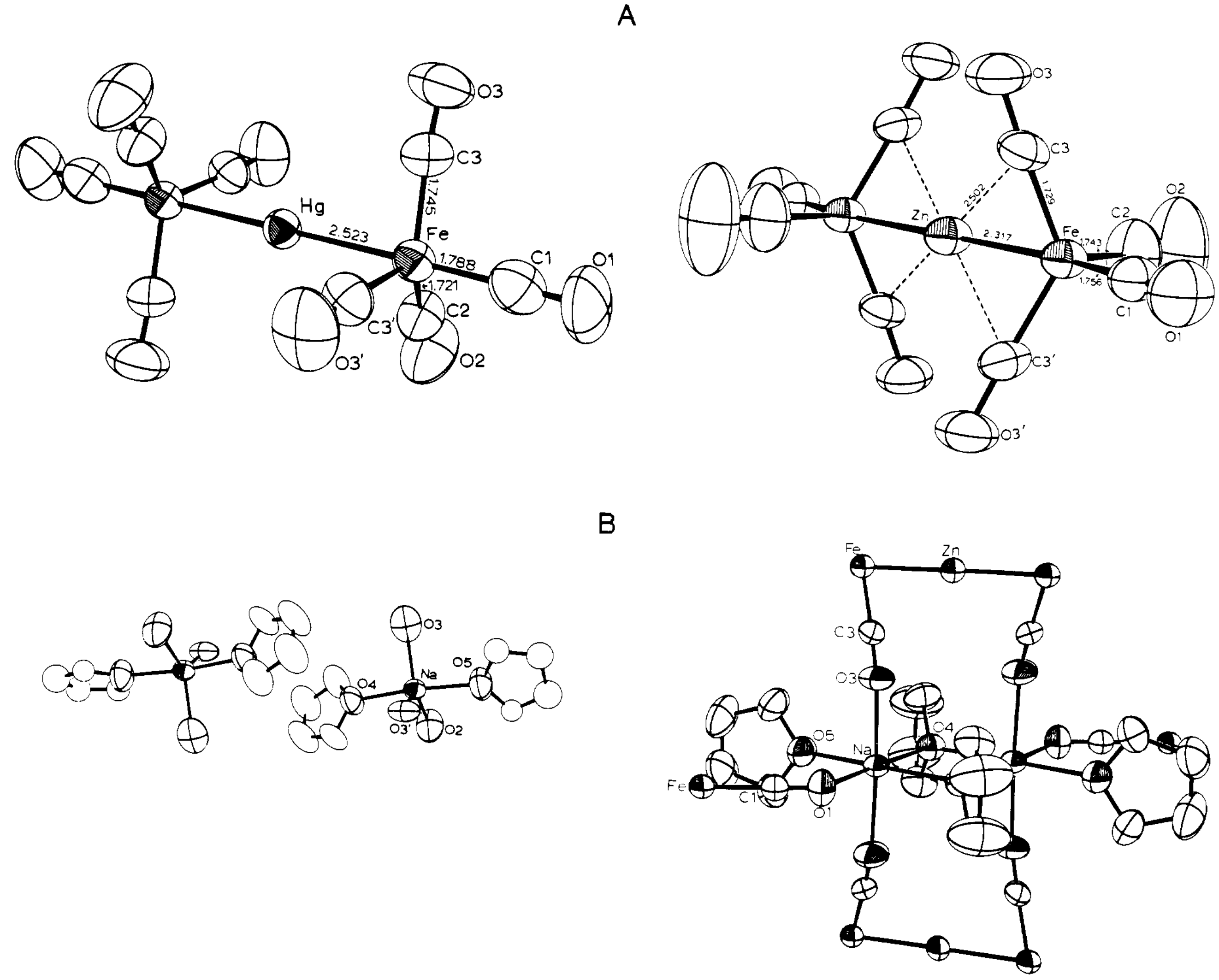

Figure 1. Geometries of the $(Na\{THF\}_2)^+{}_2[M'(Fe(CO)_4)_2]^{2-}$ (II) compounds: (A) dianion structure; (B) cation structure.

methods previously described by others. The reagents $HgCl_2$ and Hg_2Cl_2 were dried under vacuum at 110 °C for 24 h to remove adsorbed O_2 and H_2O. $NiCl_2\cdot 6H_2O$ was dried at 110 °C under vacuum until a complete color change from green to yellow-brown (6 days) took place. The reagents $HgCl_2$, Hg_2Cl_2, $NiCl_2\cdot 6H_2O$, Hg metal, Na, NaH, etc., were obtained from commercial sources.

Syntheses of $(Na\{THF\}_2)^+{}_2[M'(Fe(CO)_4)_2]^{2-}$. $(Na\{THF\}_2)^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$ (IIa). A THF (40 mL) solution of $[(NH_3)_3ZnFe(CO)_4]$ (1.0 g, 3.53 mmol) was added to a 250-mL Schlenk flask containing a 0.6% sodium (0.3 g, 13.04 mmol, of Na and 43.4 g, 216.36 mmol, of Hg) amalgam. The mixture was stirred for 30 min and then filtered through Celite and a medium-porosity sintered frit, yielding a yellow-orange solution. The product IIa (0.82 g, 63%) was obtained from a standing toluene/THF solution as very air-sensitive clear crystals with a light pink tint. Solutions of IIa are extremely air sensitive. The melting point determined in vacuo was 175 °C with decomposition IR (KBr) 1990 (sh), 1952 (m), 1894 (w), and 1809 (vs); ^{13}C NMR (CD_3CN, 25° C) 138.56 (1 (intensity)), 141.1 (2.75), 183.29 (7.89), and 233.19 ppm (5.79); conductivity (CH_3CN) 463.18 Ω^{-1} mol^{-1} cm^{-1} for M_r = 735.6; ^{57}Fe Mössbauer δ = 0.156 mm s^{-1} and Δ = 1.429 mm s^{-1}. Anal. Calcd for $Na_2Fe_2ZnC_{24}H_{32}O_{12}$: Zn, 8.89; Fe, 15.18; Na, 6.25. Found: Zn, 8.52; Fe, 14.90; Na, 6.25.

