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Preliminary communication

Synthesis and chemical characterization of some In–Fe heteronuclear carbonyl compounds; crystal structure of $[NMe_3CH_2Ph]_3[In\{Fe(CO)_4\}_3]$ and $[NEt_4]_2[In_2Br_4\{\mu\text{-}Fe(CO)_4\}_2]$

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Abstract

The reaction in THF of $Na_2[Fe(CO)_4]\cdot x$THF with $InBr_3$ in an approximate 3.5 : 1 molar ratio affords the new $[In\{Fe(CO)_4\}_3]^{3-}$ trianion, which has been isolated as its trimethylbenzylammonium salt and structurally characterized by single-crystal X-ray diffraction studies. On oxidation with two equivalents of $AgBF_4$ it stepwise affords the anions $[In_2Fe_6(CO)_{24}]^{x-}$ with $x = 4$ and 2, respectively. Its reaction with $InBr_3$ gives species of the composition $[InBr_{3-x}\{Fe(CO)_4\}_x]^{x-}$ ($x = 1, 2$), and the anion with the composition $[InBr_2\{Fe(CO)_4\}]^-$ has been structurally characterized as the dimeric species $[In_2Br_4\{\mu\text{-}Fe(CO)_4\}_2]^{2-}$.

Several neutral metal carbonyl derivatives containing Group 13 elements and displaying a trigonal planar stereochemistry of the heteroatom have been reported (e.g. $E\{Co(CO)_4\}_3$ (E = Ga, In, Tl) [1–3], $E\{Mn(CO)_5\}_3$ (E = Ga, In, Tl) [4–6], $M_2(CO)_8\{\mu\text{-}EM(CO)_5\}_2$ (E = Ga, In; M = Mn, Re) [7–9], $E\{MCp(CO)_3\}_3$ (E = Ga, Tl; M = Mo, W) [10–12]). To our knowledge the only anionic species so far reported is $[InBr_2\{Fe(CO)_4\}]^-$, for which a monomeric formulation and a trigonal planar stereochemistry at indium were suggested on the basis of conductivity and spectroscopic measurements, respectively [13]. Since trigonal planar metal carbonyl anionic moieties related to the above species could be potential building blocks for assembling low-dimensional organometallic arrays, we have undertaken a re-investigation of the reaction of the $[Fe(CO)_4]^{2-}$ dianion with indium trihalides.

The addition of one mole of solid $InBr_3$ to a stirred colourless suspension of ca. 3.5 mol of $Na_2[Fe(CO)_4]\cdot x$THF rapidly produces a yellow-orange suspension as a result of almost quantitative formation of $[In\{Fe(CO)_4\}_3]^{3-}$, and small amounts of $[Fe_2(CO)_8]^{2-}$ and $[HFe(CO)_4]^-$. The trianion was isolated as its NEt_4^+ and $NMe_3CH_2Ph^+$ salts by treatment in water or methanol with the relevant tetrasubstituted ammonium halides. Almost independent of the solvent, the salts show

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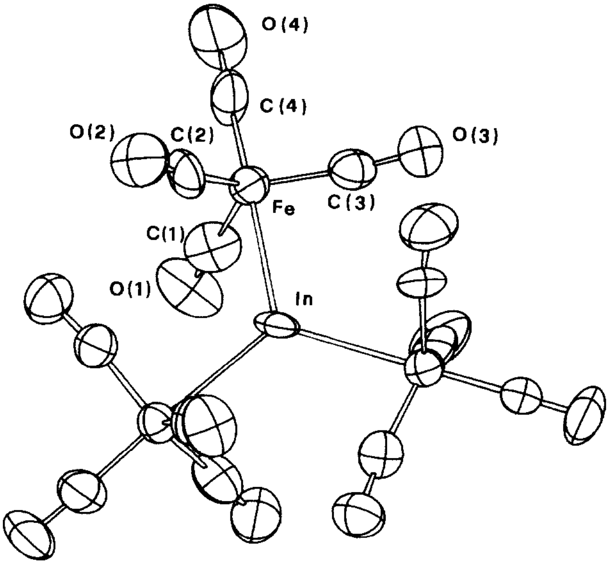

Fig. 1. Molecular structure of the $[In\{Fe(CO)_4\}_3]^{3-}$ trianion which has a C_3 crystallographic symmetry. Principal bond distance: In–Fe 2.633(1) Å.

