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Reactions of Dihalogenotriorgano-phosphorus, -arsenic and -antimony Compounds with $[Fe_2(CO)_9]$. Single-crystal Structures of the Iron(III) Complexes $[(Ph_3PO)_2H][FeBr_4]$ and $[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$ and of $[Fe(CO)_3(Ph_3P)_2]$†

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The reaction of $[Fe_2(CO)_9]$ with compounds of stoichiometry R_3EX_2 [$R_3E = Ph_3P$, $(p\text{-}MeOC_6H_4)_3P$, Me_2PhP, Me_3As or Ph_3Sb, X = I; $R_3E = Ph_3P$, Ph_3As or Me_3As, X = Br] has been investigated and shown to yield diverse products. A series of complexes with the ionic structure $[R_3EX][Fe(R_3E)X_3]$ [E = P, $R_3 = Ph_3$, Me_2Ph or $(p\text{-}MeOC_6H_4)_3$, X = I; $R_3E = Me_3As$; X = I or Br] has been obtained. The reaction of $[Fe_2(CO)_9]$ with Ph_3PBr_2 and Ph_3AsBr_2, however, resulted in the formation of the iron(III) complexes $[(Ph_3E)_2Br][FeBr_4]$. Hydrolysis of $[(Ph_3P)_2Br][FeBr_4]$ by trace quantities of water produces $[(Ph_3PO)_2H][FeBr_4]$, the crystal structure of which has been determined. Triphenylantimony diiodide reacted with $[Fe_2(CO)_9]$ yielding the surprising ionic adduct $[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$, remarkable not only for the phenyl migration at the antimony atom, but also for the formation of the rare $[FeI_4]^-$ anion from a zerovalent iron carbonyl complex. The reaction of $[Fe_2(CO)_9]$ with the milder diphosphine tetraiodide, $I_2Ph_2PCH_2CH_2PPh_2I_2$, produced $[Fe(CO)_3(Ph_2PCH_2CH_2PPh_2)I][I_3]$, a complex in which three CO ligands are retained.

Complexes of iron containing carbon monoxide and tertiary Group 15 ligands can be prepared in a number of ways, *e.g.* direct reaction of $[Fe(CO)_5]$ with Ph_3P in the absence of a solvent yields $[Fe(CO)_3(Ph_3P)_2]$,[1] whilst either $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ with Ph_3E (E = P, As or Sb) in refluxing tetrahydrofuran (thf) or dioxane yields both $[Fe(CO)_4(Ph_3E)]$ and $[Fe(CO)_3(Ph_3E)_2]$.[2] The well known $[Fe(CO)_3(Ph_3P)_2]$ is very inert of substitution, but is nonetheless useful as a starting material for the preparation of complexes *via* an oxidative route, *e.g.* reaction with diiodine in anhydrous Et_2O yields the pentaiodide adduct $Fe(CO)_2(Ph_3P)_2I_5$.[2] Substitution of CO by Ph_3P in $[Fe(CO)_5]$ requires temperatures > 90 °C, but $[Fe_2(CO)_9]$ reacts with tri(*p*-tolyl)phosphine (L) at 26 °C to yield a mixture of $[Fe(CO)_5]$, $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$.[3] Reaction of $[Fe(CO)_5]$ with dihalogens proceeds at solid CO_2 temperatures to form an intermediate $[Fe(CO)_5X_2]$ (X = I or Br)[4,5] which, on warming (−35 to 0 °C) gives the tetracarbonyl $[Fe(CO)_4X_2]$. The iron carbonyl halides react with tertiary phosphines (L) to yield $[Fe(CO)_2L_2X_2]$.[6] However, reaction of $[Fe_3(CO)_{12}]$ with triphenylphosphine in refluxing chloroform proceeds with loss of all CO ligands to form $[Fe(Ph_3P)Cl_3]$.[7]

We have recently begun to develop the chemistry of the novel oxidising agents R_3EX_2 (E = P, As or Sb; X = Br or I) and have found that the reaction of these with unactivated coarse-grain metal powders can yield previously unknown complexes,[8] novel isomers of known complexes,[9] complexes in high oxidation states[9,10] and in mixed oxidation states,[11] and complexes not previously considered to be possible of existence.[12] Of particular interest to the work reported here is our report of the reactions of iron powder with R_3PX_2 (X = Br or I) species. The reactions generally lead to the formation of highly air-sensitive materials which decompose on isolation even in a glove-box containing < 100 ppm O_2. For example, the reaction of Ph_2MePBr_2 with iron powder in anhydrous diethyl ether at room temperature (r.t.) for 12 h yields a white solid. Prolonged exposure of this solid to dioxygen leads to the formation of an orange complex which exhibits a strong ν(PO) IR band. This complex was not characterised. However, exposure of the white solid to a trace quantity of dioxygen (< 100 ppm) led to the isolation of an intensely purple complex, which was shown by X-ray crystallography to be a trigonal-bipyramidal complex of iron(III), *trans*-$[Fe(PhMe_2P)_2Br_3]$, which represented only the third reported crystallographically characterised iron(III)–phosphine complex. It also appears that only one iron(II)–phosphine complex has ever been crystallographically characterised, $[Fe(Et_3P)_2Br_2]$.[13]

We report here studies on the reaction of $[Fe_2(CO)_9]$ with some R_3EX_2 species [$R_3 = Ph_3$, $(p\text{-}MeOC_6H_4)_3$ or Me_2Ph, E = P, X = I; $R_3 = Ph_3$, E = P or As, X = Br; $R_3 = Me_3$, E = As, X = Br or I], and with Ph_3SbI_2 and $I_2Ph_2PCH_2CH_2PPh_2I_2$. In the light of our discovery of the reactions of these R_3EX_2 agents with metal powders, it is clearly of interest to examine the reactions of these new oxidising agents with other zerovalent metal species such as $[Fe_2(CO)_9]$.