$(Na\{THF\}_2)^+{}_2[Cd(Fe(CO)_4)_2]^{2-}$ (IIb). A THF (25 mL) solution of $[CdFe(CO)_4]_x$ (0.4 g, 1.43 mmol) was added to a 250-mL Schlenk flask containing a 0.4% sodium (0.1 g, 4.35 mmol, of Na/23.3 g, 116.16 mmol, of Hg) amalgam. The reaction was stirred for 10 min and then filtered through Celite and a Medium-porosity sintered frit, yielding a clear yellow-orange solution. The product IIb (400 mg, 71.4%) was obtained from a standing toluene (or hexane)/THF solution as very air-sensitive clear yellow crystals. Solutions of IIb are extremely air sensitive. The melting point determined in vacuo was 171 °C with decomposition: IR (KBr) 1952 (m), 1861 (sh), 1845 (sh), and 1799 (s) cm^{-1}; IR (THF) 1933 (s), 1867 (sh), 1848 (vs), and 1807 (s) cm^{-1}; ^{13}C NMR (CD_3CN, 25 °C) 142.07 (1.44 (intensity)), 184.17 (1), and 233.92 ppm (2.73); conductivity (CH_3CN) 394.4 Ω^{-1} mol^{-1} cm^{-1} for M_r = 782.64; ^{57}Fe Mössbauer δ = 0.492 and 1.452 mm s^{-1} and Δ = 1.11 and 0.808 mm s^{-1}, respectively, relative to iron metal.

$(Na\{THF\}_2)^+{}_2[Hg(Fe(CO)_4)_2]^{2-}$ (IIc). A THF (50 mL) *suspension* of $[HgFe(CO)_4]_x$ (2.3 g, 6.23 mmol) was added to a 250-mL Schlenk flask containing a 1.7% sodium (0.4 g, 1.43 mmol, of Na/23.3 g, 116.2 mmol, of Hg) amalgam. The reaction was stirred for 18–20 h and then filtered through Celite and a medium-porosity sintered frit, yielding a clear yellow solution. Clear gold or deep yellow crystals of IIc (1.7 g, 63%) were obtained from a standing hexane/THF solution. IIc is extremely air sensitive either in solution or in the solid state. The melting point determined in vacuo was 170 °C with decomposition: IR (KBr) 1947 (br) and 1808 (vb) cm^{-1}; IR (THF) 1962 (sh), 1934 (s), 1858 (vs), and 1815 (m) cm^{-1}; ^{13}C NMR (CD_3CN, 25 °C) 142.67 (1.11 (intensity)), 184.12 (2.17), 184.77 (1.0), and 234.61 ppm (3.22); conductivity (CH_3CN) 316 Ω^{-1} mol^{-1} cm^{-1} for M_r = 870.83; ^{57}Fe Mössbauer could not be recorded either at room temperature or at 78 K.

Reduction of $[M'Fe(CO)_4]_x$ to $[Fe_2(CO)_8]^{2-}$. A THF (25 mL) solution of Ia, Ib, or Ic (ca. 25 mg) was added to a flask containing 0.3% Na/Hg solution. $[Fe_2(CO)_8]^{2-}$ was formed in solution at reaction

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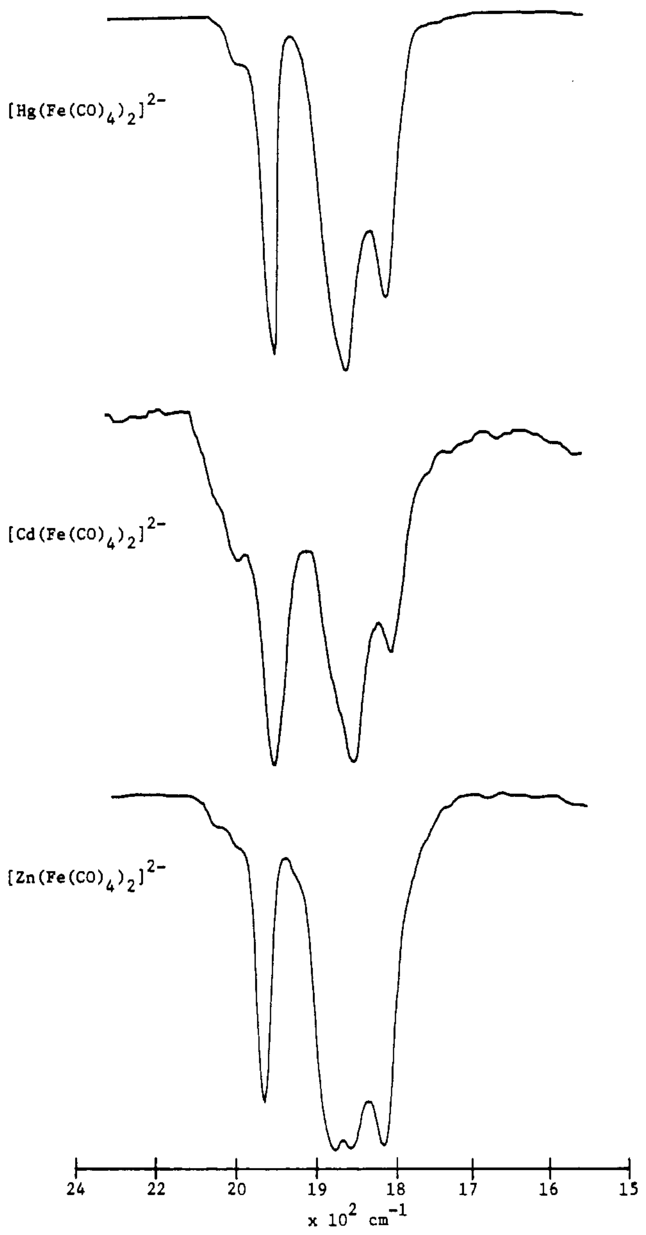

