This pattern of C–C bond lengths observed within the ring is very similar to that for [(PMDETA)Li(1,2,4-$(Me_3Si)_3C_5H_2$)].[8] The lengthening may be due to the presence of the two fairly large Me_3Si substituents on adjacent carbon atoms. However, it is apparent from Table IV that the average C–C distances in all the tris(trimethylsilyl)-substituted rings are longer than those observed in 1. The increased C–C distances observed in these rings are most probably a result of the electronic effects of the Me_3Si substituents, whose ability to stabilize, inter alia, negatively charged species such as carbanions is well documented.[19] The three Me_3Si groups in the anion of 2 provide stabilization by lowering the negative charge density through delocalization. As a result, the C–C bond order in the ring is diminished and longer C–C distances are observed. The consequent decrease in the ionic interaction may account for the relative ease with which total separation of the Li^+ ion was achieved in the case of 2. For 1, however, at H substituents on the $[C_5H_5]^-$ ion are not as effective as the silyl groups in removing negative charge density. In effect, the charge remains localized on the ring and a stronger $[Li]^+$–$[C_5H_5]^-$ attraction, which is not amenable to cleavage by 12-crown-4, results.

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Supplementary Material Available: Full tables of crystal data, data collection and refinement details, bond distances and angles, and thermal parameters (13 pages); tables of structure factors (38 pages). Ordering information is given on any current masthead page.

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Synthetic and Structural Studies on Organoiron–Indium Complexes

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The diiron–indium chloride complex $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1), has been synthesized from either the reaction between $InCl_3$ and 2 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ or from the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Compound 1 has been characterized by X-ray crystallography and exists in the solid state as a centrosymmetric dimer involving two chlorine atoms bridging between the indium centers. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.670$ (3), $b = 10.059$ (5), $c = 12.148$ (2) Å and $\alpha = 107.58$ (3), $\beta = 90.97$ (2), $\gamma = 91.32$ (4)°. The iodide complex, $[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (4), was also prepared by analogous synthetic routes by using either InI_3 or InI, although the insertion of InI into the Fe–Fe bond of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ occurs more readily than in the case for InCl. Both 1 and 4 add a further equivalent of halide ion and the compounds $[PPN][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (5), $[Me_4N][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (6), and $[Et_4N][InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (8) have been prepared and characterized. Compounds 1 and 4 also form adducts with neutral two electron donor ligands, viz. $[InCl(py)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (9) (py = pyridine), $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10), and $[InI(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (11). The structure of 10 was established by X-ray crystallography and comprises a tetrahedral indium center coordinated to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments, a chlorine atom, and the phosphorus atom of the phosphine PMe_2Ph. Compound 10 crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.646$ (2), $b = 10.621$ (4), $c = 13.586$ (4) Å and $\alpha = 92.66$ (3), $\beta = 103.62$ (2), $\gamma = 99.41$ (2)°. The iron–indium dichloride complex $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3) has also been prepared from the reaction between $InCl_3$ and 1 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and this complex is also formed as a second product in the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Full spectroscopic and analytical data are reported for all new complexes.

Introduction

Compounds containing transition metal to indium bonds have been known for many years but continue to attract the attention of a number of groups devoted to synthesis.[1] With reference to compounds containing iron, however, relatively few reports have appeared. Early work by Mays et al. demonstrated the insertion of indium(I) chloride into the Fe–Fe bond of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ which afforded the diiron–indium chloride complex formulated as $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1).[2] Later work by these authors[3] showed that 1 was also formed in reactions between $InCl_3$ and 2 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and also by displacement of mercury by InCl from $[Hg\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$. The monoiron complexes $[InX_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (X = Cl, Br) and $[InBr_2(THF)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ were also described,[3] these complexes being formed either by reaction between InX_3 and 1 equiv of $Na[Fe(CO)_2(\eta\text{-}$

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[1] For recent reviews which cover this area, see: (a) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990,** *31,* 91. (b) Whitmire, K. H. *J. Coord. Chem. Sect. B* **1988,** *17,* 95. See also: (c) Clarkson, L. M.; Clegg, W.; Norman, N. C.; Tucker, A. J.; Webster, P. M. *Inorg. Chem.* **1988,** *27,* 2653, and references therein.

[2] Hsieh, A. T. T.; Mays, M. J. *Inorg. Nucl. Chem. Lett.* **1971,** *7,* 223.

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Table I. Spectroscopic and Analytical[a] Data for the Complexes

compd	ν (C≡O),[b] cm^{-1}	NMR[c] ^1H, δ[d]	NMR[c] ^{13}C[d,e]	analysis C	analysis H	analysis N
$[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1)	1985 s, 1963 s, 1929 s	4.95 (C_5H_5)	82.4 (C_5H_5)	33.31 (33.35)	1.88 (2.00)	
$[PPN][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (5)	1980 s, 1952 s, 1920 s, 1903 m	4.81 (10 H, C_5H_5), 7.52–7.80 (30 H, Ph)		55.04 (55.70)	3.45 (3.74)	1.25 (1.30)
$[Me_4N][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (6)	1976 m, 1955 s, 1916 s	3.33 (12 H, Me_4N), 4.80 (10 H, C_5H_5)[f]		35.21 (35.22)	3.42 (3.61)	2.21 (2.28)
$[InCl(py)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (9)	1985 s, 1960 s, 1925 s, 1918 s	4.80 (C_5H_5), 8.14 (v br, py)[f]		38.84 (39.19)	2.47 (2.59)	2.29 (2.40)
$[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10)	1985 s, 1963 s, 1927 s	1.79 (d, 6 H, $P(CH_3)_2Ph$, $J(HP) = 7.1$), 4.71 (10 H, C_5H_5), 7.46–7.68 (5 H, $PMe_2C_6H_5$)[f,g]		40.85 (41.14)	3.16 (3.29)	
$[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (4)	1987 s, 1965 s, 1931 s	4.95 (C_5H_5)	83.0 (C_5H_5)	27.40 (28.23)	1.56 (1.69)	
$[Et_4N][InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (8)	1985 s, 1957 s, 1938 s, 1923 s	1.40 (tt, 12 H, $N(CH_2CH_3)_4$, $J(HH) = 7.3$, $J(^{14}NH) = 1.9$), 3.50 (q, 8 H, $N(CH_2CH_3)_4$, $J(HH) = 7.3$), 4.82 (10 H, C_5H_5)		28.31 (30.98)	3.38 (3.55)	1.67 (1.64)
$[InI(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (11)	1985 s, 1963 s, 1929 s, 1920 s	1.84 (d, 6 H, $P(CH_3)_2Ph$, $J(HP) = 7.4$), 4.66 (10 H, C_5H_5), 7.47–7.69 (5 H, $PMe_2C_6H_5$)[f,h]		35.68 (36.01)	2.82 (2.89)	
$[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3)	1991 s, 1940 s	4.92 (C_5H_5)	82.0 (C_5H_5)			