Results and Discussion

Reaction of R_3PI_2 [$R_3 = Ph_3$, $(p\text{-}MeOC_6H_4)_3$ *or* Me_2Ph] *and* Me_3AsX_2) (X = I *or* Br) *with* $[Fe_2(CO)_9]$.—Diiron nonacarbonyl was treated with a number of R_3PI_2 species in a 1:4 molar ratio in anhydrous diethyl ether under strictly anhydrous and anaerobic conditions; green or grey products formed within 1–2 h. For the trialkyl R_3PI_2 (R = Et, Pr^n or Bu^n) the products, however, proved too unstable to isolate, forming black oils on removal of the solvent, even in a dry-box under argon (< 100 ppm O_2). However, when the R_3PI_2 (R = aryl) or Me_2PhPI_2 compounds were used stable complexes could be isolated under anaerobic conditions. The three complexes **1**–**3** have the empirical formula $Fe(R_3P)_2I_4$, Table 1. Their IR spectra show no evidence of any ν(CO) bands.

Low stability in air of complexes **1**–**3** provided difficulties in obtaining magnetic moments and Raman spectra, Table 2.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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However, **1** exhibited μ_{eff} well within the accepted range for a tetrahedral iron(II) species. The Raman spectra are similar in appearance to those of the cobalt(II) species $[R_3PI][Co(R_3P)I_3]$.[8] A very strong band is exhibited at 187 cm^{-1} for **1**, Fig. 1, and 167 cm^{-1} for **3**, characteristic of ν(P–I) in the $[R_3PI]^+$ ion.[8] This suggests that, once again, the use of these oxidising agents on low-oxidation-state metallic species can produce complexes of the type $[R_3PI][M(R_3P)I_3]$. Several attempts were made to grow crystals of **1**–**3** suitable for X-ray diffraction studies in order to confirm the proposed ionic structure; however, the low solubility of these complexes in diethyl ether and their low long-term stability in more polar solvents precluded this.

The trimethylarsenic dihalides Me_3AsX_2 (X = Br or I) were also treated with $[Fe_2(CO)_9]$ in a 4:1 molar ratio and the products isolated, **4** and **5**, also had the empirical formula $Fe(Me_3As)_2X_4$; on exposure to air they quickly decompose to form orange (X = Br) or black (X = I) oils. A room-temperature magnetic moment of $\mu_{eff} = 4.98$ μ_B for **5** is consistent with a tetrahedral iron(II) species. The low-frequency bands in the Raman spectrum of **4** are less strong than those of compounds **1**–**3**. Nonetheless, there is a strong band at 315 cm^{-1}, which is probably due to ν(Fe–Br) and a fairly strong band at 167 cm^{-1}, probably due to ν(As–Br). It thus seems likely that complexes **4** and **5** also have the ionic structure $[Me_3AsX][Fe(Me_3As)X_3]$ containing the tetrahedral iron(II) cation, analogous to the phosphine derivatives **1**–**3**.

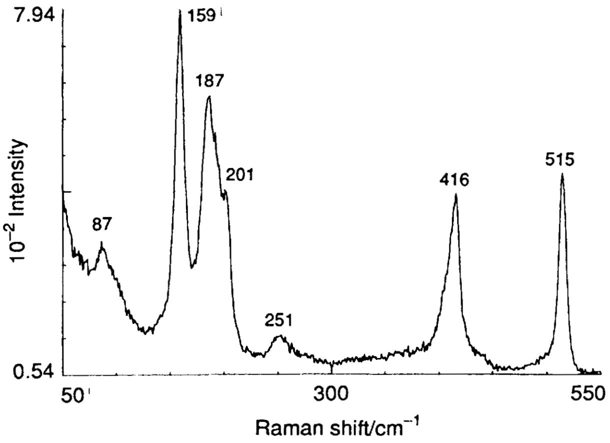

Fig. 1 Low-frequency Raman spectrum of $[Ph_3PI][Fe(Ph_3P)I_3]$

Reaction of Ph_3EBr_2 (E = P *or* As) *with* $[Fe_2(CO)_9]$.—As for the preparation of complexes **1**–**5**, the dibromo species Ph_3EBr_2 (E = P or As) were treated with $[Fe_2(CO)_9]$ in a 4:1 ratio. However, the products had the empirical formula $Fe(Ph_3E)_2Br_5$. The reactions were repeated in a 5:1 ratio and the products were identical and obtained in virtually quantitative yield, presumably according to reaction (1).

$$[Fe_2(CO)_9] + 5Ph_3EBr_2 \longrightarrow 2Fe(Ph_3E)_2Br_5 + Ph_3E + 9CO \quad (1)$$

Complete removal of all carbon monoxide ligands was confirmed by the absence of any ν(CO) bands in the infrared spectra of the $Fe(Ph_3E)_2Br_5$ (E = P **6** or As **7**) complexes. Several attempts were made to grow crystals of **6** and **7**, but their low stability made this very difficult. Trace contamination of **6** with water occurred on one such attempt and led to the isolation of single crystals of the ionic product $[(Ph_3PO)_2H][FeBr_4]$ from diethyl ether solution.

The isolation of this product of hydrolysis does, perhaps, give an insight into the possible structure of complexes **6** and **7**. The low-frequency Raman spectra of both complexes exhibit bands assignable to both ν(Fe–Br) and δ(Br–Fe–Br) in the $[FeBr_4]^-$ anion, Table 2. In addition, **6** also exhibits a band at 249 cm^{-1} attributable to ν(P–Br–P) in the $[(Ph_3P)_2Br]^+$ cation. No such absorption is discernible for the arsenic analogue **7**, but this may be hidden by the intense band centred at 203 cm^{-1}, due to ligand phenyl modes. The extreme sensitivity of both **6** and **7** to moisture made magnetic measurements difficult, but a reproducible value of $\mu_{eff} = 5.98$ μ_B for **7** supports a tetrahedral structure for this iron(III) complex. From the spectroscopic evidence it therefore seems likely that the structure of $Fe(Ph_3P)_2Br_5$ consists of $[(Ph_3P)_2Br][FeBr_4]$. Although there are no reported examples of the $[Ph_3P–Br–Ph_3P]^+$ cation in

Table 1 Elemental analyses for the iron complexes[a]

