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Gallium–boron donor–acceptor bonds

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Examples of compounds with gallium–boron donor–acceptor bonds, $\mathrm{HC[MeC(2,6\text{-}Pr^i_2C_6H_3)N]_2Ga{\rightarrow}B(C_6F_5)_3}$ 3 and $\mathrm{(\eta^5\text{-}C_5Me_5)Ga{\rightarrow}B(C_6F_5)_3}$ 4 have been prepared by treatment of the free gallanediyls with $\mathrm{B(C_6F_5)_3}$; the structures of both compounds were determined by X-ray crystallography.

Although most of the organometallic chemistry of gallium features this element in the +3 oxidation state, the recent literature reflects an emerging interest in gallium(I) derivatives. Typically, RGa species tend to aggregate into weakly bound tetrameric[1] or hexameric[2] entities; however, if a sufficient steric blockade is deployed, it is possible to isolate monomeric derivatives.[3,4] Thus, for example, $\mathrm{(Dipp_2nacnac)Ga}$ **1** ($\mathrm{HC[MeC(2,6\text{-}Pr^i_2C_6H_3)N]_2Ga}$) is monomeric in the solid state[4] while $\mathrm{(\eta^5\text{-}C_5Me_5)Ga}$ **2** (Cp*Ga) is monomeric in the vapour state.[5] Molecular orbital calculations on **1**[6] and **2**[7] indicate that both molecules adopt a singlet ground state. Accordingly, **1** and **2** are anticipated to exhibit Lewis base behaviour due to the presence of a lone pair of electrons on gallium. Indeed, it has been shown that **2** displays ligative behaviour towards transition metal moieties[8] but such complexes do not exemplify pure Lewis base behaviour because of the possibility of varying degrees of back donation on the part of the d-block element. Herein, we disclose two examples of compounds with gallium–boron donor–acceptor bonds.

The borane complexes $\mathrm{HC[MeC(2,6\text{-}Pr^i_2C_6H_3)N]_2Ga{\rightarrow}B(C_6F_5)_3}$ **3** and $\mathrm{(\eta^5\text{-}C_5Me_5)Ga{\rightarrow}B(C_6F_5)_3}$ **4** were obtained by treatment of **1** and **2**, respectively, with $\mathrm{B(C_6F_5)_3}$ in toluene solution.† The ^{11}B NMR spectra of **3** and **4** comprise broad singlets at δ −20.3 and −17.94, respectively, which fall in the tetracoordinate boron region and the ^{19}F chemical shifts of the equivalent $\mathrm{C_6F_5}$ groups are similar to those reported for other Lewis base complexes of $\mathrm{B(C_6F_5)_3}$.[9] In the ^{1}H NMR spectrum of **3** the β-diketiminate ligand resonances display a symmetric pattern thus implying *syn* η^2 bonding to gallium, while for **4** the equivalence of the methyl protons is suggestive of η^5-Cp* ring attachment. The foregoing spectroscopic indications were confirmed by means of X-ray crystallography.‡ The crystalline states of both complexes consist of individual molecules of **3** and **4** and there are no unusually short intermolecular contacts. In complex **3**, which crystallizes as two crystallographically independent but chemically identical monomeric complexes (Fig. 1), the gallium atoms have trigonal planar geometry with an average Ga–N bond distance of 1.942(6) Å. The latter distance is considerably shorter than the Ga–N bond distances (av. 2.054(2) Å) in the precursor **1**.[4] This is consistent with a decrease in the partial antibonding character of these bonds upon conversion of the gallium lone pair into a gallium–boron donor–acceptor bond, and the concomitant development of positive and negative charges on the gallium and boron atoms, respectively. The $\mathrm{C_3N_2Ga}$ array of the β-diketiminate ring is essentially planar with C–C and C–N distances (Fig. 1 legend) that are indicative of delocalization of the π-electrons. As is apparent from Fig. 1, the B–Ga–N angles differ slightly (by *ca.* 5°) which is a result of differing steric interactions caused by the orientation of the $\mathrm{C_6F_5}$ rings relative to the $\mathrm{C_6H_3Pr^i_2\text{-}2,6}$ substituents. The $\mathrm{C_5Me_5}$ group of **4** is attached to gallium in an η^5 fashion (Fig. 2) and the ring centroid–Ga–B moiety is essentially linear (176.65(6)°). While the average Ga–C

