Inorg. Chem. **1993,** *32,* 2705–2710

Preparation of [K][In{$Fe_2(CO)_8$}$_2$](THF) and Fe_2{μ-InCl(THF)}$_2(CO)_8$ (THF = Tetrahydrofuran)

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Received August 26, 1992

The compound [K][In{$Fe_2(CO)_8$}$_2$](THF) (**1**) (THF = tetrahydrofuran) has been synthesized by the reaction of $Fe_3(CO)_{12}$ with activated indium powder in the presence of potassium chloride. A single-crystal X-ray structure determination shows the iron atoms of two $Fe_2(CO)_8$ units bound to the indium in a pseudotetrahedral fashion and the potassium ion coordinated to a molecule of THF and two carbonyl oxygen atoms from each of four of the iron–indium anions to give a total coordination number of 9. Crystal data: tetragonal space group $P4/n$ (No. 85), $a = 11.850(2)$ Å, $c = 10.696(2)$ Å, $V = 1502.0(5)$ Å^3, $Z = 2$, $R = 3.61\%$, $R_w = 5.04\%$. The complex Fe_2{μ-InCl(THF)}$_2(CO)_8$ (**2**) can be prepared in high yield by the reaction of either $Na_2Fe(CO)_4$ or $Na_2Fe_2(CO)_8$ with indium(III) chloride or via the reaction of $Fe_3(CO)_{12}$ with indium(I) chloride in tetrahydrofuran. Mechanistic studies suggest that these three reactions produce the same intermediate species, $Fe(CO)_4$(THF) and InCl, which then combine to give the observed product. Fe_2{μ-InCl(THF)}$_2(CO)_8$ forms an adduct with bromide ion in the presence of tetrabutylammonium bromide, and the complex $[(C_4H_9)_4N]_2[Fe_2\{\mu\text{-InClBr}\}_2(CO)_8]$ (**3**) has been characterized crystallographically. Crystal data: triclinic space group $P\bar{1}$ (No. 2), $a = 11.510(2)$ Å, $b = 11.905(1)$ Å, $c = 12.200(2)$ Å, $\alpha = 90.373(9)°$, $\beta = 117.08(1)°$, $\gamma = 107.75(1)°$, $V = 1396.6(5)$ Å^3, $Z = 1$, $R = 4.61\%$, $R_w = 5.94\%$.

Introduction

A variety of compounds containing bonds between low-valent transition metals and the heavier group 13 elements (Ga, In, and Tl) have been prepared[1] since the pioneering studies by Hieber and Teller[2] and by Patmore and Graham.[3] In particular, metal carbonyl complexes containing iron–indium bonds have been known for some time as a result of the early work of Ruff,[4] Hsieh and Mays,[5] Preut and Haupt,[6] and Burlitch, Leonowicz, Petersen, and Hughes.[7] Of particular relevance to the present work is the initial study by Ruff of the reaction between the $Fe(CO)_4^{2-}$ anion and indium tribromide to give $Fe(CO)_4InBr_3^{2-}$ and $Fe(CO)_4InBr_2^-$, which were isolated as the bis(triphenylphosphoranylidene)ammonium (PPN) salts. More recently, Cassidy and Whitmire[8] showed that a similar reaction between $[Et_4N]_2[Fe_2(CO)_8]$ and indium trichloride forms $[Et_4N]_2[In_2Fe_6(CO)_{24}]$. They also prepared the complex $[Et_4N][(2,2'\text{-bipyridine})InFe_2(CO)_8]$ via the reaction of a mixture of $Fe(CO)_5$ and potassium hydroxide in methanol, followed by successive additions of $InCl_3$ and 2,2′-bipyridine. Albano, Cané, Iapalucci, Longoni, and Monari[9] have demonstrated in an illuminating series of experiments that the reaction of $Na_2Fe(CO)_4$ with indium tribromide in a 3.5:1 molar ratio produces the $[In\{Fe(CO)_4\}_3]^{3-}$ anion, which can be successively oxidized to the $[In_2Fe_6(CO)_{24}]^{4-}$ and $[In_2Fe_6(CO)_{24}]^{2-}$ anions or converted to $[(\mu\text{-InBr})\{Fe(CO)_4\}_2]^{2-}$ and $[(\mu\text{-InBr}_2)_2\{Fe(CO)_4\}_2]^{2-}$ by reaction with indium tribromide. The latter complex was characterized by X-ray crystallography and is believed to correspond to the complex previously formulated as $Fe(CO)_4InBr_2^-$.

The reaction of iron carbonyl compounds with indium halides is a complex process that has provided a wide variety of products. We wish to report the preparation of two new complexes in this series, as well as the results of mechanistic studies that provide additional insight into their mode of formation.

Experimental Section

Starting Materials. Activated indium powder[10] and the compounds indium(I) chloride,[11] $Fe_3(CO)_{12}$,[12] $Na_2Fe_2(CO)_8$,[13] and $Na_2Fe(CO)_4$[14] were prepared according to literature methods. Indium metal was purchased from the Aldrich Chemical Co., and indium trichloride was obtained from Johnson Matthey. Iron pentacarbonyl and triphenylphosphine were purchased from the Pressure Chemical Co. Solvents were freshly distilled under an atmosphere of dry nitrogen from sodium (hexane, toluene, xylene) or sodium benzophenone ketyl (tetrahydrofuran, diethyl ether) before use. Infrared spectra were routinely obtained on a Perkin-Elmer 1600 Series Fourier-transform spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on an IBM AF-200 (200 MHz) or AF-300 (300 MHz) Fourier-transform spectrometer, are referenced to tetramethylsilane, and were calibrated relative to $CHCl_3$, acetonitrile-d_2, or tetrahydrofuran-d_7 resonances. Mass spectra were obtained on a Hewlett-Packard Model 5995 gas chromatograph–mass spectrometer.

Reaction Procedures. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or under argon in a drybox.

