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An unprecedented mode of ligation for a bridged amido-cyclopentadienide (constrained geometry) ligand; π-olefinic interactions with gallium and indium

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The surprising reaction of $GaCl_3$ or $InBr_3$ with the di-Grignard reagent $[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)](MgCl)_2\cdot THF$ results in salts of the bimetallic anions of composition $[X_3M\{C_5Me_4(N\text{-}t\text{-}Bu)\}MX_2]^-$ (M = Ga, X = Cl; M = In; X = Br) in which the MX_2 moiety undergoes an η^2-interaction with one of the double bonds of the localized cyclopentadienide ring.

The bridged amido-cyclopentadienide ligand $[Me_2Si(C_5Me_4)N\text{-}t\text{-}Bu]^{2-}$ (**1**) has attracted considerable attention for the development of several so-called "constrained geometry complexes" of the d- and f-block elements,[1–3] some of which have proved to be important as olefin polymerization catalysts.[4] It is therefore curious that considerably less is known regarding bridged amido-cyclopentadienide complexes of the main group elements. Indeed, such complexes are limited to $[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)](MgCl)_2\cdot THF$ (**2**), a Grignard reagent of unknown structure,[5] base-stabilized group 13 complexes of the type $[Me_2Si(\eta^1\text{-}C_5Me_4)(N\text{-}t\text{-}Bu)]MMe\cdot Base$ (M = Al, Ga; Base = THF, tetramethylimadazol-2-ylidene),[6] and some group 15 monochlorides of composition $[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)]ECl$ (E = P, As, Sb) and cations derived therefrom.[7] We have now discovered that the above-mentioned Grignard reagent, **2**, undergoes an unusual type of reaction with $GaCl_3$ or $InBr_3$ to afford novel bimetallic anions in which one of the group 13 elements is bonded to the cyclopentadienide ring in an olefinic η^2-fashion.

Treatment of an equimolar quantity of the di-Grignard reagent, **2**, with $GaCl_3$ in THF solution resulted, after workup, in a 29% yield of a colourless, crystalline product, **3**.[8] The presence of an intact amido-cyclopentadienide ligand was inferred from the ^1H NMR spectrum of **3** which evidenced resonances corresponding to N-*t*-Bu, $SiMe_2$ and ring Me groups. However, the CI-mass spectrum (negative mode) indicated the presence of two gallium atoms in the product. Accordingly, it was necessary to carry out an X-ray analysis.† The crystalline state of **3** consists of an array of $[Mg_2Cl_3(THF)_6]^+$ ($\mathbf{3}^+$) cations and $[GaCl_3\{Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)\}GaCl_2]^-$ ($\mathbf{3}^-$) anions (Figure 1). There are no close interionic contacts. Regarding the structure of $\mathbf{3}^-$, the first point to note is that, in agreement with the ^1H NMR data, the amido-cyclopentadienide ligand is intact and no rearrangement has taken place (*cf.* ref. 7). Apart from the negative charge, the most conspicuous difference between the structure of $\mathbf{3}^-$ and those of composition $[Me_2Si(\eta^1\text{-}C_5Me_4)(N\text{-}t\text{-}Bu)]GaMe\cdot Base$ (the only other gallium complexes with an amido-cyclopentadienide ligand) is the presence of two gallium atoms. A $GaCl_3$ group is attached to C(1) of the C_5Me_4 ring and constitutes part of what can be regarded as an alkyltrichlorogallate moiety. Although there is a slight scatter of bond angles, the geometry at this gallium centre is close to tetrahedral and the average Cl–Ga–Cl bond angle of 106.07(4)° is similar to those reported for *e.g.* $[MeGaCl_3]^-$ (108.2(6)° and 107.1(2)°).[9] A $GaCl_2$ fragment occupies a position between the C(4) and C(5) carbon atoms and the N-*t*-Bu group. The C_5Me_4 ring is completely planar (sum of internal bond angles = 540.0(2)°) with a localized diene structure as shown by the fact that the C(2)–C(3) and C(4)–C(5) bonds (av. 1.371(3) Å) are appreciably shorter than the remaining three carbon–carbon bonds (av. 1.478(3) Å). The environment around Ga(1) can be construed as an η^2-olefin complex of an amidodichlorogallane. Such a view is supported by the following facts: (i) the C(4)–C(5) bond (1.385(3) Å) is longer than the C(2)–C(3) bond (1.357(3) Å), (ii) the $NGaCl_2$ moiety departs from trigonal planarity (sum of angles at Ga = 338.26(7)°) due to interaction with the C(4)–C(5) π-bond, (iii) the methyl groups attached to C(4) and C(5) are bent out of the Cp ring plane by 0.211(4) Å [C(14)] and 0.276(4) Å [C(15)], and (iv) the Ga(1)–C(4) and Ga(1)–C(5) bond lengths of 2.406(3) and 2.393(2) Å, respectively, are very similar to those reported recently for a Ga-alkyne π-interaction (av. 2.361(5) Å).[10] Although short η^1-arene carbon interactions with Ga(III) or In(III) centres have been observed previously,[11] we believe that the π-olefinic interactions in $\mathbf{3}^-$ and $\mathbf{4}^-$ (see later) are unprecedented. The structure of $\mathbf{3}^+$ has been reported previously[12] and our metrical parameters are very similar to the literature values.

