Crystal Structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})]^+(\text{BF}_4)^-\cdot 3\text{CH}_2\text{Cl}_2$

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The crystal structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})]^+(\text{BF}_4)^-\cdot 3\text{CH}_2\text{Cl}_2$ was obtained, revealing the following properties: triclinic, space group $P\bar{1}$ with $a = 13.9482(2)$, $b = 14.7621(2)$, $c = 18.9520(2)\text{\AA}$, $\alpha = 104.9195(6)$, $\beta = 93.6985(7)$, $\gamma = 97.1409(5)^\circ$, $Z = 2$, $R = 0.059$ and $wR2 = 0.133$ for all 19611 unique reflections. The In-F-In bridging unit is characterized by In-F distances of 2.1674(18) and 2.1637(18) $\text{\AA}$ and by an In-F-In angle of $171.28(11)^\circ$; each indium centre is planar three-coordinate (Σ angles at indium = 360° , within the standard 3σ limit, in each case) with In-Fe distances of 2.4740(5) and 2.4760(5) $\text{\AA}$ and Fe-In-C_{ipso} angles of $153.75(8)$ and $154.79(9)^\circ$.

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Studies of the structure, bonding and reactivity of transition-metal complexes containing low coordinate group-13 ligands have been the main focus of considerable recent research interest. We have developed a halide abstraction methodology to generate cationic transition metal complexes featuring multiply bonded boron-containing ligands {e.g. $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})]^+(\text{BAr}^f_4)^-$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{BN}(\text{c-C}_6\text{H}_{11})_2]^+(\text{BAr}^f_4)^-$, $\text{Ar}^f = \text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}$ }.¹ Recently we extended this approach to the heavier group-13 elements, and in particular gallium,² leading to a successful synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{dppe})(\text{GaI})]^+(\text{BAr}^f_4)^-$ [dppe = 1,2-bis(diphenylphosphino)ethane].^{2c} This complex contains a terminally coordinated GaI moiety, and therefore represents the first group 13/17 analogue of classical N₂ and CO ligand systems. In attempting to further develop this approach towards the synthesis of cationic systems containing indanediyl (InR) ligands, we were mindful of previous reports describing the use of aromatic N-donor ligands to trap cationic systems as base stabilized adducts.³ Thus, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Ga}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\text{dtbpy})]^+(\text{BAr}^f_4)^-$ (dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) can be isolated from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Ga}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})\text{I}$ with Na(BAr^f₄) in the

presence of dtbpy.^{3b} Targetting similar chemistry for indium, we therefore examined the reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})\text{Br}$ (**1**)^{2a} with a commercially available halide abstraction agent, AgBF₄ in the presence of 4-picoline. In this event, the greater affinity of fluoride (over 4-picoline) for group-13 Lewis acids is presumably responsible for the formation of the observed product.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})]^+(\text{BF}_4)^-\cdot 3\text{CH}_2\text{Cl}_2$ (**2**) was synthesized as follows: A mixture of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})\text{Br}$ (**1**; 0.050 g, 0.073 mmol) and 4-picoline (0.010 cm³, 0.103 mmol) in CD₂Cl₂ (3 cm³) was added to a slurry of AgBF₄ (0.014 g, 0.072 mmol) in CD₂Cl₂ (0.5 cm³) at -78°C under the exclusion of light. The reaction mixture was allowed to warm to room temperature and sonicated for 1 h. The resulting yellow solution was decanted, concentrated (to ca. 1 cm³) and layered with hexanes. Crystals of **2** were obtained from the layered solution at -30°C . Isolated yield 0.010 g, 35%. ¹H (CD₂Cl₂, 300 MHz): δ_{H} 1.24 (s, 36H, *ortho*-Bu of Mes*), 1.84 (s, 18H, *para*-Bu of Mes*), 1.90 (s, 15H, CH₃ of Cp*), 7.16 (s, 2H, CH of Mes*). ¹³C (CD₂Cl₂, 75

Fig. 1 The chemical structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})]^+(\text{BF}_4)^-$, **2**, in the solid state.

Fig. 2 Molecular structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})]^+(\text{BF}_4)^-\cdot 3\text{CH}_2\text{Cl}_2$, **2**. Relevant bond lengths and angles are included in Table 2; hydrogen atoms, anion and three molecules of dichloromethane have been omitted for clarity. ORTEP ellipsoids set at the 40% probability level.

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Table 1 Crystal data and structure refinement details for **2**

CCDC	682164
Empirical formula	C ₆₃ H ₉₄ BCl ₆ F ₅ Fe ₂ In ₂ O ₄
Formula weight	1575.24
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 13.9482(2)\text{Å}$ $\alpha = 104.9195(6)^\circ$ $b = 14.7621(2)\text{Å}$ $\beta = 93.6985(7)^\circ$ $c = 18.9250(2)\text{Å}$ $\gamma = 97.1409(5)^\circ$
Volume	3717.20(8) Å ³
Z, calculated density	2, 1.41 g cm ⁻³
Absorption coefficient	1.264 mm ⁻¹
$F(0\ 0\ 0)$	1612
Crystal size	0.60 × 0.40 × 0.22 mm
θ range for data collection	5.10 to 29.14°
Limiting indices	$-19 \leq h \leq 19$, $-20 \leq k \leq 19$, $0 \leq l \leq 25$
Reflections collected/unique	65280/19611 [$R(\text{int}) = 0.044$]
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	19611/27/748
Goodness-of-fit on F^2	0.978
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.1249$
R indices (all data)	$R_1 = 0.0591$, $wR_2 = 0.1325$
Largest diff. peak and hole	3.39 and -2.37 eÅ^{-3} (see text)

