Synthesis and characterization of $[Fe(NCCH_3)_6][\textit{cis}\text{-}Fe(InX_3)_2(CO)_4]$ (X = Cl, Br, I) containing two terminal indium fragments

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COMMUNICATION

Synthesis and Characterization of [Fe(NCCH$_3$)$_6$][*cis*-Fe(InX$_3$)$_2$(CO)$_4$] (X = Cl, Br, I) Containing Two Terminal Indium Fragments†

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Iron complexes, [Fe(NCCH$_3$)$_6$][*cis*-Fe(InX$_3$)$_2$(CO)$_4$] (X = Cl: 1, Br: 2, I: 3) containing two terminal indium fragments, were synthesized. Their structures were determined using X-ray analysis. The bonding mode of the Fe–In bonds in the anionic part was investigated using ^{57}Fe Mössbauer and IR spectroscopy. These complexes represent the first example of transition metal complexes containing two terminal indium fragments.

The chemistry of complexes in which transition metals are involved in a Z-type interaction with group 13 elements has been developed rapidly, and interesting reactivity has been reported.[1,2] A Z-type interaction (M→E, M = transition metal and E = group 13 element) is formed by the donation of two electrons from electron-rich M to electron-deficient EX$_3$. In group 13 elements, syntheses and reactivities of M→borane complexes are well investigated, whereas much less information is available on M→indane complexes; however, different bonding fashions between M and In have been reported (Fig. 1).[3-8]

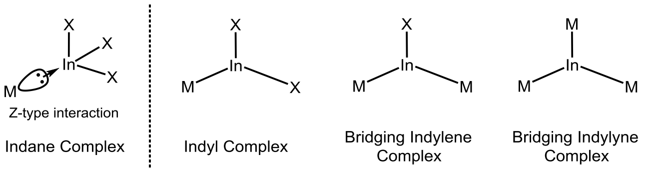


Fig. 1 Various coordination modes of M–In complex.

In 1942, Hieber and Teller reported the first M–In complex [In{Co(CO)$_4$}$_3$] having M–In σ bonds.[9] Since then, a large number of transition metal complexes containing M–In σ bond(s) have been synthesized. We also reported the bridging indylene (W–In–W) complex with tungsten [{Cp(CO)$_3$W}$_2$InCl(py)].[10] However, only a few examples of indane complexes (M→InX$_3$, X = Cl, Br, I) have been reported, and group 6 transition metal complexes have been crystallographically authenticated.[11] In addition, the group of Bourissou synthesized a palladium indane complex [(TPI)Pd] (TPI = triphosphine-indane).[12] Only three examples of iron indane complexes (Fe→In(III)) have been reported so far (Fig. 2).[13]

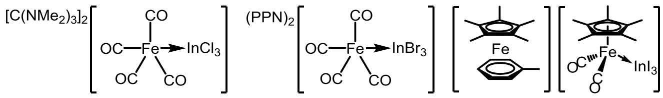
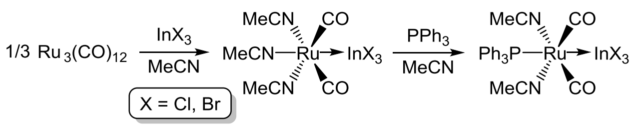


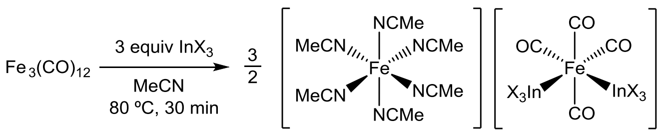
Fig. 2 Examples of previously reported Fe→In(III) complexes.

Previously, we reported the first ruthenium indane complexes *fac*-[Ru(NCMe)$_3$(CO)$_2$(InX$_3$)] (X = Cl, Br) and their reactivity with PPh$_3$ (eqn (1)).[14] In this paper, the synthesis and characterization of iron complexes containing two terminal indium fragments are described, and the bonding mode of the two Fe–In bonds based on ^{57}Fe Mössbauer and IR data are discussed.



(1)

Triiron dodecacarbonyl Fe$_3$(CO)$_{12}$ was treated with 3 equiv of InX$_3$ (X = Cl, Br, I) in acetonitrile at 80 °C for 30 min to produce an iron complex with two InX$_3$ groups, [Fe(NCMe)$_6$][*cis*-Fe(InX$_3$)$_2$(CO)$_4$] (X = Cl: **1**, Br: **2**, I: **3**), in high yields (Scheme 1).