A. Synthesis of [K][In{$Fe_2(CO)_8$}$_2$](THF) (1). A mixture of activated indium metal powder and potassium chloride was prepared according to the literature method[10] by refluxing indium trichloride (2.21 g, 9.99 mmol) and potassium metal (1.17 g, 29.9 mmol) in dry xylene (15 mL) for 6 h. To this slurry was added a solution of $Fe_3(CO)_{12}$ (1.5 g, 3.0 mmol) in tetrahydrofuran, and the resulting mixture was refluxed for 18 h, during which time the color of the solution changed from green to red. The solution was filtered via cannula, and all volatile materials were removed under vacuum to give a red solid. This was redissolved in dry diethyl ether (50 mL), the solution was again filtered, and solvent was removed under vacuum until the solution was saturated. Cooling to −35 °C resulted in the formation of dark red crystals. Yield: 1.5 g (80% based on iron). Anal. Calcd for $C_{20}H_8Fe_4InKO_{17}$: C, 26.76; H, 0.90. Found: C, 26.82; H, 0.87. Melting point: the crystals decompose over

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the temperature range 220–235 °C. Infrared spectrum (KBr disk): 2965 (w), 2932 (w), 2882 (w), 2043 (sh), 2003 (s), 1974 (s), 1905 (sh), 1773 (sh), 1752 (m), 1490 (m), 1372 (m), 1261 (w), 1049 (w), 908 (w), 802 (w), 603 (s) $\mathrm{cm^{-1}}$. Infrared spectrum (ν_{CO}, diethyl ether solution): 2041 (m), 2010 (s), 1970 (m), 1962 (m), 1951 (sh) $\mathrm{cm^{-1}}$.

B. Synthesis of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (2). A mixture of $Fe_3(CO)_{12}$ (7.40 g, 14.7 mmol) and indium(I) chloride (6.54 g, 43.6 mmol) in dry tetrahydrofuran (50 mL) was refluxed for 20 h to give a dark brown solution and a yellow powder precipitate. The solution was filtered while hot, then allowed to cool to 23 °C, and filtered again to yield an additional portion of yellow powder. Both portions of yellow powder exhibited identical infrared spectra. Yield: 11.8 g (85.1% based on iron). Melting point: the compound decomposes over the temperature range 230–245 °C. Infrared spectrum (ν_{CO}, THF solution): 2064 (variable), 2041 (variable), 1985 (s), 1898 (m) $\mathrm{cm^{-1}}$ (see explanation under Results). Infrared spectrum (ν_{CO}, KBr disk): 2083 (sh), 2050 (s), 1999 (s), 1964 (s) $\mathrm{cm^{-1}}$. The latter two peaks at 1999 and 1964 $\mathrm{cm^{-1}}$ are small minima on either side of a large, broad absorption centered at approximately 1985 $\mathrm{cm^{-1}}$.

C. Synthesis of $[(C_4H_9)_4N]_2[Fe_2(\mu\text{-}InClBr)_2(CO)_8]$ (3). A mixture of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (0.95 g, 1.22 mmol) and tetrabutylammonium bromide (0.96 g, 2.98 mmol) was stirred in dry tetrahydrofuran (50 mL) at 23 °C for 14 h to give a yellow solution with a yellow powder precipitate. Volatile materials were removed under vacuum, and the residue was recrystallized from tetrahydrofuran to give yellow crystals. Yield: 1.43 g (91.5% based on iron). Melting point: the crystals melt over the temperature range 231–234 °C. Infrared spectrum (ν_{CO}, KBr disk): 2005 (s), 1953 (sh), 1943 (s), 1880 (w) $\mathrm{cm^{-1}}$. Anal. Calcd for $C_{40}H_{72}Br_2Cl_2Fe_2In_2N_2O_8$: C, 37.50; H, 5.67; Fe, 8.72. Found: C, 36.99; H, 5.74; Fe, 8.89. ^1H NMR spectrum in CD_3CN: 3.346 (m, 2H), 1.772 (m, 2H), 1.415 (m, 2H), 0.967 (t, 3H, J = 6.24 Hz) ppm. ^{13}C NMR spectrum in CD_3CN: 212.34, 59.52, 24.51, 20.38, 13.88 ppm.

D. Reactions of $Na_2Fe_2(CO)_8$ with $InCl_3$. (i) A solution of indium trichloride (0.12 g, 0.54 mmol) in dry tetrahydrofuran (30 mL) was added to $Na_2Fe_2(CO)_8$ (0.12 g, 0.31 mmol) which had been cooled to −78 °C. The mixture was stirred at this temperature to give a brown solution. The infrared spectrum of the solution in the metal carbonyl region (2200–1600 $\mathrm{cm^{-1}}$) was taken after a period of 80 min, and the solution was then allowed to warm to 23 °C. Additional spectra were taken at 22 and 48 h after the initial addition of the THF solution. The initial spectrum exhibited peaks at 2067, 2038, 2004, 1984, 1970, and 1790 $\mathrm{cm^{-1}}$, none of which corresponded to those of the starting material, $Na_2Fe_2(CO)_8$, which has absorptions at 1916 (m), 1866 (s), and 1842 (w) $\mathrm{cm^{-1}}$. When the sample was allowed to warm to room temperature, the peak at 1790 $\mathrm{cm^{-1}}$ disappeared and was replaced by a new peak at 1897 $\mathrm{cm^{-1}}$. As the reaction progressed, the peaks at 2038, 2004, and 1970 $\mathrm{cm^{-1}}$ gradually decreased in intensity, and peaks at 2067, 1984, and 1897 $\mathrm{cm^{-1}}$ gradually increased. After a total reaction time of 48 h, all volatile materials were removed under vacuum to give a yellow-brown powder that was kept under dynamic vacuum for 1 h. The powder was washed with hexane and toluene, and then redissolved in THF to give a yellowish-brown solution that exhibited infrared absorptions at 2064 (m), 2030 (sh), 1986 (s, broad), and 1897 $\mathrm{cm^{-1}}$. The THF was again removed under vacuum, and the powder was dried under dynamic vacuum for 4 h. The infrared spectrum of the powder in a KBr disk showed absorptions at 2079 and 2054 $\mathrm{cm^{-1}}$ and a strong broad absorption centered at 1988 $\mathrm{cm^{-1}}$. The sample was kept under vacuum for 2 days and then redissolved in THF to give an infrared spectrum with peaks at 2065 (w, sh), 2035 (s), 1988 (vs, broad), and 1897 (m) $\mathrm{cm^{-1}}$, which closely matches the spectrum for $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$.

(ii) Indium trichloride (0.1565 g, 0.71 mmol) and $Na_2Fe_2(CO)_8$ (0.16 g, 0.42 mmol) were stirred vigorously in dry toluene (50 mL) at −78 °C for 24 h to give a dark green solution. This was allowed to warm to 23 °C, and after 10 days the flask contained a yellow precipitate and a colorless solution. The solution was removed, and the precipitate was dried under vacuum. Infrared spectrum of the yellow precipitate (ν_{CO}, KBr disk): 2078 (sh), 2049 (s), 1997 (s), 1970 (s) $\mathrm{cm^{-1}}$.