Figure 2. Solution infrared spectra (in THF) of IIa–c in the ν_{CO} region.

times greater than those previously indicated. After 1 h solutions of IIa and IIb were fully reduced to $[Fe_2(CO)_8]^{2-}$; 48 h was required to fully reduce IIc. $[Fe_2(CO)_8]^{2-}$ was characterized by its infrared and Mössbauer spectra. Filtration of the solution and addition of PPN^+Cl^- ((μ-nitrido)triphenylphosphorus(1+) chloride) and hexane yielded off-white colored $(PPN)^+{}_2[Fe_2(CO)_8]^{2-}$ in 90% yield.

Synthesis of IIc with NaH. A 100-mL round-bottom flask was charged with Ic (100 mg, 0.27 mmol) and 40 mg of NaH. The sodium hydride commercially available as a suspension in mineral oil was washed earlier with CH_2Cl_2 to remove the oil. THF was added to the reaction, and the mixture was stirred. No immediate gas evolution occurred, but the suspension turned progressively orange. After 2 weeks the suspension was filtered through Celite and a medium-porosity frit, yielding a clear yellow solution of IIc (85 mg, 72%), isolated as before.

Reaction of Ia with $[Fe(CO)_4]^{2-}$. A 100-mL round-bottom flask was charged with Ia (100 mg, 0.35 mmol) in the form $[(NH_3)_3Zn\text{-}Fe(CO)_4]$ and $Na^+{}_2[Fe(CO)_4]^{2-}\cdot 1.5$(dioxane) (121 mg, 0.35 mmol) and 25 mL of THF. The reaction was stirred and monitored by solution IR for the appearance of IIb ν_{CO} bands. Rapid reaction ensued, and after 10 min all the $[Fe(CO)_4]^{2-}$ was consumed and the yellow-orange solution of IIa was isolated as before, yielding crystalline IIa (250 mg, 0.34 mmol, 96%).

Reaction of IIa with $HgCl_2$. A flask was charged with IIa (70 mg, 0.10 mmol), $HgCl_2$ (200 mg, 0.74 mmol), 10 mL of THF, and a stir bar, and the mixture was stirred for 20 min. Monitoring the solution by infrared spectroscopy revealed the presence of only a strong sharp doublet, ν_{CO} 2079 and 2010 cm^{-1}. Light yellow crystalline $[(HgCl)_2Fe(CO)_4]$ (90 mg, 73.8%) was deposited from the solution, filtered, dried, and identified from an authentic sample prepared by an alternate literature procedure.[9]

Table I. Crystallographic Data for $(Na\{THF\}_2)^+{}_2[Hg(Fe(CO)_4)_2]^{2-}$

fw: 870.83
monoclinic
space group: $C2/m$
$a = 12.39$ (3) Å
$b = 8.54$ (1) Å
$c = 16.01$ (1) Å
$\beta = 105.5$ (2)°
$V = 1636$ Å^3
$Z = 2$
$\mu = 57.6\ cm^{-1}$

d(calcd) = 1.768 g cm^{-3}
Mo Kα radiation ($\lambda = 0.71069$ Å)
scan rate: 4°/min
scan range: ±0.7°
2θ limits: $0° \leq 2\theta \leq 45°$
data collected: 1152
data $F_o^2 > 3\sigma(F_o^2)$: 973
$p = 0.04$
$R_F = 0.043$
$R_{wF} = 0.052$

Reaction of IIa with Hg_2Cl_2. HgCl (reagent grade, calomel, Merck & Co.) was predried by heating (110 °C) under high vacuum for 24 h. A THF (10 mL) solution of IIa (100 mg, 0.14 mmol) was added to a 50-mL round-bottom flask containing Hg_2Cl_2 (30 mg, 0.13 mmol). An immediate reaction was observed by a solution color charge from clear pink to green. A gray precipitate was also formed. The solution was evaporated and placed in a ^{13}C NMR tube. Analysis of the ^{13}C NMR spectrum and infrared spectrum revealed the presence of III as the major product with minor amounts of IIa and IIc.

Reaction of IIa with Hg and IIc with Zn. A THF (10 mL) solution of IIa (100 mg, 0.14 mmol) was added to a 50-mL round-bottom flask containing Hg (ca. 2 g). The mixture was stirred and monitored by solution IR for changes in the IIa ν_{CO} bands. After 6 days of stirring at room temperature, no reaction occurred. A mixture of IIc (100 mg, 0.11 mmol) in THF (10 mL) and Zn metal (0.1 g, 1.5 mmol) for 1 week at reflux showed no reaction.