Complex	Colour	Analysis (%)		
		C	H	X[b]
1 $[Ph_3PI][Fe(Ph_3P)I_3]$	Dark green	39.8 (39.7)	2.6 (2.8)	4.6 (46.7)
2 $[Me_2PhPI][Fe(Me_2PhP)I_3]$	Grey	21.9 (22.9)	2.6 (2.6)	61.5 (60.5)
3 $[(p\text{-}MeOC_6H_4)_3P][Fe\{(p\text{-}MeOC_6H_4)_3P\}I_3]$	Dark green	39.4 (39.7)	3.0 (3.3)	40.5 (40.1)
4 $[Me_3AsBr][Fe(Me_3As)Br_3]$	Cream	11.4 (11.7)	2.7 (2.9)	51.9 (51.9)
5 $[Me_3AsI][Fe(Me_3As)I_3]$	Brown	9.0 (9.0)	2.4 (2.2)	61.4 (63.2)
6 $[(Ph_3P)_2Br][FeBr_4]$	Peach	43.8 (44.1)	2.9 (3.1)	40.6 (40.8)
7 $[(Ph_3As)_2Br][FeBr_4]$	Orange	39.1 (40.4)	2.6 (2.8)	38.2 (37.5)
8 $[Fe(CO)_3(dppe)I][I_3]$	Dark brown	33.3 (33.3)	2.3 (2.3)	48.7 (48.6)
9 $[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$	Black	30.0 (31.5)	2.1 (2.2)	48.9 (47.6)

[a] Calculated values in parentheses. [b] X = I or Br.

Table 2 Spectroscopic and magnetic data for some of the iron complexes

Complex	μ_{eff}/μ_B[a]	ν(EX)[b]/cm^{-1}	ν(Fe–Br)/cm^{-1}	δ(Br–Fe–Br)/cm^{-1}	ν(CO)/cm^{-1}
1	5.3	187	—	—	—
3	5.2	167	—	—	—
5	4.98	167	—	—	—
6	—	249	297	85	—
7	5.98	—	294	91	—
8	—	—	—	—	2037.1w 2023.6w 1985.0s

[a] $\mu_B \approx 9.274\,02 \times 10^{-24}$ JT^{-1}. [b] E = P or As, X = I or Br.

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the solid state, it is not without precedence. From conductiometric studies of the reactions of tertiary phosphines with dibromine in acetonitrile solution under anhydrous conditions, Harris and McKechnie[14] postulated that 1:1 complexes of stoichiometry $[(R_3P)_2Br]Br_3$ were formed for R = Bu^n, C_8H_{17} or C_6H_{11}. No other bromine-bridged cations of this type have been reported, but in view of the recently reported iodine-bridged cations in the complexes $[(Ph_3AsI)_2I][Co(Ph_3As)I_3]$[15] and $[(Bu^n{}_3PI)_2I][Co(Bu^n{}_3PI)(\mu\text{-}I)I_3]$[16] it seems likely that cations of this nature could also be formed with a bromine bridge.

Crystal Structure of $[(Ph_3PO)_2H][FeBr_4]$.—Dark orange crystals of $[(Ph_3PO)_2H][FeBr_4]$ were isolated from a slurry containing $Fe(Ph_3P)_2Br_5$ **6** in diethyl ether. Formation of the former can be explained by trace contamination of the slurry with moist air. The structure, Fig. 2, consists of a tetrahedral $[FeBr_4]^-$ anion with a hydrogen-bonded $[(Ph_3PO)_2H]^+$ counter ion. Selected bond distances and angles are given in Table 3, atomic coordinates in Table 4. Complexes containing the $[FeBr_4]^-$ anion are not uncommon and nine other examples have been structurally characterised.[17] The anion revealed here is typical of all $[FeBr_4]^-$ anions, all bond lengths being close to 2.3 Å and angles close to that of a regular tetrahedron, 109°. The cation is probably produced by reaction (2).

$$[(Ph_3P)_2Br]^+ + 2H_2O \longrightarrow [(Ph_3PO)_2H]^+ + HBr \quad (2)$$

Crystal Structure of $[Fe(CO)_3(Ph_3P)_2]$.—After isolation of the bulk product, $Fe(Ph_3P)_2Br_5$ **6**, from the reaction of Ph_3PBr_2 with $[Fe_2(CO)_9]$ in a 4:1 molar ratio, pale yellow crystals were formed in the diethyl ether filtrate. These were thought to be of complex **6**; however, subsequent single-crystal X-ray studies showed that they were of $[Fe(CO)_3(Ph_3P)_2]$. Although this complex has been known for a long time[1] and is a common product of the reaction of iron carbonyl complexes with triphenylphosphine,[18] the crystal structure has never been reported. This structure, Fig. 3, consists of a trigonal-bipyramidal iron centre with *trans* phosphine groups, consistent with that predicted from vibrational spectroscopic studies. Some disordered diethyl ether of crystallisation is incorporated into the structure. Selected bond lengths and angles are given in Table 5, atomic coordinates in Table 6.

The IR spectrum of the bulk product **6** from this reaction exhibits no ν(CO) bands, thus implying that all $[Fe(CO)_3(Ph_3P)_2]$ formed remains in solution. Complex **6** was isolated in *ca.* 80% yield (the maximum calculated), and so we propose that the formation of the tricarbonyl species $[Fe(CO)_3(Ph_3P)_2]$ is due to reaction of the excess of Ph_3P and $[Fe_2(CO)_9]$ after