(iii) Indium trichloride (0.258 g, 1.17 mmol) and $Na_2Fe_2(CO)_8$ (0.26 g, 0.68 mmol) were stirred vigorously in dry diethyl ether (30 mL) at −78 °C for 7 h to give a dark purple solution. This was allowed to warm to 23 °C, whereupon the solution turned dark green, and after 24 h the flask contained a dark green solution and a white precipitate. The solution was decanted from the precipitate via cannula, and the solution volume was reduced under vacuum. Cooling to −35 °C resulted in the formation of dark green crystalline material that was identified by infrared spectroscopy as $Fe_3(CO)_{12}$. Infrared spectrum (ν_{CO}, KBr disk): 2049 (s), 2022 (s), 1999 (m), 1861 (w), 1830 (w) $\mathrm{cm^{-1}}$. Literature values[15] for $Fe_3(CO)_{12}$ (ν_{CO}, hexane solution): 2048 (s), 2027 (m), 1866 (w), 1841 (w) $\mathrm{cm^{-1}}$. The mass spectrum of the green solid matched very well with that of an authentic sample of $Fe_3(CO)_{12}$, and it also revealed the presence of indium(I) chloride.

E. Reactions of $Na_2Fe(CO)_4$ with $InCl_3$. (i) A suspension of indium trichloride (0.3379 g, 1.53 mmol) in dry diethyl ether (8 mL) was transferred via cannula to a suspension of $Na_2Fe(CO)_4$ (0.27 g, 1.26 mmol) in ether (19 mL), and the mixture was stirred at 23 °C for 24 h to give a clear solution and a yellow precipitate. The solution was removed via cannula, and the yellow precipitate was dissolved in two 100-mL portions of tetrahydrofuran, which were transferred via cannula to another flask, leaving behind an insoluble white powder. The yellow THF solution was evaporated under vacuum to give a yellow powder identified by its infrared spectrum as $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. Infrared spectrum ($\nu_{CO}$, KBr disk): 2080 (sh), 2054 (s), 2003 (s), 1968 (s) $\mathrm{cm^{-1}}$. Yield: 0.1692 g (42% based on iron).

(ii) A solution of indium trichloride (0.8149 g, 3.69 mmol) in dry tetrahydrofuran (20 mL) was transferred via cannula to a suspension of $Na_2Fe(CO)_4$ (0.7501 g, 3.51 mmol) in THF (20 mL), and the mixture was stirred at −78 °C for 30 min. The mixture was then allowed to warm to 24 °C, and after 7 h a clear orange solution and a white precipitate were observed. The solution was filtered via cannula, and the orange THF solution was evaporated under vacuum to give a yellow powder, which was washed with hexane (2 × 25 mL), toluene (20 mL), and diethyl ether (2 × 5 mL). The product was identified by infrared spectroscopy as $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. Infrared spectrum ($\nu_{CO}$, KBr disk): 2080 (sh), 2051 (s), 1999 (s), 1969 (s) $\mathrm{cm^{-1}}$. Infrared spectrum (ν_{CO}, THF): 2064 (sh), 2031 (s), 1985 (s), 1898 (s) $\mathrm{cm^{-1}}$. Yield: 1.21 g (88% based on iron).

F. Reaction of $Na_2Fe_2(CO)_8$ with $InCl_3$ and PPh_3. A suspension of $Na_2Fe_2(CO)_8$ (0.13 g, 0.34 mmol) in dry tetrahydrofuran (10 mL) was transferred into a solution containing triphenylphosphine (0.18 g, 0.68 mmol) and indium trichloride (0.09 g, 0.40 mmol) in THF (20 mL) which was precooled to −78 °C. The mixture was stirred as it gradually warmed to 23 °C and was then stirred at this temperature for 2 days. Volatile materials were removed under vacuum to leave a brown powder. This was washed with three successive portions of hexane (3 x 10 mL), which were removed by filtration to give a yellow solution and a yellow residue. The solution was evaporated under vacuum to give $Fe(CO)_4(PPh_3)$. Yield: 0.13 g (44% based upon iron). Infrared spectrum (ν_{CO}, hexane solution): 2051 (m), 1978 (m), 1945 (s) $\mathrm{cm^{-1}}$. Literature values[16] (ν_{CO}, CCl_4 solution): 2055, 1978, 1943 $\mathrm{cm^{-1}}$.

G. Reaction of $Na_2Fe_2(CO)_8$ with PPh_3. A mixture of $Na_2Fe_2(CO)_8$ (0.13 g, 0.34 mmol) in dry tetrahydrofuran (30 mL) was transferred into a flask containing triphenylphosphine (0.18 g, 0.68 mmol) which was precooled to −78 °C. The mixture was stirred for 20 min and then gradually warmed to 23 °C. It was then stirred at this temperature for 2 days. Volatile materials were removed under vacuum to leave a brown powder. This was washed with three successive portions of hexane (3 × 10 mL), which were removed by filtration and combined. The powder was then washed with three successive portions of toluene (3 × 10 mL), which were also removed by filtration and combined. The remaining powder was dissolved in THF (10 mL), and the resulting solution was removed by filtration, leaving a small amount of grayish-brown residue (0.0015 g). An infrared spectrum of the hexane solution revealed a small amount of $Fe(CO)_4(PPh_3)$. The solution was evaporated under vacuum to give a white powder with a small amount of yellow coloration (0.1543 g). This was purified by redissolving the material in hexane and passing the resulting solution through a silica gel column, followed by evaporation of the eluent to give a white powder that was identified as pure triphenylphosphine (0.1519 g, 84% recovery) by its infrared spectrum. An IR spectrum of the toluene solution showed only a single peak at 1886 $\mathrm{cm^{-1}}$ corresponding to $Fe(CO)_3(PPh_3)_2$ (literature value[16] (ν_{CO}, $CHCl_3$ solution): 1887 $\mathrm{cm^{-1}}$). The solvent was evaporated under vacuum to give an orange powder. Yield: 0.0235 g (10% based upon iron). An infrared spectrum of the THF solution showed only $Na_2Fe_2(CO)_8$, and evaporation under vacuum at 50 °C for 30 min gave a yellow powder (0.0933 g, 72% recovery).

