

Novel dimeric ring systems containing gallium

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A gallole (gallacyclopentadiene) is found to dimerise in a different fashion than boroles; the corresponding diazabutadiene complex is also dimeric.

Until recently, very little was known about the chemistry of metallacyclopentadienes involving the heavier group 13 elements. However, this situation has begun to change with the reports of galla- and inda-cyclopentadienes¹ being added to the prior disclosure of an aluminacyclopentadiene.² As in the case of the somewhat better known boracyclopentadienes (boroles),³ the strategies for monomer isolation involve the use of bulky substituents,^{1b} benzannulation,⁴ or Lewis-base complexation^{1a,c} at the group 13 site. When such features are absent, as in the case of 1-phenyl-2,3,4,5-tetramethylborole,⁵ a Diels–Alder dimerisation takes place. We have prepared and structurally characterised the first gallacyclopentadiene (gallole) dimer and discovered that the mode of dimerisation is quite different from that of the boron analogue.

Treatment of the requisite zirconacycle **1** with Bu^tGaCl₂ **2** afforded the gallole dimer **3** (Scheme 1).[†] The dimeric nature of the product in the solid state was established by an X-ray crystallographic study.[‡]

Whereas the borole, PhBC₄Me₄, dimerises in the classical Diels–Alder fashion,⁵ the related gallole **3** dimerises by means of gallium–carbon bond formation (Fig. 1). The central Ga₂C₂ core of each individual dimer resides on a crystallographic inversion centre and is therefore planar; there are no unusually short intermolecular contacts. While the Ga–C bond distances in the core differ only slightly (<0.02 Å), there is over 30° difference in the C–Ga–C and Ga–C–Ga bond angles.⁶ As expected on the basis of a three-centre bonding description,⁷ the Ga–C bond distance in the Ga₂C₂ core [Ga(1)–C(1)] is longer (by ca. 0.2 Å) than that in the gallole rings [Ga(1)–C(4)]. The geometry at C(1) is remarkable. Owing to the acute angle at this centre, the cross-ring Ga...Ga distance is quite short (2.599 Å) and only slightly longer than those reported for the digallanes Ga₂[CH(SiMe₃)₂]₄ [2.541(1) Å⁸], Ga₂[(C₆H₂)Pr₃-2,4,6]₄ [2.513(3) Å⁹], and Ga₂[C₆H₂(CF₃)₃-2,4,6]₄ [2.479(1) Å¹⁰]. However, we have found no theoretical evidence¹¹ for a Ga–Ga bonding interaction. The metrical parameters for the gallole ring are also of interest. The C(3)–C(4) and C(2)–C(3) bond distances of 1.341(5) and 1.497(5) Å correspond roughly to bond orders of two and one respectively and, as expected, these carbon atoms adopt a trigonal-planar geometry within experimental error. Note, however, that the C(1)–C(2) bond distance [1.359(4) Å] is only slightly longer than the C(3)–C(4) distance even though C(1) is four-coordinate!¹⁷ Moreover, the fragment

containing Ga(1), C(1), C(5), and C(2) [sum of bond angles 343.2(3)°] adopts a geometry which is midway between trigonal planar and tetrahedral. The implication of the foregoing structural features is that the dimer is rather weakly bonded and this surmise is borne out by the following additional observations: (a) the solution-phase ¹³C NMR spectra which reveal that the chemical shifts for C(1) and C(4) and C(2) and C(3) are identical,[§] and (b) the solution molecular mass which corresponds to that of the monomer (thf solution, calc. 235.0; found 203.5).

Gallole dianions are isoelectronic with the corresponding diazabutadiene–gallium complexes and, since both ring systems involve six π electrons, they are potentially aromatic.¹² Unfortunately, however, galloles are not stable with respect to reduction. It therefore became important to prepare the diazabutadiene (DAB) analogue of **3**. The synthesis of **4** was effected by treatment of Bu^tGaCl₂ with Li₂(Bu^tNCHCHNBu^t) (Scheme 2).