[a] Calculated values are given in parentheses. [b] Measured in THF solution unless otherwise stated. [c] Chemical shifts in ppm, coupling constants in Hz; measurements at room temperature. [d] Measured in acetone-d_6 unless otherwise stated. [e] ^1H NMR decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [f] Measured in CD_2Cl_2. [g] $^{31}P\{^1H\}$, (CD_2Cl_2), δ −34.3. [h] $^{31}P\{^1H\}$, (CD_2Cl_2) δ −45.4.

Table II. Selected Bond Distances (Å) and Angles (deg) for $[(InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$ (1)[a]

Bond Distances			
In–Fe(1)	2.553 (1)	In–Fe(2)	2.558 (1)
In–Cl	2.625 (2)	In–Cl′	2.708 (2)
Bond Angles			
Fe(1)–In–Fe(2)	131.5 (1)	Fe(1)–In–Cl	111.1 (1)
Fe(1)–In–Cl′	106.9 (1)	Fe(2)–In–Cl	111.4 (1)
Fe(2)–In–Cl′	102.4 (1)	Cl–In–Cl′	80.0 (1)
In–Cl–In′	100.0 (1)		

[a] Estimated standard deviations in the least significant digit are given in parentheses in this and all subsequent tables.

$C_5H_5)]$ or by insertion of InX into the iron–halogen bond in the complexes $[FeX(CO)_2(\eta\text{-}C_5H_5)]$ (X = Cl, Br). Other complexes which are known include the iron–manganese cluster $[Fe_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2]$, reported by Haupt and Preut,[4] and the anionic complexes $[InPh_3\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]^-$ [5] and $[InBr_3\{Fe(CO)_4\}]^{2-}$, $[InBr_2\{Fe(CO)_4\}]^-$, and $[InBr_2(L)\{Fe(CO)_4\}]^-$ (L = C_5H_5N, NEt_3).[6]

We have reported the synthesis and spectroscopic characterization of $[In\{Fe(CO)_2(\eta\text{-}C_5H_4R)\}_3]$ (R = H, Me)[7a] together with additional results on the insertion reactions of indium monohalides into $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[8] Herein we report full details on the latter reactions along with further studies on the reactions between indium trihalides and $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$. Preliminary aspects of the reactivity of some of these complexes are also described.

Results and Discussion

The diiron–indium complex $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1) was originally reported by Mays et al.[2,3] being formed either from the reaction between $InCl_3$ and 2 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ or by the insertion of InCl into the Fe–Fe bond in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. We have also studied these reactions in some detail. The reaction between $InCl_3$ and $2Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ in THF afforded 1 as orange crystals after workup with typical isolated yields of between 65 and 70%. No other iron–indium products were formed in appreciable quantities and this route is the best method for obtaining synthetically useful amounts of 1. It is interesting to note, however, that we obtained no evidence for the formation of the dichloro anionic complex $Na[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (2) in this reaction which is in contrast to results we observed for the analogous chromium, molybdenum and tungsten systems for which the reaction between $InCl_3$ and 2 equiv of $Na[M(CO)_3(\eta\text{-}C_5H_5)]$ under very similar conditions afforded high yields of $Na[InCl_2\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$[1c,9] (M = Cr, Mo, W). We are not sure of the reasons for these differences but will discuss this matter in a more general context later. Spectroscopic data for a compound which we formulated as 2 is given in ref 8, this complex being occasionally observed as a minor product in the formation of $[In\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]$ from $InCl_3$ and 3 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$.[7a]

The other route to 1 involves the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in refluxing toluene. Although 1 was formed as the major product (typical isolated yields were about 40%) significant amounts of $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3) were also obtained[8] together with traces of $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ and unreacted $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. The latter two complexes could be readily extracted with toluene, in which 1 and 3 were insoluble, but crystallization procedures (solvent diffusion, THF/hexane) were not very effective for isolating either 1 or 3 as pure materials, which limits the synthetic utility of this reaction. These results are broadly in line with those reported by Mays et al.[2,3] in which refluxing dioxane was used instead of toluene.

Spectroscopic and analytical data for 1 are presented in Table I and Figure 1a and were fully consistent with the anticipated formula. However, we considered it unlikely that 1 would be monomeric in view of the pronounced Lewis acidity of three-coordinate indium and there was no evidence from either ^1H NMR or microana-

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(9) Clarkson, L. M.; Norman, N. C. Unpublished results.