Reaction of IIa with $NiCl_2$. A 50-mL round-bottom flask was charged with IIa (100 mg, 0.14 mmol) and $NiCl_2$ (20 mg, 0.15 mmol) and 10 mL of THF. The reaction was stirred and monitored by solution IR. Reaction was noticeable after 3 days of stirring and complete after 5 days, yielding III.

Structure Determination of $(Na\{THF\}_2)^+{}_2[Hg(Fe(CO)_4)_2]^{2-}$ (IIc). Crystals of $(Na\{THF\}_2)_2{}^+{}_2[Hg(Fe(CO)_4)_2]^{2-}$ obtained from THF were found to form in the monoclinic space group $C2/m$. A crystal suitable for data collection was mounted in a glass capillary tube and aligned on a Syntex $P\bar{1}$ automated diffractometer. The centered settings of 15 reflections were used to calculate the cell constants given in Table I. Data were collected at ambient room temperature over the angular range $3° \leq 2\theta \leq 45°$. The structure was solved with use of conventional heavy-atom techniques. Calculational procedures and sources of tables have been described in a previous publication.[15] Of the 1152 reflections measured, 973 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement. The final cycle of refinement converged with $R_F = 0.043$ and $R_{wF} = 0.052$. The standard deviation of an observation of unit weight was 1.452. Final positional and thermal parameters and their estimated standard deviations are listed in Table II. Values of F_o and F_c (x10) are available as supplementary material.

Results and Discussion

Description of the $(Na\{THF\}_2)^+{}_2[Hg(Fe(CO)_4)]^{2-}$ Structure. The results of a molecular structure determination of IIc show that the mercury atom is located at a site of $2/m$ symmetry with the iron atom and two carbonyl ligands (CO(1) and CO(2)) of the independent $Fe(CO)_4$ moiety located on a crystallographic mirror plane. The two remaining carbonyl ligands (CO(3) and CO(3)′) are symmetrically related across the mirror plane. A view of the $[Hg(Fe(CO)_4)_2]^{2-}$ dianion is shown in Figure 1A with pertinent bond distances and angles listed in Tables III and IV, respectively.[16] Coordination about iron approximates a regular trigonal bipyramid with the mercury atom at an axial site. We visualize this geometry as arising from a distortion of the tetrahedral array of $Fe(CO)_4{}^{2-}$

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(16) Structure factor tables are available as supplementary material.

Table II. Positional Parameters for the Atoms of $[\mathrm{Na}\{\mathrm{THF}\}_2]^{+}{}_2[\mathrm{Hg}(\mathrm{Fe}(\mathrm{CO})_4)_2]^{2-}$

atom	*x*	*y*	*z*
Hg	0	0	0
Fe	0.0445 (1)	0	0.2108 (2)
Na	0.3611 (4)	0	0.1840 (5)
C(1)	0.078 (1)	0	0.360 (2)
O(1)	0.099 (1)	0	0.453 (1)
C(2)	0.145 (1)	0	0.185 (1)
O(2)	0.2144 (8)	0	0.175 (1)
C(3)	−0.0152 (7)	0.173 (2)	0.1933 (9)
O(3)	−0.0525 (7)	0.289 (1)	0.1899 (8)
O(4)	0.3790 (9)	0	0.3745 (10)
R1C(1)	0.366 (1)	0.139 (2)	0.433 (1)
R1C(2)	0.355 (1)	0.086 (2)	0.537 (1)
O(5)	0.3195 (8)	0	−0.0053 (10)
R2C(1)[a]	0.386 (2)	0.045 (4)	−0.064 (3)
R2C(2)	0.339 (2)	0.033 (6)	−0.179 (3)
R2C(3)	0.236 (2)	0.053 (3)	−0.080 (2)
R2C(4)	0.246 (3)	0.033 (8)	−0.187 (3)
R2C(5)	0.330 (5)	0.15 (1)	−0.078 (6)
R2C(6)	0.279 (4)	0.097 (7)	−0.186 (5)

[a] R2C(1), R2C(3), and R2C(5) symbolize a carbon atom which is disordered, being in three different positions. R2C(2), R2C(4), and R2C(6) symbolize another carbon atom which is disordered, being in three different positions.

Table III. Bond Distancess (Å) for the $[\mathrm{Na}\{\mathrm{THF}\}_2]^{+}{}_2[\mathrm{Hg}(\mathrm{Fe}(\mathrm{CO})_4)_2]^{2-}$ Compound[a]

Fe–Hg	2.522 (5)	O(5)–Na	2.27 (1)
Fe–C(1)	1.79 (2)	O(4)–R1C(1)	1.44 (1)
Fe–C(2)	1.72 (2)	R1C(1)–R1C(2)	1.41 (2)
Fe–C(3)	1.75 (2)	R1C(2)–R1C(2)′	1.47 (3)
Hg–C(2)	2.80 (2)	O(5)–R2C(1)	1.49 (3)
Hg–C(3)	2.88 (1)	R2C(1)–R2C(2)	1.44 (4)
C(1)–O(1)	1.11 (2)	R2C(2)–R2C(4)	1.48 (5)
C(2)–O(2)	1.15 (2)	O(5)–R2C(3)	1.48 (3)
C(3)–O(3)	1.15 (1)	R2C(3)–R2C(4)	1.38 (5)
O(2)–Na	2.32 (2)	O(5)–R2C(5)	1.58 (8)
O(3)–Na	2.26 (1)	R2C(5)–R2C(6)	1.44 (8)
O(4)–Na	2.30 (1)	R2C(6)–R2C(6)′	1.65 (13)

[a] The prime indicates a position transformed by *x*, −*y*, *z*. R2C(1), R2C(3), and R2C(5) symbolize a carbon atom which is disordered, being in three different positions. R2C(2), R2C(4), and R2C(6) symbolize a carbon atom which is disordered, being in three different positions.

