

significant  $\pi$ -bonding contribution to the energetics of substitution.

Finally, the fact that the displacement of the second amine molecule is much slower than that of the first one indicates that in these complexes the *trans*-labilizing effect of the amine is higher than that of thioethers. Since other observations show that thioethers are easily replaced by amines from the complexes *trans*-Pd(RSR')<sub>2</sub>Cl<sub>2</sub>, we must conclude that a good *trans* labilizer is at the same time a good entering reagent. This seems to be a general rule for the reactions at platinum(II) substrates<sup>5</sup> and it agrees with the proposed associative mechanism *via* the trigonal-bipyramidal transition state, owing to the equivalence of the leaving group and the *trans* partner in the transition state. The increasing number of available data relative to the substitutions on Pd(II) complexes seems to confirm the expected similarity of behavior between Pt(II) and Pd(II) derivatives.

### Experimental Section

The complexes *trans*-Pd(am)<sub>2</sub>Cl<sub>2</sub> were obtained by following the methods reported in the literature.<sup>8</sup> The analytical figures correspond to the proposed formula, and the melting points, to the values reported in the literature.<sup>8</sup> Thioethers were pure commercial samples, and the solvent, 1,2-dimethoxyethane, was distilled over sodium before use.

**Kinetics.**—The method used to follow the kinetics was similar to that reported previously.<sup>1,3</sup> Known volumes of thermostated solutions of the complex and reagent were mixed in the thermostated cell of an Optica CF4 double-beam recording spectrophotometer. The spectral changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region of the spectrum at known intervals. Afterward, a suitable wavelength was chosen to study the reaction (usually 340 m $\mu$ ) and the kinetics were followed by recording the changes of optical density as a function of time.

**Acknowledgments.**—We thank the Italian Council for Research (CNR, Rome) for financial support.

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CONTRIBUTION FROM ROHM AND HAAS COMPANY, REDSTONE RESEARCH LABORATORIES  
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## Lewis Adducts of the $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Co}(\text{CO})_4^-$ Ions

By J. K. RUFF

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The metal carbonyl anions  $\text{Fe}(\text{CO})_4^{2-}$  and  $\text{Co}(\text{CO})_4^-$  form adducts with indium tribromide or gallium tribromide of the type  $\text{M}(\text{CO})_4\text{M}'\text{Br}_3^{2-}$ . The complex ion  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  dissociates in solution to give a new ion  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$ . This new ion will form adducts with amines and the preparation of the ions  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot (\text{C}_2\text{H}_5)_3\text{N}^-$  and  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_6\text{H}_5\text{N}^-$  is also described.

The ability of metal carbonyls to react with numerous Lewis bases has been well documented, whereas the ability of pure metal carbonyl anions to function as Lewis bases has received only slight attention. The first examples of such adducts to be reported were the complex anions  $\text{Mn}(\text{CO})_5\text{BH}_3^-$  and  $(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4\text{BH}_3^-$ .<sup>1</sup> More recently complex anions of the type  $\text{M}(\text{CO})_5\text{Mn}(\text{CO})_5^-$  (where M = Cr, Mo, or W) were obtained by the direct interaction of the Lewis base  $\text{Mn}(\text{CO})_5^-$  and the group VI metal carbonyl.<sup>2</sup> In a similar manner, the adduct  $\text{W}(\text{CO})_5\text{Co}(\text{CO})_4^-$  was prepared.<sup>3</sup> Indium tribromide also forms stable adducts with the  $\text{Cr}(\text{CO})_5^{2-}$  and  $\text{W}(\text{CO})_5^{2-}$  anions although the synthetic route to these materials does not involve the direct combination of the components.<sup>4</sup>

### Experimental Section

All operations described herein, except the weighing of reactants and products, were carried out under a nitrogen atmosphere. The analytical data for the compounds prepared in this study are summarized in Table I.

**Materials.**—The metal carbonyl anions were prepared and isolated as described previously.<sup>3</sup> The anhydrous metal halides were obtained from Alfa Inorganics, Inc. and used without further purification.

**Preparation of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4\text{MBr}_3$  (M = In or Ga).**—The preparation of both of the adducts was performed in an analogous manner. Therefore only the preparation of the indium derivative will be described. To a 1.41-g sample of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$  dissolved in 40 ml of  $\text{CH}_2\text{Cl}_2$ , a 0.72-g sample of  $\text{InBr}_3$  was added. The mixture was stirred for 0.5 hr and filtered and then concentrated to 20 ml. A 1.45-g sample of product was obtained upon the addition of approximately 80 ml of ether.