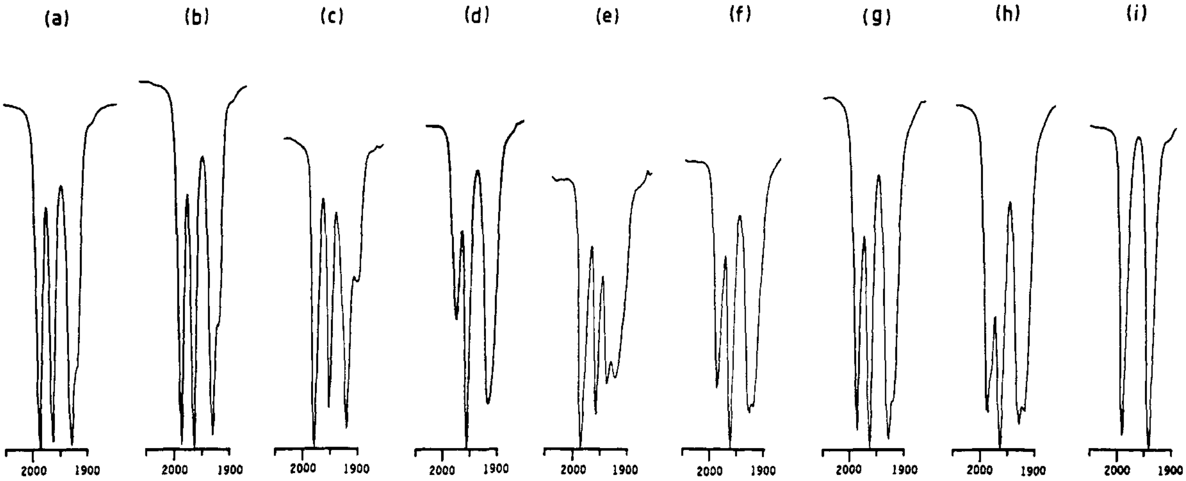

Figure 1. Solution infrared spectra for the complexes measured in THF in the carbonyl stretching region: (a) 1; (b) 4; (c) 5; (d) 6; (e) 8; (f) 9; (g) 10; (h) 11; (i) 3.

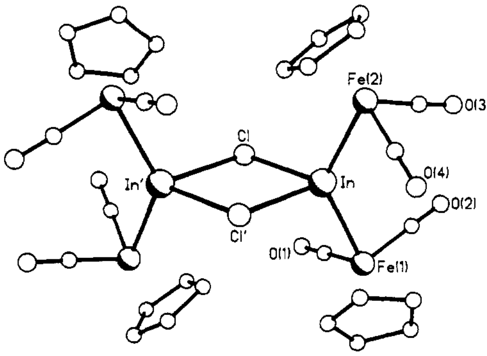

Figure 2. A view of the molecular structure of 1 showing the atom numbering scheme adopted. Hydrogen atoms are omitted for clarity.

lytical data for a THF adduct analogous to the molybdenum complex $[InCl(THF)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$.[8] A structure involving additional indium–chlorine bonding was considered likely and this was confirmed by X-ray crystallography the results of which (Figure 2, Tables II and III) revealed that 1 is a centrosymmetric dimer. The central unit consists of a In_2Cl_2 parallelogram with In–Cl bond lengths of 2.625 (2) and 2.708 (2) Å and angles at In and Cl of 80.0 (1) and 100.0 (1)°, respectively. Each indium center is also bonded to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments by unsupported Fe–In bonds such that the overall coordination geometry around the indium center is approximately tetrahedral. Distortions are apparent, however, both in the acute Cl–In–Cl angle and in the large value for the Fe–In–Fe angle, 131.5 (1)°. Such distortions are quite general and are also seen in the related manganese and rhenium complexes, $[(InX\{Mn(CO)_5\}_2)_2]$ (X = Cl, Br, I; X–In–X 79.98 (5), 82.58 (2), 85.65 (2)°; Mn–In–Mn 123.59 (3), 124.97 (3), 126.37 (4)°)[10a] and $[(InX\{Re(CO)_5\}_2)_2]$ (X = Cl, Br, I; X–In–X av 97.2 (2), av 94.8 (1), 96.47 (5)°; Re–In–Re av 127.5 (1), av 128.4 (1), 126.34 (5)°)[10b] prepared by Haupt and co-workers. A comparison can also be made with the chlorobismuthinidene complex $[(BiCl\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$, prepared by Huttner and co-workers, which is formally isoelectronic with 1. Important angles in this centrosymmetric, chloride-bridged dimer are Mn–Bi–Mn 141.0 (2), Cl–Bi–Cl 76.7 (2), Bi–Cl–Bi 103.3 (2)°.[11] A superposition of the structures of 1 and $[(BiCl\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$ is shown in Figure 3. These large deviations from idealized tetrahedral values probably result from constraints due to the presence of the In_2Cl_2 four-mem-

Table III. Final Positional Parameters (Fractional Coordinates) and Isotropic Thermal Parameters (Å^2) (Equivalent Isotropic Parameters U_{eq} for Anisotropic Atoms) for $[(InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$ (1) ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$)

atom	*x/a*	*y/b*	*z/c*	U_{eq}
In	−0.01525 (6)	0.11496 (4)	0.16983 (3)	0.030
Fe(1)	0.12734 (13)	0.36435 (8)	0.21908 (7)	0.033
Fe(2)	−0.11108 (14)	−0.03545 (8)	0.29820 (7)	0.033
Cl	−0.2383 (2)	0.0500 (2)	−0.0201 (1)	0.038
O(1)	−0.1453 (8)	0.4090 (5)	0.0456 (4)	0.057
O(2)	−0.1660 (8)	0.4581 (5)	0.3955 (5)	0.061
O(3)	−0.2878 (9)	0.1990 (5)	0.4623 (5)	0.067
O(4)	0.2890 (9)	0.0443 (7)	0.3961 (5)	0.077
C(1)	−0.0354 (10)	0.3896 (6)	0.1132 (6)	0.042
C(2)	−0.0516 (11)	0.4184 (6)	0.3272 (5)	0.041
C(3)	−0.2182 (10)	0.1087 (6)	0.3954 (5)	0.038
C(4)	0.1280 (12)	0.0122 (8)	0.3564 (6)	0.051
C(11)	0.4047 (11)	0.2727 (8)	0.2327 (7)	0.057
C(12)	0.4075 (11)	0.3270 (9)	0.1464 (7)	0.062
C(13)	0.3777 (13)	0.4723 (10)	0.1881 (9)	0.080
C(14)	0.3573 (12)	0.5027 (8)	0.3097 (8)	0.069
C(15)	0.3677 (12)	0.3793 (11)	0.3359 (7)	0.069
C(21)	−0.1412 (16)	−0.2340 (7)	0.3170 (7)	0.064
C(22)	−0.3292 (14)	−0.1779 (8)	0.3138 (6)	0.061
C(23)	−0.3569 (12)	−0.1502 (7)	0.2103 (7)	0.055
C(24)	−0.1837 (13)	−0.1933 (7)	0.1440 (6)	0.052
C(25)	−0.0525 (14)	−0.2414 (7)	0.2135 (8)	0.068