By means of X-ray crystallography[‡] it was established that, like **3**, **4** is dimeric in the solid state (Fig. 2). The Ga₂N₂ core of **4** is planar and much less rhombically distorted than the Ga₂C₂

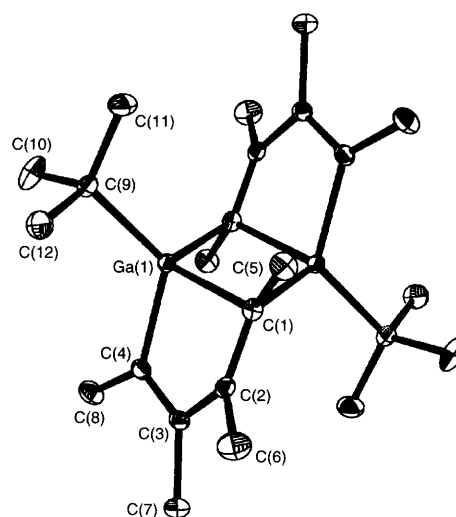
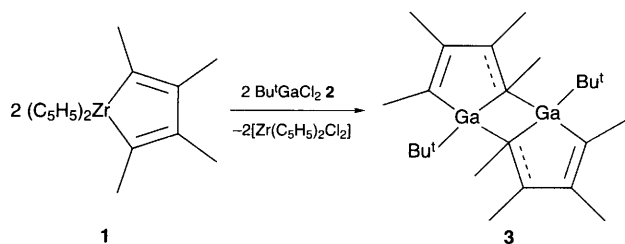
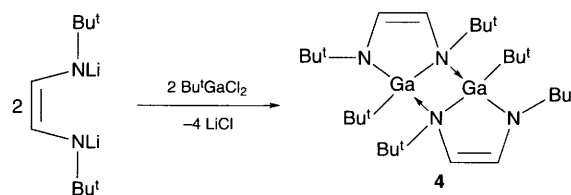


Fig. 1 View of **3** showing the atom numbering scheme of one of the independent molecules. Important bond distances (Å) and angles (°): Ga(1)–C(1) 2.164(3), Ga(1)–C(1') 2.146(3), Ga(1)–C(4) 1.980(3), Ga(1)–C(9) 1.991(3), C(1)–C(2) 1.359(4), C(2)–C(3) 1.497(5), C(3)–C(4) 1.341(5); C(4)–Ga(1)–C(1) 87.61(13), Ga(1)–C(1)–C(2) 99.1(2), C(1)–C(2)–C(3) 121.4(3), C(2)–C(3)–C(4) 117.4(3), C(3)–C(4)–Ga(1) 108.8(2), C(1)–Ga(1)–C(1') 105.81(10), Ga(1)–C(1)–Ga(1') 74.19(10).



Scheme 1



Scheme 2

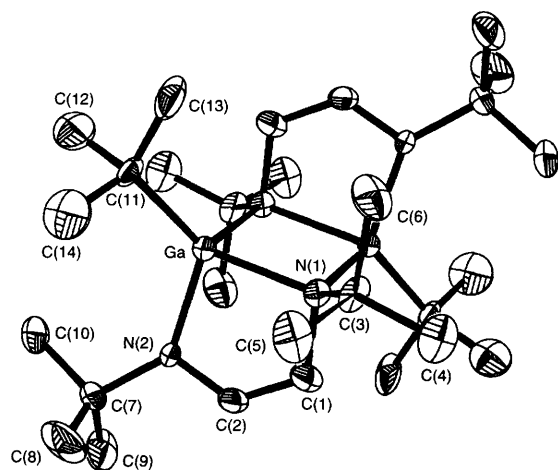


Fig. 2 View of **4** showing the atom numbering scheme. Important bond distances (Å) and angles (°): Ga–N(1) 2.056(12), Ga–N(1') 2.041(8), Ga–N(2) 1.928(5), Ga–C(11) 2.021(11), N(1)–C(1) 1.473(11), C(1)–C(2) 1.36(2), C(2)–N(2) 1.31(2); N(2)–Ga–N(1) 90.1(4), Ga–N(1)–C(1) 100.0(7), N(1)–C(1)–C(2) 118.2(13), C(1)–C(2)–N(2) 125.1(9), C(2)–N(2)–Ga 106.0(6), N(1)–Ga–N(1') 83.8(5), Ga–N(1)–Ga' 96.2(5).

core of **3**. Furthermore, the geometry at N(1) is fully tetrahedral (albeit with a range of bond angles) thus suggesting a more strongly bound dimer. Indeed, it was observed on the basis of ^1H and ^{13}C NMR spectroscopy that, in contrast to **3**, dimer **4** persists in solution at ambient temperature.¹³ Finally, we note that a saturated analogue of **4** has been reported.¹⁴