H. Reaction of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ with PPh_3. Triphenylphosphine (0.20 g, 0.76 mmol) and $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (0.18 g, 0.19 mmol) were stirred in dry tetrahydrofuran (20 mL) at 23 °C for 3 days, and the solution was monitored by infrared spectroscopy. Only peaks

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due to $Fe_2\{\mu\text{-InCl(THF)}\}_2(CO)_8$ were observed, and no traces of either $Fe(CO)_4(PPh_3)$ or $Fe(CO)_3(PPh_3)_2$ were detected by infrared spectroscopy.[16]

X-ray Crystallography. Suitable crystals were sealed in thin-walled glass capillaries under a nitrogen atmosphere. Data collection was performed on a Siemens Model P4 automated diffractometer using Mo Kα radiation. The unit cell parameters were determined and refined by a least-squares fit of 25 reflections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on ψ-scans were applied. The space group determinations were based upon a check of the Laue symmetry and systematic absences present and were confirmed by the structure solution. The structures were determined by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-Ray Instruments, Inc. Scattering factors were taken from ref 17a. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms unless otherwise specified. ORTEP[17b] drawings are shown with 30% ellipsoids in Figure 1 and 50% probability ellipsoids in Figures 2 and 3. Full details for the structure solutions and refinements are available in the supplementary material.

A. $[K][In\{Fe_2(CO)_8\}_2](THF)$ (1). The tetrahydrofuran molecule is situated on a crystallographic 4-fold axis that lies in the plane of the ring and passes through the oxygen, with one-fourth of the oxygen and two of the carbons in the asymmetric unit. This results in the observation of eight carbon positions rather than the four required for a tetrahydrofuran, and hence the molecule has a 2-fold disorder in the crystal lattice. The two unique carbons were therefore refined with a site occupancy of 0.5, and the oxygen was refined with an occupancy of 0.25. Hydrogen atoms were not located.

B. $[(C_4H_9)_4N]_2[Fe_2(\mu\text{-InClBr})_2(CO)_8]$ (3). Both halide positions are disordered with respect to chloride/bromide occupancy, and therefore the least-squares refinement was carried out so that for each halide atom site a single set of coordinates and temperature factors was used, but the site occupancy was refined as a fraction of a chlorine atom and a fraction of a bromine atom such that the two fractions summed to unity. This resulted in values of 0.71 Br and 0.29 Cl for the Br(1)/Cl(1) position and 0.56 Br and 0.44 Cl for the Br(2)/Cl(2) site. The tetrabutylammonium cation also shows a slight disorder, with residual peaks near the butyl groups. The four largest residual peaks were within bonding distance of the nitrogen atom. All of the butyl carbons of the primary orientation were refined with site occupancy factors of unity, except for the carbons attached to the nitrogen, which were given a common occupancy factor that was also refined. The four residual peaks near the nitrogen corresponding to the alternate orientation were refined with a common occupancy factor that, when added to the occupancy factor for the primary orientation, gave a value of 1. The final value for the site occupancy of the primary carbons attached to nitrogen was 0.73. No attempt was made to refine the small residual peaks for carbons of the secondary orientation other than the ones attached to nitrogen. The largest residual peak in the final difference Fourier map was 1.17 Å from the indium.

Results

$[K][In\{Fe_2(CO)_8\}_2](THF)$ (1). Although the preparation of transition metal complexes of indium via the direct reaction of indium metal with a metal carbonyl has been known for some time,[6,18] these reactions are few in number and generally involve the use of sealed tubes and high temperatures. A recent report by Rieke[10] of a method for preparing activated indium powders led us to attempt the synthesis of new transition metal complexes of indium by reaction of this form of the metal with a variety of transition metal carbonyls. Reduction of indium trichloride by potassium in refluxing xylene under a nitrogen atmosphere afforded a mixture of the finely divided indium and potassium chloride, to which was added a solution of $Fe_3(CO)_{12}$ in tetrahydrofuran. Further heating resulted in the formation of dark red $[K][In\{Fe_2(CO)_8\}_2](THF)$, which was recrystallized from ether in high yield.

Table I. Crystallographic Data for $[K][In\{Fe_2(CO)_8\}_2](THF)$ (1) and $[(C_4H_9)_4N]_2[Fe_2\{\mu\text{-InClBr}\}_2(CO)_8]$ (3)

	1	3
chem formula	$C_{20}H_8Fe_4InKO_{17}$	$C_{40}H_{72}Br_{2.54}Cl_{1.46}$-$Fe_2In_2N_2O_8$
fw	897.6	1305.2
space group	tetragonal $P4/n$ (No. 85)	triclinic, $P\bar{1}$ (No. 2)
a, Å	11.850(2)	11.510(2)
b, Å		11.905(1)
c, Å	10.696(2)	12.200(2)
α, deg		90.373(9)
β, deg		117.08(1)
γ, deg		107.75(1)
V, Å^3	1502.0(5)	1396.6(5)
Z	2	1
temp, °C	23	23
λ, Å (Mo Kα)	0.710 73	0.710 73
ρ(calc), g cm^{-3}	1.985	1.552
μ(Mo Kα), cm^{-1}	28.53	32.55
transm coeff	0.7380–1.0000	0.6115–1.0000
R^a	0.0361	0.0461
$R_w{}^b$	0.0504	0.0594

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 1

	x	y	z	U(eq)^a
In	7500	2500	5000	30(1)
Fe	7971(1)	1371(1)	2952(1)	31(1)
K	12500	2500	4147(4)	40(1)
O(1)	8643(8)	1067(8)	326(6)	90(3)
O(2)	8336(5)	–859(6)	3999(8)	75(3)
O(3)	10266(5)	1960(6)	3688(7)	74(3)
O(4)	5582(5)	814(6)	2603(8)	77(3)
O(11)	12500	2500	1586(14)	87(5)
C(1)	8337(7)	1240(7)	1319(9)	47(3)
C(2)	8190(7)	32(7)	3595(9)	48(3)
C(3)	9345(8)	1774(7)	3425(9)	48(3)
C(4)	6481(8)	1102(7)	2752(9)	47(3)
C(11)	12611(73)	3465(21)	855(21)	168(18)
C(12)	12116(49)	3137(43)	–456(19)	109(21)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

An X-ray crystal structure determination revealed that the anion is composed of an indium atom coordinated to two $Fe_2(CO)_8$ moieties in a manner analogous to the isoelectronic tin complex $Sn\{Fe_2(CO)_8\}_2$.[19] The complex lies on a crystallographic 4-fold inversion axis that bisects the two Fe–Fe bonds, with the indium residing on the inversion center, and there is one $Fe(CO)_4$ group in the asymmetric unit. The Fe–In bond distance of 2.627(1) Å is comparable to those found in $[(bpy)InFe_2(CO)_8]^-$ (2.545(3) and 2.552(3) Å),[8] $[In\{Fe(CO)_4\}_3]^{3-}$ (2.633(1) Å),[9] $Fe_2(CO)_8$-$[InMn(CO)_5]_2$ (2.662(1) and 2.663(1) Å),[6] $[(\mu\text{-InBr}_2)_2\text{-}\{Fe(CO)_4\}_2]^{2-}$ (2.668(1) Å),[9] and $[In_2Fe_6(CO)_{24}]^{2-}$ (2.698(2)–2.708(1) Å).[8] Crystal data for $[K][In\{Fe_2(CO)_8\}_2](THF)$ (1) are given in Table 1. Atomic coordinates and a list of bond distances and angles are given in Tables II and III, respectively. An ORTEP diagram of the anion is shown in Figure 1.