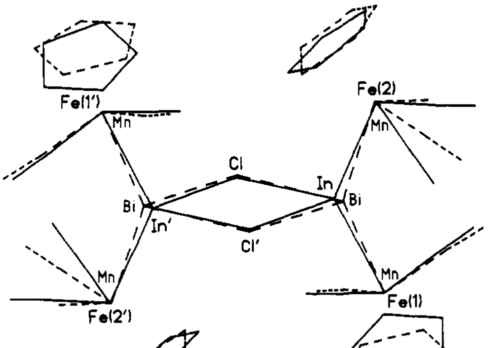

Figure 3. A best fit superposition of 1 (—) and $[(BiCl\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$ (- - -). Coordinates for the bismuth manganese complex were taken from ref 11.

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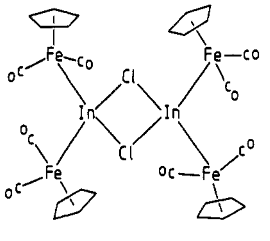
bered ring, since for structures of the general type, $[InCl_2(ML_n)_2]^-$, e.g. $[Na(THF)_2][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[1c] $[PPN][InCl_2\{Co(CO)_4\}_2]$[12] (PPN = $Ph_3PNPPh_3^+$), $[Co(CO)_3(PPh_3)_2][InCl_2\{Co(CO)_4\}_2]$,[12] and $[Et_4N][InBr_2\{Co(CO)_4\}_2]$[13] the X–In–X and M–In–M angles are, for the former, 90.4 (1), av 102.4 (3), 102.5 (1), 103.5 (3)° and, for the latter, 129.4 (1), av 121.9 (2), 121.5 (1), 124.3 (4)°, respectively, i.e. somewhat closer to tetrahedral values. The Fe–In bond lengths in **1** are 2.553 (1) and 2.558 (1) Å which are substantially shorter than the sum of the covalent radii for the two elements which is approximately 2.71 Å[14] although caution is advisable when attempting to draw too many conclusions from facts such as these. We note, however, that π-bonding is *possible* between filled iron d orbitals and vacant In–Cl σ*-orbitals of π-symmetry, i.e., a form of negative hyperconjugation.[16] We have recently reported details for a similar situation in the related bismuth complexes, $[BiCl_2\{M(CO)_x(\eta\text{-}C_5H_5)\}_2]^-$ (M = Fe, $x = 2$; M = Mo, $x = 3$)[17] and possible π-bonding interactions for **1** are shown in A and B. If we consider the nature of the d functions on the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments, then, as described by Hoffmann et al.,[18] two π-donor orbitals are present, one orthogonal to, and one in the symmetry plane of the fragment. Any overlap of the kind depicted in A and B should, therefore, lead to slight orientational preferences for the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments with respect to the $InCl_2$ unit. Specifically, the torsion angles defined by the Cl,Cl-midpoint–In–Fe–C_5H_5 ring centroid should be 0, 90, 180, or 270° in order to achieve maximum overlap.[19] The observed values in **1** are Cl,Cl–In–Fe(1)–cC_5H_5 −82.9° and Cl,Cl–In–Fe(2)–cC_5H_5 −16.1° which are thus consistent with the presence of some type of π-interaction of the kind discussed above. Moreover, in the bismuth complex $[(BiCl\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2)_2]$ the analogous torsion angles are −84.4° and −3.9°, i.e. very close to those in **1** (Figure 3), which further highlights the similarity between these two compounds and indicates that the orientations of the manganese fragments may also be dictated by electronic factors. Similar arguments can be advanced for a range of complexes containing the $In\{M(CO)_3(\eta\text{-}C_5H_5)\}_2$ (M = Cr, Mo) unit and we will discuss this general topic in more detail in a future publication on the basis of more quantitative results obtained from extended Hückel molecular orbital calculations.



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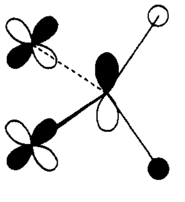

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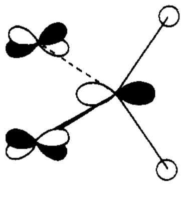

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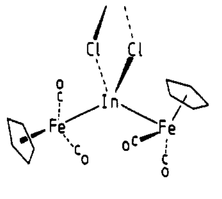
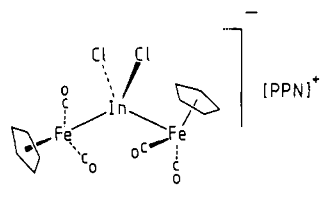


1



5

The iodide compound $[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**4**) can be similarly prepared and in higher yields. The reaction between InI_3 and $2Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ afforded **4** with isolated yields of around 90% while the insertion reaction between InI and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ also afforded reasonable, although lower, yields of **4**. Moreover, in the latter reaction we found no evidence for the iron–indium diiodide $[InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$, analogous to **3**, although small amounts of $[FeI(CO)_2(\eta\text{-}C_5H_5)]$ and unreacted $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ were present.[20] Spectroscopic and analytical data for **4** are presented in Table I and Figure 1b and we presume that the structure is probably similar to that found for **1**, although we were unable to obtain X-ray quality crystals of **4** due to rapid loss of solvent of crystallization.