**Preparation of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4\text{CdBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ .**—Cadmium dibromide, 0.28 g, was added to a solution of 0.74 g of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$  in 25 ml of tetrahydrofuran (THF). The mixture was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was dissolved in 20 ml of  $\text{CH}_2\text{Cl}_2$  and filtered. The addition of 30 ml of ether resulted in the crystallization of 0.73 g of product. A proton nmr spectrum showed the presence of ethyl groups as well as phenyl groups but gave no evidence for the presence of THF. The area ratio of the phenyl groups to ethyl groups was 3.1:1.0.

**Preparation of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}[\text{Fe}(\text{CO})_4\text{InBr}_2]$ .**—(A) A mixture of 0.51 g of  $\text{Fe}_2(\text{CO})_{12}$ , 25 g of 1% sodium amalgam, and 40 ml of THF was stirred overnight. The excess amalgam was drained out of the bottom of the flask and then 0.7 g of  $\text{InBr}_3$  was added to the mixture. After stirring 15 min, 2.5 g of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NBr}$  in 100 ml of  $\text{CH}_2\text{Cl}_2$  was added to the mixture. It was then filtered and the filtrate was evaporated to dryness under reduced pressure.

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(2) A. Anders and W. A. G. Graham, *ibid.*, **89**, 539 (1967).

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TABLE I  
 ANALYTICAL DATA FOR THE COMPOUNDS PREPARED

Anion	Mp, °C	Yield, %	Analyses, %									
			Calcd			Found						
			C	H	N	Br	M	C	H	N	Br	M
Co(CO) <sub>4</sub> InBr <sub>3</sub> <sup>-</sup>	152-153	91	45.2	2.82	1.32	22.6	5.5 (Co)	45.0	2.72	1.33	22.7	5.3 (Co)
Co(CO) <sub>4</sub> GaBr <sub>3</sub> <sup>-</sup>	173-175	57	47.1	2.94	1.37	23.7	5.8 (Co)	46.9	3.24	1.40	24.0	5.5 (Co)
Co(CO) <sub>4</sub> CdBr <sub>2</sub> ·(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>-</sup>	74-80 dec	81	50.1	3.79	1.33	15.2	...	49.9	3.59	1.43	15.1	...
Fe(CO) <sub>4</sub> GaBr <sub>3</sub> <sup>2-</sup>	219-222 dec	48	58.7	3.86	1.80	15.4	3.6 (Fe)	58.6	3.79	1.91	15.4	3.3 (Fe)
Fe(CO) <sub>4</sub> InBr <sub>3</sub> <sup>2-</sup>	220-225 dec	79	57.1	3.76	1.75	15.0	3.5 (Fe)	56.9	3.82	1.79	15.1	3.0 (Fe)
Fe(CO) <sub>4</sub> InBr <sub>2</sub> <sup>-</sup>	208-211	15	49.0	3.88	1.43	16.3	5.7 (Fe)	49.0	3.88	1.40	16.3	5.5 (Fe)
Fe(CO) <sub>4</sub> InBr <sub>2</sub> ·C <sub>6</sub> H <sub>5</sub> N <sup>-</sup>	140-142	28	51.0	3.30	2.64	15.1	...	50.8	3.50	2.73	15.2	...
Fe(CO) <sub>4</sub> InBr <sub>2</sub> ·(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>-</sup>	N148-149	33	51.1	4.16	2.59	14.8	...	51.2	4.09	2.89	14.7	...

The residue was dissolved in 25 ml of CH<sub>2</sub>Cl<sub>2</sub>. The addition of approximately 30 ml of ethyl acetate resulted in the precipitation of 2.0 g of product.

(B) A mixture of 1.33 g of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NHFe(CO)<sub>4</sub> and 0.35 g of InBr<sub>3</sub> in 35 ml of CH<sub>2</sub>Cl<sub>2</sub> was stirred for 1 hr. The mixture was then filtered and 50 ml of ethyl acetate was added to the filtrate. Upon standing a 1.22-g sample of impure product was obtained. It consisted of the desired anion Fe(CO)<sub>4</sub>InBr<sub>3</sub><sup>2-</sup>, contaminated with a small amount of the Fe(CO)<sub>4</sub>InBr<sub>2</sub><sup>-</sup> anion. It can be purified by recrystallization from a solution of 25 ml of CH<sub>2</sub>Cl<sub>2</sub> and 25 ml of ethyl acetate to which a small amount of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NBr has been added.

