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Fe–Ga multiple bonding? Synthesis, spectroscopic and structural characterization of a transition metal complex containing a cationic two-coordinate gallium centre†

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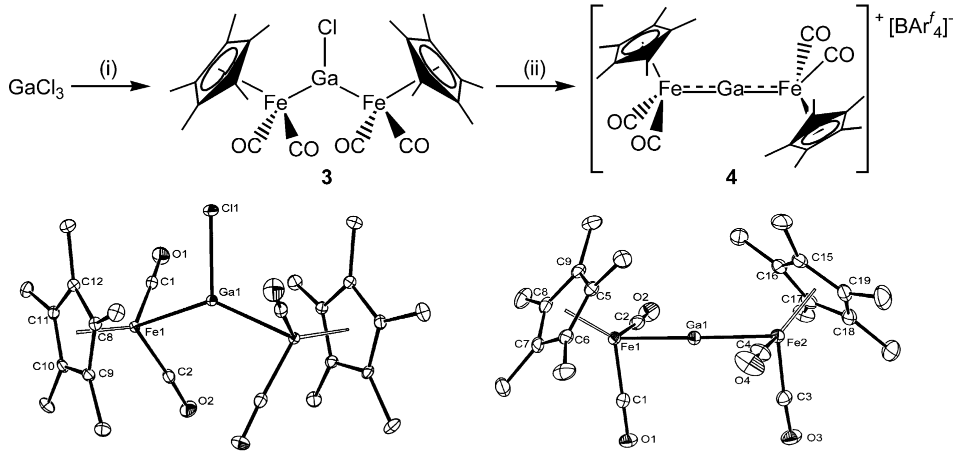
This communication reports the synthesis and characterization of the cationic iron complex [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}$_2$Ga]$^+$[BAr$^f_4$]$^-$ [Ar^f = C$_6$H$_3$(CF$_3$)$_2$-3,5] containing a symmetrically bridging two-coordinate gallium atom and a delocalised Fe–Ga–Fe π system incorporating partial Fe–Ga multiple bond character.

The chemistry of transition metal complexes featuring low coordinate Group 13 ligands continues to attract significant research interest,[1] in part with a view to better understanding the fundamental issues of structure and bonding. Thus, the nature of the interaction between the ligand and the metal centre in diyl systems [L$_n$M(ER)], such as (OC)$_4$Fe(GaAr) [**1**, Ar = C$_6$H$_3$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$-2,6] has been the subject of considerable debate.[2] The description of superficially similar complexes as being bound *via* multiple bonds (*e.g.* L$_n$M=ER or L$_n$M≡ER) or *via* donor–acceptor interactions (*e.g.* L$_n$M←ER) reflects not only the fundamental questions of structure and bonding posed by such systems, but also the scarcity of structural data available.[1–3]

Although several recent theoretical studies have sought to characterize the metal–Group 13 element bond by quantifying its various components,[4] experimental validation has been impaired by the paucity of available synthetic routes. For the heavier Group 13 elements these are confined principally to salt elimination {as used for [(η^5-C$_5$Me$_5$)Fe(dppe)]Ga[Fe(CO)$_4$], **2**},[2a,5] and to reactions of suitable alkyl or aryl precursors, (RE)$_n$, with transition metal complexes containing labile ligands (*e.g.* Ni{Ga[C(SiMe$_3$)$_3$]}$_4$[3a]). Recently we have demonstrated a new synthetic approach to two-coordinate diyl complexes, using halide abstraction to generate the Fe=B double bond in [(η^5-C$_5$Me$_5$)Fe(CO)$_2$(BMes)]$^+$[BAr$^f_4$]$^-$ [Ar^f = C$_6$H$_3$(CF$_3$)$_2$-3,5].[6] Given the continuing debate surrounding charge neutral diyl systems, we have sought to extend this methodology to *cationic* species offering the potential for M=E multiple bonding involving the heavier Group 13 elements. Herein we report the synthesis of [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}$_2$Ga]$^+$ which features a naked symmetrically bridging gallium atom and a significant Fe–Ga π bonding component.