X = Cl: **1** 82%, Br: **2** 85%, I:**3** 89%

Scheme 1 Synthesis of [Fe(NCCH$_3$)$_6$][*cis*-Fe(InX$_3$)$_2$(CO)$_4$] (X = Cl, Br, I).

Complex **2** was obtained in 88% yield in the reaction of Fe$_2$(CO)$_9$ with 2 equiv of InBr$_3$ in acetonitrile at 80 °C for 1 h.

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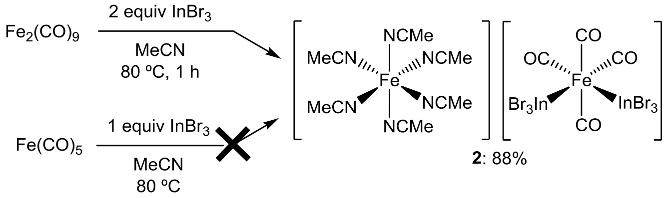
†Dedicated to Professor Kohtaro Osakada on the occasion of his 60th birthday

However, when $Fe(CO)_5$ was used instead of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$, **2** was not formed (Scheme 2).



Scheme 2 Reaction of $InBr_3$ with $Fe_2(CO)_9$ or $Fe(CO)_5$.

The $^{13}C\{^1H\}$ NMR spectrum of **1** at 25 °C showed a broad singlet at δ 216.03 corresponding to the carbonyl groups. This signal split into two singlets (δ 218.38, 219.87) at –40 °C, indicating that **1** in solution shows fluxional behavior.

The electric charge of $[Fe(NCMe)_6]$ is known to be 2+;[15,16] therefore, the electric charge of *cis*-$[Fe(InX_3)_2(CO)_4]$ should be 2–. As **1**–**3** were prepared from $Fe_3(CO)_{12}$, charge disproportionation among neutral Fe(0) species took place. Previously, Scheer *et al.* reported the synthesis of the analogous iron complex $[Na(OEt)]_2[Fe(GaCl_3)_2(CO)_4]$.[17] However, this complex was not synthesized by charge disproportionation but by the reaction of 2 equiv of $GaCl_3$ with the dianion iron complex $Na_2[Fe(CO)_4]$.

The structures of **1**–**3** were determined by X-ray crystallography. The molecular structures of the anionic part of **1**–**3**, *i.e.*, *cis*-$[Fe(InX_3)_2(CO)_4]^{2-}$ (X = Cl, Br, I), are shown in Figs. 3–5, respectively. Two independent molecules of **2** crystallized in the unit cell. As these are basically the same, only one anionic part, *i.e.*, *cis*-$[Fe(InBr_3)_2(CO)_4]^{2-}$ (Fe1 molecule), is shown in Fig. 4. In all cases, the Fe atom for the cationic part is coordinated by six MeCN ligands, and the Fe atom for the anionic part is coordinated by two indium ligands and four terminal CO ligands. These InX_3 ligands are in a mutual *cis* position. The Fe–In bond distances (2.5817(5), 2.5896(6) Å for **1**, 2.5861(13)–2.6039(11) Å for **2**, and 2.6001(7), 2.6233(7) Å for **3**) are longer than those of previously reported Fe–InX_3 (X = Cl, I) complexes (2.517(2) Å for Cl,[13b] 2.5275(9) Å for I[13a]). The distances of Fe–C bonds *trans* to In (1.805(4), 1.811(4) Å for **1**, 1.782(9)–1.816(8) Å for **2**, and 1.805(5), 1.801(5) Å for **3**) are similar to those of Fe–C bonds *trans* to CO (1.802(4), 1.782(4) Å for **1**, 1.786(9)–1.812(7)Å for **2**, and 1.795(5), 1.804(5) Å for **3**). In contrast to the Ru case, the InX_3 ligands of **1**–**3** do not show a greater *trans*-influence than CO.[14] The interaction between Fe and InX_3 in **1**–**3** seems to be weaker than that in the previously reported indane iron complex, because the In–X bond distances for **1**–**3** (X = Cl: 2.3865(9)–2.4153(10) Å for **1**, X = I: for 2.7413(6)–2.7956(5) Å for **3**) are shorter than those for the indane iron complex (X = Cl: 2.432(3)–2.469(3) Å,[13b] X = I: for 2.7942(6)–2.8060(6) Å[13a]).