infrared carbonyl absorptions in solution at 1935(m) and 1849(s) cm^{-1}; the IR pattern suggests a C_{3v} symmetry of the $Fe(CO)_4$ moieties. Crystals of $[NMe_3CH_2Ph]_3[In\{Fe(CO)_4\}_3]$ were grown from an acetonitrile solution by precipitation with di-isopropyl ether, and a single-crystal X-ray structure determination was carried out *. As shown in Fig. 1, the structure of $[In\{Fe(CO)_4\}_3]^{3-}$ is based on a trigonal planar array of three iron atoms surrounding the unique indium atom. Around each iron atom the four carbonyl ligands occupy the three equatorial and one of the two axial sites of a trigonal bipyramid; the indium atom is bound to the second axial site and is in-plane with the three iron atoms, the three axial carbonyls and three out of nine equatorial CO ligands. The trianion has C_3 crystallographic and C_{3h} idealized symmetry, and its structure closely resembles that of $In\{Co(CO)_4\}_3$ [3] and $[E\{Fe(CO)_4\}_3]^{2-}$ (E = Sn, Pb) [14].

Only a few potential condensation reactions of $[In\{Fe(CO)_4\}_3]^{3-}$ have so far been investigated, and some preliminary results are as follows. Addition to $[In\{Fe(CO)_4\}_3]^{3-}$ of one equivalent of $AgBF_4$ in acetonitrile causes a darkening of the solution and a shift of the carbonyl infrared absorptions to higher frequencies

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* *Crystal data:* Data were collected on an Enraf-Nonius CAD-4 diffractometer with the ω-scan method. For $[NMe_3CH_2Ph]_3[In\{Fe(CO)_4\}_3]$: $C_{42}H_{48}Fe_3InN_3O_{12}$, $M = 1069.22$, hexagonal, space group $P6_3$ (No. 173), $a = b = 18.19(1)$, $c = 8.507(8)$ Å, $U = 2438.3$ Å, $F(000) = 1088$, $\mu(\text{Mo-}K_\alpha) = 13.11$ cm^{-1}, $Z = 2$, $D_c = 1.46$ g cm^{-3}, θ-range 2–25°; $R = 0.0600$ for 1240 absorption-corrected reflections with $F_o/\sigma(F_o) > 4.0$. For $[NEt_4]_2[In_2Br_4\{Fe(CO)_4\}_2]$: $C_{24}H_{40}Br_4Fe_2In_2N_2O_8$, $M = 1145.28$ tetragonal, space group $I4_1/acd$ (No. 142), $a = b = 13.611(5)$, $c = 41.049(9)$ Å, $U = 7604.9$ Å^3, $F(000) = 4416$, $\mu(\text{Mo-}K_\alpha) = 59.85$ cm^{-1}, $Z = 8$, $D_c = 2.00$ g cm^{-3}, θ-range 2–28°; $R = 0.0321$ for 1353 absorption corrected reflections with $F_o/\sigma(F_o) > 4.0$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

(ν(CO) at 1970(m) and 1885(s) cm^{-1}). Precipitation allowed the isolation of a red diamagnetic salt having the composition $[NEt_4]_2[In\{Fe(CO)_4\}_3]$, for which a dimeric structure, with tetracoordinate In atoms and two $Fe(CO)_4$ bridging groups (*vide infra*), is suggested on the basis of its diamagnetism. Correspondingly, the reaction of $[In\{Fe(CO)_4\}_3]^{3-}$ with two equivalents of $AgBF_4$ affords the red $[In_2Fe_6(CO)_{20}(\mu\text{-}CO)_4]^{2-}$ dianion (ν(CO) in CH_3CN at 2037(w), 2008(s), 1954(m), 1927(w) and 1781(w) cm^{-1}), which was recently obtained from the reaction of $[Fe_2(CO)_8]^{2-}$ with $InCl_3$ and structurally characterized [15]. These two dimeric anions $[In_2Fe_6(CO)_{24}]^{x-}$ ($x = 2$, 4) are formed directly, along with some $[In\{Fe(CO)_4\}_3]^{3-}$, by reaction of $InBr_3$ with ca. 4 mol of $[HFe(CO)_4]^-$.