The diindium salt, $[Mg_2BrCl_2(THF)_6][InBr_3\{Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)\}InBr_2]$ (**4**: X = Cl, Br) was prepared in 34% yield *via* the reaction of **2** with $InBr_3$ in THF solution in an analogous fashion to that described for **3**.[8] The X-ray crystal structure of **4**† is very similar to that of **3**. The exclusive presence of bromide ligands in the anion and a $\mu_3\text{-}Cl_2Br$ bridging unit in the cation was established on the basis that the R_1 values for alternative structural models were significantly higher. As in the structure of $\mathbf{3}^-$, the planar C_5Me_4 ring of $\mathbf{4}^-$

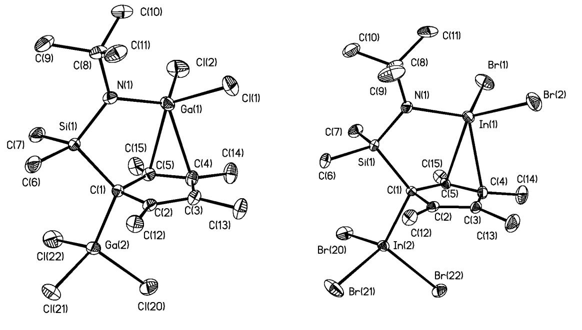

Fig. 1 Structures of anions $\mathbf{3}^-$ (left) and $\mathbf{4}^-$ (right). Important bond lengths [Å] and angles [°] (the corresponding values for $\mathbf{4}^-$ are shown in parentheses): Ga(1)–C(4) 2.406(3) (2.551(7)), Ga(1)–C(5) 2.393(2) (2.566(6)), Ga(1)–N(1) 1.864(2) (2.072(6)), Ga(1)–Cl(1) 2.2071(10) (2.5341(12)), Ga(1)–Cl(2) 2.1962(9) (2.5102(12)), C(1)–C(2) 1.495(3) (1.487(8)), C(2)–C(3) 1.357(3) (1.360(10), C(3)–C(4) 1.450(3) (1.445(10)), C(4)–C(5) 1.385(3) (1.386(9)), C(1)–Ga(2) 2.012(2) (2.215(6)), Ga(2)–Cl(20) 2.2030(10) (2.5154(11)), Ga(2)–Cl(21) 2.2012(9) (2.5159(11)), Ga(2)–Cl(22) 2.2037(10) (2.5175(10)), C(1)–Si(1) 1.913(2) (1.909(6)), Si(1)–N(1) 1.725(2) (1.710(6)), C(4)–Ga(1)–C(5) 33.55(8) (31.4(2)), Ga(1)–C(4)–C(5) 72.70(14) (74.9(4)), Ga(1)–C(5)–C(4) 73.75(15) (73.7(4)), Cl(1)–Ga(1)–Cl(2) 103.14(4) (103.77(4)), C(2)–C(1)–C(5) 103.3(4) (103.3(5)), C(1)–C(2)–C(3) 110.2(2) (110.1(6)), C(2)–C(3)–C(4) 108.5(2) (108.9(6)), C(3)–C(4)–C(5) 109.4(2) (108.9(6)), C(1)–C(5)–C(6) 108.6(9) (108.8(6)), Cl(20)–Ga(2)–Cl(21) 107.97(4) (103.86(5)), Cl(21)–Ga(2)–Cl(22) 104.13(4) (107.30(4)), Cl(20)–Ga(2)–Cl(22) 106.11(4) (107.90(4)), Si(1)–N(1)–Ga(1) 115.32(11) (112.9(3)), Ga(1)–N(1)–C(8) 118.42(16) (119.3(5)) Si(1)–N(1)–C(8) 126.27(17) (127.5(5)).

