

*Electronic Supplementary Information (ESI)*

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

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**General considerations:** All of the manipulations were carried out by using standard Schlenk techniques under nitrogen. Acetonitrile and dichloromethane were distilled from  $\text{CaH}_2$  and were stored under a nitrogen atmosphere. Diethyl ether was distilled from sodium metal and was stored under a nitrogen atmosphere. The other chemicals used were commercially available. NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) were recorded at ambient temperature on a JNM AL-400 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data were analyzed with reference to the residual peaks of the solvent. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. IR spectra were recorded on a Perkin-Elmer TIR-Spectrum One spectrometer.  $^{57}\text{Fe}$  Mössbauer spectrum was obtained by using a Wissel Mössbauer spectrometer and a cryostat. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

**Synthesis of  $[\text{Fe}(\text{CH}_3\text{CN})_6][\text{cis-Fe}(\text{InCl}_3)_2(\text{CO})_4]$  (1):** An acetonitrile solution (10 mL) of  $\text{Fe}_3(\text{CO})_{12}$  (0.26 mmol, 132.5 mg) and  $\text{InCl}_3$  (0.79 mmol, 174.6 mg) was stirred for 30 min at 80 °C. The color of the solution turned to pale yellow, along with generation of CO gas. Removal of the volatile materials by vacuum afforded a colorless powder. Complex **1** (0.32 mmol, 294.1 mg, 82%) was isolated by crystallization from acetonitrile/diethyl ether.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , r.t.):  $\delta$ , 11.06 (br,  $\text{CH}_3\text{CN}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.4 MHz,  $\text{CD}_3\text{CN}$ , r.t.):  $\delta$ , 216.03 (br, CO).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.4 MHz,  $\text{CD}_3\text{CN}$ , -40 °C):  $\delta$ , 218.38 (s, CO), 219.87 (s, CO). IR (KBr): 1984(s)  $\text{cm}^{-1}$ , 2030(s), 2076(m)  $\nu(\text{CO})$ . Elemental analysis; calcd for  $\text{C}_{16}\text{H}_{18}\text{Cl}_6\text{Fe}_2\text{In}_2\text{N}_6\text{O}_4$ : C, 20.06; H, 1.99; N, 9.21; found: C, 20.51; H, 2.02; N, 8.58.

**Synthesis of  $[Fe(CH_3CN)_6][cis-(InBr_3)_2Fe(CO)_4]$  (2):** *Method (i).* An acetonitrile solution (10 mL) of  $Fe_3(CO)_{12}$  (0.21 mmol, 103.4 mg) and  $InBr_3$  (0.62 mmol, 218.4 mg) was stirred for 30 min at 80 °C. The color of the solution turned to yellow, along with generation of CO gas. Removal of the volatile materials by vacuum afforded an oily yellow residue. Complex **2** (0.26 mmol, 307.7 mg, 85%) was isolated by crystallization from acetonitrile/diethylether. *Method (ii).* An acetonitrile solution (10 mL) of  $Fe_2(CO)_9$  (0.48 mmol, 174.5 mg) and  $InBr_3$  (0.96 mmol, 340.1 mg) was stirred for 1 h at 80 °C. CO gas was evolved and the color change to yellow occurred. Removal of the volatile materials by vacuum afforded an oily yellow residue. **2** (0.42 mmol, 499.6 mg, 88%) was isolated by crystallization from acetonitrile/diethyl ether.

$^1H$  NMR (400 MHz,  $CD_3CN$ , r.t.):  $\delta$ , 10.21 (br,  $CH_3CN$ ).  $^{13}C\{^1H\}$  NMR (100.4 MHz,  $CD_3CN$ , r.t.):  $\delta$ , 215.86 (s, CO). IR (KBr): 1984(s)  $cm^{-1}$ , 2016(s), 2076(m)  $\nu(CO)$ . Elemental analysis; calcd for  $C_{16}H_{18}Br_6Fe_2In_2N_6O_4$ : C, 16.30; H, 1.54; N, 7.13; found: C, 16.25; H, 1.71; N, 6.88.