The attempted condensation of $[In\{Fe(CO)_4\}_3]^{3-}$ with $InBr_3$ results in successive formation of the yellow products of the compositions shown in eqs. (1) and (2); these products were separately obtained in quantitative yield by addition of ca. 0.5 and 2 mol of $InBr_3$ respectively, per mole of starting $[In\{Fe(CO)_4\}_3]^{3-}$.

$$2\,\left[In\{Fe(CO)_4\}_3\right]^{3-} + InBr_3 \rightarrow 3\,\left[InBr\{Fe(CO)_4\}_2\right]^{2-} \qquad (1)$$

$$\left[InBr\{Fe(CO)_4\}_2\right]^{2-} + InBr_3 \rightarrow 2\,\left[InBr_2\{Fe(CO)_4\}\right]^{-} \qquad (2)$$

Both the $[InBr\{Fe(CO)_4\}_2]^{2-}$ (ν(CO) at 1960(m) and 1865(s) cm^{-1}) and $[InBr_2\{Fe(CO)_4\}]^-$ (ν(CO) at 2014(m) and 1959(s) cm^{-1}) anions were isolated as crystals as NEt_4^+ salts. The latter shows identical composition, infrared absorptions, and reactivity to the compound isolated by Ruff in his pioneering investigation of the reactions of metal carbonyl anions with Group 13 Lewis acids [13]. However, IR monitoring of reaction (2) indicated the intermediate formation of yet another carbonyl species. This seemed to argue against a progressive substitution of

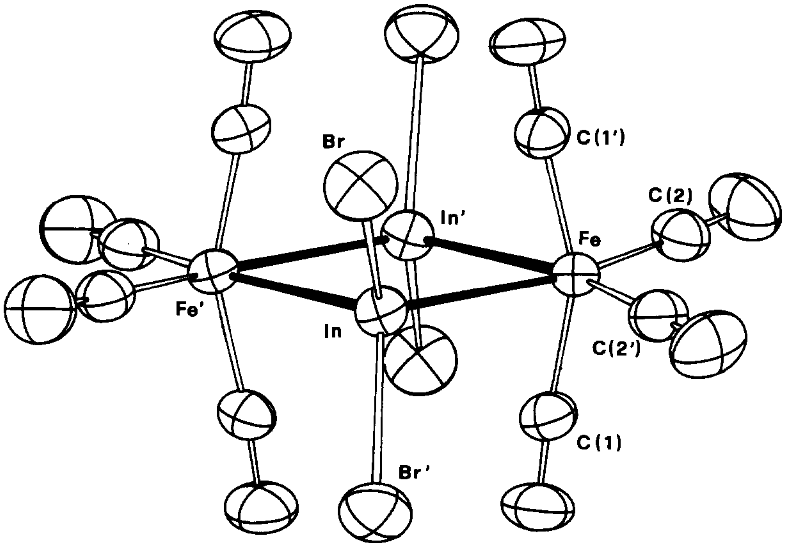

Fig. 2. ORTEP drawing of the $[In_2Br_4\{Fe(CO)_4\}_2]^{2-}$ dianion, D_2 crystallographic symmetry; principal distances (Å) and angles (°) are: In–Fe, 2.668(1); In–Br 2.584(1); Fe···Fe', 4.264(1); In···In', 3.212(1); Fe–C(1), 1.792(5); C(1)–O(1), 1.146(7); Fe–C(2), 1.803(6); C(2)–O(2), 1.134(7); Fe–In–Fe', 106.0(2); In–Fe–In', 74.0(2); Br–In–Br', 102.4(1); C(1)–Fe–C(1'), 157.0(5); C(2)–Fe–C(2'), 102.2(5).

$[Fe(CO)_4]^{2-}$ moieties in $[In\{Fe(CO)_4\}_3]^{3-}$ by bromide ions in the above reactions, and suggested the need to carry out X-ray diffraction studies of the above $[InBr_{3-x}\{Fe(CO)_4\}_x]^{x-}$ ($x = 1, 2$) species.

As shown in Fig. 2, the legend to which lists the most relevant bond interactions, $[NEt_4][InBr_2\{Fe(CO)_4\}]$ * consists of a dimer with two $InBr_2$ and two $Fe(CO)_4$ fragments arranged in a diamond. The coordination geometry is tetrahedral for indium and octahedral for iron. The dianion has D_2 symmetry imposed by the crystal packing, but its idealized symmetry is D_{2h}. The presence of μ-$Fe(CO)_4$, rather than μ-Br, bridges probably arises from the necessity for all the involved atoms to attain the effective atomic number combined with the tendency to delocalize the negative free charge also over the acidic $InBr_2$ moieties. It is conceivable, although not certain because of the high free charge of the resulting dimer, that the corresponding $[InBr\{Fe(CO)_4\}_2]^{2-}$ derivative could adopt a related stereochemistry.

Further reactions of both the $[In_2Fe_6(CO)_{24}]^{x-}$ ($x = 2, 4$) and $[InBr_{3-x}\{Fe(CO)_4\}_x]^{x-}$ ($x = 1, 2$) anions with In^I and In^{III} salts or with $AgBF_4$ provide new series of compounds of increasing complexity, the characterization of which is currently in progress.

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