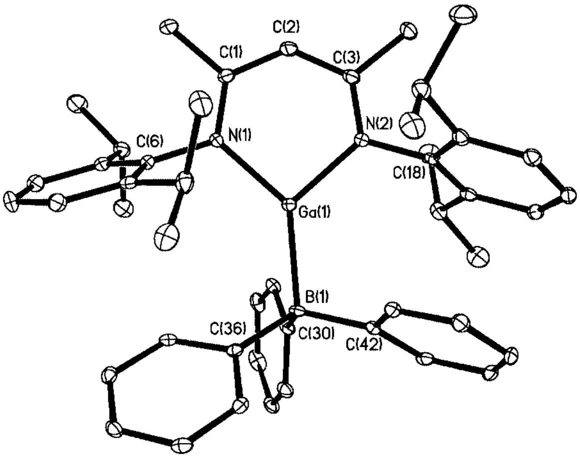

Fig. 1 Thermal ellipsoid plot (30%) one of the two crystallographically independent molecules of **3**. H and F atoms are not shown. Selected bond distances (Å) and angles (°) Ga(1)–B(1) 2.156(1), Ga(2)–B(2) 2.142(3), Ga–N(av.) 1.942(6), N(1)–C(1) 1.331(4), C(1)–C(2) 1.395(4), C(2)–C(3) 1.388(4), C(3)–N(2) 1.339(4), B–C(av.) 1.641(6); N(1)–Ga(1)–N(2) 96.1(1), N(3)–Ga(2)–N(4) 95.7(1), Σ°CB(1)C 334.3(2), Σ°CB(2)C 332.8(2).

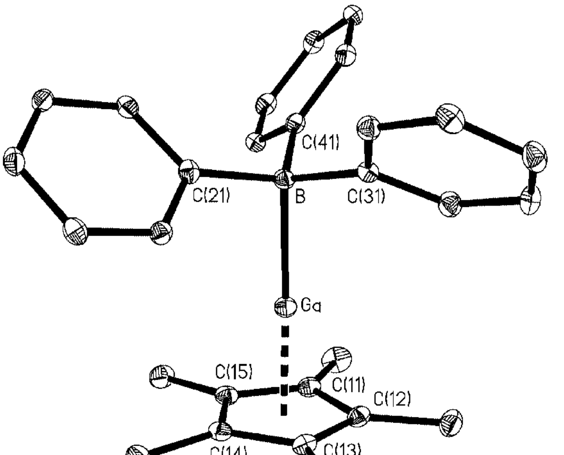

Fig. 2 Thermal ellipsoid plot (30%) of $\mathrm{(\eta^5\text{-}C_5Me_5)Ga{\rightarrow}B(C_6F_5)_3}$ **4** showing the atom-labeling scheme. Hydrogen and fluorine atoms have been removed for clarity. Selected bond distances (Å) and angles (°) Ga–B 2.160(2), Ga–$\mathrm{Cp^*_{centroid}}$ 1.8648(9), Ga–C(11) 2.217(2), Ga–C(12) 2.226(2), Ga–C(13) 2.227(2), Ga–C(14) 2.238(2), Ga–C(15) 2.230(2), B–C(21) 1.623(3), B–C(31) 1.629(3), B–C(41) 1.633(3); C(21)–B–C(31) 113.15(15), C(21)–B–C(41) 115.7(2), C(31)–B–C(41) 113.23(15), Σ°CBC 342.2(2).