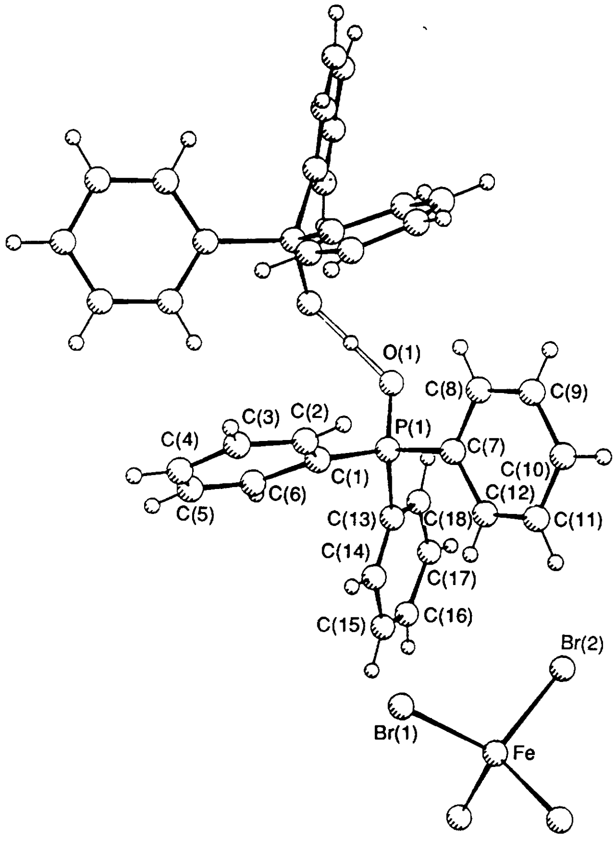

Fig. 2 Crystal structure of $[(Ph_3PO)_2H][FeBr_4]$

Table 3 Selected bond distances (Å) and angles (°) for $[(Ph_3PO)_2H][FeBr_4]$*

Br(1)–Fe	2.336(6)	P(1)–O(1)	1.53(2)
Br(2)–Fe	1.330(5)		
Br(1)–Fe–Br(1)	107.1(3)	Br(2)–Fe–Br(2)	107.0(3)
Br(1)–Fe–Br(2)	111.3(1)	O(1)–P(1)–C(1)	113(1)
Br(1)–Fe–Br(2)	110.1(2)	O(1)–P(1)–C(7)	109(1)
Br(1)–Fe–Br(2)	110.1(2)	O(1)–P(1)–C(13)	112(1)
Br(1)–Fe–Br(2)	111.3(1)		

* Estimated standard deviations in the least significant figure are given in parentheses.

Table 4 Fractional atomic coordinates for non-hydrogen atoms of $[(Ph_3PO)_2H][FeBr_4]$

Atom	*x*	*y*	*z*
Br(1)	0.5659(3)	0.1645(3)	0.1736(4)
Br(2)	0.5960(2)	−0.0079(3)	0.3671(3)
Fe	$\frac{1}{2}$	0.0781(4)	$\frac{1}{4}$
P(1)	0.8685(6)	0.0257(6)	0.2559(8)
O(1)	0.949(1)	−0.022(1)	0.285(2)
C(1)	0.860(2)	0.100(3)	0.175(3)
C(2)	0.886(2)	0.178(3)	0.195(3)
C(3)	0.885(2)	0.236(2)	0.120(3)
C(4)	0.852(2)	0.218(2)	0.022(3)
C(5)	0.826(2)	0.142(3)	−0.004(3)
C(6)	0.830(2)	0.084(2)	0.066(3)
C(7)	0.870(2)	0.078(2)	0.363(2)
C(8)	0.945(2)	0.101(2)	0.439(3)
C(9)	0.944(2)	0.141(2)	0.520(3)
C(10)	0.869(3)	0.158(3)	0.530(4)
C(11)	0.794(2)	0.136(3)	0.455(3)
C(12)	0.795(2)	0.096(2)	0.377(3)
C(13)	0.780(3)	−0.038(3)	0.203(3)
C(14)	0.705(3)	−0.013(2)	0.149(3)
C(15)	0.638(3)	−0.060(3)	0.117(4)
C(16)	0.647(3)	−0.141(5)	0.134(4)
C(17)	0.724(4)	−0.177(2)	0.194(4)
C(18)	0.794(2)	−0.126(3)	0.224(3)

Table 5 Selected bond lengths (Å) and angles (°) for $[Fe(CO)_3(Ph_3P)_2]$*

Fe–P(1)	2.225(3)	Fe–C(3)	1.755(8)
Fe–P(2)	2.207(3)	O(1)–C(1)	1.136(7)
Fe–C(1)	1.783(7)	O(2)–C(2)	1.150(7)
Fe–C(2)	1.779(8)	O(3)–C(3)	1.157(7)
P(1)–Fe–P(2)	172.54(8)	P(2)–Fe–C(2)	87.7(2)
P(1)–Fe–C(1)	94.8(2)	P(2)–Fe–C(3)	88.8(2)
P(1)–Fe–C(2)	87.3(2)	C(1)–Fe–C(2)	117.1(3)
P(1)–Fe–C(3)	89.7(2)	C(1)–Fe–C(3)	116.9(3)
P(2)–Fe–C(1)	92.4(2)	C(1)–Fe–C(3)	125.9(3)

* Estimated standard deviations in the least significant figure are given in parentheses.

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Table 6 Fractional atomic coordinates for non-hydrogen atoms of $[Fe(CO)_3(Ph_3P)_2]$

Atom	*x*	*y*	*z*
Fe	0.916 28(8)	0.305 90(7)	0.835 7(1)
P(1)	1.085 1(1)	0.208 5(1)	0.799 6(2)
P(2)	0.749 9(1)	0.385 5(1)	0.883 5(2)
O(1)	0.930 3(4)	0.486 2(4)	0.794 8(6)
O(2)	1.009 6(4)	0.217 6(4)	1.119 2(5)
O(3)	0.802 8(4)	0.234 7(4)	0.595 0(6)
C(1)	0.925 5(5)	0.415 6(5)	0.809 2(7)
C(2)	0.973 4(5)	0.251 9(5)	1.007 7(8)
C(3)	0.848 5(5)	0.262 7(5)	0.690 4(8)
C(4)	1.100 3(5)	0.086 2(5)	0.756 5(7)
C(5)	1.151 6(8)	0.036 7(6)	0.660(1)
C(6)	1.160(1)	−0.056 1(7)	0.627(1)
C(7)	1.114(1)	−0.096 2(7)	0.690(1)
C(8)	1.061 3(8)	−0.048 4(6)	0.789(1)
C(9)	1.054 1(7)	0.043 2(5)	0.820 2(8)
C(10)	1.207 9(5)	0.188 3(4)	0.947 9(6)
C(11)	1.211 5(5)	0.266 3(5)	1.023 4(7)
C(12)	1.304 4(6)	0.257 0(6)	1.129 2(7)
C(13)	1.397 4(6)	0.168 7(7)	1.164 0(8)
C(14)	1.396 2(6)	0.089 0(6)	1.093 4(9)
C(15)	1.302 4(6)	0.098 7(5)	0.984 5(7)
C(16)	1.125 7(5)	0.246 4(4)	0.662 9(6)
C(17)	1.045 0(6)	0.289 3(6)	0.538 5(9)
C(18)	1.075 7(8)	0.315 3(7)	0.431 1(9)
C(19)	1.183 6(9)	0.298 2(6)	0.442(1)
C(20)	1.264 3(7)	0.256 2(6)	0.563 9(9)
C(21)	1.236 2(6)	0.229 2(5)	0.670 3(7)
C(22)	0.667 1(5)	0.316 3(4)	0.875 5(6)
C(23)	0.550 6(5)	0.357 6(4)	0.843 5(7)
C(24)	0.491 5(6)	0.303 7(6)	0.848 4(8)
C(25)	0.551 8(7)	0.206 5(6)	0.888(1)
C(26)	0.669 1(7)	0.163 0(6)	0.922(1)
C(27)	0.726 3(6)	0.217 8(5)	0.911(1)
C(28)	0.646 2(5)	0.496 0(4)	0.774 6(6)
C(29)	0.562 6(5)	0.572 7(5)	0.823 2(7)
C(30)	0.484 5(5)	0.654 1(5)	0.737(1)
C(31)	0.488 2(6)	0.660 8(5)	0.602 8(9)
C(32)	0.569 0(7)	0.586 6(6)	0.554 4(7)
C(33)	0.647 7(6)	0.505 2(5)	0.639 9(7)
C(34)	0.759 5(5)	0.427 4(4)	1.060 0(6)
C(35)	0.809 9(6)	0.489 9(5)	1.101 4(7)
C(36)	0.823 3(6)	0.520 7(5)	1.235 0(8)
C(37)	0.787 1(6)	0.487 1(6)	1.328 6(7)
C(38)	0.739 9(6)	0.424 5(5)	1.289 8(7)
C(39)	0.725 7(6)	0.394 2(5)	1.155 4(7)