An interesting feature of the structure is the coordination of the potassium counterion to a molecule of tetrahydrofuran and two carbonyl oxygen atoms (one from each iron of an $Fe_2(CO)_8$ moiety) from each of four anions to give a total coordination number of 9. An ORTEP diagram of the potassium ion coordination sphere is shown in Figure 2. The potassium is located on a crystallographic 4-fold axis, as is the tetrahydrofuran, which of necessity experiences a 2-fold disorder (only one of these orientations is shown in Figure 2). The arrangement of the metal carbonyl oxygens around the potassium can be described as approximating a square antiprism, with the potassium lying

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Table III. Unique Bond Distances (Å) and Bond Angles (deg) for **1**

Bond Distances			
In–Fe	2.627(1)	Fe–C(1)	1.806(9)
Fe–C(2)	1.749(9)	Fe–C(3)	1.771(9)
Fe–C(4)	1.807(9)	Fe–FeA	2.900(2)
K–O(3)	2.767(6)	K–O(11)	2.739(15)
K–O(2)	2.949(8)	O(1)–C(1)	1.141(12)
O(2)–C(2)	1.154(11)	O(3)–C(3)	1.148(11)
O(4)–C(4)	1.130(11)	O(11)–C(11)	1.392(26)
C(11)–C(12)	1.569(48)		
Bond Angles			
Fe–In–FeA	67.0(1)	Fe–In–FeB	134.1(1)
In–Fe–C(1)	154.3(3)	In–Fe–C(2)	99.5(3)
C(1)–Fe–C(2)	105.5(4)	In–Fe–C(3)	79.6(3)
C(1)–Fe–C(3)	94.5(4)	C(2)–Fe–C(3)	89.8(4)
In–Fe–C(4)	88.9(3)	C(1)–Fe–C(4)	96.0(4)
C(2)–Fe–C(4)	91.8(4)	C(3)–Fe–C(4)	168.5(4)
In–Fe–FeA	56.5(1)	C(1)–Fe–FeA	99.9(3)
C(2)–Fe–FeA	153.4(3)	C(3)–Fe–FeA	96.0(3)
C(4)–Fe–FeA	77.7(3)	O(3)–K–O(11)	79.8(2)
O(3)–K–O(2A)	69.2(2)	O(11)–K–O(2A)	132.3(2)
O(3)–K–O(2B)	126.4(2)	O(2A)–K–O(2B)	95.5(3)
O(3)–K–O(2C)	132.2(2)	O(2A)–K–O(2C)	63.1(2)
O(3)–K–O(2D)	64.3(2)	O(3)–K–O(3A)	159.6(3)
O(3)–K–O(3B)	88.2(1)	C(2)–O(2)–KA	143.6(6)
K–O(3)–C(3)	175.5(7)	K–O(11)–C(11)	124.2(11)
C(11)–O(11)–C(11A)	111.6(22)	C(11)–O(11)–C(11B)	71.6(11)
Fe–C(1)–O(1)	172.7(8)	Fe–C(2)–O(2)	178.8(9)
Fe–C(3)–O(3)	174.6(8)	Fe–C(4)–O(4)	172.4(8)
O(11)–C(11)–C(12)	105.3(30)	O(11)–C(11)–C(11B)	54.2(5)
C(12)–C(11)–C(11B)	63.5(30)	C(12)–C(11)–C(11C)	92.2(20)
C(11B)–C(11)–C(11C)	90.0(1)	O(11)–C(11)–C(12C)	99.6(27)
C(12)–C(11)–C(12C)	44.9(29)	C(11B)–C(11)–C(12C)	92.0(20)
C(11C)–C(11)–C(12C)	56.6(25)	C(11)–C(12)–C(11B)	60.0(17)
C(11)–C(12)–C(12A)	91.1(32)	C(11B)–C(12)–C(12A)	83.9(34)
C(11)–C(12)–C(12B)	109.3(18)	C(11B)–C(12)–C(12B)	62.7(36)
C(12A)–C(12)–C(12B)	45.0(1)	C(11)–C(12)–C(12C)	72.4(42)
C(11B)–C(12)–C(12C)	108.0(20)	C(12A)–C(12)–C(12C)	45.0(1)
C(12B)–C(12)–C(12C)	90.0(1)		

slightly below a square face that is capped by the oxygen of the THF molecule. Each anion contributes an oxygen to the top square and the bottom square of the antiprism. The K–O distances for the two sets of symmetry-related carbonyl oxygens are 2.767(6) and 2.949(8) Å, and the distance between the potassium and the oxygen of the THF molecule is 2.739(15) Å. The infrared spectrum of **1** in the solid state shows absorptions attributable to THF and also exhibits an absorption at 1752 cm^{-1}, which is in the region appropriate for C–O stretching vibrations of transition metal carbonyls having an oxygen atom attached to an alkali metal cation.[20] The infrared spectrum of the complex in ether does not exhibit an absorption in this region, and therefore it appears likely that this strong association does not persist in solution. The presence of tetrahydrofuran in the crystals is presumably from traces of the solvent that remain in the crude product before recrystallization from ether.

$Fe_2\{\mu$-InCl(THF)$\}_2(CO)_8$ (2). Although the best route for the preparation of this complex is the reaction of indium(I) chloride with $Fe_3(CO)_{12}$ in refluxing tetrahydrofuran, it can also be obtained by reacting either $Na_2Fe_2(CO)_8$ or $Na_2Fe(CO)_4$ with indium(III) chloride. The compound will form crystals from THF; however these lose solvent rapidly when removed from solution. Prolonged exposure (over 1 week) to dynamic vacuum does not completely remove all traces of THF. When the complex is first formed, it is highly soluble and has a yellowish brown color, with infrared peaks at 2064 and 1896 cm^{-} and a broad peak centered at 1986 cm^{-1}. Removal of the solvent results in a bright yellow solid, the infrared spectrum of which is strikingly different from the spectrum of the complex in solution. The solid-state spectrum exhibits peaks at 2083 (sh) and 2050 (s) cm^{-1} and a broad, strong peak centered at 1985 with minima at 1999 and 1964 cm^{-1}. This effect is presumably due to displacement of the THF coordinated to indium by chloride atoms of adjacent molecules, resulting in the formation of chloride-bridged oligomers. Compound **2** redissolves in THF very slowly at room temperature to give a bright yellow solution with infrared absorptions at 2064 (sh), 2041 (s), 1985 (s), and 1898 (m) cm^{-1}. Increasing the exposure of the complex to dynamic vacuum results in subsequent solution spectra that show a decrease in the intensity of the peak at 2064 cm^{-1}, which is diagnostic for the highly-solvated THF complex, and an increase in the intensity of the peak at 2041 cm^{-1}, which is indicative of the less soluble chloride-bridged oligomers.