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distance of 2.228(2) Å is considerably shorter than those reported for (η^5-C_5Me_5)Ga (2.405(4) Å)[5] and [(η^5-C_5Me_5)Ga]$_6$ (2.380(9) Å),[10] they are in good agreement with those reported for the transition metal derivatives (η^5-C_5Me_5)-GaFe(CO)$_4$ (2.226(2) Å) and (η^5-C_5Me_5)GaCr(CO)$_5$ (2.260(3) Å).[8] The cause of this Ga–C bond shortening upon coordination is similar to that described above for the Ga–N bond shortening of **3**. The Ga–B bond distances in **3** (2.142(3) Å, Ga(2)–B(2) and 2.156(3) Å, Ga(1)–B(1)) and **4** (2.160(2) Å) are slightly longer than that predicted for a single bond from the sum of the covalent radii of Ga (1.25 Å) and B (0.85 Å). These bond distances may be compared with the average Ga–B distances reported for a variety of gallium-substituted carboranes (2.14–2.33 Å).[11] Due to the donor action of the (Dipp$_2$nacnac)Ga and (η^5-C_5Me_5)Ga fragments, the geometry of the B(C_6F_5)$_3$ changes from trigonal planar to distorted tetrahedral. The extent of the geometrical change from trigonal planar toward tetrahedral of B(C_6F_5)$_3$ has been taken to be an indication of the strength of the donor–acceptor interactions.[9] The sums of the C–B–C bond angles at boron in compound **3** (334.3(2), B(1); 332.8(2)°, B(2)) and **4** (342.2(2) Å) may be compared with the 339.8(2)° reported previously[12] for (η^5-C_5Me_5)Al$\rightarrow$B(C_6F_5)$_3$, suggesting that (η^5-C_5Me_5)Ga is a slightly weaker Lewis base than (η^5-C_5Me_5)Al whereas (Dipp$_2$-nacnac)Ga appears to be a slightly stronger base than either molecule. It remains to be seen if this is an accurate measure of the Lewis basicity of (Dipp$_2$nacnac)Ga where high steric effects may also play a role.§