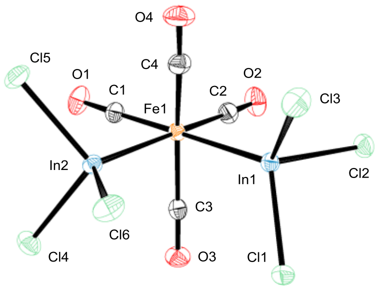


Fig. 3 ORTEP drawing of *cis*-$[Fe(InCl_3)_2(CO)_4]^{2-}$ anionic part of **1** in the crystal (30% thermal ellipsoidal plots). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–In1 2.5896(6), Fe1–In2 2.5817(5), Fe1–C1 1.805(4), Fe1–C2 1.811(4), Fe1–C3 1.802(4), Fe1–C4 1.782(4), C1–O1 1.133(5), C2–O2 1.129(5), C3–O3 1.139(4), C4–O4 1.148(5), In1–Cl1 2.3965(10), In1–Cl2 2.3996(10), In1–Cl3 2.4153(10), In2–Cl4 2.4025(10), In2–Cl5 2.4089(10), In2–Cl6 2.3865(9), In1–Fe1–In2 92.930(17).

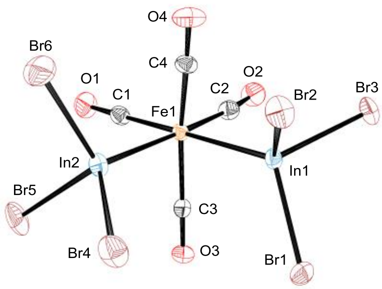


Fig. 4 ORTEP drawing of *cis*-$[Fe(InBr_3)_2(CO)_4]^{2-}$ anionic part (Fe1 molecule) of **2** in the crystal (30% thermal ellipsoidal plots). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–In1 2.6039(11), Fe1–In2 2.5883(10), Fe1–C1 1.782(9), Fe1–C2 1.816(8), Fe1–C3 1.812(7), Fe1–C4 1.794(8), C1–O1 1.134(10), C2–O2 1.121(9), C3–O3 1.125(8), C4–O4 1.126(9), In1–Br1 2.5456(9), In1–Br2 2.5532(10), In1–Br3 2.5655(10), In2–Br4 2.5496(11), In2–Br5 2.5539(12), In2–Br6 2.5369(11), In1–Fe1–In2 93.38(3) for Fe1 molecule. Fe2–In3 2.5861(13), Fe2–In4 2.5910(12), Fe2–C5 1.799(11), Fe2–C6 1.802(8), Fe2–C7 1.786(9), Fe2–C8 1.791(9), C5–O5 1.132(12), C6–O6 1.134(10), C7–O7 1.140(10), C8–O8 1.144(10), In3–Br7 2.5576(11), In3–Br8 2.5504(13), In3–Br9 2.5364(14), In4–Br10 2.5314(14), In4–Br11 2.5505(15), In4–Br12 2.5351(13), In3–Fe2–In4 91.77(4) for Fe2 molecule.

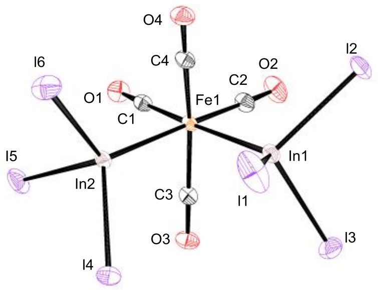


Fig. 5 ORTEP drawing of *cis*-$[Fe(InI_3)_2(CO)_4]^{2-}$ anionic part of **3** in the crystal (30% thermal ellipsoidal plots). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–In1 2.6001(7), Fe1–In2 2.6233(7), Fe1–C1 1.805(5), Fe1–C2 1.801(5), Fe1–C3 1.795(5), Fe1–C4 1.804(5), C1–O1 1.139(6), C2–O2 1.136(6), C3–O3 1.147(6), C4–O4 1.133(6), In1–I1 2.7493(6), In1–I2 2.7956(5), In1–I3 2.7512(6), In2–I4 2.7607(5), In2–I5 2.7845(6), In2–I6 2.7413(6), In1–Fe1–In2 95.33(2).

Next, we focused on the Fe–In bonding mode in the anionic part *cis*-$[Fe(InX_3)_2(CO)_4]^{2-}$. Three possible combinations concerning Fe–In bonds for $[Fe(InX_3)_2(CO)_4]^{2-}$ are conceivable (Fig. 6): (i) two Z-type bonds (electron donation from $[Fe(CO)_4]^{2-}$ to two InX_3 serving as a Lewis acid), (ii) two covalent bonds (two $Fe–In^{-}X_3$, that is, two indate portions), (iii) one Z-type bond and one covalent bond (a situation between (i) and (ii)). The formal oxidation number of Fe is considered to be –II for (i), 0 for (ii), and –I for (iii).