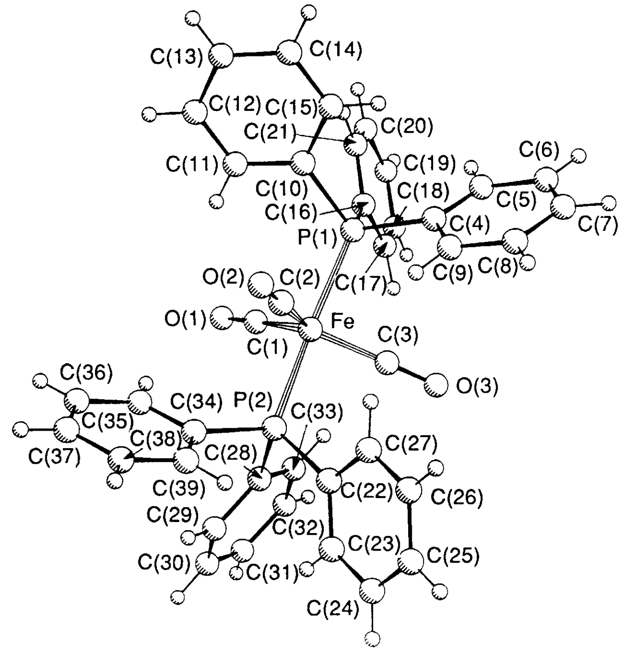

Fig. 3 Crystal structure of $[Fe(CO)_3(Ph_3P)_2]$

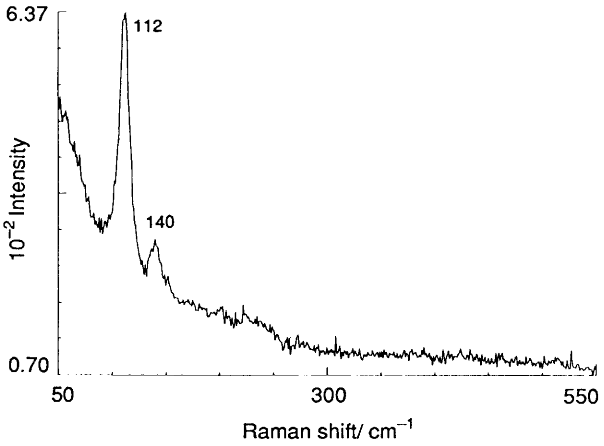

Fig. 4 Low-frequency Raman spectrum of $[Fe(CO)_3(dppe)I][I_3]$

formation of **6** was complete. In the light of the proposed structure for **6** it seems unlikely that $[Fe(CO)_3(Ph_3P)_2]$ is formed as an intermediate in the reaction, as this would involve the formation and then cleavage of Fe–P bonds. However, as the mechanistic route of the reaction is not known a phosphine-containing iron intermediate cannot entirely be ruled out.

The reaction was successfully repeated in a 5:1 Ph_3PBr_2 : $[Fe_2(CO)_9]$ ratio; complex **6** was formed and no other product could be isolated which contained carbon monoxide as a ligand.

Reaction of $I_2Ph_2PCH_2CH_2PPh_2I_2$ *with* $[Fe_2(CO)_9]$.—In vivid contrast to the reaction of the R_3PI_2 species above, the diphosphine tetraiodide $I_2Ph_2PCH_2CH_2PPh_2I_2$ does not react with $[Fe_2(CO)_9]$ (2:1 molar ratio) under anhydrous conditions in diethyl ether to remove all carbon monoxide ligands from the iron. Instead, a dark brown solid of stoichiometry $Fe(CO)_3(dppe)I_4$ **8** (dppe = $Ph_2PCH_2CH_2PPh_2$) is produced, Table 1; the presence of carbon monoxide in the complex is shown by three bands in the IR spectrum in the range 1980–2040 cm^{-1}, Table 2. The ultraviolet spectrum in acetonitrile solution consists of two bands at 360.5 and 293.5 nm, indicative of the presence of the I_3^- anion,[19] and the presence of I_3^- in the solid state is confirmed by the weak low-frequency Raman absorption at 140 cm^{-1} and a strong absorption at 112 cm^{-1}, Fig. 4, both attributable to ν(I–I) in the I_3^- anion.[20] Thus, this complex is the iron(II) complex, $[Fe(CO)_3(dppe)I][I_3]$.