Reaction of gallium trichloride with two equivalents of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] leads to the formation of chlorogallylene complex **3** (Scheme 1).‡ Spectroscopic data are consistent with the proposed formulation,§ which was confirmed crystallographically.¶ The steric bulk of the (η^5-C$_5$Me$_5$)Fe(CO)$_2$ fragment appears to have a strong influence on structural and reaction chemistry. Hence, in contrast to the corresponding (η^5-C$_5$H$_5$) derivative, **3** is monomeric in the solid state [Σ(angles at Ga) = 360.00(3)°],‖ shows no hint of oligomerization *via* Ga–Cl–Ga bridges, and can be crystallised from thf without coordination at gallium.[7] **3** therefore represents a suitable precursor for the formation of a two-coordinate cationic gallium centre by halide abstraction.

Monitoring of the reaction of **3** with a single equivalent of Na[BAr$^f_4$] in CD$_2$Cl$_2$ (by ^{1}H NMR) reveals quantitative conversion to a single η^5-C$_5$Me$_5$ containing species;‡ the significantly higher carbonyl stretching frequencies (2016, 1994, 1963 *vs.* 1960, 1925, 1910 cm^{-1}) are consistent with the development of a net positive charge implied by chloride abstraction.[6] Multinuclear NMR, IR and mass spectral data for the isolated crystalline product are consistent with [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}$_2$Ga]$^+$ and [BAr$^f_4$]$^-$ ions,§ and these spectroscopic inferences were subsequently confirmed crystallo-



Scheme 1 Syntheses of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$]$_2$GaCl (**3**) and [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}$_2$Ga] [BAr$^f_4$] (**4**). Reagents and conditions: (i) Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] 2 equiv., toluene, 20 °C, 12 h; (ii) Na[BAr$^f_4$] 1 equiv., dichloromethane, −78 °C to 20 °C, 30 min. Relevant bond lengths (Å), angles (°) and torsion angles (°): for **3** Fe(1)–Ga(1) 2.3524(4), Fe(1)–C(1) 1.760(3), Fe(1)–centroid 1.725(3), Ga(1)–Cl(1) 2.283(1), Fe(1)–Ga(1)–Fe(1′) 138.90(3), Fe(1)–Ga(1)–Cl(1) 110.55(1); for the cationic component of **4** Fe(1)–Ga(1) 2.272(1), Fe(2)–Ga(1) 2.266(1), Fe(1)–C(1) 1.764(3), Fe(1)–centroid 1.728(3), Fe(1)–Ga(1)–Fe(2) 178.99(2), centroid-Fe(1)–Fe(2)-centroid 84.62(3).

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† Electronic supplementary information (ESI) available: *xyz* file corresponding to the fully optimised geometry of [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}$_2$Ga]$^+$ and full details of the crystal structures of **3** and **4**. See http://www.rsc.org/suppdata/cc/b4/b405943c/

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graphically.¶ Thus halide abstraction from **3** proceeds cleanly as outlined in Scheme 1, leading to the generation of the cationic dinuclear complex $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\}_2\text{Ga}][\text{BAr}^f{}_4]$ (**4**). To our knowledge **4** represents the second structurally characterized example of a two-coordinate cationic gallium centre, and the first featuring bonds to a transition metal.[8]