**Preparation of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>GaBr<sub>3</sub>.**—A solution of 0.32 g of GaBr<sub>3</sub> in 10 ml of THF was added dropwise to a solution of 1.47 g of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NHFe(CO)<sub>4</sub> in 25 ml of THF which was cooled to -10°. The mixture was stirred for 15 min, and then the solvent was removed at this temperature under reduced pressure. Precooled CH<sub>2</sub>Cl<sub>2</sub>, 30 ml, was added to the residue, and the new mixture was filtered while still cold. Precooled ethyl acetate, 50 ml, was added to the filtrate which recurred in the precipitation of 0.8 g of product. Attempted recrystallization of the product often resulted in its decomposition.

**Preparation of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>InBr<sub>2</sub>.**—The compound [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>InBr<sub>2</sub> could be obtained in minor amounts in preparation B described above for [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>InBr<sub>3</sub> and could be isolated by fractional crystallization. However, better yields were obtained by the procedure described below, although fractional crystallization was still necessary. A mixture of 0.53 g of Fe<sub>3</sub>(CO)<sub>12</sub> and 25 g of 1% sodium amalgam in 25 ml of THF was stirred overnight. The excess amalgam was drained off and 1.0 g of InBr<sub>3</sub> was added. After stirring for 15 min, 50 ml of ether was added and the mixture was filtered. A solution of 1.5 g of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NBr in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> was then added to the filtrate. The new mixture was filtered and the solvent was removed from the filtrate at reduced pressure. The residue is fractionally recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethyl acetate. A yield of 0.35 g of product was obtained.

**Preparation of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>InBr<sub>2</sub>-am (am = Amine).**—The preparation of the pyridine and triethylamine derivatives was carried out in an analogous manner. The procedure described above for the preparation of the Fe(CO)<sub>4</sub>InBr<sub>2</sub><sup>-</sup> anion was followed exactly. After the addition of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NBr to the mixture, 5 ml of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N was then added. After filtration, the solvent was evaporated under reduced pressure and the residue was dissolved in 20 ml of CH<sub>2</sub>Cl<sub>2</sub>. A 5-ml portion of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N and 20 ml of THF were added. The product, 1.04 g, was precipitated by the addition of ether. Both of the amine derivatives were dried at ambient temperature at a pressure of 1.5 mm for several hours.

**Conductivity Measurements.**—The conductivity of the cobalt derivatives was determined on solutions of approximately 10<sup>-3</sup> M nitromethane using equipment previously described.<sup>5</sup> In addition, the conductivity of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NFe(CO)<sub>4</sub>InBr<sub>2</sub> was determined as a function of concentration in nitromethane solution. The specific conductivity of the nitromethane employed was 4.28 × 10<sup>-7</sup>. The anion, molar concentration, and molar

conductance (cm<sup>2</sup>/ohm equiv) are: Co(CO)<sub>4</sub>GaBr<sub>3</sub><sup>-</sup>, 1.025 × 10<sup>-3</sup>, 71.6; Co(CO)<sub>4</sub>InBr<sub>3</sub><sup>-</sup>, 1.023 × 10<sup>-3</sup>, 69.0; and, Co(CO)<sub>4</sub>CdBr<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O<sup>-</sup>, 1.005 × 10<sup>-3</sup>, 63.9. The molar concentration and molar conductance for the Fe(CO)<sub>4</sub>InBr<sub>2</sub><sup>-</sup> anion are: 11.91 × 10<sup>-3</sup>, 61.6; 5.953 × 10<sup>-3</sup>, 68.0; 2.977 × 10<sup>-3</sup>, 72.0; 1.488 × 10<sup>-3</sup>, 75.6; and 0.992 × 10<sup>-3</sup>, 76.8. Extrapolation to infinite dilution gives a value for Λ equal to 82.7. A plot of Λ<sub>∞</sub> - Λ<sub>c</sub> vs. √V has a slope of 210.

