A novel multidecker sandwich complex from the reaction of ferrocene with GaCl₃

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A redox reaction takes place between GaCl₃ and an excess of ferrocene, leading to the multidecker sandwich complex 1, [–Ga(C₅H₅)Fe(C₅H₅)Ga(C₅H₅)Fe(C₅H₅)–]ₙ[GaCl₄]₂ₙ, which features an array of alternating Ga(I) and Fe(II) ions bridged by cyclopentadienyl moieties.

Transition metals as well as main group elements form a wide variety of complexes with the cyclopentadienyl ligand.[1,2] Many of these compounds have been investigated by X-ray crystallography. Two species are particularly noteworthy in the context of this paper: (i) ferrocene, (η⁵-C₅H₅)₂Fe,[3] the bis(cyclopentadienyl) complex of Fe(II) and (ii) the pentamethylcyclopentadienyl complex of Ga(I), which forms a hexameric cluster (η⁵-C₅Me₅Ga)₆[4] in the solid state. Related, but less stable π-complexes of main group elements with uncharged aromatic systems are also known. Schmidbaur et al., for example, succeeded in the synthesis and structural characterisation of various Ga(I) arene complexes.[5,6]

A landmark in the field was the discovery of multidecker sandwich complexes (e.g. of nickel and rhodium) with the 2,3-dihydro-1,3-diborolyl ligand, which is able to coordinate two transition metal atoms in an η⁵ fashion, thereby adopting a bridging position.[7] Analogous compounds consisting of a main group element and a transition metal are, however, very rare {cf. (C₅H₅)Co(C₂Me₂B₂Me₂C)Tl[8] and [(C₅H₅)Co(C₂Et₂B₂Me₂-C)]₂Sn[9]}.

Herein we report on the polymeric multidecker sandwich complex 1 featuring an array of alternating Ga(I) and Fe(II) ions bridged by cyclopentadienyl moieties (Scheme 1). When an equimolar solid mixture of ferrocene and GaCl₃ is treated with benzene,† a blue–green solution is obtained, which contains paramagnetic species (¹H NMR spectroscopic monitoring). From this solution, a first crop of blue–green crystals was isolated and identified as [(C₅H₅)₂Fe][GaCl₄] by means of X-ray crystallography.[10] The mother-liquor was evaporated and the pulpy residue recrystallised from CH₂Cl₂ to give a second crop consisting of red platelets, which are highly sensitive to air and moisture. An X-ray crystal structure determination‡ of the material revealed the multidecker sandwich complex 1 featuring Ga(I) centers, each coordinated to two different ferrocene molecules (Scheme 1). This leads to the conclusion that a redox process has taken place [Scheme 1, eqn. 1(a)] in the system ferrocene/GaCl₃, rather than an electrophilic substitution of the Cp ring as in the case of the related system ferrocene/BBr₃[11] [Scheme 1, eqn. 1(b)].

When a smaller amount of benzene is employed, we observe the immediate precipitation of microcrystalline [(C₅H₅)₂Fe]-[GaCl₄], as well as the formation of two separate liquid phases. A similar phenomenon has been reported by Schmidbaur et al.[12] upon dissolving Ga[GaBr₄] in aromatic solvents and has been attributed to the presence of solvent clathrates at higher concentrations.

GaCl₃ as well as GaCl₃·dioxane, can be reduced not only with ferrocene, but also with decamethylferrocene and cobaltocene.

The corresponding oxidation products, [(C₅Me₅)₂Fe][GaCl₄] and [(C₅H₅)₂Co][GaCl₄], have been identified by X-ray crystal structure analysis.[13]

A comparison of the ¹H NMR spectra (d₆-benzene) of 1 (4.38 ppm; $h_{1/2}$ 20.4 Hz) and ferrocene (4.00 ppm) reveals a downfield shift of 0.38 ppm for the former. The Ga(I) ion of Ga[GaCl₄] exhibits a resonance at δ −715 in its ⁷¹Ga NMR spectrum (d₆-benzene), which is shifted by 45 ppm to lower field (δ −670) when ferrocene is added to the solution. This leads to the conclusion that a certain proportion of the Ga(I) centers remain coordinated to the electron-rich ferrocene molecules, even in the presence of an excess of benzene. Compound 1 crystallises in the monoclinic space group $P2_1/n$ (Fig. 1).‡