We have already mentioned that the reaction between $InCl_3$ and $2Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ gave no appreciable quantities of the dichloro anionic complex **2** in contrast to the situation observed for the molybdenum-based system. One possible reason for this may be the apparent stability of the dimeric unit in **1**, the formation of which facilitates chloride ion loss under the reaction conditions. However, dichloro anionic complexes can be readily prepared as was demonstrated by the following reactions. Treatment of **1** with 1 equiv of either [PPN]Cl (PPN = $Ph_3PNPPh_3^+$) or $[Me_4N]Cl$ afforded the complexes $[PPN][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**5**) and $[Me_4N][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**6**) spectroscopic and analytical data for which are given in Table I. These data were consistent with the anticipated formulas, but it was apparent from the infrared spectra (**5**, Figure 1c; **6**, Figure 1d) that the solution-state structures were in some way dissimilar. We suspect that this difference lies in the orientation of the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments with respect to the $InCl_2$ unit, i.e. the conformation about the Fe–In bonds. It is clear from Figure 1 that **5** (Figure 1c) is similar to **1** (Figure 1a) and we therefore propose that similar conformations are adopted (see diagrams). The spectrum for **6**, however, is very similar to that observed for the triiron complex $[In\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]$ (**7**).[7a] Since we were not able to obtain an X-ray structure of **7** we cannot be sure of the precise iron fragment orientation but on the basis of the structure we suggested in ref 7a, for electronic reasons, we propose that in **6** the conformations about the Fe–In bonds are similar as shown in the diagrams.

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(12) Clarkson, L. M.; McCrudden, K.; Norman, N. C.; Farrugia, L. J. *Polyhedron* **1990**, *9*, 2533.

(13) Cradwick, P. D. *J. Organomet. Chem.* **1971**, *27*, 251.

(14) This value is derived from a literature value of 1.44 Å for In(III) (see: Ball, M. C.; Norbury, A. H. *Physical Data for Inorganic Chemists*; Longman: London, 1974) and a value for iron derived from the bond length in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.534 (2) Å) taken from ref 15.

(15) Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390.

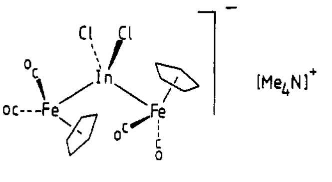
(16) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

(17) Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G. *Polyhedron* **1991**, *10*, 123.

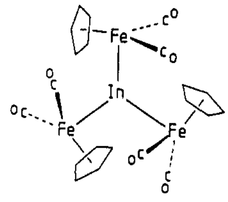
(18) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(19) The lowest energy conformation will depend critically on the precise energies of the orbitals involved. Moreover, the energy difference between the conformations which maximize overlap is likely to be small.

(20) Small amounts of unreacted $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ are always observed during work up of the InCl and InI insertion reactions even when the indium monohalides are present in slight excess.



6

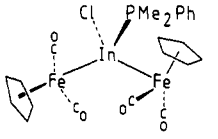


7

The explanation as to why the anion, $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^-$, should have a slightly different structure in THF solution depending on whether the counter cation is PPN^+ (5) or Me_4N^+ (6) is not clear. The most likely reason is that a significant degree of ion pairing is responsible but we are unable to be more specific with the data at hand.

The diiodide anionic complex $[Et_4N][InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (8) was prepared from the reaction between $[Et_4N]I$ and 4, spectroscopic and analytical data for which are presented in Table I and Figure 1e.

The ease with which the neutral monochloride and monoiodide complexes 1 and 4 formed adducts with chloride and iodide anions, respectively, indicated that adducts with neutral two electron donor ligands might also be reasonable targets for synthesis. Treatment of 1 with pyridine afforded an orange crystalline complex after workup which analyzed correctly for $[InCl(py)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (9). ^1H NMR data were also in accord with this formulation although only a broad signal was observed for the pyridine ligands suggesting the possibility of rapid reversible dissociation. We also carried out the reactions of both 1 and 4 with the phosphine PMe_2Ph which afforded the orange crystalline complexes $[InX(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10, X = Cl; 11, X = I), spectroscopic and analytical data for which are given in Table I and Figure 1g,h. The structure of 10 was confirmed by X-ray crystallography the results of which are presented in Figures 4 and 5 and Tables IV and V. The structure consists of a central, tetrahedral indium bonded to a chlorine, two iron atoms, and the phosphorus of the PMe_2Ph phosphine ligand. The distortions of the interbond angles are in a manner that is common to the examples of $[InX_2(ML_n)_2]$ species, discussed earlier, with a large angle for Fe(1)–In–Fe(2), 124.8 (1)°, and a small angle between the chlorine and phosphorus atoms, Cl–In–P 89.0(1)°. The only bond length of note is for the In–P bond, 2.739 (2) Å. Very few bonds for indium(III)–phosphine adducts have been measured by X-ray methods, the only others, of which we are aware, being for the complexes $[InCl_2(PPh_3)\{Co(CO)_4\}]$ (2.607 (5) and 2.611 (5) Å for two crystallographically independent molecules),[12] $[InCl_3(PPh_3)_2]$ (2.701 (5) and 2.723 (5) Å),[21a] and $[(Me_3In)_2(Ph_2PCH_2CH_2PPh_2)]$ (2.755 (4) Å).[21b] The overall conformation of the $In\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$ fragment is similar to that found in 1 and this similarity in structure is clearly maintained in solution as is evident from the infrared spectra (Figure 1a vs Figure 1g).



10

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10)

Bond Distances			
In–Fe(1)	2.582 (1)	In–Fe(2)	2.569 (1)
In–Cl	2.486 (2)	In–P	2.739 (2)
Bond Angles			
Fe(1)–In–Fe(2)	124.8 (1)	Fe(1)–In–Cl	115.0 (1)
Fe(1)–In–P	105.8 (1)	Fe(2)–In–Cl	107.9 (1)
Fe(2)–In–P	108.1 (1)	Cl–In–P	89.0 (1)