Close consideration of the ν(CO) bands in the IR spectrum allows the probable structure of complex **8** to be deduced. The spectrum consists of a strong band at 1985.0 and two weak bands at 2023.6 and 2037.1 cm^{-1}. This is typical of an octahedral complex with carbon monoxide ligands in facial geometry,[21] and this structure is shown in **A**. The strong band corresponds to the A″ mode of vibration for the axial carbonyl ligand, the two weaker bands being attributed to the A″ modes of the equatorial carbonyls. This type of structure would also be expected from a consideration of the relative substitution lability of carbonyl ligands in an octahedral complex.[22] Carbonyls *trans* to one another are considered to be more labile

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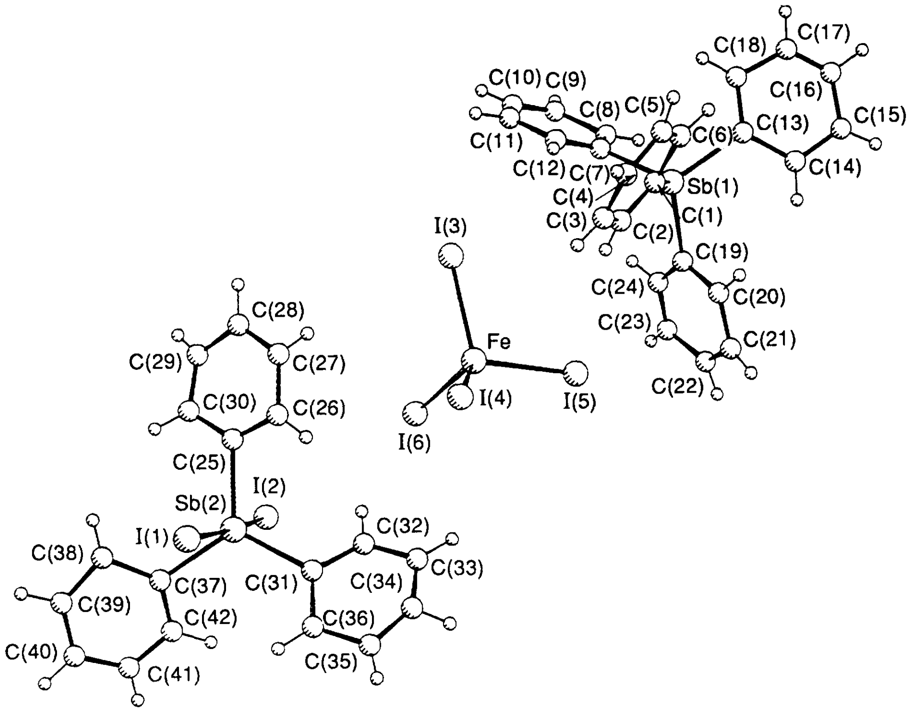
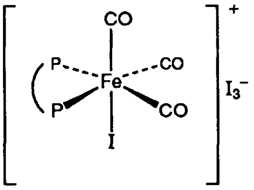


Fig. 5 Crystal structure of $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$



A

Table 7 Selected bond distances (Å) and angles (°) for $[Ph_4Sb]$-$[FeI_4]{\cdot}Ph_3SbI_2$*

I(1)–Sb(2)	2.910(4)	I(4)–Fe	2.525(7)
I(2)–Sb(2)	2.850(4)	I(5)–Fe	2.541(6)
I(3)–Fe	2.545(7)	I(6)–Fe	2.553(7)
I(1)–Sb(2)–I(2)	174.8(1)	I(4)–Fe–I(5)	109.5(2)
I(3)–Fe–I(4)	108.3(2)	I(4)–Fe–I(6)	111.9(2)
I(3)–Fe–I(5)	108.6(2)	I(5)–Fe–I(6)	106.9
I(3)–Fe–I(6)	111.6(3)		

* Estimated standard deviations in the least significant figure are given in parentheses.

than those *trans* to another ligand, and thus a facial structure with *cis* carbonyls is favoured.

Reaction of Ph_3SbI_2 *with* $[Fe_2(CO)_9]$.—Triphenylantimony diiodide was treated with $[Fe_2(CO)_9]$ in 2:1, 3:1, 4:1 and 5:1 molar ratios under anhydrous and anaerobic conditions in diethyl ether; in each case a dark solid was formed, which defied our attempts at characterisation being of variable composition and extremely insoluble. However, after filtration of the bulk solids from each of these reactions, black crystals rapidly formed in the filtrates. X-Ray diffraction studies showed that the crystals formed from the 4:1 molar ratio reaction filtrate were of the ionic complex $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$, Fig. 5. X-Ray powder diffraction studies of the crystals formed from the filtrates of the reactions involving other mole ratios of Ph_3SbI_2 and $[Fe_2(CO)_9]$ confirmed that the common crystalline product isolated was $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$, and this extremely soluble complex is the bulk product of these reactions.

Crystal Structure of $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$.—This structure is remarkable. Not only has the iron in $[Fe_2(CO)_9]$ been oxidised from Fe^0 to Fe^{III} under anaerobic conditions, but, less remarkably, phenyl migration has occurred to yield the tetraphenylantimony cation. It is generally believed that iron(III) and the I^- anion are incompatible because of the highly oxidising nature of the former and the strongly reducing properties of the latter.[23] However, a small number of examples of the $[FeI_4]^-$ anion are known. It has been seen to exist in conjunction with heterometallic clusters, as in $[Fe\{Cr_2(\eta\text{-}C_5H_5)_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2\}_2]^+[FeI_4]^-$,[24] with other iron(III) ions, *e.g.* $[Fe(CH_2O)_6][FeI_4]_2{\cdot}I_2$,[25] and also with simple ammonium cations such as NEt_4^+.[26] In this complex the $[FeI_4]^-$ moiety is close to a regular tetrahedron with angles of 106.9–111.9° and bond lengths close to 2.5 Å (Table 7; atomic coordinates in Table 8). These are typical values for the $[FeI_4]^-$ anion.

Migration of the phenyl group in Ph_3SbI_2 has been observed previously. Although most R_3EI_2 (E = P, As or Sb) adducts ionise in polar solvents to form the $[R_3EI]^+$ cation, it has recently been shown that the weaker E–C bond in Ph_3SbI_2 leads to this type of migration in acetonitrile solution.[27] The $[R_3PI]^+$ cation has frequently been seen in complexes prepared by the reaction of tertiary phosphine dihalide compounds with coarse-grain metal powders and also with transition-metal carbonyl complexes. Thus it seems likely that ionisation of their antimony analogue Ph_3SbI_2 also occurs, leading to the tetraphenylantimony cation $[Ph_4Sb]^+$ rather than to $[Ph_3SbI]^+$.