A number of structural features are worthy of further comment. (i) The linear Fe–Ga–Fe unit [$\angle$ Fe(1)–Ga(1)–Fe(1′) = 178.99(2)°] is consistent with a two-coordinate gallium centre engaging in no significant secondary interactions (*e.g.* with the anion).[8] This geometry is consistent with that found in the only other complex containing a ‘naked’ bridging gallium atom (*i.e.* **2**) and contrasts with the bent geometry found in base-stabilized analogues.[5,9–11] (ii) The Fe–Ga bond lengths [2.266(1) and 2.272(1) Å] are significantly shorter than those found in **3** [2.3524(4) Å] and in compounds conventionally thought of a possessing Fe–Ga single bonds (2.36–2.46 Å).[1a] Furthermore, they are similar to that found in the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(dppe)}]$Ga unit of **2** [2.248(1) Å], which possesses unsaturated character as a result of significant π back-bonding from the electron-rich $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(dppe)}$ fragment.[5] (iii) The centroid–Fe(1)–Fe(2)–centroid torsion angle [84.62(3)°] implies a relative alignment of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]$ fragments which allows for optimal Fe→Ga π back-bonding. For related carbene complexes, most effective back-bonding involves the HOMO of the $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe(CO)}_2]^+$ fragment (an a″ symmetry orbital roughly co-planar with the cyclopentadienyl ligand).[12] In the case of **4**, optimal stabilization of the mutually perpendicular pair of formally vacant Ga p orbitals would therefore be achieved by orthogonal alignment of the HOMOs of the two $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]$ fragments and consequently by a torsion angle of *ca.* 90°.

In order to provide a fuller basis for discussion of the bonding in **4**, DFT analysis was carried out at the BLYP/TZP level using established methods.[13] The fully optimised geometry [d(Fe–Ga) = 2.338, 2.337 Å; $\angle$(Fe–Ga–Fe) = 177.9°, $\angle$(Ct–Fe–Fe–Ct) = 86.5°] is consistent with that determined crystallographically. A *bond population analysis* was carried out to quantify the relative importance of σ and π components to the Fe–Ga covalent interaction using a method previously applied to the borylene cation $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2(\text{BMes})]^+$ and to boryl complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{Fe(CO)}_2(\text{BX}_2)$.[6,13] This reveals a 61 : 38 σ : π breakdown of the covalent Fe–Ga interaction {*c.f.* 86 : 14 for the Fe–Ga single bond in the model compound $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{GaCl}_2$, and a 62 : 38 breakdown for $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2(\text{BMes})]^+$}.[6,13b] Further evidence for a significant Fe–Ga π component is provided by analysis of the atomic orbital contributions to the MOs HOMO-3 to HOMO-6, each of which features in-phase contributions from gallium- and iron-centred π symmetry orbitals (Ga 4p_x and 4p_y and Fe 3d_{xz} and 3d_{yz}).

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Notes and references

‡ *Syntheses of* $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]_2\text{GaCl}$ (**3**) *and* $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\}_2\text{Ga}][\text{BAr}^f{}_4]$ (**4**). Reaction of GaCl_3 (0.163 g, 0.93 mmol) with a suspension of $\text{Na}[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2]$ (0.500 g, 1.85 mmol) in toluene (30 cm^3) at 20 °C for 12 h, followed by filtration, concentration to *ca.*10 cm^3 and cooling to −50 °C yielded **3** as a bright yellow microcrystalline material (0.200 g, 36%). X-ray quality crystals were grown by layering a solution in thf with hexanes, and cooling to −50 °C for 1 week. Treatment of **3** (0.045 g, 0.075 mmol) with 1 equiv. of $\text{Na}[\text{BAr}^f{}_4]$ in CH_2Cl_2 (20 ml) at −78 °C, followed by warming to 20 °C over 30 min., filtration and removal of volatiles *in vacuo* yielded **4** as a golden yellow powder (0.050 g, 46%). X-ray quality crystals were grown by layering a CH_2Cl_2 solution with hexanes.

