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Synthesis and characterization of the monomer Ga{(NDippCMe)$_2$CH} (Dipp = C$_6$H$_3$Pr$^i{}_2$-2,6): a low valent gallium(I) carbene analogue

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The reaction between solvent free Li{(NDippCMe)$_2$CH} (Dipp = C$_6$H$_3$Pr$^i{}_2$-2,6), 'GaI' and potassium in toluene afforded Ga{(NDippCMe)$_2$CH} 1 which features a V-shaped, two-coordinate, six-electron gallium(I) center electronically analogous to a singlet carbene carbon.

Neutral, molecular derivatives of low-valent gallium usually exist as Ga–Ga bonded tetramers[1] or hexamers[2] of formula (GaR)$_4$ or (GaR)$_6$ which may dissociate to monomers in either the vapor or the solution phase.[3] Lower degrees of aggregation than four are extremely rare in the solid state, and the monomeric compound Ga(Tp$^{\mathrm{Bu^t}_2}$) [Tp$^{\mathrm{Bu^t}_2}$ = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato] is the only such example to have been well characterized. In this species, the bulky tridentate Tp$^{\mathrm{Bu^t}_2}$ ligand prevents association by coordinatively saturating the gallium center to afford a complex with four electron pairs in the metal valence shell.[4] In related work it has been demonstrated that the anion of the salt [K(18-crown-6)(thf)$_2$][Ga{N(Bu^t)CH}$_2$] contains a two-coordinate gallium center that has just three valence electron pairs and is electronically analogous to a carbene carbon.[5] In addition, the use of extremely bulky terphenyl ligands in the compounds MC$_6$H$_3$Trip$_2$-2,6 (M = In or Tl; Trip = C$_6$H$_2$Pr$^i{}_3$-2,4,6) has shown that unassociated, low valent, one-coordinate, monomers with only two electron pairs in the metal valence shell can be stabilized.[6]† In attempting to extend this work to lower valent gallium we were struck by the close steric resemblance (Fig. 1) between the terphenyl ligand C$_6$H$_3$Trip$_2$-2,6[7] and the Dipp substituted β-diketiminate ligand (NDippCMe)$_2$CH (Dipp = C$_6$H$_3$Pr$^i{}_2$-2,6).[8] This led to the hypothesis that the use of a crowded β-diketiminate ligand should stabilize a Ga(I) derivative with a low degree of aggregation. The synthesis and characterization of such a compound are now described.

Yellow crystals of Ga{(NDippCMe)$_2$CH} **1** were obtained‡ by the reaction of Li{(NDippCMe)$_2$CH} with "GaI"[9] and subsequent treatment with potassium to reduce any I$_2$Ga{(N-DippCMe)$_2$CH} formed in the reaction. Compound **1** was characterized by ^{1}H and ^{13}C NMR spectroscopy, UV-VIS and IR spectroscopy and C, H elemental analyses. These data were consistent with the structure (Fig. 2) obtained by X-ray crystallography§ which showed that the molecule is monomeric and has a V-shaped two-coordinate geometry at gallium. The central GaN$_2$C$_3$ ring atoms, the C(4) and C(5) methyl carbons, and the *ipso*-carbons C(6) and C(18) are essentially coplanar. The substituent aryl (Dipp) ring planes are oriented at angles of 88.2 and 89.2° with respect to the plane of the GaN$_2$C$_3$ ring. The C–C and N–C distances within this ring are similar to those previously reported for this ligand.[10]

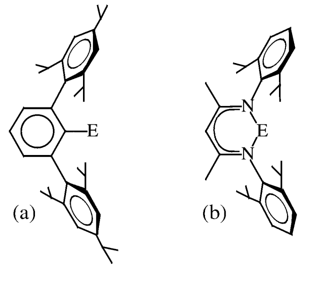

Fig. 1 Schematic drawing of the C$_6$H$_3$Trip$_2$-2,6 (Trip = C$_6$H$_2$Pr$^i{}_3$-2,4,6) and (NDippCMe)$_2$CH (Dipp = C$_6$H$_3$Pr$^i{}_2$-2,6) ligands illustrating their steric resemblance and the protection they afford the bound site E.

The most interesting structural features in **1** concern; (a), the two-coordinate environment at gallium, (b), the Ga–N distances which average 2.054(2) Å, and (c) the NGaN angle of 87.56(6)°. The Ga–N distances in **1** are relatively long in view of the low coordination number of the gallium atom, and do not support the presence of significant multiple Ga–N bond character which might have arisen from delocalization of the π-electrons of the C$_3$N$_2$ ring moiety. Instead, the bonding in **1** is probably best viewed as involving a Ga$^+$ ion complexed by the bidentate, monoanionic ligand [(NDippCMe)$_2$CH]$^-$. The increased ionic and less directional character of the Ga–N bonds are also consistent with the narrow N–Ga–N angle. The Ga–N distances in **1** are shorter than the 2.230(5) Å observed in Ga(Tp$^{\mathrm{Bu^t}_2}$)[4] as a result of the lower metal coordination number. On the other hand, the Ga–N distances in [Ga{N(Bu^t)CH}$_2$]$^-$ [Ga–N 1.985(6) Å][5] are shorter than those observed in **1**, probably as a result of the lower steric effects of the {N(Bu^t)CH}$_2$ ligand.¶ The relatively long Ga–N distances in these monovalent complexes are underlined by the fact that the trivalent digallium species {HC(Bu^t)N}$_2$Ga–Ga{N(Bu^t)CH}$_2$[11] {which has the same ligand as that in [Ga{N(Bu^t)CH}$_2$]$^-$} has Ga–N distances of 1.836(4) and 1.839(6) Å. These values are typical of those found for three-coordinate Ga–N bond lengths in trivalent complexes with similarly sized ligands.[12]

A significant feature of interest in **1** is the presence of a lone pair of electrons at gallium which suggests that this ligand will display significant Lewis base chemistry. Experiments on this aspect of **1** are in progress.