Conclusion

The novel complexes $[R_3EX][Fe(R_3E)X_3]$ have been prepared by the reaction of 4 molar equivalents of R_3EX_2 with diiron nonacarbonyl. This general ionic structure is the most common structure seen for complexes prepared by the reaction of R_3EX_2

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Table 8 Fractional atomic coordinates for non-hydrogen atoms of $[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	0.9440(1)	0.4056(4)	0.2731(1)	C(18)	0.172(2)	1.122(5)	0.358(2)
I(2)	0.9467(2)	0.7528(4)	0.4571(1)	C(19)	0.358(2)	0.881(4)	0.458(1)
I(3)	0.5607(2)	0.9344(4)	0.3198(1)	C(20)	0.339(2)	0.750(5)	0.466(2)
I(4)	0.6201(2)	0.5292(3)	0.3252(1)	C(21)	0.368(2)	0.659(4)	0.507(2)
I(5)	0.5295(1)	0.6853(3)	0.4439(1)	C(22)	0.414(2)	0.747(5)	0.550(2)
I(6)	0.7243(2)	0.8032(4)	0.4430(2)	C(23)	0.436(3)	0.887(6)	0.544(2)
Sb(1)	0.3069(1)	0.9757(3)	0.3871(1)	C(24)	0.405(2)	0.937(4)	0.495(2)
Sb(2)	0.9414(1)	0.5723(3)	0.3679(1)	C(25)	0.878(2)	0.717(4)	0.316(1)
Fe	0.6102(3)	0.7377(6)	0.3824(2)	C(26)	0.810(2)	0.680(4)	0.298(2)
C(1)	0.309(2)	0.847(4)	0.321(1)	C(27)	0.769(3)	0.781(6)	0.266(2)
C(2)	0.364(2)	0.777(5)	0.316(2)	C(28)	0.794(3)	0.904(6)	0.257(2)
C(3)	0.366(2)	0.698(5)	0.268(2)	C(29)	0.865(3)	0.940(6)	0.282(2)
C(4)	0.311(2)	0.698(4)	0.229(2)	C(30)	0.908(2)	0.836(6)	0.303(2)
C(5)	0.253(2)	0.774(5)	0.232(2)	C(31)	0.888(2)	0.411(4)	0.399(1)
C(6)	0.247(2)	0.841(5)	0.277(2)	C(32)	0.827(2)	0.443(5)	0.413(2)
C(7)	0.360(2)	1.157(4)	0.372(2)	C(33)	0.782(2)	0.353(5)	0.427(2)
C(8)	0.354(3)	1.269(6)	0.405(2)	C(34)	0.809(2)	0.232(5)	0.428(2)
C(9)	0.393(2)	1.396(5)	0.392(2)	C(35)	0.864(2)	0.165(5)	0.414(2)
C(10)	0.426(2)	1.391(5)	0.355(2)	C(36)	0.911(2)	0.263(6)	0.401(2)
C(11)	0.427(2)	1.285(6)	0.327(2)	C(37)	1.050(2)	0.565(4)	0.382(1)
C(12)	0.392(2)	1.161(4)	0.334(1)	C(38)	1.085(2)	0.628(4)	0.344(1)
C(13)	0.204(2)	1.020(4)	0.390(1)	C(39)	1.157(2)	0.593(5)	0.360(2)
C(14)	0.174(2)	0.944(5)	0.429(2)	C(40)	1.187(2)	0.516(6)	0.402(2)
C(15)	0.108(2)	0.971(5)	0.430(2)	C(41)	1.152(3)	0.481(6)	0.438(2)
C(16)	0.078(3)	1.071(6)	0.394(2)	C(42)	1.082(3)	0.499(6)	0.427(2)
C(17)	0.104(3)	1.145(6)	0.365(2)				

species with both coarse-grain metal powders and transition-metal carbonyl complexes.[8] The dibromo-adducts Ph_3PBr_2 and Ph_3AsBr_2 react with $[Fe_2(CO)_9]$ to yield the iron(III) complexes $[(Ph_3E)_2Br][FeBr_4]$. The oxidation of the iron atom from the 0 to +III state provides a further example of the use of the R_3EX_2 species as powerful oxidising agents. This is reinforced by the formation of the ionic complex $[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$ from Ph_3SbI_2 and $[Fe_2(CO)_9]$.

The diphosphine analogue of the dihalogenophosphoranes, $I_2Ph_2PCH_2CH_2PPh_2I_2$, has been seen to act as a much milder reagent than are the R_3EX_2 species. Whilst still oxidising the iron atom of $[Fe_2(CO)_9]$ to the +II state, three CO groups are retained at the iron centre. This is the only complex prepared from the reaction of $[Fe_2(CO)_9]$ with a tertiary phosphine dihalide adduct in which any carbon monoxide ligands have been retained.

It should be noted that previous studies of the reaction of dihalogenotriorganophosphorus compounds with coarse-grain iron powder have led almost exclusively to the formation of highly substitution-labile complexes which could not be characterised due to their severe reactivity with trace quantities of dioxygen. Although this extreme sensitivity is seen to some extent in the reaction of these species with $[Fe_2(CO)_9]$, the complexes formed are generally less labile than those prepared from the metal powder, thus indicating that this novel reaction route may be useful in the preparation of more stable transition metal–phosphine complexes.

Experimental

The extreme sensitivity of all of the iron complexes described to air and moisture required strictly anaerobic and anhydrous conditions to be employed throughout both preparation and sample handling. All manipulations of the complexes were made inside a Vacuum Atmospheres HE-493 glove-box under an argon atmosphere. Diethyl ether (BDH) was dried over sodium wire for 24 h and then distilled over CaH_2 under a nitrogen atmosphere; it was distilled directly into the reaction vessel and degassed thoroughly prior to use. Diiron nonacarbonyl (Aldrich) was used as received. It was stored in a dark glass, gas-tight jar under nitrogen in a refrigerator (*ca.* −4 °C). All manipulations of $[Fe_2(CO)_9]$ were made in a dry-box under argon. The preparation of the tertiary phosphine diiodide species, R_3PI_2, is described elsewhere.[28] Triphenylphosphine dibromide and the arsenic and antimony adducts, Ph_3AsBr_2 and Ph_3SbI_2, were prepared in an analogous manner by the reaction of equimolar quantities of R_3E with the dihalogen in diethyl ether, under anhydrous and anaerobic conditions.