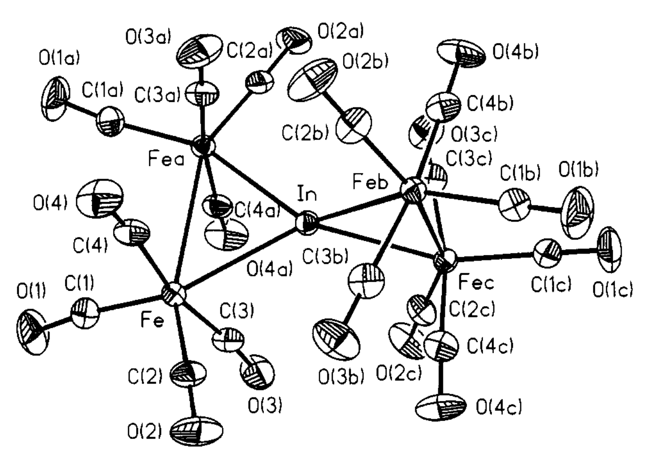

Figure 1. ORTEP drawing of the $[In\{Fe_2(CO)_8\}_2]^-$ anion of compound **1**.

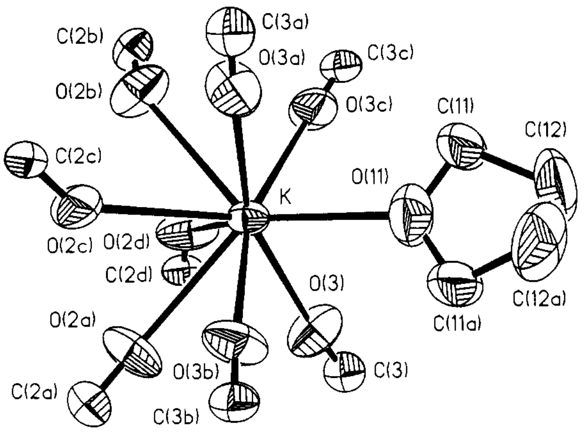

Figure 2. ORTEP drawing of the coordination sphere of the potassium cation of compound **1** showing the eight carbonyl groups and one orientation of the disordered tetrahydrofuran.

Repeated attempts to obtain crystals of $Fe_2\{\mu$-InCl(THF)$\}_2(CO)_8$ suitable for X-ray diffraction were unsuccessful due to their pronounced tendency to lose solvent, and hence the complex was characterized as its tetrabutylammonium bromide adduct, $[n\text{-}Bu_4N]_2[Fe_2(\mu\text{-}InClBr)_2(CO)_8]$ (**3**). The adduct can be formed quite readily from a stirred solution of $Fe_2\{\mu$-InCl(THF)$\}_2(CO)_8$ and $[n\text{-}Bu_4N][Br]$ in THF. Coordination of the bromide ion to the indium of the complex results in a dramatic shift to lower frequency of the carbonyl stretching frequencies in the infrared spectrum, although the peak pattern remains similar. The average magnitude of the shift is on the order of 45 cm^{-1}. This change would be expected for the alteration of a complex from a neutral species to a dianion with minimal change in the geometry of the carbonyl groups.

The X-ray crystal structure determination for $[n\text{-}Bu_4N]_2[Fe_2(\mu\text{-}InClBr)_2(CO)_8]$ was performed, and the crystallographic data, atomic coordinates, and important bond distances and angles are given in Tables I, IV, and V, respectively. An ORTEP diagram of the anion is shown in Figure 3, with the disordered halide

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(20) Edgell, W. F.; Lyford, J., IV; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403.

Table IV. Atomic Coordinates ($\times 10^j$ and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for the Anion of 3

	x	*y*	*z*	*U*(eq)[a]
X(1)	3117(2)	2046(1)	5610(2)	94(1)
X(2)	1588(2)	4621(1)	4897(2)	90(1)
In	3675(1)	4153(1)	5103(1)	57(1)
Fe	4006(1)	4226(1)	3079(1)	62(1)
O(1)	5124(11)	4846(9)	1353(9)	136(7)
O(2)	1336(10)	2357(9)	1536(9)	135(6)
O(3)	2956(8)	6197(7)	2880(7)	103(5)
O(4)	5547(8)	2642(6)	4256(8)	98(5)
C(1)	4672(13)	4589(10)	2036(10)	89(7)
C(2)	2411(13)	3101(11)	2162(11)	92(7)
C(3)	3390(11)	5429(9)	3004(10)	78(6)
C(4)	4948(11)	3274(8)	3818(10)	71(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Unique Bond Distances (Å) and Bond Angles (deg) for the Anion of 3

Bond Distances			
X(1)–In	2.547(2)	X(2)–In	2.531(2)
In–Fe	2.663(2)	In–In′	3.223(2)
In–Fe′	2.680(1)	Fe–C(1)	1.757(15)
Fe–C(2)	1.740(10)	Fe–C(3)	1.768(13)
Fe–C(4)	1.774(11)	Fe–In′	2.680(1)
O(1)–C(1)	1.165(20)	O(2)–C(2)	1.167(12)
O(3)–C(3)	1.149(16)	O(4)–C(4)	1.145(14)
Bond Angles			
X(1)–In–X(2)	100.2(1)	X(1)–In–Fe	112.1(1)
X(2)–In–Fe	115.4(1)	X(1)–In–Fe′	114.6(1)
X(2)–In–Fe′	109.0(1)	Fe–In–Fe′	105.8(1)
In–Fe–C(1)	163.8(3)	In–Fe–C(2)	93.2(5)
C(1)–Fe–C(2)	103.0(6)	In–Fe–C(3)	79.9(4)
C(1)–Fe–C(3)	97.7(6)	C(2)–Fe–C(3)	98.1(6)
In–Fe–C(4)	80.7(5)	C(1)–Fe–C(4)	97.0(6)
C(2)–Fe–C(4)	96.8(5)	C(3)–Fe–C(4)	156.1(5)
In–Fe–In′	74.2(1)	C(1)–Fe–In′	89.5(3)
C(2)–Fe–In′	167.4(5)	C(3)–Fe–In′	81.2(3)
C(4)–Fe–In′	80.2(3)	Fe–C(1)–O(1)	179.0(11)
Fe–C(2)–O(2)	179.1(11)	Fe–C(3)–O(3)	176.0(10)
Fe–C(4)–O(4)	177.6(11)		