**Infrared Spectra.**—The infrared spectra were obtained on degassed solutions of approximately 0.010 g/ml of the pure compound in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub>, or CH<sub>3</sub>CN. The instrument, a Perkin-Elmer 521 spectrometer, was calibrated with indene. In several cases, either excess bromide or pyridine was added to the solutions containing the Fe(CO)<sub>4</sub>InBr<sub>2</sub><sup>-</sup> or Fe(CO)<sub>4</sub>InBr<sub>3</sub><sup>2-</sup> anion. Absorbance spectra were obtained in CH<sub>2</sub>Cl<sub>2</sub> solutions of these anions as a function of added bromide. The relative intensities of the four observed peaks (neglecting one shoulder) vs. the amount of bromide added are presented in Table II. A summary of the CO stretching frequencies for the compounds prepared in this study is given in Table III.

 TABLE II  
 INFRARED SPECTRA OF THE IRON CARBONYL-INDIUM  
 BROMIDE DERIVATIVES AS A FUNCTION OF ADDED BROMIDE

Concn of anions, M × 10 <sup>2</sup>			Rel intens of CO peaks				10K
Fe(CO) <sub>4</sub> InBr <sub>3</sub> <sup>2-</sup>	Fe(CO) <sub>4</sub> InBr <sub>2</sub> <sup>-</sup>	Br <sup>-</sup>	2012 cm <sup>-1</sup>	1984 cm <sup>-1</sup>	1956 cm <sup>-1</sup>	1871 cm <sup>-1</sup>	
1.85		0.00	35	28	40	51	4
1.81		0.26	28	27	32	49	6
1.79		0.70	24	32	27	59	4
1.58		1.10	17	31	19	57	3
1.52		1.63	13	31	15	57	3
1.49		7.22	0	35	0	66	...
	2.12	0.00	78	0	89	0	...
	1.87	0.74	55	10	63	18	2
	2.09	1.67	48	23	55	42	2
	2.17	2.52	27	25	32	46	5

## Results and Discussion

Adducts formed between metal carbonyl anions, Mn(CO)<sub>5</sub><sup>-</sup> and Re(CO)<sub>5</sub><sup>-</sup>, and the Lewis acid, borane (BH<sub>3</sub>), were prepared by the interaction of the components in solution.<sup>1</sup> This approach has now been extended to include two isoelectronic metal carbonyl anions, Co(CO)<sub>4</sub><sup>-</sup> and Fe(CO)<sub>4</sub><sup>2-</sup>. However, the Lewis acids employed in this study were the group III metal bromides instead of diborane. Adducts were isolated only when gallium tribromide and indium tribromide were used. Although reaction was observed when the two carbonyl anions were allowed to interact with boron tribromide or aluminum tribromide, no simple adducts could be isolated.

**The Co(CO)<sub>4</sub>-MBr<sub>3</sub> System**—The reaction of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NCo(CO)<sub>4</sub> with either indium tribromide or

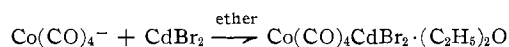
TABLE III  
THE INFRARED SPECTRA IN THE CARBONYL STRETCHING  
REGION FOR THE COMPOUNDS PREPARED

Anion	Freq, $\text{cm}^{-1}$
$\text{Co}(\text{CO})_4\text{InBr}_3^-$	2080 m, 2013 m, sh, 1989 s
$\text{Co}(\text{CO})_4\text{GaBr}_3^-$	2084 m, 2018 m, sh, 1991 s
$\text{Co}(\text{CO})_4\text{CdBr}_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2^-$	2041 m, 1996 w, sh, 1956 vs
$\text{Fe}(\text{CO})_4\text{InBr}_3^{2- a}$	1984 m, 1890 m, sh, 1871 s
$\text{Fe}(\text{CO})_4\text{InBr}_3^{2- b}$	1977 m, 1883 m, sh, 1867 s, dbt
$\text{Fe}(\text{CO})_4\text{InBr}_2^{2-}$	2012 s, 1956 s
$\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}^- c$	1996 ms, 1910 m, 1881 s
$\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}^- b$	1994 ms, 1911 ms, 1881 s, dbt, 1833 w, sh
$\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{N}(\text{C}_2\text{H}_5)_3^- b$	1973 ms, 1878 m, sh, 1864 s, dbt, 1828 w, sh
$\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{N}(\text{C}_2\text{H}_5)_3^-$	1982 m, br, 1890 m, sh, 1874 s, br
$\text{Fe}(\text{CO})_4\text{GaBr}_3^{2- b}$	1978 ms, 1876 m, sh, 1864 s, dbt

<sup>a</sup> Spectrum taken in  $\text{CH}_3\text{CN}$  solution. This spectrum is identical with that taken in the presence of excess bromide.