Table IV. Bond Angles (deg) for the $[\mathrm{Na}\{\mathrm{THF}\}_2]^{+}{}_2[\mathrm{Hg}(\mathrm{Fe}(\mathrm{CO})_4)_2]^{2-}$ Compound[a]

Hg–Fe–C(1)	179.0 (6)	O(5)–Na–O(3)	92.6 (4)
Hg–Fe–C(2)	80.4 (6)	O(2)–Na–O(3)	127.1 (3)
Hg–Fe–C(3)	82.7 (4)	O(3)–Na–O(3)′	105.7 (6)
C(1)–Fe–C(2)	98.6 (8)	R1C(1)–O(4)–R1C(1)′	111.0 (14)
C(1)–Fe–C(3)	97.8 (5)	R1C(2)–R1C(1)–O(4)	105.7 (13)
C(2)–Fe–C(3)	119.0 (4)	R1C(1)–R1C(2)–R1C(2)′	108.5 (9)
C(3)–Fe–C(3)′	116.1 (7)	R2C(1)–O(5)–R2C(3)	105.0 (17)
Fe–C(1)–O(1)	179.9 (19)	R2C(2)–R2C(1)–O(5)	102.2 (24)
Fe–C(2)–O(2)	175.8 (15)	R2C(1)–R2C(2)–R2C(4)	108.8 (29)
Fe–C(3)–O(3)	175.2 (11)	R2C(2)–R2C(4)–R2C(3)	107.5 (31)
O(4)–Na–O(2)	84.6 (6)	R2C(4)–R2C(3)–O(5)	104.7 (27)
O(4)–Na–O(3)	93.1 (4)	R2C(5)–O(5)–R2C(5)′	105.3 (59)
O(4)–Na–O(5)	170.4 (5)	R2C(6)–R2C(5)–O(5)	100.0 (58)
O(5)–Na–O(2)	85.8 (6)	R2C(5)–R2C(6)–R2C(6)′	107.3 (45)

[a] The prime indicates a position transformed by *x*, −*y*, *z*. R2C(1), R2C(3), and R2C(5) symbolize a carbon atom which is disordered, being in three different positions. R2C(2), R2C(4), and R2C(6) symbolize a carbon atom which is disordered, being in three different positions.

as it is face capped by a mercury atom. An alternate description is that slight ionicity in the Hg–Fe bond induces an umbrella distortion of the equatorial carbonyls inwards toward the mercury atom. The Hg–Fe bond length of 2.523 (5) Å compares closely with those found previously for the neutral species $[\mathrm{Hg}(\mathrm{Fe}(\mathrm{CO})_2\mathrm{NO}(\mathrm{P}(\mathrm{C}_2\mathrm{H}_5)_3))_2]$,[17] $[\mathrm{Hg}(\mathrm{Fe}(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)(\mathrm{CO})_2(\mathrm{Co}(\mathrm{CO})_4)]$,[18] and $[\mathrm{Hg}(\mathrm{Co}(\mathrm{CO})_4)_2]$[19] of 2.534, 2.49, and 2.50 Å, respectively. The sum of the Pauling metallic radii[20] for Fe and Hg is 2.605 Å, suggesting that additional electron density in Ic is not localized on M′–Fe bonds. A central Feature of IIa, namely, the unusual carbonyl bending configuration interactions, are largely missing in IIc although some bending normally associated with polar heterobimetallic bonds are exhibited here. Thus Hg–Fe–C(2) and Hg–Fe–C(3) angles are 80.4 (6) and 82.7 (4)°, respectively, and compare favorably with bending in $[\mathrm{Hg}(\mathrm{Fe}(\mathrm{CO})_2\mathrm{NO}(\mathrm{P}(\mathrm{C}_2\mathrm{H}_5)_3))_2]$,[17] $[\mathrm{Hg}(\mathrm{Co}(\mathrm{CO})_4)_2]$,[19] and $[\mathrm{Zn}(\mathrm{Co}(\mathrm{CO})_4)_2]$[21] M′–M–C(eq) bond angles of 86°, 83°, and 81.1°, respectively. IIa shows[1] a Zn–Fe–C(eq) angle of 74.80° and a Zn–C(eq) distance of 2.502 Å for C(2) and C(3). These Hg–C(eq) distances are outside the range normally considered for semibridging carbonyls, 2.1–2.55 Å,[15,22] and compare to M′–C contacts in the range of 2.70 Å for base adduct complexes previously reported.[23,24] For both IIa and IIc little deviation from linearity for bent carbonyls is observed, and recent theoretical calculations suggest little or no interaction between carbonyl base orbitals and empty $\mathrm{M'}_{\mathrm{p}\pi}$ orbitals.[25]

For IIa, the sodium counterion occurs[1] as an unusual dimeric structure with six-coordination about each sodium, while in IIc an equally unusual five-coordinate geometry with monomeric sodium cations was observed as shown in Figure 1B. Geometry about sodium which is tight ion paired appears to be principally governed by the configuration of the dianion rather than by strong intermolecular forces. The two independent carbon atoms in the THF molecule, which has oxygen O(5) as a member, are disordered about the crystallographic mirror plane on which the Na atom and the two THF oxygen atoms lie.