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Notes and references

† All manipulations were carried out under anaerobic and anhydrous conditions. **3**: With rapid stirring, a pale yellow toluene solution (20 mL) of (Dipp$_2$nacnac)Ga (0.768 g, 1.5 mmol) was added dropwise to B(C_6F_5)$_3$ (0.730 g, 1.5 mmol) in toluene (10 mL). After several minutes the solution became colourless. The toluene was removed under reduced pressure and the residue was dissolved in hexane (30 mL). The hexane solution was concentrated to a volume of approximately 10 mL, and allowed to cool to *ca.* −20 °C overnight. After 20 h, large colorless crystals of **3** were obtained (1.21 g, 81%). mp 160–162 °C. ^{1}H NMR (300 MHz, 298 K, C_6D_6) δ 7.02 (t, *p*-H, $^3J_{HH}$ 7.5 Hz, 2H), 6.79 (d, *m*-H on phenyl, $^3J_{HH}$ 7.8 Hz), 4.99 (s, 1H, methine CH), 2.81 (sept, $^3J_{HH}$ 6.6 Hz, 4H, C*H*Me), 1.39 (s, 6H, CMe), 1.02 (d, $^3J_{HH}$ 6.6 Hz, 12H, CH*Me*$_2$), 0.88 (d, $^3J_{HH}$ 6.6 Hz, 12H, CH*Me*$_2$): ^{11}B NMR (128 MHz, C_6D_6) δ −20.30: ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 170.72 (CN), 149.98 (br, *o*-C_6F_5), 146.82 (br, *p*-C_6F_5), 142.38 (*C*Me), 141.31 (*o*-C on phenyl; *C*CHCMe$_2$), 138.56 (br, *m*-C_6F_5), 135.40 (br, *ipso*-C_6F_5), 128.47 (*p*-C on phenyl), 124.63 (*m*-C on phenyl), 101.25 (γ-C), 29.80 (*C*HMe$_2$), 24.78 (CH*Me*$_2$), 24.45 (C*Me*), 23.05 (CH*Me*$_2$). ^{19}F{^{1}H} NMR (376.0 MHz, 300 K, C_6D_6) δ −129.43 (*m*-C_6F_5), −156.19 (*p*-C_6F_5), −160.20 (*o*-C_6F_5). **4**: A solution of B(C_6F_5)$_3$ (0.62 g, 1.22 mmol) in 30 mL of toluene was added to a pale yellow solution of [(C_5Me_5)Ga]$_6$ (0.25 g, 1.22 mmol of (C_5Me_5)Ga units) in 20 mL of toluene at −78 °C. The stirred yellow-coloured reaction mixture was maintained at −78 °C for 1 h, following which it was allowed to warm slowly to room temperature and stirred for an additional 4 h. The resulting tan coloured solution was filtered through Celite. The filtrate was concentrated *in vacuo* until the volume was *ca.* 10 mL; slow cooling to −20 °C afforded a crop of colourless crystals, 0.65 g, 0.91 mmol, 75% yield; mp 125–135 °C (decomp.). ^{1}H NMR (300.00 MHz, 295 K, C_6D_6): δ 1.465 (s, C_5Me_5, 15 H); ^{11}B{^{1}H} NMR (96.28 MHz, 295 K, C_6D_6): δ −17.94 (br, $w_{1/2}$ = 2887 Hz]; ^{13}C{^{1}H} NMR (75.48 MHz, 295 K, C_6D_6): δ 147.62 (d, *o*-C_6F_5, $^1J_{CF}$ 239 Hz), 141.36 (d, *p*-C_6F_5, $^1J_{CF}$ 254 Hz), 137.62 (d, *m*-C_6F_5, $^1J_{CF}$ 252 Hz), 129.28 (s, *ipso*-C_6F_5), 114.64 (s, *C*$_5$(CH$_3$)$_5$), 8.54 (s, C$_5$(*C*H$_3$)$_5$); ^{19}F{^{1}H} NMR (282.0 MHz, 295 K, C_6D_6): δ −131.28 (s, *m*-C_6F_5), −153.81 (s, *p*-C_6F_5), −163.05 (s, *o*-C_6F_5).

‡ *Crystal data* for **3**: monoclinic, space group $P2_1/c$, a = 18.1799(15), b = 23.8400(19), c = 21.5818(18) Å, β = 111.279(2)°, V = 8716.0(12) Å^3, Z = 8, D_c 1.523 g cm^{-3}, R_1 = 0.0431, wR_2 = 0.1138. For **4**: monoclinic, space group $P2_1/c$, a = 9.2222(18), b = 24.000(5), c = 12.063(2) Å, β = 93.67(3)°, V = 2664.5(9) Å^3, Z = 4, D_c = 1.787 g cm^{-3}, R_1 = 0.0332, wR_2 = 0.0910. Suitable single crystals of **3** and **4** were covered with mineral oil and mounted on a Bruker Smart AXS 1000 diffractometer at 90 K (**3**) or a Nonius-Kappa CCD diffractometer at 133 K (**4**). Data sets for **3** and **4** were collected using Mo-Kα radiation (λ = 0.71073 Å). For **3**, there were a total of 17 805 independent reflections in the range $1.2 < \theta < 26.38°$ and, of these, 11 235 reflections were observed ($I > 2.0\sigma(I)$) for the solution (direct methods) and refinement (full matrix, least squares on F^2). For **4**, a total of 6009 independent reflections were collected in the range $5.98 < 2\theta < 54.94°$. Of these, 5306 (R_{int} = 0.0413) were considered observed ($I > 2.0\sigma(I)$) and were used to solve (direct methods) and refine (full matrix, least squares on F^2) the structure of **4**. CCDC reference numbers 168666 and 168667. See http://www.rsc.org/suppdata/cc/b1/b106599h/ for crystallographic data in CIF or other electronic format.

§ *Note added in proof*: after this work had been submitted, another paper that described the synthesis and structure of **4** was published.[13]

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