MHz): δ_C 11.2 (CH₃ of Cp*), 31.4 (*para*-¹Bu quaternary carbon of Mes*), 31.7 (*para*-¹Bu CH₃ of Mes*), 34.1 (*ortho*-¹Bu quaternary carbon of Mes*), 35.2 (*ortho*-¹BuCH₃ of Mes*), 94.9 (quaternary carbon of Cp*), 119.8 (CH of Mes*), 150.5 (*para*-quaternary carbon of Mes*), 157.2 (*ortho*-quaternary carbon of Mes*), 218.1 (CO). ¹¹B (CD₂Cl₂, 96 MHz): δ_B 2.2 (BF₄⁻). IR (CD₂Cl₂, cm⁻¹): $\nu(\text{CO})$ 1937 (st), 1988 (st).

The crystal structure [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})\}^+(\text{BF}_4)^-\cdot 3\text{CH}_2\text{Cl}_2$, **2**], was solved and refined by full-matrix least squares using the programs SIR-92 and Crystals, respectively.⁴ The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The hydrogen atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C-H distances in the range 0.93 to 0.98 Å and $U_{\text{iso}}(\text{H})$ in the range 1.2 to 1.5-times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The *tert*-butyl group C(165)–C(168) was best modelled as a librating group (angle of libration 21.2°) leading to large tangential anisotropic atomic displacement parameters. Soft restraints were applied to the C–C distances, and similarity restraints were applied to the anisotropic atomic displacement parameters. Similar restraints were applied to the dichloromethane of solvation lying near the void at (1/2, 1/2, 0). The diffuse electron density could be seen in this region, but could not be modelled with any sensible chemical. The density was modelled with a discrete Fourier transform of the residual (SQUEEZE) integrated over a volume of 227 Å³. This contribution to the structure factor was saved as the A and B parts, and added into F_c rather than being subtracted from F_o .

The solid-state structure of **2** contains the dinuclear cation [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-F})\}^+$ (Fig. 2), in which two [$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})$] units are linked by a single fluorine atom. The parameters associated with the In($\mu\text{-F}$)In moiety [$d(\text{In}\text{--F}) = 2.1674(18)$, $2.1637(18)\text{Å}$ and $\angle\text{In}\text{--F}\text{--In} = 171.28(11)^\circ$] are consistent with a symmetrical, but slightly bent, bridging unit. The In–F distances are slightly longer than those measured for [(2,4,6-Me₃C₆H₂)₂InF]₃ [2.095(5) – 2.140(5)Å], presumably reflecting the greater steric bulk of the

Table 2 Key bond lengths (Å) and angles (°) for **2**

Fe(1)–C(2)	1.755(3)	Fe(101)–C(145)	2.096(3)
Fe(1)–C(4)	1.764(4)	C(102)–O(103)	1.146(5)
Fe(1)–In(12)	2.4740(5)	C(104)–O(105)	1.152(5)
Fe(1)–C(41)	2.127(3)	In(112)–C(151)	2.163(3)
Fe(1)–C(42)	2.110(3)	In(112)–F(1)	2.1637(18)
Fe(1)–C(43)	2.106(3)		
Fe(1)–C(44)	2.091(3)	C(2)–Fe(1)–C(4)	96.31(17)
Fe(1)–C(45)	2.094(4)	Fe(1)–C(2)–O(3)	178.0(3)
C(2)–O(3)	1.148(4)	Fe(1)–C(4)–O(5)	176.8(3)
C(4)–O(5)	1.140(5)	Fe(1)–In(12)–C(51)	153.75(8)
In(12)–C(51)	2.154(3)	Fe(1)–In(12)–F(1)	106.41(6)
In(12)–F(1)	2.1674(18)	C(51)–In(12)–F(1)	99.81(10)
Fe(101)–C(102)	1.760(4)	C(102)–Fe(101)–C(104)	96.68(18)
Fe(101)–C(104)	1.760(4)	Fe(101)–C(102)–O(103)	177.7(4)
Fe(101)–In(112)	2.4760(5)	Fe(101)–C(104)–O(105)	176.6(3)
Fe(101)–C(141)	2.127(3)	Fe(101)–In(112)–C(151)	154.79(9)
Fe(101)–C(142)	2.102(4)	Fe(101)–In(112)–F(1)	103.74(5)
Fe(101)–C(143)	2.104(4)	C(151)–In(112)–F(1)	101.38(10)
Fe(101)–C(144)	2.095(3)	In(12)–F(1)–In(112)	171.28(11)

[$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{In}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})$] moieties.⁵ The overall structure of the cationic component of **2** resembles that of the related chloride-bridged dinuclear gallium species [$\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Ga}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-Cl})\}^+$], which has recently been isolated as the (BARf₄)⁻ salt.^{2b} In particular, the relatively wide Fe–In–C_{ipso} angles at the three coordinate indium centres [153.75(8) and 154.79(9)°] are very similar to the corresponding Fe–Ga–C_{ipso} angles [149.07(8) and 150.50(9)°] in [$\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Ga}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_2(\mu\text{-Cl})\}^+$]. Contraction of the Fe–In bond lengths in **2** [2.4740(5) and 2.4760(5)Å] compared to the charge neutral precursor **1** [2.509(1)Å] also mirrors the behavior of analogous gallium-containing systems.^{2b}

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