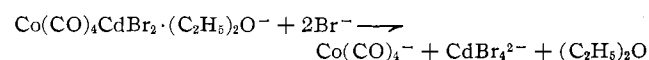
<sup>b</sup> Spectra taken on Nujol mulls. <sup>c</sup> Spectra taken on solutions containing excess  $\text{C}_5\text{H}_5\text{N}$ .

gallium tribromide proceeded readily in methylene chloride solution to produce the anionic adducts  $\text{Co}(\text{CO})_4\text{InBr}_3^-$  and  $\text{Co}(\text{CO})_4\text{GaBr}_3^-$  in moderate to high yields. No evidence for a halide-displacement reaction and the resultant formation of the neutral species  $\text{Co}(\text{CO})_4\text{MBr}_2$  was observed in these systems. This is contrary to the reported reaction between  $\text{NaCo}(\text{CO})_4$  and  $\text{InBr}_3$  in THF to give  $\text{Co}(\text{CO})_4\text{InBrCo}(\text{CO})_4 \cdot \text{THF}$ .<sup>6</sup> The reason for this difference probably lies in the fact that  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NBr}$  is very soluble in methylene chloride, so solubility contributes no driving force to the displacement reaction. However, when an attempt was made to replace the  $\text{Co}(\text{CO})_4^-$  ion with  $\text{Mn}(\text{CO})_5^-$ , a displacement reaction was observed and it was not possible to isolate an analytically pure adduct,  $\text{Mn}(\text{CO})_5\text{MBr}_3^-$ . The use of trimethylindium instead of  $\text{InBr}_3$  would probably lead to the successful isolation of an adduct with the manganese carbonyl anion since no good leaving group is present. It was possible to use cadmium dibromide instead of either of the tribromides, and a 1:1 adduct could be isolated as a monoetherate



The 2:1 adduct,  $\text{CdBr}_2[\text{Co}(\text{CO})_4]_2^{2-}$ , was not formed under these experimental conditions even when an excess of the carbonyl anion was employed.

All three of the adducts are white to pale yellow solids which are stable in air for short periods of time. In solution they are oxidized by atmospheric oxygen. All of the complex salts are soluble in polar organic solvents such as THF,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ , or  $\text{CH}_2\text{Cl}_2$ . The adduct formed with  $\text{InBr}_3$  appears to be the least active while that formed with  $\text{CdBr}_2$  is the most active. Only the latter adduct reacts with excess bromide ion at ambient temperature according to

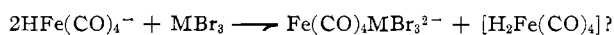


The proton nmr shows no evidence for any paramagnetic impurities or the presence of metal-hydride

bonds. The area ratio of the ethyl groups to the phenyl groups (in the cation) confirms the presence of 1 mol of ether in the cadmium adduct. The conductivity of these salts in nitromethane is in the range attributable to 1:1 electrolytes.<sup>7</sup> The infrared spectra in the carbonyl region of the cobalt derivatives are summarized in Table III.

The presence of three active infrared bands in the spectra of the two tribromide derivatives is consistent with  $\text{C}_{3v}$  symmetry in which the metal tribromide is bonded to an apical position in a trigonal bipyramid.<sup>8</sup> This geometric arrangement has been proposed for a large number of other substituted tetracarbonylcobalt derivatives including the isoelectronic species  $\text{Co}(\text{CO})_4\text{-GeBr}_3$  and  $\text{Co}(\text{CO})_4\text{SnX}_3$ .<sup>9,10</sup> The presence of the negative charge in these adducts results in a shift to lower frequencies by approximately 30–50  $\text{cm}^{-1}$  over that observed in the isoelectronic species. Since the frequencies of the observed bands for both the indium and the gallium derivatives are practically identical, it is apparent that their relative  $\pi$ -acceptor abilities are similar. Only three of the four expected carbonyl modes were observed in the spectrum of the  $\text{Co}(\text{CO})_4\text{-CdBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}^-$  ion assuming that it has  $\text{C}_s$  symmetry. Thus, it cannot be definitely concluded that this anionic adduct has the same structure as the  $\text{Co}(\text{CO})_4\text{InBr}_3^-$  ion. However, if a local site symmetry is applicable or if the resolution is poor (as might be expected for polar materials in polar solvents), less than the expected number of bands would be observed. Therefore, the spectral data are insufficient to determine the structure unambiguously.