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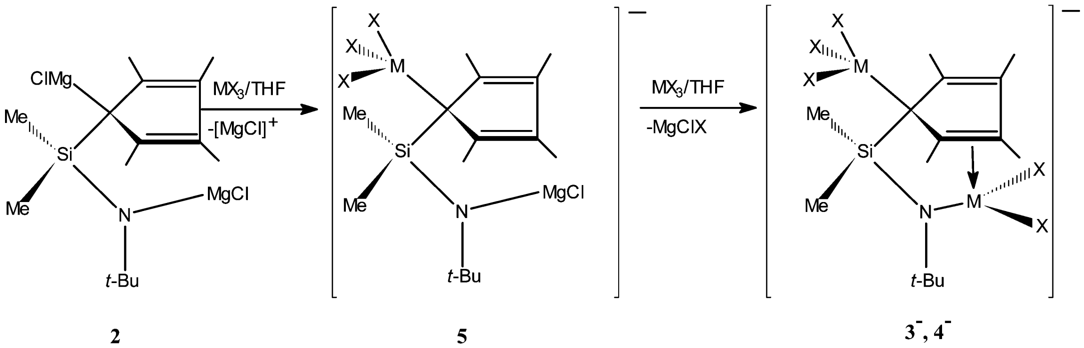

M = Ga, X = Cl; M = In, X = Br

Scheme 1

features localized double bonds and the C(4)–C(5) distance (1.386(10) Å) is longer than the C(2)–C(3) distance (1.360(10) Å). Moreover, the amidoindium dibromide moiety is distorted from a trigonal planar geometry (sum of angles at N(1) = 339.71(4)°) and the C(4) and C(5) methyl groups are bent out of the Cp ring plane in a similar fashion and extent to those in **3**$^-$, leading to the conclusion that In(1) experiences an olefinic π-type interaction with the C(4)–C(5) double bond. The overall structural features of **4**$^+$ are similar to those of **3**$^+$.

Although the mechanism of formation of **3** and **4** is not known, some plausible steps that could account for the observed products are illustrated in Scheme 1. Starting with a postulated structure for the di-Grignard reagent, **2**, Lewis acid attack at the carbanionic centre could result in the anions, **5**. A metathetical reaction of the second MgCl moiety could then form the observed anions, **3**$^-$ and **4**$^-$. The counter cations $[Mg_2Cl_2X(THF)_6]^+$ would result from the combination of $[MgCl]^+$ with MgClX and the requisite number of THF ligands.

Notes and references

† *Crystal data*. Single crystals were covered with mineral oil and mounted on a Nonius KAPPA-CCD at 153(2) K using Mo–Kα radiation (λ = 0.71069 Å). Both structures were solved by direct methods. **3**: $C_{39}H_{75}Cl_8Ga_2Mg_2NO_6Si$, monoclinic, $P2_1/n$, a = 12.464(5), b = 19.300(5), c = 23.142(5) Å, β = 100.558(5)°, V = 5473(3) Å^3, Z = 4, D_{calcd} = 1.400 g cm^{-3}, μ (Mo–Kα) = 1.460 mm^{-1}; wR_2 = 0.0863, R_1 = 0.0364. **4**: $C_{39}H_{75}Br_6Cl_2In_2Mg_2NO_6Si$, monoclinic $P2_1/c$, a = 20.235(4), b = 19.009(4), c = 15.175(3), V = 5695(2) Å^3, Z = 5, D_{calcd} = 1.762 g cm^{-3}, μ = 5.195 mm^{-1}, wR_2 = 0.1572, R_1 = 0.601. CCDC 211521 and 211522. See http://www.rsc.org/suppdata/cc/b3/b304940j/ for crystallographic data in CIF or other format.

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8 Compounds **3** and **4** were synthesized in a similar fashion except that in the case of **4**, the reaction mixture was heated at 60 °C for 5.0 h. A solution of $[Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)(MgCl)_2{\cdot}THF]$[5] (1.60 g, 3.6 mmol) in 30 mL of THF was added slowly to a solution of $GaCl_3$ (0.64 g, 3.6 mmol) in 40 mL of THF at −78 °C. The stirred reaction mixture was allowed to come to room temperature overnight, following which the solvent and volatiles were removed under reduced pressure. The resulting residue was extracted with 50 mL of toluene and filtered through a glass frit covered with diatomaceous earth. Storage of the filtrate at 20 °C afforded a crop of colourless crystals of **3** (mp 120–2 °C) in 29% yield. **3**: ^1H ^{1}NMR (300 MHz, C_6D_6) δ 0.60 (s, 6H, $SiMe_2$), 1.49 (s, 9H, $NCMe_3$), 1.9 (s, br., 12H, C_5Me_4). **4**: (colourless crystals, mp 143–5 °C): ^1H NMR (300 MHz, C_6D_6) δ 0.76 (s, 6H, $SiMe_2$), 1.71 (s, 9H, $NCMe_3$), 2.27 (s, 6H, C_5Me_2), 2.53 (s, 6H, C_5Me_2).
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