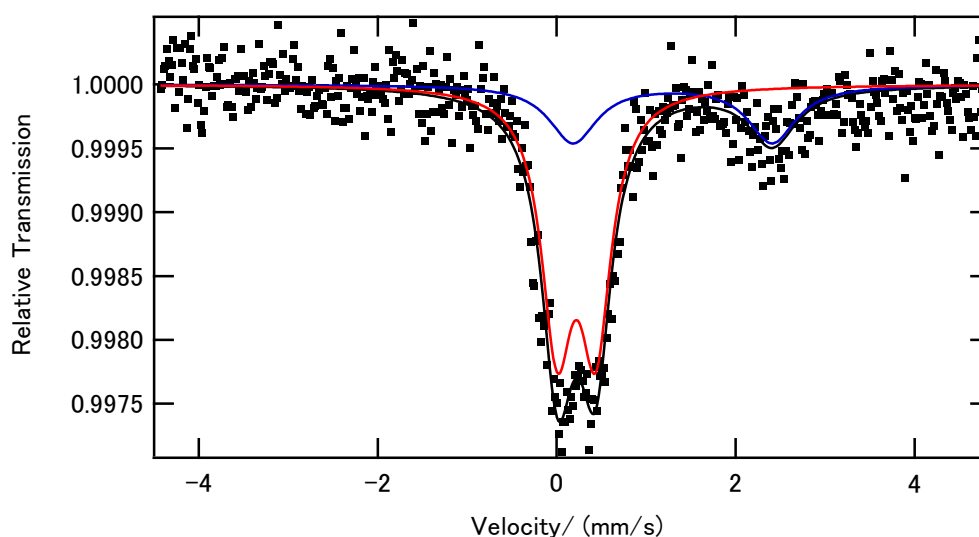
**Synthesis of  $[Fe(CH_3CN)_6][cis-Fe(InI_3)_2(CO)_4]$  (3):** An acetonitrile solution (10 mL) of  $Fe_3(CO)_{12}$  (0.22 mmol, 112.5 mg) and  $InI_3$  (0.67 mmol, 332.1 mg) was stirred for 30 min at 80 °C. The color of the solution turned to orange, along with generation of CO gas. Removal of the volatile materials by vacuum afforded an oily orange residue. Complex **3** (0.30 mmol, 434.7 mg, 89%) was isolated by crystallization from acetonitrile/diethyl ether.

$^1H$  NMR (400 MHz,  $CD_3CN$ , r.t.):  $\delta$ , 7.31 (br,  $CH_3CN$ ).  $^{13}C\{^1H\}$  NMR (100.4 MHz,  $CD_3CN$ , r.t.):  $\delta$ , 214.37 (s, CO). IR (KBr): 1988(s)  $cm^{-1}$ , 2009(s), 2064(m)  $\nu(CO)$ . Elemental analysis; calcd for  $C_{16}H_{18}I_6Fe_2In_2N_6O_4$ : C, 13.15; H, 1.24; N, 5.75; found: C, 12.69; H, 1.25; N, 5.29.

**X-ray crystallography measurements:** Crystals of **1–3** suitable for X-ray diffraction studies were separately mounted in a glass capillary. All of data were collected at 200(1) K on Rigaku AFC-7/Mercury CCD area-detector diffractometer equipped with monochromated  $MoK\alpha$  radiation. All of calculations were performed with the CrystalClear software package of Molecular Structure Corporation. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1403939, 1403940 and 1403941 for **1–3**, respectively.

Table S1. Crystallographic data and details of structure refinement of complexes 1–3.

	1	2	3
empirical formula	C <sub>16</sub> H <sub>18</sub> Cl <sub>6</sub> Fe <sub>2</sub> In <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>18</sub> Br <sub>6</sub> Fe <sub>2</sub> In <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>18</sub> Fe <sub>2</sub> I <sub>6</sub> In <sub>2</sub> N <sub>6</sub> O <sub>4</sub>
formula weight	912.40	1179.16	1461.10
<i>T</i> (K)	200(2)	200(2)	200(2)
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	12.4367(7)	24.0932(7)	13.7811(16)
<i>b</i> (Å)	15.9921(9)	11.7087(3)	11.8004(14)
<i>c</i> (Å)	16.2630(10)	25.1339(7)	23.661(3)
$\beta$ (°)		93.6994(16)	91.9235(17)
volume (Å <sup>3</sup> )	3234.5(3)	7088.0(5)	3845.7(8)
<i>Z</i>	4	8	4
$\rho_{\text{calcd}}$ (mg m <sup>-3</sup> )	1.874	2.214	2.524
$\mu$ (mm <sup>-1</sup> )	2.813	8.896	6.767
<i>F</i> (000)	1760	4384	2624
crystal size (mm <sup>3</sup> )	0.20 × 0.20 × 0.10	0.45 × 0.23 × 0.12	0.17 × 0.17 × 0.15
reflections collected	31914	43522	29054
independent reflections	7395	12366	8679
( <i>R</i> (int))	(0.0449)	(0.0515)	(0.0344)
<i>R</i> 1 ( <i>I</i> > 2σ( <i>I</i> ))	0.0302	0.0556	0.0365
w <i>R</i> 2 (all data)	0.0586	0.1539	0.0884
Goodness of fit	1.064	1.063	1.068



**Fig. S1** <sup>57</sup>Fe Mössbauer spectrum of solid **1** recorded at 300 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<sup>2+</sup> component (blue, 27%)  $\delta = 1.30$  mm/s,  $\Delta E_Q = 0.65$  mm/s and Fe<sup>0</sup> component (red, 73%)  $\delta = 0.22$  mm/s,  $\Delta E_Q = 0.42$  mm/s.