Me_3AsI_2 *and* Me_3AsBr_2.—The reaction between trimethylarsine and the dihalogens is violent and thus a more cautious method was employed for their preparation. The adducts were prepared in pre-dried reaction tubes fitted with a Rotaflo tap, in a dry-box under argon. To a solution of dihalogen (8.3 mmol) in anhydrous diethyl ether (*ca.* 50 cm^3) was added dropwise a solution of trimethylarsine (1 g, 8.3 mmol). The resultant mixture was stirred for *ca.* 24 h and the white solid product was isolated using standard Schlenk techniques.

$I_2Ph_2PCH_2CH_2PPh_2I_2$.—The diphosphine tetraiodide species was prepared by a similar method to that for R_3PI_2. Two molar equivalents of diiodine were added to a slurry of dppe in anhydrous diethyl ether under argon.

$[Ph_3PI][Fe(Ph_3P)I_3]$.—The compound Ph_3PI_2 (0.60 g, 1.2 mmol) was slurried in anhydrous diethyl ether (*ca.* 50 cm^3) in a Rotaflo tube under argon. The complex $[Fe_2(CO)_9]$ (0.11 g, 0.3 mmol) in a preweighed argon-filled ampoule in a dry-box under argon was added to the slurried Ph_3PI_2 against a stream of argon. The resultant dark green solid was collected by standard Schlenk techniques.

Prepared similarly were: $[R_3EX][Fe(R_3E)X_3]$ ($E = P$, $R_3 = Me_2Ph$ or $(p\text{-}MeOC_6H_4)_3$, $X = I$; $E = As$, $R_3 = Me_3$, $X = I$ or Br), all yields quantitative; $[(Ph_3E)_2Br][FeBr_4]$ ($E = As$ or P), using a 5:1 molar ratio of Ph_3EBr_2:$[Fe_2(CO)_9]$; $[Fe(CO)_3(dppe)I][I_3]$, by reaction of 2 molar equivalents of $I_2Ph_2PCH_2CH_2PPh_2I_2$ with $[Fe_2(CO)_9]$.

$[Ph_4Sb][FeI_4]\cdot Ph_3SbI_2$.—The reaction of 4 molar equivalents Ph_3SbI_2 with $[Fe_2(CO)_9]$ was carried out in diethyl ether as for $[Ph_3PI][Fe(Ph_3P)I_3]$. The resultant black bulk solid was removed by standard Schlenk techniques and the black filtrate

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Table 9 Crystal data and details of refinement for the complexes $[(Ph_3PO)_2H][FeBr_4]$, $[Fe(CO)_3(Ph_3P)_2]$ and $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$

	$[(Ph_3PO)_2H][FeBr_4]$	$[Fe(CO)_3(Ph_3P)_2]$	$[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$
M	933.05	701.52	1600.51
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	17.329(6)	13.51(1)	20.143(7)
b/Å	16.077(5)	15.34(1)	9.717(3)
c/Å	14.596(5)	10.040(9)	25.397(9)
α/°	90	93.85(8)	90
β/°	112.63(3)	105.84(8)	102.62(3)
γ/°	90	63.92(6)	90
U/Å^3	3754(4)	1795(3)	4851(5)
Z	4	2	4
D_c/g cm^{-3}	1.651	1.298	2.191
$F(000)$	1836	730	2932
μ/cm^{-1}	47.32	5.43	52.15
Total data measured	2936	6624	9398
Maximum 2θ/°	50.0	50.0	50.1
No. of unique reflections	2818	6315	9112
No. of observed reflections $[I_o > 2\sigma(I_o)]$	655	2952	2359
No. of parameters	179	406	250
ρ_{min}, ρ_{max}/e Å^{-3}	−0.44, 0.49	−0.25, 0.48	−0.96, 0.98
Maximum least-squares shift-to-error ratio	0.04	0.20	0.13
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.01	0.03	0.03
Final R	0.068	0.045	0.062
Final R'	0.061	0.055	0.079

was collected in a dry, argon-filled Rotaflo tube. Dark black crystals of $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$ immediately formed in the filtrate and were collected by standard Schlenk techniques.

Elemental analyses (Table 1) were performed by the analytical laboratory in this department. Infrared spectra were recorded on a Nicolet 5PC FT-IR spectrophotometer for Nujol mulls mounted between KBr plates. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5 W argon-ion laser and Spex 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. T.E. 177 RF-005 cooler housing. The data were processed using a Spex DM1B data station. X-Ray powder patterns were recorded on a Sintag XRD2000 powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å) in the range 2θ 2–25°. Magnetic susceptibility measurements were made using an Oxford Instruments Faraday balance with a 4 in electromagnet (Newport Series N100) employing a CI Robal microbalance and an Oxford Instruments ITC4 temperature controller. The calibrant used was mercury tetrathiocyanatocobaltate(II) ($\chi = 16.44 \times 10^{-6}$ cgs; $\chi_{SI} = \chi_{cgs} \times 4\pi/10^6$). The effective magnetic moment was calculated from $\mu_{eff} = 2.84\,(\chi_{corr}T)^{\frac{1}{2}}$.

Crystallography.—Crystal data and refinement details for $[(Ph_3PO)_2H][FeBr_4]$, $[Fe(CO)_3(Ph_3P)_2]$ and $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$ are presented in Table 9. All three compounds were mounted in glass capillaries under argon. Measurements were performed on a Rigaku AFC6S diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω-2θ scans for $[Fe(CO)_3(Ph_3P)_2]$ and $[(Ph_3PO)_2H][FeBr_4]$, and ω scans for $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$. The structures were solved by heavy-atom methods using SHELXS 86[29] and refined by full-matrix least squares using TEXSAN.[30] Heavy atoms were treated anisotropically and hydrogen atoms were placed in chemically reasonable positions. Carbon atoms were subjected to isotropic refinement in $[Ph_4Sb][FeI_4]{\cdot}Ph_3SbI_2$, however anisotropic carbon parameters were used for $[Fe(CO)_3(Ph_3P)_2]$ and all but five carbon atoms were treated anisotropically for $[(Ph_3PO)_2H][FeBr_4]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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