A preliminary study of IIb (M′ = Cd) indicates that it is isostructural with IIc. The small differences in bond angles and distances are due to the different sizes of the M′ cations. This was to be expected since they are found in the same crystallographic space group.

Characterization of $[\mathrm{M'}(\mathrm{Fe}(\mathrm{CO})_4)_2]^{2-}$ (II). The structures of complex II are shown in Figure 1, and the solution ν_{CO} infrared spectra of IIa–c are illustrated in Figure 2. Previous work by Behrens et al. assigned[8] idealized D_{3d} (axially substituted trigonal bipyramidal) geometry to IIa–c. IIc (M′ = Hg) maintains close to a D_{3d} geometry but IIa (M′ = Zn) is best treated as C_{2h} geometry. A normal-coordinate analysis[26] suggests four infrared bands. The C_{2h} geometry of Ia is maintained in solution as evidenced by the appearance of four ν_{CO} bands, which we assign in the order of decreasing frequency to an $\mathrm{A_u}$ mode followed by three $\mathrm{B_u}$ modes. In D_{3d} geometry three infrared bands labeled $\mathrm{A_{2u}}$, $\mathrm{E_u}$, and $\mathrm{A_{2u}}$ in order

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of decreasing ν_{CO} are expected and found for IIc, thus suggesting D_{3d} geometry is retained in solution at least on the infrared time scale. Solution ν_{CO} infrared data on IIb show it to be an intermediate case, and the solid-state structure of IIb shows it to be very similar to IIc.

The dianions IIa–c have fairly low carbonyl stretching frequencies compared to the complexes I and are very close in energies to those of the base adduct complexes $[(M'\{B\}_nFe(CO)_4]$ (IV). The lowest energy band (A_{2u} in D_{3d} (IIb,c) B_u in C_{2h} (IIa)) for IIa, IIb, and IIc is found at 1817, 1807, and 1815 cm^{-1}, respectively, while those found[11,24] in the starting compounds $[M'Fe(CO)_4]_x$ (Ia–c) are found (Nujol mull) at 1904, 1871, and 1917 cm^{-1}, respectively. By comparison, the lowest ν_{CO} stretching frequency in IIa–c may be found to be intermediate between the ν_{CO} of the $[Fe(CO)_4]^{2-}$ dianion (1730 cm^{-1} (DMF)) and that of the $[Fe_2(CO)_8]^{2-}$ dianion (1816 cm^{-1} (DMF)).[26] This is to be expected as a considerable amount of negative charge for the reduced mixed-metal bimetallic compound fills π^* levels of the carbonyl ligands through back-bonding, thus lowering ν_{CO} frequencies.

The ^{57}Fe Mössbauer spectrum of IIa was a doublet centered at $\delta = 0.156$ mm s^{-1} (relative to iron) with $\Delta = 1.429$ mm s^{-1}. A series of diamagnetic covalent iron carbonyls and iron carbonyl anions decrease in isomer shift with increasing charge at iron.[27] This value for IIa corresponds nicely to a charge of 1– as found[27] for $[Fe_2(CO)_8]^{2-}$, where $\delta = 0.16$ mm s^{-1} (relative to iron foil). For the complexes $[LFe(CO)_4]$ a plot of Δ vs. Δ of a series of axially substituted complexes investigated by Lalor et al.[28] falls on a line with positive slope. Equatorial complexes (and pseudoequatorial) of this type investigated by Collins and Pettit[29] define a line with negative slope. Both lines intersect at $[Fe(CO)_5]$. IIa may be seen to lie above ($>\Delta$) the C–P line with an isomer shift near the high side of the plot. Deviance from both lines of behavior occurs because of increasing iron d-orbital occupancy. We attribute the higher Δ value to the intermediacy of zinc in IIa between axial and equatorial substitution. The reader is referred elsewhere for a more complete discussion.[7]

One of the most interesting aspects of the work is the observation that IIb has a resolved three-peak iron-57 Mössbauer spectrum. This spectrum may be fit by any of the following solutions: as three singlets ($\delta = -0.064$, 1.048, and 1.856 mm s^{-1} relative to iron metal), as two doublets ($\delta = 0.492$ and 1.452 mm s^{-1}; $\Delta = 1.112$ and 0.808 mm s^{-1}, respectively), and as a doublet around a singlet ($\delta = 1.048$ (Δ small) and 0.896 ($\Delta = 1.921$) mm s^{-1}). Most consistent with the known structure of IIb is the two-doublet scheme. The empirical formula $M'Fe_2$ argues against three singlets, as well as asymmetry in the middle peak, and isomer shifts for two of the singlets above the range normally encountered for a d^8–d^{10}-Fe description. The location and symmetry of the peak argue against a doublet around a singlet scheme as well. The two-doublet scheme has isomer shifts consistent with two inequivalent iron atoms having isomer shifts and quadrupole splittings above that normally encountered for d^8-Fe^0 equatorially substituted TBP $[Fe(CO)_4L]$ or for d^{10}-Fe^{2-} T_d $[Fe(CO)_4L]$ cases. We are unable to record a Mössbauer spectrum for IIc due to an apparent relaxation effect.

We have attempted to establish whether complexes II are stereochemically nonrigid but have been unsuccessful in establishing this. At –45 °C, complexes IIa,c show no change in the ^{13}C NMR spectra. High-temperature spectra of IIa–c at 80 °C also show no change. We expected to find fluxionality because orbital occupancy might be variable between structures exhibited by IIa and IIc, with a small enough energy difference to be observable on the NMR time scale.