**The  $\text{Fe}(\text{CO})_4\text{-MBr}_3$  System.**—The reaction between the  $\text{Fe}(\text{CO})_4^{2-}$  ion and the group III metal bromide proceeded readily in THF solution. The anion was generated as the sodium salt from sodium amalgam and  $\text{Fe}_3(\text{CO})_{12}$  since a crystalline salt was not available. However, it was found that the  $\text{HFe}(\text{CO})_4^-$  anion could be used in its place and these reactions could be carried out in  $\text{CH}_2\text{Cl}_2$ . Generally, the best yields were obtained when a twofold excess of the  $\text{HFe}(\text{CO})_4^-$  ion was employed. No attempt was made to determine the fate of the hydrogen or the remaining iron carbonyl moiety.



During the isolation of the anionic adduct  $\text{Fe}(\text{CO})_4\text{-InBr}_3^{2-}$ , another product was observed. This product was found in varying amounts regardless of which preparative procedure was used. It was isolated in low yield by a fractional crystallization process and identified as the complex anion  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$ . Attempts to improve the yield of this new adduct were only partially successful, and a clean preparation was never achieved. However, it was found that this ion would form a complex with amines which could be isolated in moderate yield by choosing the appropriate solvent system. This

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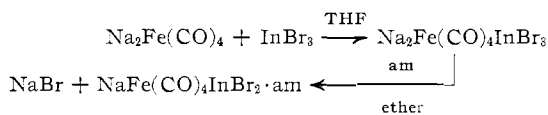
(8) F. A. Cotton and R. V. Parrish, *ibid.*, 1440 (1960).

(9) W. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

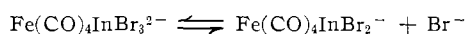
(10) A. P. Hagen and A. G. MacDiarmid, *ibid.*, **6**, 686 (1967).

(6) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

apparently forced the halogen-displacement reaction to occur by precipitation of sodium bromide ( $\text{am} = (\text{C}_2\text{H}_5)_3\text{N}$  or  $\text{C}_5\text{H}_5\text{N}$ )



A reversible equilibrium between the two species  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  and  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  was found to exist in  $\text{CH}_2\text{Cl}_2$  solution. The infrared spectra of both ions

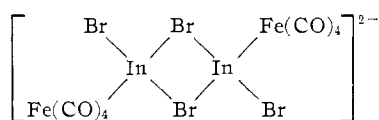


were taken as functions of added bromide ion. The data are summarized in Table II. Using the expression

$$K_d = \frac{[\text{Fe}(\text{CO})_4\text{InBr}_2^-][\text{Br}^-]}{[\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}]}$$

a value of the dissociation constant of  $0.4 \pm 0.2$  mol/l. was obtained. Figure 1 shows the infrared spectrum in the carbonyl region of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  ion in  $\text{CH}_2\text{Cl}_2$  and the spectrum of the same ion to which some bromide ion has been added. In basic solvents such as  $\text{CH}_3\text{NO}_2$  or  $\text{CH}_3\text{CN}$  the dissociation of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  ion was not observed by infrared spectroscopy. Figure 2 shows the spectrum of this ion in  $\text{CH}_3\text{CN}$ . However, the exact nature of the species present in the polar solutions formally containing the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  ion is not known. It is quite possible that dissociation has occurred followed by complexation of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion with the solvent. The infrared spectrum of the complex  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot (\text{C}_2\text{H}_5)_3\text{N}^-$  (except for poor resolution) is practically identical with that of the dianion  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$ . Furthermore, the spectrum of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  anion in  $\text{CH}_3\text{NO}_2$  shows two weak bands at 1984 and 1874  $\text{cm}^{-1}$  not present when the spectrum is taken on  $\text{CH}_2\text{Cl}_2$  solutions (see Figure 2). This probably arises from complexation of the anion by the solvent.