positions labeled as X's. While this work was in progress, the crystal structure of $[Et_4N]_2[Fe_2(\mu\text{-}InBr_2)_2(CO)_8]$ was reported,[9] and as the structure of 3 differs very little from that reported for the tetraethylammonium bromide complex, a detailed discussion of this structure will not be presented here. However, our study does provide two valuable pieces of information, the first being that the conclusive identification of complex 3 provides strong confirming evidence for the identity and structure of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. The second feature of interest is the coordination of the halides to the indium atoms. The anion is situated on a crystallographic inversion center, with one indium and two halides in the asymmetric unit. Both halide positions are disordered with respect to chloride/bromide occupancy. The Br(1)/Cl(1) position refines to a value of 0.71 for the bromine occupancy (and consequently a value of 0.29 for chlorine), and the Br(2)/Cl(2) position refines to 0.56 bromine and 0.44 chlorine. Experimental limitations do not allow us to distinguish between a disordered array of $[Fe_2(\mu\text{-}InClBr)_2(CO)_8]$ anions and a situation in which the crystal lattice contains a mixture of $[Fe_2(\mu\text{-}InClBr)_2(CO)_8]$ ions and $[Fe_2(\mu\text{-}InBr_2)_2(CO)_8]$ ions. However, both the crystal structure and the elemental analysis data provide strong evidence for the retention of chlorine in the complex, and another crystal study that we have performed for the same complex with a different cation showed a bromine–chlorine distribution much closer to 50% for each. Although this is suggestive of a situation in which the bromide ion adds to the complex without displacement of chlorine, we have not yet determined conclusively whether or not halide exchange occurs in solution.

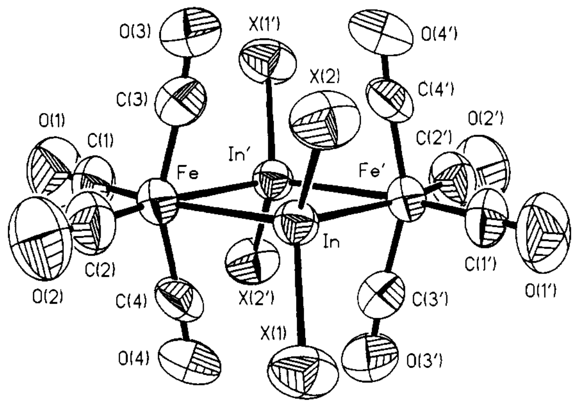

Figure 3. ORTEP drawing of the $[Fe_2\{\mu\text{-}InClBr\}_2(CO)_8]^{2-}$ anion of compound 3. The disordered halide positions are labeled as X's.

Discussion

Reactions of Iron Carbonyl Anions with Indium Trihalides. Recent work has demonstrated that a wide variety of iron carbonyl complexes of indium can be prepared by the reaction of iron carbonyl anions with indium trihalides.[4,8,9] In the course of our studies over the past few years, we were surprised to find that three rather different reactions of iron carbonyl species with indium halides all led to the same product, $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. The ubiquitous presence of this complex leads us to speculate that it may be an intermediate in the formation of other known compounds that are formed in similar reactions under slightly different conditions.

The initial preparation of $[(Ph_3P)_2N][Fe(CO)_4(InBr_2)]$ by Ruff[3] was carried out via the reduction of $Fe_3(CO)_{12}$ with sodium amalgam in tetrahydrofuran, followed by the addition of indium tribromide and the subsequent addition of bis(triphenylphosphoranylidene)ammonium bromide. Later work by Albano et al.[9] clearly indicates that this compound is the dimeric complex $[(Ph_3P)_2N]_2[Fe_2(CO)_8(\mu\text{-}InBr_2)_2]$. We propose that this procedure initially forms the sodium salt of an iron carbonyl anion, either $Na_2Fe_2(CO)_8$ or $Na_2Fe(CO)_4$ or a mixture of both, which reacts with the indium tribromide to form $Fe_2\{\mu\text{-}InBr(THF)\}_2(CO)_8$, which then adds $[(Ph_3P)_2N][Br]$ to give the observed product. The latter two steps are entirely analogous to syntheses described in this paper in which either $Na_2Fe_2(CO)_8$ or $Na_2Fe(CO)_4$ reacts with indium trichloride to give $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$, and this complex reacts with tetraethylammonium bromide to give $[Et_4N]_2[Fe_2(\mu\text{-}InBr_2)_2(CO)_8]$.

The reaction of indium tribromide with 3.5 equiv of $Na_2Fe(CO)_4$ is known to produce the $[In\{Fe(CO)_4\}_3]^{3-}$ anion in nearly quantitative yield,[9] whereas a similar reaction between indium trichloride and 1 equiv of $Na_2Fe(CO)_4$ gives $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. We have reason to believe that the initial step in the latter reaction is reduction of the indium trihalide by the $Fe(CO)_4^{2-}$ anion to give solvent-stabilized $Fe(CO)_4$ and the indium(I) halide (vide infra). Although we have no strong evidence that indicates the subsequent course of the reaction, one can envision a sequence in which a transient, solvent-stabilized species such as $Fe(CO)_4(InX)$ (X = Cl or Br) is formed that is similar to the known complex $Cr(CO)_5\{InBr(THF)\}$.[21] This intermediate either could dimerize to give $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ or, in the presence of additional $Fe(CO)_4^{2-}$, could add two of these dianions in a stepwise fashion to give the known complexes[9] $[XIn\{Fe(CO)_4\}_2]^{2-}$ and $[In\{Fe(CO)_4\}_3]^{3-}$. It is interesting to note that the Et_4N^+ salt of $[BrIn\{Fe(CO)_4\}_2]^{2-}$ reacts with 1 equiv of $InBr_3$ to give an unidentified intermediate complex, possibly $Fe_2\{\mu\text{-}InBr(THF)\}_2(CO)_8$, which goes on to add $[Et_4N][Br]$ to form $[Et_4N]_2[Fe_2(\mu\text{-}InBr_2)_2(CO)_8]$.[9]

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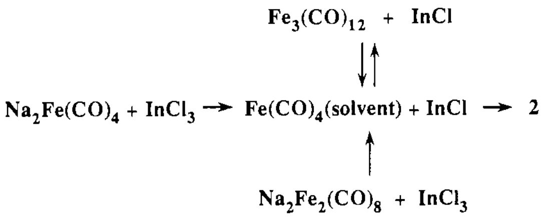
(21) Behrens, H.; Moll, M.; Sixtus, E.; Thiele, G. *Z. Naturforsch., B* **1977**, *32b*, 1109.