The Ga(I) centers are coordinated by two chelating [GaCl₄]⁻ moieties and two cyclopentadienyl ligands. Each [GaCl₄]⁻ anion links two Ga(I) centres, thereby creating polymeric rods running through the crystal lattice. Perpendicular to these rods, zigzag chains consisting of Ga(I) ions and ferrocene molecules are established. Each Ga(I) centre is coordinated to two Cp rings of two different ferrocene molecules in an η⁵ fashion. The mean
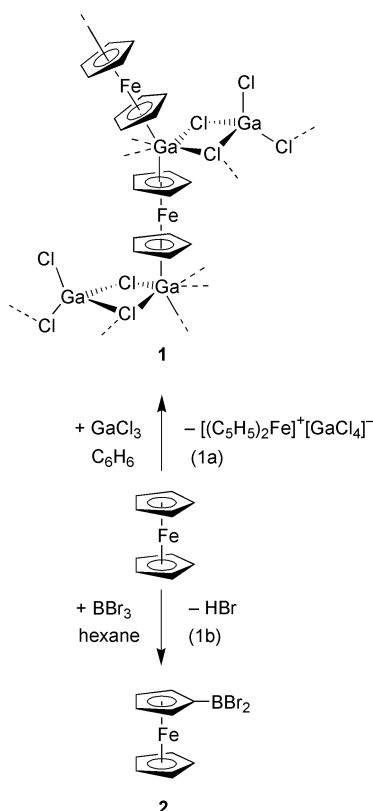
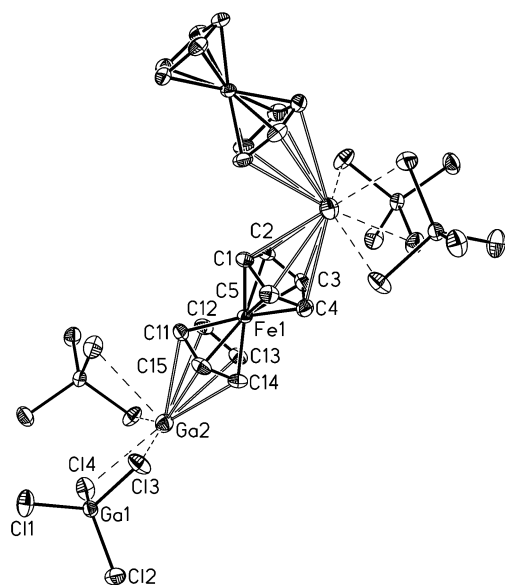Scheme 1 Reactions of EX₃ (E = B, Ga; X = Cl, Br) with ferrocene.

Fig. 1 Solid state structure of **1**. H atoms have been omitted for clarity. Selected bond lengths (pm) and angles (°): Ga(2)–C(1) 299.8(3), Ga(2)–C(2) 301.5(3), Ga(2)–C(3) 312.0(3), Ga(2)–C(4) 315.4(3), Ga(2)–C(5) 308.4(3), Ga(2)–C(11) 334.6(3), Ga(2)–C(12) 331.5(3), Ga(2)–C(13) 316.6(3), Ga(2)–C(14) 311.3(3), Ga(2)–C(15) 322.4(3), Ga(2)–Cl(2) 338.0(1), Ga(2)–Cl(3) 314.9(1), Ga(2a)–Cl(3) 326.6(1); Cl(1)–Ga(1)–Cl(2) 110.77(3), Cl(1)–Ga(1)–Cl(4) 109.97(3), Cl(2)–Ga(1)–Cl(4) 111.60(3), Cl(1)–Ga(1)–Cl(3) 109.81(3), Cl(2)–Ga(1)–Cl(3) 107.49(3), Cl(4)–Ga(1)–Cl(3) 107.10(3); mean value Ga(2)–COG(Cp) 291.2.

distance Ga(2)–C(Cp) between Ga(I) and the Cp carbon atoms is 315.3 pm, a value very close to the mean Ga–C(benzene) distance of 316 pm observed in the complex $[Ga(C_6H_6)_2]^+[GaCl_4]^-$.[5] Compared to $(\eta^5-C_5Me_5Ga)_6$, which features a mean Ga–C(Cp*) distance of 240.0 pm,[4] the Ga(2)–C(Cp) bond lengths in **1** are elongated by 75.3 pm. An average distance of 291.2 pm is found between Ga(2) and the centres of gravity (COG) of the cyclopentadienyl rings in compound **1** {*cf.* $[Ga(C_6H_6)_2]^+[GaCl_4]^-$: average distance Ga–COG(C_6H_6) 284.7 pm[5]}. The $[Fe(C_5H_5)_2]_2Ga$ fragment is bent by an angle Cp(COG)–Ga(2)–Cp(COG) of 110.3°.

To gain further insight into the relative stability of Ga(I)–benzene *vs.* Ga(I)–ferrocene complexes, DFT calculations were performed.§ The optimised structure of $[Fe(C_5H_5)_2]_2Ga^+$ had an average Ga–C distance of 293 pm and an angle Cp(COG)–Ga(2)–Cp(COG) of 158°. The optimised angle for the unit is sufficiently different from that found in the crystal structure to suggest that the coordination of the Ga(I) to the $[GaCl_4]^-$ units partly determines the angle. The optimisation was repeated with the angle fixed at 110° as found experimentally; the average Ga–C distance lengthened to 305 pm, closer to that found experimentally. The energy of the species with an angle of 110° is 22 kJ mol^{-1} above the ground state species, indicating a soft surface for bending. The binding energy of two ferrocene molecules to Ga$^+$ was calculated as 213 kJ mol^{-1} while that for formation of $[Ga(C_6H_6)_2]^+$ from two benzene molecules and Ga$^+$ is calculated to be less at 136 kJ mol^{-1}. Fragment analysis of $[Fe(C_5H_5)_2]_2Ga^+$ indicated a transfer of 0.4 electrons into the gallium 4p orbitals compared with a zero occupancy for Ga$^+$. This points towards a small covalent interaction between the ferrocenes and the Ga(I) ion.

Notes and references

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