The nature of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion in solution is not known with certainty. However, conductance measurements over a concentration range strongly suggest the presence of a 1:1 electrolyte in the nitromethane solution.<sup>7</sup> Thus, the formation of bridged dimers such as



can be eliminated. The infrared spectrum of this ion in nitromethane shows only a slight degree of solvation. Because of the instability of the  $\text{Fe}(\text{CO})_4\text{GaBr}_3^{2-}$  ion in solution, it was not possible to demonstrate the formation of the simple monoanion  $\text{Fe}(\text{CO})_4\text{GaBr}_2^-$ . The infrared spectrum of the ion changed at an appreciable rate, and the addition of excess bromide did not prevent decomposition.

The infrared spectrum of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  anion in the carbonyl region is shown in Figure 2a and summarized in Table III for both a  $\text{CH}_3\text{CN}$  solution and the solid state. This spectrum appears to be typical

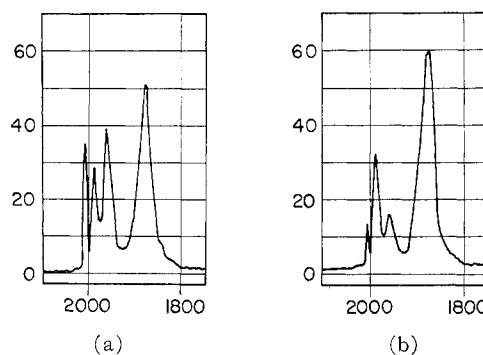


Figure 1.—(a) The infrared spectrum of  $[[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}]_2\text{Fe}(\text{CO})_4\text{InBr}_3$  in  $\text{CH}_2\text{Cl}_2$  solution. (b) The infrared spectrum of the same solution after the addition of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NBr}$ .

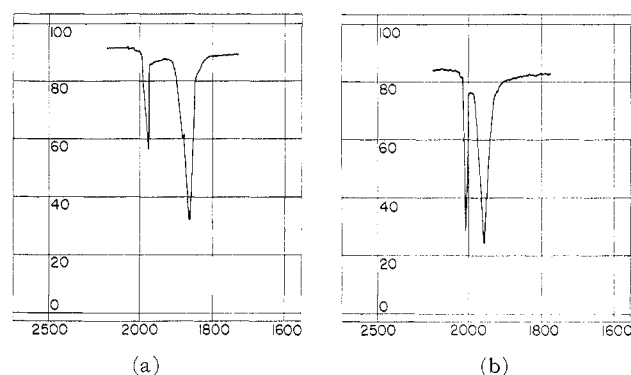


Figure 2.—(a) The infrared spectrum of  $[[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}]_2\text{Fe}(\text{CO})_4\text{InBr}_3$  in  $\text{CH}_3\text{CN}$  solution. (b) The infrared spectrum of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFe}(\text{CO})_4\text{InBr}_2$  in  $\text{CH}_2\text{Cl}_2$  solution.

of a number of substituted iron pentacarbonyl derivatives which have  $\text{C}_{3v}$  symmetry except for the frequency of the carbonyl stretching bands. These bands are shifted to lower frequency in this compound, presumably owing to the presence of the two excess electrons. Thus, like the cobalt carbonyl adducts, the indium tribromide is probably attached at the apical position in a trigonal bipyramid. The infrared spectrum of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion in the carbonyl region is less definitive and indicates that perhaps only local site symmetry is observed.<sup>11</sup> It is compatible with either  $\text{C}_{4v}$  symmetry or  $\text{C}_{3v}$  symmetry assuming that two bands are accidentally degenerated in the latter case.<sup>3</sup> Thus, the possibility that the indium dibromide moiety is attached at the apical position of a tetragonal pyramid rather than the apical position on a trigonal bipyramid must be considered.

The close similarity in the carbonyl region of the infrared spectra of the two amine complexes  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}^-$  and  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot (\text{C}_2\text{H}_5)_3\text{N}^-$  and the spectrum of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  ion suggests a closely related geometry. Therefore it is probable that (a) the amine is bonded to the indium and (b) the indium dibromide amine unit is bonded to the apical position of a trigonal bipyramid.<sup>12</sup> This structure would also mean that the iron had achieved the rare gas configura-

(11) This also appeared to be the case for the adduct  $\text{Co}(\text{CO})_4\text{CdBr}_2 \cdot (\text{C}_6\text{H}_5)_2\text{O}^-$  (see earlier discussion) and for the insertion products described in ref 3.

(12) This assumes that only local site symmetry is observed since the ion  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{am}^-$  would have  $\text{C}_s$  symmetry and four active carbonyl stretching modes would be expected.

tion and that the indium was tetracoordinate. Further coordination of the  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}^-$  ion was not observed in solution since the infrared spectrum of this ion in the presence of excess pyridine was essentially the same as the solid-state spectrum.