Table V. Final Positional Parameters (Fractional Coordinates) and Isotropic Thermal Parameters ($Å^2$) (Equivalent Isotropic Parameters U_{eq} for Anisotropic Atoms) for $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10) ($U_{eq} = 1/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$)

atom	x/a	y/b	z/c	U_{eq}
In	0.24936 (3)	0.35400 (2)	0.78626 (2)	0.033
Fe(1)	0.17170 (7)	0.15833 (5)	0.88201 (4)	0.037
Fe(2)	0.07645 (7)	0.52750 (5)	0.73909 (4)	0.038
Cl	0.53721 (13)	0.46166 (10)	0.84271 (9)	0.057
P	0.31169 (13)	0.25688 (9)	0.61219 (8)	0.043
O(1)	0.0108 (5)	0.0266 (3)	0.6860 (3)	0.068
O(2)	−0.1143 (4)	0.2570 (3)	0.9001 (3)	0.071
O(3)	0.2061 (5)	0.5632 (3)	0.5643 (3)	0.080
O(4)	−0.1605 (4)	0.3055 (3)	0.6422 (3)	0.074
C(1)	0.0754 (5)	0.0804 (4)	0.7629 (3)	0.047
C(2)	0.0019 (5)	0.2215 (4)	0.8925 (3)	0.047
C(3)	0.1578 (6)	0.5466 (4)	0.6351 (3)	0.051
C(4)	−0.0688 (5)	0.3950 (4)	0.6808 (3)	0.049
C(11)	0.3441 (8)	0.2175 (5)	1.0175 (4)	0.082
C(12)	0.4202 (6)	0.1738 (5)	0.9460 (4)	0.070
C(13)	0.3546 (7)	0.0478 (5)	0.9156 (4)	0.068
C(14)	0.2383 (7)	0.0084 (5)	0.9680 (4)	0.066
C(15)	0.2280 (7)	0.1101 (6)	1.0308 (3)	0.077
C(21)	0.1572 (7)	0.5893 (5)	0.8945 (3)	0.069
C(22)	0.2133 (6)	0.6841 (4)	0.8360 (4)	0.064
C(23)	0.0767 (8)	0.7211 (4)	0.7739 (4)	0.071
C(24)	−0.0607 (7)	0.6485 (6)	0.7918 (4)	0.078
C(25)	−0.0140 (7)	0.5657 (5)	0.8645 (4)	0.071
C(111)	0.3928 (5)	0.1105 (4)	0.6291 (3)	0.045
C(112)	0.5341 (6)	0.1137 (4)	0.7025 (3)	0.055
C(113)	0.5966 (7)	0.0036 (5)	0.7224 (4)	0.072
C(114)	0.5180 (8)	−0.1112 (5)	0.6687 (5)	0.084
C(115)	0.3787 (8)	−0.1149 (5)	0.5948 (5)	0.080
C(116)	0.3145 (6)	−0.0055 (4)	0.5744 (4)	0.060
C(121)	0.4633 (7)	0.3635 (5)	0.5696 (4)	0.078
C(131)	0.1429 (7)	0.2235 (5)	0.5024 (4)	0.071

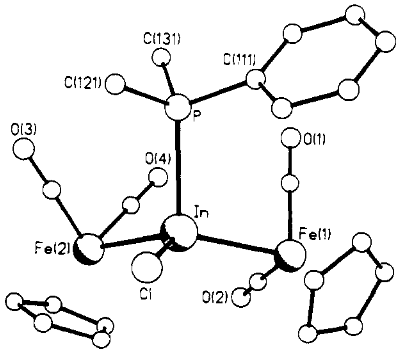


Figure 4. A view of the molecular structure of 10 showing the atom numbering scheme adopted. Hydrogen atoms are omitted for clarity.

In concluding this section we note that the iron–indium dichloride complex $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3) previously mentioned as a product of the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, can be obtained in high yield from the reaction between $InCl_3$ and 1 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$. Spectroscopic and analytical data (Table I, Figure 1i) were consistent with the anticipated formula but since we were unable to obtain X-ray quality crystals, we cannot comment further on the structure except to say that it is

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(21) (a) Veidis, M. V.; Palenik, G. J. *Chem. Commun.* **1969**, 586. (b) Bradley, D. C.; Chudzynska, H.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Smith, L. M. *Polyhedron* **1988**, 7, 1289.

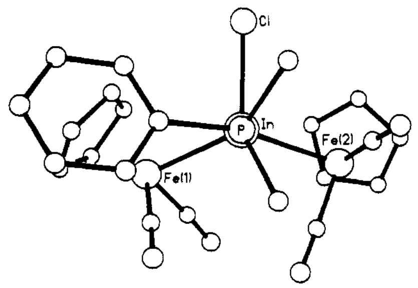

Figure 5. A Newman projection view of **10** looking along the In–P bond.

almost certainly not monomeric.

Further studies are in progress, particularly with respect to the reactivity of the complexes 1 and 4.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen by using standard Schlenk techniques. All solvents were dried over suitable drying agents [Na/benzophenone for THF, Et_2O, hexane, and toluene; CaH_2 for CH_2Cl_2] and distilled immediately prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP200 spectrometer operating at 200.13 and 50.324 MHz, respectively, and referenced to residual solvent signals, values for which were taken from ref 22. ^{31}P NMR spectra [proton decoupled] were obtained on a Bruker WM300 instrument operating at 121.49 MHz and referenced to 85% H_3PO_4, external. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle. Mass spectra (EI mode) were obtained on AE MS9 and Kratos MS80 instruments.

$InCl_3$, InI_3, InCl, PMe_2Ph, [PPN]Cl, $[Me_4N]Cl$, $[Et_4N]I$, and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ were procured commercially and used as received. InI was prepared according to the procedure given by Tuck.[23]

Infrared, ^1H and ^{13}C NMR, and microanalytical data for all new complexes are presented in Table I.

Preparations. $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1). Method A. A THF solution of $InCl_3$ (0.084 g, 0.379 mmol) was added to a stirred solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ (prepared by sodium amalgam reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.134 g, 0.379 mmol) in THF (20 mL) over a period of 12 h) cooled to 0 °C. A color change from dark yellow-brown to red-brown and then to yellow-brown was observed during the addition. The reaction mixture was warmed to room temperature and stirred for a further 3 h. The THF was removed by vacuum, affording a yellow-brown residue, which was extracted in 30 mL of THF, and filtered through Celite. The orange filtrate obtained was reduced in volume to 6 mL over which hexane (40 mL) was layered. Crystallization by solvent diffusion at −30 °C over a period of 6 days afforded orange crystalline 1 in 65% yield.