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Footnotes

† *Experimental procedure.* A solution of Bu^tGaCl_2 (1.00 g, 5.05 mmol) in pentane was added dropwise to a stirred solution of $[\text{Zr}(\text{C}_5\text{H}_5)_2(\text{C}_4\text{Me}_4)]$ (1.66 g, 5.05 mmol) in pentane at -78°C and allowed to warm slowly to room temp. The reaction mixture was concentrated to 15 ml and cooling resulted in colourless X-ray quality crystals of **3**, which decompose at 75°C , in 90% yield. A solution of Bu^tGaCl_2 (1.00 g, 5.05 mmol) in toluene was added dropwise to a stirred solution of $\text{Li}(\text{Bu}^t\text{NCHCHNBu}^t)\text{Li}$ (0.92 g, 5.05 mmol) in 30 ml of toluene at -78°C . The solution was allowed to warm slowly to room temp. The reaction mixture was filtered and the solution was concentrated to 15 ml and cooling resulted in yellow X-ray quality crystals of **4** (mp 118°C) in 40% yield.

‡ *Crystal data:* for **3**, $\text{C}_{24}\text{H}_{42}\text{Ga}$, triclinic, space group $P\bar{1}$, $a = 8.793(1)$, $b = 9.160(1)$, $c = 17.180(3)$ Å, $\alpha = 94.16(1)$, $\beta = 104.68(1)$, $\gamma = 112.50(1)^\circ$, $Z = 2$, $U = 1214.2(3)$ Å³, $D_c = 1.286$ g cm⁻³, Mo-K α ($\lambda = 0.71073$ Å), $\mu = 22.24$ cm⁻¹. 5504 unique data were collected at 173 K on a Siemens P4 diffractometer (2θ – θ scan technique, $4.9 < 2\theta < 55.0^\circ$). The structure was refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms to an $R_w = 0.0847$ and conventional $R = 0.0372$, with a goodness of fit = 1.021. The hydrogen atoms were calculated in idealized positions (C–H 0.96 Å) with isotropic displacement parameters set and refined to a common value for the *tert*-butyl and methyl hydrogens.

4, $\text{C}_{14}\text{H}_{29}\text{GaN}_2$, monoclinic, space group $P2_1/c$, $a = 8.594(2)$, $b = 19.491(4)$, $c = 10.069(3)$ Å, $\beta = 112.65(2)^\circ$, $U = 1556.5(7)$ Å³, $D_c = 1.259$ g cm⁻³, Mo-K α ($\lambda = 0.71073$ Å), $\mu = 17.52$ cm⁻¹. 2368 data were collected at 293 K on an Enraf-Nonius CAD 4 diffractometer (2θ – θ scan technique, $4.18 < 2\theta < 49.94^\circ$). The structure was refined by full-

matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms to an $R_w = 0.1350$ and conventional $R = 0.0449$, with a goodness of fit = 1.009. The hydrogen atoms were calculated in idealized positions (C–H 0.96 Å) with isotropic displacement parameters set and refined to a common value. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/231.

§ *Selected spectroscopic data:* **3**, ^1H NMR (300.15 MHz, C_6D_6 , 295 K, SiMe_4 ext) δ 1.14 (s, 9 H, Bu^t), 1.79 (s, 6 H, 2,5-Me₂), 1.87 (s, 6 H, 3,4-Me₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 295 K, SiMe_4 ext.) δ 16.83, 20.97 (s, Me), 26.68 [s, $\text{C}(\text{CH}_3)_3$], 30.91 [s, $\text{C}(\text{CH}_3)_3$], 136.05 (s, 3,4-C₂), 145.23 (s, 2,5-C₂), MS (CI, CH_4), m/z 413 ($\text{M}^+ - \text{Bu}^t$, 100%). HRMS (CI, CH_4) calc. for $\text{C}_{24}\text{H}_{43}\text{Ga}_2$ m/z 469.1876, found 469.1876.

4, ^1H NMR (300.15 MHz, C_6D_6 , 295 K, SiMe_4 ext) δ 1.29 (s, 36 H, Bu^tN), 1.46 (s, 18 H, Bu^tGa), 4.91 (d, J 4.5 Hz, 2 H, C-1), 6.42 (d, J 4.8 Hz, 2 H, C-2); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 295 K, SiMe_4 ext.) δ 30.07 [$(\text{CH}_3)_3\text{CN}$], 32.12 [$(\text{CH}_3)_3\text{CN}$], 32.20 (CGa), 33.51 [$(\text{CH}_3)_3\text{CGa}$], 52.85 (CN), 56.56 (CN), 103.55 (CH), 137.34 (CH). MS (CI, CH_4), m/z 589 ($\text{M}^+ + \text{H}$, 77%). HRMS (CI, CH_4), calc. for $\text{C}_{28}\text{H}_{59}\text{Ga}_2\text{N}_4$ 589.3213, found 589.3261.

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