The infrared spectrum of the pyridine complex of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion when taken on a  $\text{CH}_2\text{Cl}_2$  solution indicates that dissociation of this adduct also occurs. Figure 3 shows the infrared spectrum in the carbonyl

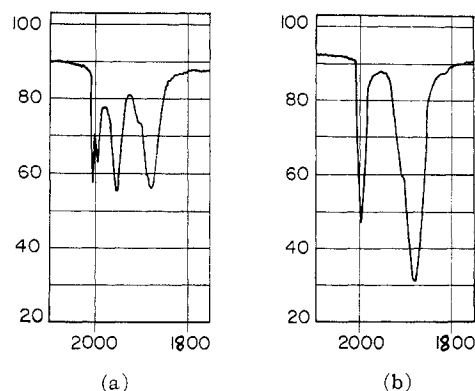


Figure 3.—(a) The infrared spectrum of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}$  in  $\text{CH}_2\text{Cl}_2$  solution. (b) The infrared spectrum of the same solution after the addition of a twofold excess of pyridine.

region of (a) the  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{C}_5\text{H}_5\text{N}^-$  ion in  $\text{CH}_2\text{Cl}_2$  and (b) the same solution to which a twofold excess of pyridine has been added. It is clear that the course of dissociation involves cleavage of the indium–nitrogen bond rather than cleavage of a bromine–indium bond since the ion  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  can be identified in solution by its spectrum. Therefore, the equilibrium may be written as



The resolution of the infrared spectrum of the other amine complex  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot (\text{C}_2\text{H}_5)_3\text{N}^-$  under the same conditions was too poor to observe dissociation if it had occurred to only a small extent. However, if it had occurred to the extent shown in Figure 3a, it would have been observed. Therefore, it appears as if the triethylamine complex is more stable than the pyridine complex. This is also supported by the slight increase in the stretching frequencies of the carbonyl modes of the latter complex.

In comparing the carbonyl frequencies of the isoelec-

tronic anions  $\text{Co}(\text{CO})_4\text{InBr}_3^-$  and  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$ , it is expected that, while the spectra will be similar, a shift to lower frequencies will occur for the more negatively charged ion. This is exactly what happens. The carbonyl stretching modes of the latter ion are approximately 100 wave numbers lower than for the cobalt derivative. However, the total charge is not the only factor in determining the frequency. The amine complexes of the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion have spectra that are essentially identical with the spectrum of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  ion even though the charge has been reduced. Furthermore, the frequency of the carbonyl modes in the spectrum of the uncomplexed ion  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  are higher by 30–75 wave numbers than the corresponding bands in the spectrum of the complexed ion  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot (\text{C}_2\text{H}_5)_3\text{N}^-$ . Thus, the formal coordination state of the indium appears to be an important factor in determining the position of these bands in addition to the total negative charge in the anion. The question of why the dissociation of the  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  occurs also has to be answered. No dissociation of the  $\text{InBr}_4^-$  ion was observed from molecular weight determinations. Therefore, the substitution of a  $\text{Fe}(\text{CO})_4^{2-}$  ion for a bromide ion results in a reduction of the Lewis acidity of the indium to a point where a bromide ion or pyridine is fairly easily lost. This, coupled with the fact that the frequency of the infrared bands in the carbonyl stretching region indicates a much lower iron–carbon interaction for the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion than for either of the adducts  $\text{Fe}(\text{CO})_4\text{InBr}_3^{2-}$  or  $\text{Fe}(\text{CO})_4\text{InBr}_2 \cdot \text{am}^-$ , suggests that a very strong  $d\pi$ – $p\pi$  interaction between the iron and indium is occurring. Thus the iron carbonyl moiety in the  $\text{Fe}(\text{CO})_4\text{InBr}_2^-$  ion competes successfully with either a bromide ion or pyridine for the vacant p orbital on the indium. This in turn should lead to a shortening of the iron–indium bond distance. A similar situation is found in comparing the boron–nitrogen bond distances in amine boranes and aminoboranes. The latter has a shorter distance owing to back-bonding of the nitrogen to the boron. Whether the shortening of the bond is as extensive in the iron carbonyl complex anion as in the boron–nitrogen system can only be answered by X-ray studies.

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