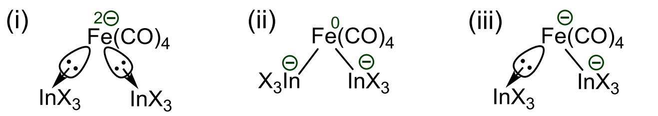


Fig. 6 Three possible structures for the anionic part *cis*-$[Fe(InX_3)_2(CO)_4]^{2-}$.

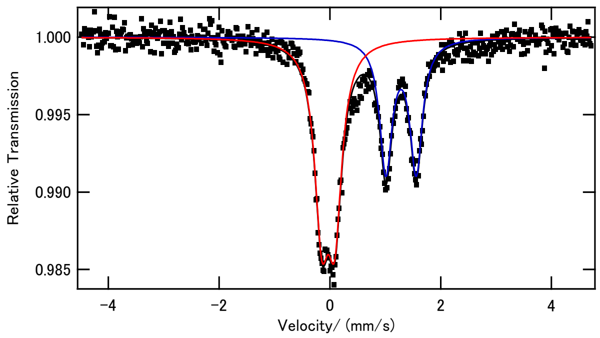


Fig. 7 ^{57}Fe Mössbauer spectrum of solid **1** recorded at 80 K. The black dot marks are the raw data, and the solid lines were obtained from least-squares fits of the spectrum with two doublets, Fe^{2+} component (blue, 40%) δ = 1.28 mm/s, ΔE_Q = 0.55 mm/s and Fe^{0} component (red, 60%) δ = –0.03 mm/s, ΔE_Q = 0.24 mm/s.

The ^{57}Fe Mössbauer spectrum of solid **1**, collected at 80 K, is shown in Fig. 7. Complex **1** displays two doublets with δ = 1.28 mm/s, ΔE_Q = 0.55 mm/s (blue, 40% of Fe) and δ = –0.03 mm/s, ΔE_Q = 0.24 mm/s (red, 60% of Fe). The area ratio of the present sample is 40:60 at 80 K, which is different from the expected ratio. We measured the same sample at 300 K. The ratio (40:60) at 80 K changed to 27:73 at 300 K (see Figure S1). The intensity of Mössbauer absorption changes depending on the molecular vibration. The results suggest that the site of 40% at 80 K is easier to vibrate even at 80 K. The expected ratio would be observed at lower temperature than 80 K. The δ value of the former signal (1.28mm/s) is in the range of the reported values for Fe(+II) species (δ = 0.8–1.4 mm/s).[18] Thus, the doublet can be reasonably assigned to $[Fe(NCMe)_6]^{2+}$. The δ value of the latter signal (–0.03mm/s) is close to that of an Fe(0) complex, such as $Fe(CO)_5$ (0.009 mm/s),[19] and is quite different from that of an Fe(–II) complex, such as $Na_2Fe(CO)_4$ (–0.251 mm/s).[20] The IR spectra of **1**–**3** show ν_{CO} absorptions at 1984, 2030, 2076 cm^{-1} for **1**, 1984, 2016, 2076 cm^{-1} for **2**, and 1988, 2009, 2064 cm^{-1} for **3**. The ν_{CO} absorptions of **1**–**3** are similar to that of the zero-valent iron complex $Fe(CO)_5$ (2000, 2022 cm^{-1})[21] and far from the ν_{CO} absorption of the dianion iron complex $Na_2[Fe(CO)_4]$ (1730 cm^{-1}).[22]

The data obtained from the Mössbauer and IR spectra suggest that the formal oxidation number of the Fe atom in *cis*-$[Fe(InX_3)_2(CO)_4]^{2-}$ is 0 (zero). In addition, there are no large difference between two Fe–In distances and among six In–X distances in **1**-**3**. Therefore, (ii) in Fig. 6 seems to be an appropriate expression for *cis*-$[Fe(InX_3)_2(CO)_4]^{2-}$.

In summary, we synthesized and characterized the first iron complexes $[Fe(NCMe)_6]$[*cis*-$Fe(InX_3)_2(CO)_4$] (X = Cl: **1**, Br: **2**, I: **3**) containing two terminal indium fragments. In solid state and in solution state at –40 °C, two InX_3 fragments are situated in a *cis* position. However, they show *cis*/*trans* fractional behavior in solution at room temperature. The ^{57}Fe Mössbauer and IR data suggest that $Fe^{0}(CO)_4$ has two indate ($Fe–In^{-}X_3$) portions.

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