Measured conductivities of IIa–c 463.18, 394.4 and 316 Ω^{-1} mol^{-1} cm^{-1} are nearly 4 times higher than that found[6] for $[Fe(CO)_4(SnMe_2)]^{2-}$ (109 Ω^{-1} mol^{-1} cm^{-1}) and nearly 1.5–2.0 times higher than that of $[Fe(CO)_4]^{2-}$. These large conductivities, to a first approximation, reflect the size over which charge is distributed in the various molecules.

Lewis Base Reduction of $[M'Fe(CO)_4]_x$ (Ia–c). The base homolysis of metal–metal (M–M') bonds has been known for some time and occurs whenever the strength of the metal–base bond in the adduct is of strength similar to the metal–metal bond.[30] This process (eq 1) may be thought of as an equilibrium with the lability of the Lewis base directly dependent upon base strength.[31] Multiple base adduct formation can occur in many cases and serves to render the metal attached (M') less likely to re-form a new M'–M bond, presumably because of the buildup of excess negative charge on M'. Base adduct formation is most expected when the metal (M) is relatively electron rich as in d^8–d^{10} tetracarbonylferrates presently under study.

$$\underset{\mathrm{I}}{[M'Fe(CO)_4]_x} \overset{nB}{\rightleftharpoons} \underset{\mathrm{II}}{[(M'\{B\}_n)Fe(CO)_4]} \qquad (1)$$

Base adduct formation ($M'\{B\}_n$) has the concomitant effect of changing iron d^n-electron configuration and overall coordination number. In $[M'Fe(CO)_4]_x$ complexes which exist as chains or cycles and have normally cis-octahedral units, the bending in of axial carbonyls toward M' has been noted in structural studies and properly assigned to buildup of $Fe(CO)_4{}^{\delta-}$ character induced by the ionicity of the M'–M bond.[23,24,32] With progressive base adduct formation charge separation is reduced, leading to assumption of the favored d^8-Fe^0 trigonal-bipyramidal array. A series of compounds have been isolated and structurally characterized[23,24] where these competitive trends in oligomerization and base adduct formation can be clearly seen.

The lability of the Lewis base in metal–base adducts has been used widely as a general organometallic reaction pathway particularly in substitution reactions and reactions that may formally be considered as reductions.[33] Base adduct formation is, in fact, a process similar to reduction. It remains to be established, possibly by our intended future electrochemical studies, whether the electron-transfer process involves prior base loss by an inner-sphere type mechanism or whether an outer-sphere process is involved. In regard to this question, it is worthwhile noting that the isolation of the intermediate reduced compounds $[M'(Fe(CO)_4)_2]^{2-}$ (II) formally involves base attack of an $[Fe(CO)_4]^{2-}$ molecule on $[(M'\{B\}_n)Fe(CO)_4]$ (IV). While the lability of the base in this latter molecule is unquestioned, it does not necessarily imply that reduction of $[(M'\{B\}_n)Fe(CO)_4]$ requires prior base loss. $[Fe(CO)_4]^{2-}$ may be in the reaction mixture at about the time $[Fe_2(CO)_8]^{2-}$ begins to form. Eventually all the $[Fe(CO)_4]^{2-}$ converts to the final product $[Fe_2(CO)_8]^{2-}$. The isolation of the final species $[Fe_2(CO)_8]^{2-}$ suggests that with sodium amalgam $[Fe(CO)_4]^{2-}$ can be converted back to neutral $[Fe(CO)_4\{B\}]$ species. We visualize the base reduction of the group 2B tetracarbonyl ferrates as involving steps 2–5. The intermediate

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$$[(M'\{B\}_n)Fe(CO)_4]\ (IV) \xrightarrow[-M']{2e^-} [Fe(CO)_4]^{2-} \qquad (2)$$

$$[Fe(CO)_4]^{2-} + [(M'\{B\}_n)Fe(CO)_4] \overset{-B}{\rightleftharpoons} M'(Fe(CO)_4)_2]^{2-} \quad \text{fast} \qquad (3)$$

$$[Fe(CO)_4]^{2-} \overset{+2e^-(Na/Hg)+B}{\rightleftharpoons} [Fe(CO)_4\{B\}] \quad \text{slow} \qquad (4)$$

$$[Fe(CO)_4\{B\}] + [Fe(CO)_4]^{2-} \rightarrow [Fe_2(CO)_8]^{2-}\ (III) \qquad (5)$$

isolation of $[M'(Fe(CO)_4)_2]^{2-}$ (II) we ascribe to kinetic factors. $[Fe(CO)_4]^{2-}$, being a good base, inhibits the back-reaction (3), which occurs only to a limited extent. Reaction (3) of a 1:1 solution of $[Fe(CO)_4]^{2-}$ and $[Zn(NH_3)_3Fe(CO)_4]$ was rapid and gave IIa in excellent yield (ca. 90%) after workup. In reaction 2 M′ is lost, we believe, as the native metal and incorporated into the amalgam. A possible complication in the reaction of $[Zn(NH_3)Fe(CO)_4]$ with Na/Hg is the production of $NaNH_2$ or $Zn(NH_2)_2$ plus H_2 gas. This may account for the lower yield of IIa (63%) when it is synthesized by this method vs. a near-quantitative synthesis (90%) of IIa when $[Fe(CO)_4]^{2-}$ was reacted with $[Zn(NH_3)_3Fe(CO)_4]$ in a 1:1 ratio.

Compounds II may be synthesized by reaction of I with sodium hydride. The route gives similar yields of II but faster subsequent reduction to $[Fe_2(CO)_8]^{2-}$. Closer monitoring of solutions of II exposed to NaH is necessary to optimize the yield.