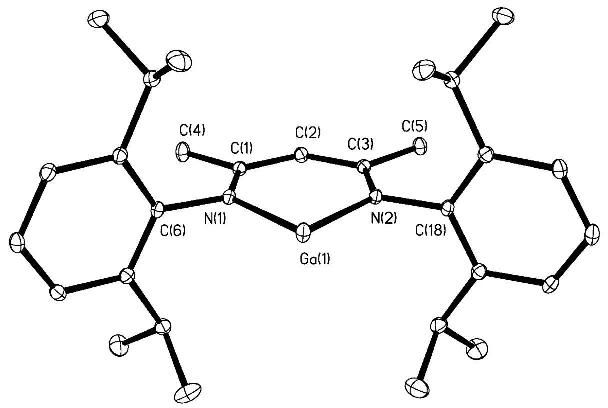

Fig. 2 Thermal ellipsoid (30%) plot of **1**. H atoms are not shown. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.0528(14), Ga(1)–N(2) 2.0560(13), N(1)–C(1) 1.337(2), N(1)–C(6) 1.446(2), N(2)–C(3) 1.338(2), N(2)–C(18) 1.442(2), C(1)–C(2) 1.399(2), C(2)–C(3) 1.401(3); N(1)–Ga(1)–N(2) 87.53(5), Ga(1)–N(1)–C(1) 129.04(1), Ga(1)–N(2)–C(3) 129.31(11), N(1)–C(1)–C(2) 123.44(15), C(1)–C(2)–C(3) 127.74(16), C(2)–C(3)–N(2) 122.91(14).

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Notes and references

† $GaC_6H_3Trip_2$-2,6 has been stabilized as an iron carbonyl complex in which the gallium is two coordinate.[6c]

‡ All manipulations were carried out under anaerobic and anhydrous conditions. Crystals of Li{(NDippCMe)$_2$CH} were synthesized by the reaction of H{(NDippCMe)$_2$CH}[8] with Bu^{n}Li and grown from toluene. The structure of this lithium salt consists of weakly associated monomers in the crystal phase. Crystals of Li{(NDippCMe)$_2$CH} (2.2 g, 5.2 mmol) in toluene (30 mL) were added dropwise to a well stirred slurry of 'GaI'[9] (1.5 g, 7.6 mmol) in toluene with cooling in a dry ice/acetone bath. The mixture was allowed to come to room temperature overnight and cooled again with a dry ice/acetone bath, whereupon excess potassium (0.5 g, 12.8 mmol) was added by a solids-addition tube. After stirring for 1 h the solution was allowed to warm to room temperature overnight. The resultant red solution was filtered and the volume was reduced to incipient crystallization (10 mL). Storage at *ca.* −20 °C for 48 h afforded yellow crystals of **1** (0.97 g, yield 39%); Anal. Calc. (found) for $C_{29}H_{41}GaN_2$: C, 71.46 (71.90), H, 8.48 (8.86)%. Mp 202–204 °C; UV–VIS λ_{max} = 340 nm; ^{1}H NMR (300 MHz C_6D_6) δ 7.17 (m, 6H, aromatic H of Dipp group, partially obscured by resonances due to impurities in the solvent C_6D_6) 5.19 (s, 1H, methine CH), 3.14, (sept, $^3J_{HH}$ 6.9 Hz, 4H, C*H*Me$_2$), 1.67 (s, 6H, C*Me*), 1.25 (d, $^3J_{HH}$ 6.9 Hz, 12H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$): ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 163.49 (*p*-C), 143.65 (*C*Me) 142.92 [*o*-C(Dipp)], 126.49 [*p*-C(Dipp], 123.96 [*m*-C(Dipp], 99.55 (γ-C), 28.76 (*C*HMe$_2$), 25.72 (CH*Me*$_2$), 24.02 (C*Me*), 23.85 (CH*Me*$_2$).

§ *Crystal data* at 90 K for **1** with Mo-Kα radiation (λ = 0.71073 Å): $C_{29}H_{41}GaN_2$, M = 487.36, yellow parallelpipeds, monoclinic, space group $P2_1/n$, a = 12.6570(4), b = 15.9025(6), c = 13.9390(5) Å, β = 105.099(1)°, V = 2689.49(16) Å, Z = 4, D_c = 1.204 g cm^{-3}, μ = 1.041 mm^{-1}, $R1$ = 0.0375 for 6190 [$I > 2\sigma(I)$] data. CCDC 182/1774. See http://www.rsc.org/suppda/cc/b0/b005686n/ for crystallographic files in .cif format.

¶ In this compound the formal valence of the gallium is two (one unit higher than that in **1**) although its formal oxidation state is +1.

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