Method B. InCl (0.129 g, 0.858 mmol) and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.304 g, 0.858 mmol) were stirred in refluxing toluene (20 mL) for 3 h, which afforded a yellow-brown solution, a yellow powder, and indium metal. The solvent was removed by vacuum and the residue washed with hexane to remove unreacted $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ which was formed as a byproduct. The yellow powder which remained was dried by vacuum and then extracted in THF, and filtered through Celite. The dark orange filtrate was reduced in volume by vacuum to about 6 mL over which hexane (40 mL) was layered. Solvent diffusion over a period of 5 days at −30 °C afforded crystals of 1 in 41% yield. Recrystallization of the mother liquor and a yellow powder which formed during the first crystallization was effected from THF/hexane mixtures and afforded a yellow-brown powder, $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3) (yield 40%). Mass spectrum for 1, *m/z* 469, P − Cl (P = $InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$); 413, P − Cl + 2CO; 476, P − 1CO; 448, P − 2CO; 420, P − 3CO.

$[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (4). Method A. A solution of InI_3 (0.214 g, 0.431 mmol) in THF (10 mL) was added to a stirred solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ (freshly prepared from Na/Hg reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.153 g, 0.431 mmol) in THF (20 mL) over 12 h), at 0 °C. An increase in the intensity of the yellow color of the solution was observed during the addition. The temperature was maintained at 0 °C for 15 min and then the ice bath was removed and the reaction solution stirred at room temperature for 24 h. Removal of the THF by vacuum followed by extraction of the residue in CH_2Cl_2 and filtration through Celite afforded a dark yellow-brown solution from which long yellow needles were obtained after reduction of the solvent volume to 6 mL and crystallization by slow diffusion of hexane (60 mL) at −30 °C over a period of several days (yield 90%). The yellow needles lost solvent and turned powdery on drying and were unsuitable for X-ray diffraction. The red-brown mother liquor was shown to be a mixture of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[FeI(CO)_2(\eta\text{-}C_5H_5)]$ by infrared spectroscopy.

Method B. InI (0.045 g, 0.186 mmol) and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.066 g, 0.186 mmol) were heated in toluene (10 mL) under reflux conditions for 1 h. During this time the solution changed color from red-brown to yellow-brown and deposits of indium metal were observed. The solvent was removed by vacuum, and the residue was washed repeatedly with hexane until the washings were colorless (to remove excess $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[FeI(CO)_2(\eta\text{-}C_5H_5)]$ which formed as a byproduct). The yellow powder which remained was extracted in THF and filtered through Celite. The solvent volume was reduced to ~6 mL over which hexane (40 mL) was layered. Solvent diffusion at −30 °C over a period of days afforded a yellow powder.

Long yellow needles were obtained in low yield (20%) by recrystallization from CH_2Cl_2/hexane mixtures, but readily lost solvent on removal of the mother liquor.

The washings obtained from the reaction mixture were shown to be $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[FeI(CO)_2(\eta\text{-}C_5H_5)]$ by IR spectroscopy. Using an excess of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ did not improve the yield of 4.

Mass spectrum, *m/z* 568, P − 1CO (P = $InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$); 540, P − 2CO; 512, P − 3CO; 469, P − I; 419, P − $Fe(CO)_2(\eta\text{-}C_5H_5)$; 391, P − $Fe(CO)_2(\eta\text{-}C_5H_5)$ + 1 CO; 363, P − $Fe(CO)_2(\eta\text{-}C_5H_5)$ + 2CO.

$[PPN][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (5). [PPN]Cl (0.057 g, 0.099 mmol) was added to a solution of 1 (0.050 g, 0.099 mmol) in THF (15 mL) at room temperature and stirred for 24 h. Removal of the THF by vacuum, extraction of the oily residue in CH_2Cl_2 (10 mL) and filtration through Celite afforded a yellow solution which was reduced in volume (3 mL) and set up to crystallize by solvent diffusion using hexane (25 mL) at −30 °C. After a period of 7 days, a golden flaky crystalline material was isolated, washed with hexane (2 × 10 mL), and dried.

$[Me_4N][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (6). A few drops of dried and degassed MeOH were added to a mixture of $[Me_4N]Cl$ in CH_2Cl_2 (2 mL) until all the solid dissolved. The resulting colorless solution was then added to solid 1 and shaken until all the solid had dissolved to give a yellow-orange solution. Crystallization by solvent diffusion using Et_2O (20 mL) over a period of 4 days afforded an orange microcrystalline solid.

$[Et_4N][InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (8). Compound 4 (0.053 g, 0.089 mmol) and $[Et_4N]I$ (0.023 g, 0.089 mmol) were dissolved in CH_2Cl_2 (4 mL). The slightly turbid solution was filtered through Celite and the dark yellow filtrate was reduced in solvent volume and set up to crystallize by solvent diffusion using hexane at −30 °C. Dark red needles and an oily solid were obtained after a few days. All solvent was removed by vacuum and the oily residue stirred in hexane (10 mL) overnight, which afforded a yellow powder. The hexane extracts were discarded, and the yellow powder was dried by vacuum.

A red-brown crystalline solid was obtained by redissolution of the yellow powder in CH_2Cl_2 (5 mL), filtration through Celite, and crystallization by solvent diffusion using hexane (25 mL) at −30 °C over a period of 24 h.

$[InCl(py)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (9). Pyridine (0.5 mL, 0.063 mmol, 0.124 M in THF) was added to a solution of 1 (0.032 g, 0.063 mmol) in THF (3 mL) at room temperature. After thorough mixing, the resulting yellow solution was set up to crystallize by solvent diffusion using hexane (20 mL) at −30 °C. Orange nee-

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[22] Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Oxford, 1987.

[23] Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.