The structure and bonding in II is discussed in a subsequent section and spectroscopic Mössbauer evidence for the variable iron d^n-configuration elsewhere.[7] In the series II(M′ = Zn, Cd, Hg) solution IR data correlate with solid-state structural studies to show progressive changes in geometry about iron. Slippage of the zinc atom away from the site capping the face of an $[Fe(CO)_4]^{2-}$ tetrahedron, as in the mercury case, is highly suggestive of a loss in σ-donor ability for Zn, which in this system correlates with increased nuclear shielding of the Zn^{2+} ion. Calculations by Hoffmann et al.[34] suggest that the site of substitution is directly related to the σ-donor ability of the ligand in $[LFe(CO)_4]$. Fajan's rules suggest that a small highly charged cation will distort a large polarizable anion. This serves to lower zinc's ability to share Fe d-electron density, and zinc slips off the axis that defines the Fe t_{2g} level. This is consistent with the fact that in a tetrahedral field the t_{2g} levels lie $10Dq$ above the e_g set. Loss of σ-donor ability allows iron to choose a smaller crystal field. Geometric preferences play some role in the distribution of carbonyls toward a square-planar array about zinc in IIa, but a preliminary calculation by T. A. Albright (University of Houston) suggests a nonbonding interaction between CO-based orbitals and zinc 3p levels. The potential energy barriers for the three-dimensional energy surface connecting various geometries of monosubstituted five-coordinate tetracarbonylferrates have been calculated to be quite low.[35]

In the base reduction process (eq 1–5) reactivity I → II increases in the order Zn > Cd >> Hg. Mercury tetracarbonylferrate is nearly insoluble in THF; however, we have observed by solution IR that over a long period of time suspensions of Ic contain mercury base adduct compound(s). In 1 day in the presence of Na/Hg, suspensions of Ic are converted to clear solutions of IIc. All three compounds IIa–c convert relatively rapidly (ca. 1 h) to $[Fe_2(CO)_8]^{2-}$ once all I is consumed. Essentially, reactions 3–5 are autocatalytic when III is absent.

The alternate route to II to react $[Fe_2(CO)_8]^{2-}$ with the native group 2B metals.[8] After periods of *weeks* at 100–120 °C[8] about 30% yields have been obtained. The long reaction times are needed to decompose the $[Fe_2(CO)_8]^{2-}$. Re-formation of III occurs preferentially to M′–Fe bond formation.

Krumholz and co-workers have reported[36] on the aqueous reaction of carbonylferrate anions $[Fe(CO)_4]^{2-}$ and $[HFe(CO)_4]^-$ with zinc(II) salts potentiometrically. Evaluation of $[H^+]$ shows four distinct equilibria in mildly acidic solution. In a subsequent study in mildly basic aqueous solution a number of mixed zinc tetracarbonylferrate hydroxides are claimed[37] again from potentiometric studies. Without further characterization we consider that the claims of these authors may be in error. In our hands IIa–c are rapidly decomposed by water.

The reaction chemistry of IIa with small molecules displays no evidence of covalency. IIa may be reduced in refluxing THF (with Ar or CO gas) very slowly to $[Fe_2(CO)_8]^{2-}$. Hydrogen rapidly reduces IIa to $[Fe_2(CO)_8]^{2-}$ with CO acting as a catalyst for this process. IIa is unreactive toward polyolefins, allyl bromide, and diphenylacetylene.

Transmetalation reactions (eq 6–8) are a feature of ionic

$$[M'\text{–}ML_n] + M'' \rightarrow [M''\text{–}ML_n] + M' \qquad (6)$$

$$[M'\text{–}ML_n] + M''X \rightarrow [M''\text{–}ML_n] + M'X \qquad (7)$$

$$[M'\text{–}ML_n] + M''X_2 \rightarrow [M''\text{–}ML_n] + M'X_2 \qquad (8)$$

bonding with a general tendency for a more ionic bond to be replaced with a more covalent bond. With this feature in mind we decided to test the ionicity of the zinc–iron bond in IIa toward a variety of reagents, Hg^0, Hg_2Cl_2, $HgCl_2$, and $NiCl_2$. IIa does not react with the Hg^0, reacts sluggishly with $NiCl_2$, yielding III, and sluggishly with Hg_2Cl_2, yielding mainly III and traces of IIa and IIc, and reacts rapidly with $HgCl_2$, yielding $[(HgCl)_2Fe(CO)_4]$. The relative ability of these reagents to react with IIa roughly parallels their reducing ability. Only mercuric ion is sufficiently strong to undergo the transmetalation reaction (8); however, it is not sufficiently strong to further reduce $Fe(CO)_4{}^{2-}$ and $[(HgCl)_2Fe(CO)_4]$ is produced.

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Registry No. Ib, 9038-79-3; Ic, 56378-57-5; IIa, 82110-39-2; IIb, 86784-88-5; IIc, 86784-89-6; III, 58281-28-0; $(PPN)^+{}_2[Fe_2(CO)_8]^{2-}$, 76419-41-5; $Na^+{}_2[Fe(CO)_4]^{2-}$, 14878-31-0; $[(NH_3)_3ZnFe(CO)_4]$, 34720-06-4; $[(HgCl)_2Fe(CO)_4]$, 15281-84-2; Zn, 7440-66-6; Cd, 7440-43-9; Hg, 7439-97-6; Fe, 7439-89-6.

Supplementary Material Available: Listings of anisotropic thermal parameters and calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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