Scheme I. Mechanism for the Formation of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (**2**)



$$\begin{tikzcd}
 & Fe_3(CO)_{12} + InCl \arrow[d, shift right] & \\
Na_2Fe(CO)_4 + InCl_3 \arrow[r] & Fe(CO)_4(solvent) + InCl \arrow[u, shift right] \arrow[r] & 2 \\
 & Na_2Fe_2(CO)_8 + InCl_3 \arrow[u] &
\end{tikzcd}$$

Cassidy and Whitmire[8] have shown that either $[Et_4N]_2[Fe_2(CO)_8]$ or a mixture of $Fe(CO)_5$ and KOH in methanol will react with indium trichloride to give $[Et_4N]_2[In_2Fe_6(CO)_{24}]$. We have observed that $Na_2Fe_2(CO)_8$ reacts with indium trichloride in THF to give $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. Once again, these observations suggest a pathway for the former reaction in which $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ is formed as an intermediate, which then reacts with two additional $Fe_2(CO)_8^{2-}$ anions that replace the two halides to give $In_2Fe_6(CO)_{24}^{2-}$.

Mechanism for the Formation of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (2). The isolation of a single major product, $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ (**2**), from reactions involving three different iron carbonyl complexes as starting materials led us to speculate as to the path taken by these three reactions and the possibility of a common intermediate. We therefore carried out a series of spectroscopic studies and trapping experiments, the results of which have led us to propose the mechanistic scheme shown in Scheme I.

The reaction between $Fe_3(CO)_{12}$ and indium(I) chloride gives a high yield (85%) of $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$, and it clearly must involve the cleavage of Fe–Fe bonds. The reaction is carried out in refluxing tetrahydrofuran (67 °C) and does not proceed to any appreciable extent at 23 °C. It appears likely that the rate-determining step in this reaction involves breaking the Fe–Fe bonds to form solvated $Fe(CO)_4$ units which are then free to react with the indium(I) chloride to give the observed product.

The reaction of $Na_2Fe_2(CO)_8$ with indium(III) chloride in THF was monitored by infrared spectroscopy, and the iron dianion was found to react completely at -78 °C. We have never observed unreacted starting material in THF, even within 5 min after the reaction started. The reaction proceeds smoothly at 23 °C to give $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. Similar reactions in toluene and diethyl ether also produce complex **2**, accompanied by a green compound that was identified as $Fe_3(CO)_{12}$. Indium(I) chloride was also observed in the ether reaction. These observations are consistent with a process in which the indium trichloride is first reduced to indium(I) chloride by the iron dianion, which is itself oxidized to the solvent-stabilized $Fe(CO)_4$ complex. In solvents of low coordinating ability, such as toluene and ether, the reactive $Fe(CO)_4$ units also form $Fe_3(CO)_{12}$. The reaction between $Na_2Fe(CO)_4$ and indium trichloride in weakly coordinating diethyl ether gives a moderate yield (42%) of complex **2**. When the same reaction is carried out in tetrahydrofuran, which has a much higher coordinating ability, the iron–indium complex is isolated in a much higher yield (88%). This overall process is quite different from that observed for the reaction of $HFe(CO)_4^-$ with thallium trichloride in which the Tl^{3+} ion, rather than Tl^+, is the key intermediate that reacts with the iron carbonyl anion to give $Tl_2Fe_4(CO)_{16}^{2-}$. When a similar reaction is performed with thallium(I) carbonate, disproportionation occurs to give Tl^{3+} and thallium metal.[22]

In an attempt to trap the reactive intermediate $Fe(CO)_4(THF)$, the reaction of $Na_2Fe_2(CO)_8$ with indium(III) chloride was carried out in the presence of triphenylphosphine. This led to the isolation of $Fe(CO)_4(PPh_3)$ in 44% yield and a trace of $Fe(CO)_3(PPh_3)_2$, identified by its infrared spectrum, that was too small to weigh accurately. However, the possibility remained that these products could have been formed by the interaction of the triphenylphosphine with either $Na_2Fe_2(CO)_8$ or $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. The reaction of $Na_2Fe_2(CO)_8$ with triphenylphosphine under identical conditions produced only a small amount of $Fe(CO)_3(PPh_3)_2$ (10% yield) with a trace of $Fe(CO)_4(PPh_3)$ observed after 2 days, and $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$ did not react with triphenylphosphine after stirring at 23 °C for 3 days. We therefore conclude that the $Fe(CO)_4(PPh_3)$ obtained previously was formed via the reaction of $Fe(CO)_4(THF)$ with triphenylphosphine.

The results of these studies lead us to propose that, in the proper stoichiometry, the reaction of either $Na_2Fe(CO)_4$ or $Na_2Fe_2(CO)_8$ with indium(III) chloride and the reaction of $Fe_3(CO)_{12}$ with indium(I) chloride in tetrahydrofuran all proceed via the intermediates $Fe(CO)_4(THF)$ and indium(I) chloride to give $Fe_2\{\mu\text{-}InCl(THF)\}_2(CO)_8$. This information has guided us in the preparation of new complexes containing bonds between indium and transition metals, which will be the subject of future reports.

Acknowledgment. The authors gratefully acknowledge support from the Robert A. Welch Foundation (Grant No. D-1180), as well as from the Texas Higher Education Coordinating Board's Advanced Research Program (Grant No. 3644180). The X-ray diffractometer was purchased with funds from Texas Tech University and the Texas Higher Education Coordinating Board's Energy Research in Applications Program (Grant No. 3644-039).

Supplementary Material Available: Tables giving full details of the crystal data, data collection, and structure solution parameters for compounds **1** and **3** (Tables S1 and S2), complete atomic coordinates and bond distances and angles for **3** (Tables S3 and S4), and anisotropic thermal parameters for **1** and **3** (Tables S5 and S6) (10 pages). Ordering information is given on any current masthead page.

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