Table VI. Crystallographic and Intensity Data Collection Parameters for 1 and 10

	1	10
formula	$C_{28}H_{20}Cl_2Fe_4In_2O_8$	$C_{22}H_{21}ClFe_2InO_4P$
fw	1008.4	642.4
cryst class	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.670 (3)	8.646 (2)
b, Å	10.059 (5)	10.621 (4)
c, Å	12.148 (2)	13.586 (4)
α, deg	107.58 (3)	92.66 (3)
β, deg	90.97 (2)	103.62 (2)
γ, deg	91.32 (4)	99.41 (2)
V, Å^3	776.5 (6)	1191.5 (7)
Z	1	2
ρ(calcd), g cm^{-3}	2.16	1.79
F(000)	488	636
μ(Mo Kα), cm^{-1}	34.81	23.52
2θ range, deg	4–50	4–50
no. of rflns measd	2973	4487
no. of rflns obsd	2315	3762
data omission factor	$I > 3.0\sigma(I)$	
R	0.029	0.033
R_w	0.049	0.042

dle-like crystals were obtained after 3 days.

The yields of **5**, **6**, **8**, and **9** are essentially quantitative as judged by IR although recrystallized yields are invariably lower.

[InCl(PMe$_2$Ph){Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] (10). PMe$_2$Ph (0.0175 g, 0.018 mL, 0.127 mmol) was added to a solution of **1** (0.064 g, 0.127 mmol) in THF (2 mL) at room temperature. The solution was shaken gently to ensure thorough mixing (5 min) and then set up to crystallize by solvent diffusion using hexane (20 mL) at −30 °C. Bright red-orange crystals were obtained after 3 days; yield 0.06 g, 74%. The PMe$_3$ analogue was prepared similarly and identified by infrared spectroscopy; ν (C ≡ O) (cm^{-1}) 1976 s, 1957 s, 1916 s.

[InI(PMe$_2$Ph){Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] (11). PMe$_2$Ph (0.021 g, 0.021 mL, 0.151 mmol) was added to a THF solution of **4** (0.090 g, 0.151 mmol) at room temperature. The solution was shaken for about 5 min and then left to stand for 30 min. Crystallization by solvent diffusion using hexane (20 mL) afforded dark red crystals after 7 days; yield 47%.

[InCl$_2${Fe(CO)$_2$(η-C$_5$H$_5$)}] (3). A freshly prepared solution of Na[Fe(CO)$_2$(η-C$_5$H$_5$)] (prepared by Na/Hg reduction of [Fe$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.059 g, 0.167 mmol) in 15 mL of THF) was added to a stirred solution of InCl$_3$ (0.074 g, 0.334 mmol) in THF (10 mL) at 0 °C. The resulting turbid dirty yellow reaction mixture was warmed to room temperature with continuous stirring for 5 h. Removal of the THF by vacuum, followed by extraction in THF (insoluble in CH$_2$Cl$_2$) and filtration through Celite afforded a yellow filtrate. Yellow crystals were obtained by reduction of the solvent volume to 4 mL and solvent diffusion using hexane (30 mL) at −30 °C over a period of a few days. The crystals lost solvent and became opaque on isolation from the mother liquor and drying by vacuum.

Mass spectrum, m/z 362, P (P = InCl$_2${Fe(CO)$_2$(η-C$_5$H$_5$)}); 327, P − Cl; 306, P − 2CO; 689, 2P − Cl; 696, 2P − 1CO; 668, 2 P − 2CO.

X-ray Crystallography. X-ray Analysis of 1 (Values for 10 in Parentheses). An orange crystal of approximate dimensions 0.4 × 0.4 × 0.3 (0.6 × 0.4 × 0.3) mm was mounted in a general position on a glass fiber and coated with acrylic resin. Data were collected at ambient temperatures by using the $\theta/2\theta$ scan mode on a CAD4F automated diffractometer with graphite monochromated X-radiation (λ = 0.710 69 Å). Unit cell parameters were determined by refinement of the setting angles ($10 \geq \theta \geq 14°$) of 23 reflections ($15 \geq \theta \geq 16°$ for 24 reflections for **10**). The standard reflections $\bar{3}\bar{1}\bar{3}$ and $20\bar{6}$ (173, $5\bar{4}4$, $3,\bar{1},\overline{10}$) were measured every 2 h, and no significant decay was noted (linear 1% decay corrected). Lorentz-polarization and absorption/extinction (DIFABS[24]) corrections were applied. A total of 2973 (4487) measured reflections (θ range 2–25°, h 0 to 7, k −11 to +11, l −14 to +14) (h 0 to 10, k −12 to +12, l −16 to +16) yielded 2713 (4183) independent data, of which 2315 (3762) having an intensity $>3.0\sigma(I)$ were considered observed and used for structure solution and refinement. The distribution of normalized structure factors indicated the centrosymmetric space group $P\bar{1}$, and this was confirmed by successful structure solution and refinement. The structure was solved by direct methods (MITHRIL[25]) and subsequent electron density difference syntheses. The structure was refined by using full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weighting scheme $w = [\sigma^2(F_o)]^{-1}$ was used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. All non-H atoms were allowed anisotropic thermal motion, while H atoms were assigned a fixed isotropic thermal parameter of 0.05 Å^2. H atoms were included at calculated positions (C–H = 1.0 Å). Refinement using a total of 199 (280) parameters converged at R (R_w) = 0.029 (0.049) (0.033 (0.042)), with mean and maximum Δ/σ values of 0.006 and 0.033 (0.01 and 0.045), respectively, in the final cycle. A final electron density difference synthesis showed no chemically significant features (max $\Delta\rho$ = +0.8 (+0.9), min $\Delta\rho$ = −0.84 (−1.13) eÅ^{-3} in vicinity of the In atom). The esd of an observation of unit weight (S) was 2.61 (2.38). Neutral atom scattering factors were taken from ref 26 with corrections applied for anomalous scattering. All calculations were carried out on a MicroVAX 3600 computer with the Glasgow GX suite of programs.[27]

Crystallographic and intensity data collection parameters are presented in Table VI.

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Supplementary Material Available: Tables of bond lengths, bond angles, torsion angles, thermal parameters, and hydrogen positional parameters for 1 and 10 (18 pages); listings of observed and calculated structure factors for 1 and 10 (29 pages). Ordering information is given on any current masthead page.

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