§ *Spectroscopic data for* **3** *and* **4**. **3**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.68 (s, 30H, $\eta^5\text{-C}_5\text{Me}_5$); (300 MHz, CD_2Cl_2): δ 1.85 (s, 30H, $\eta^5\text{-C}_5\text{Me}_5$). ^{13}C NMR (76 MHz, C_6D_6): δ 9.7 (Me of $\eta^5\text{-C}_5\text{Me}_5$), 94.4 ($\eta^5\text{-C}_5\text{Me}_5$ quaternary), 217.2 (CO). IR (cm^{-1}): ν(CO) (KBr disc) 1955 st, 1932 st, 1919 m sh; (CH_2Cl_2 solution) 1960 st, 1925 st, 1910 m sh. EI-MS: *m/z* 598 (M$^+$, 5%), correct isotope distribution for 2 Fe, 1 Ga and 1 Cl atoms, significant fragment ions at *m/z* 570 ([M − CO]$^+$, 35 %), 542 ([M − 2CO]$^+$, 25%). Exact mass (M$^+$): calc. 597.9782, meas. 597.9780. **4**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 30H, $\eta^5\text{-C}_5\text{Me}_5$), 7.54 (s, 4H, *p*-H of $\text{BAr}^f{}_4{}^-$), 7.70 (s, 8H, *o*-H of $\text{BAr}^f{}_4{}^-$). ^{13}C NMR (76 MHz, CD_2Cl_2): δ 10.3 (Me of $\eta^5\text{-C}_5\text{Me}_5$), 97.5 ($\eta^5\text{-C}_5\text{Me}_5$ quaternary), 117.5 (*p*-CH of $\text{BAr}^f{}_4{}^-$), 122.8 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3 of $\text{BAr}^f{}_4{}^-$), 128.8 (q, $^2J_{\text{CF}}$ = 34 Hz, *m*-C of $\text{BAr}^f{}_4{}^-$), 134.8 (*o*-CH of $\text{BAr}^f{}_4{}^-$), 160.8 (q, $^1J_{\text{CB}}$ = 53 Hz, *ipso*-C of $\text{BAr}^f{}_4{}^-$), 211.4 (CO). ^{19}F NMR (283 MHz, CD_2Cl_2): δ −62.8 (CF_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ −7.6 ($\text{BAr}^f{}_4{}^-$). IR (cm^{-1}): ν(CO) (CH_2Cl_2 solution) 2016 m, 1994 st, 1963 st. ES-MS (neg.): *m/z* 863 ($\text{BAr}^f{}_4{}^-$); ES-MS (pos.): *m/z* 563 (M$^+$, 5%), correct isotope distribution for 2 Fe and 1 Ga atoms. Exact mass (M$^+$): calc. 563.0093, meas. 563.0092.

¶ *Crystallographic data for* **3** *and* **4**. $\text{C}_{24}\text{H}_{30}\text{ClFe}_2\text{GaO}_4$, **3**: orthorhombic, *Pcnb*, a = 11.1946(2), b = 12.9307(3), c = 16.9269(4) Å, U = 2450.24(9) Å^3, Z = 4, d_c = 1.625 Mg m^{-3}, M_r = 599.34, T = 150(2) K. 29314 reflections collected, 3574 independent [R(int) = 0.1124] which were used in all calculations. R_1 = 0.0486, wR_2 = 0.0981 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0678, wR_2 = 0.1050 for all unique reflections. Max. and min. residual electron densities: 1.310 and −0.761 e Å^{-3}, respectively. $\text{C}_{56}\text{H}_{42}\text{BF}_{24}\text{Fe}_2\text{GaO}_4$, **4**: triclinic, $P\bar{1}$, a = 14.442(3), b = 15.004(3), c = 15.541(3) Å, α = 66.25(3), β = 71.75(3), γ = 75.17(3)°, U = 2894.5(10) Å^3, Z = 2, d_c = 1.637 Mg m^{-3}, M_r = 1427.13, T = 150(2) K. 43319 reflections collected, 13120 independent [R(int) = 0.0770] which were used in all calculations. R_1 = 0.0443, wR_2 = 0.1038 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0599, wR_2 = 0.1119 for all unique reflections. Max. and min. residual electron densities: 1.069 and −0.699 e Å^{-3}, respectively. CCDC 237193 and 237194. See http://www.rsc.org/suppdata/cc/b4/b405943c/ for crystallographic data in .cif or other electronic format.

‖ Bridging gallylene (gallanediyl) complexes featuring three-coordinate gallium centres have previously been reported only in association with very bulky gallylene substituents.[14]

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