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The crystal structure of the 'pentamethylcyclopentadienyl cation' is that of the pentamethylcyclopentenyl cation†

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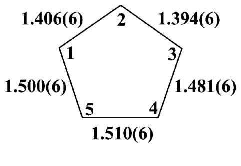
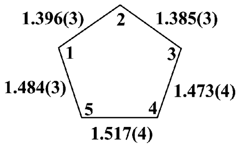
The recently reported X-ray crystal structure of the $[B(C_6F_5)_4]^-$ salt of the 'pentamethylcyclopentadienyl cation' is actually that of pentamethylcyclopentenyl tetrakis(pentafluorophenyl)borate.

Recently, we reported $[In(\eta^5\text{-}C_5Me_5)In]^+$, the first example of an inverse-sandwich main group cation.[1] Originally, this species was isolated as the $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ salt; however, more recently we have been able to prepare the corresponding $[B(C_6F_5)_4]^-$ salt.[2] In an effort to prepare the analogous digallium cation, we treated $[Ga(\eta^5\text{-}C_5Me_5)]_6$[3] with the Brønsted acid, $[(toluene)H][B(C_6F_5)_4]$. However, this experiment resulted in the isolation of a small quantity of the pentamethylcyclopentenyl salt, $[C_5Me_5H_2][B(C_6F_5)_4]$ (**1**).[4a] We have examined **1** by single-crystal X-ray diffraction.‡ To our surprise, we discovered that, within experimental error, the space group and unit cell dimensions for **1** are the same as those reported very recently for the pentamethylcyclopentadienyl salt, $[C_5Me_5][B(C_6F_5)_4]$.[5] The crystal structure of **1** is shown in Fig. 1 and a view of the pentamethylcyclopentenyl cation is presented in Fig. 2. Clearly, the most conspicuous difference between the pentamethylcyclopentenyl and pentamethylcyclopentadienyl cation structures is the addition of hydrogen atoms to C(4) and C(5) in the latter. Note that, in the case of **1**, all hydrogen atoms were located and refined whereas in the structure of Lambert *et al.*,[5] the hydrogens were placed in idealized positions. A comparison of intra-ring C–C bond lengths (Å) is shown below:



Lambert *et al.*[5]



Present work

The C(4)–C(5) bond length is close to the value of 1.54 Å anticipated for a single bond between sp^3 hybridized carbon atoms. Moreover, tetrahedral geometries are evident at C(4) and C(5) and the methyl groups attached to these carbon atoms are arranged above and below the five-carbon ring in a *trans* fashion. The CH_3–C(4)–C(5)–CH_3 dihedral angle of 104.6(3)° is identical to that reported by Lambert *et al.* (106.9(6)°) within experimental error; the H–C(4)–C(5)–H dihedral angle is 135.0(2)°. The cyclopentenyl ring is somewhat non-planar, the internal ring dihedral angles being −2.1(3), 0.9(3), 2.7(3), −2.1(3) and 0.7(3)°.

In order to develop a rational, higher yield synthesis of **1**, we treated pentamethylcyclopentadiene with an equimolar quantity of $[(toluene)H][B(C_6F_5)_4]$.[4b] The product of this reaction was examined by X-ray crystallography and found to possess the same structure as the material that was isolated from the reaction of $[(toluene)H][B(C_6F_5)_4]$ with $[Ga(\eta^5\text{-}C_5Me_5)]_6$.

Calculations on the pentamethylcyclopentenyl cation have been performed using Gaussian 98 at the B3PW91/6-311G(d) level of theory (see ESI for details†). The global minimum is the structure with a *trans* arrangement of CH_3 groups at ring carbon atoms C(4) and C(5). As shown below, the calculated structure is in excellent accord with the X-ray crystallographic data. The geometries at C(4) and C(5) are tetrahedral and the computed CH_3–C(4)–C(5)–CH_3 and H–C(4)–C(5)–H dihedral angles of 107.8 and 134.0°, respectively, agree very well with the experimental values. The slightly nonplanar five-membered ring has computed dihedral angles of −1.18, 0.77, 1.62, −1.38, and 0.32°.

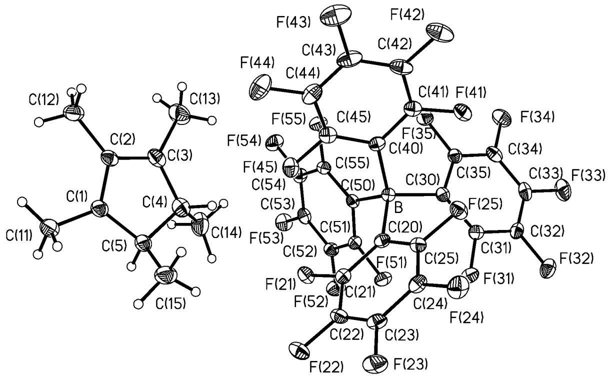


Fig. 1 Structure of crystalline $[C_5Me_5H_2][B(C_6F_5)_4]$ (**1**). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.396(3), C(2)–C(3) 1.385(3), C(3)–C(4) 1.473(4), C(4)–C(5) 1.517(4), C(5)–C(1) 1.484(3), C(4)–H(4) 1.032(4), C(5)–H(5) 0.955(4), C(1)–C(11) 1.461(4), C(2)–C(12) 1.494(4), C(3)–C(13) 1.488(4), C(4)–C(14) 1.518(4), C(5)–C(15) 1.527(4); C(2)–C(1)–C(5) 111.5(2), C(1)–C(2)–C(3) 108.0(2), C(2)–C(3)–C(4) 111.8(2), C(3)–C(4)–C(5) 104.8(2), C(4)–C(5)–C(1) 103.9(2).

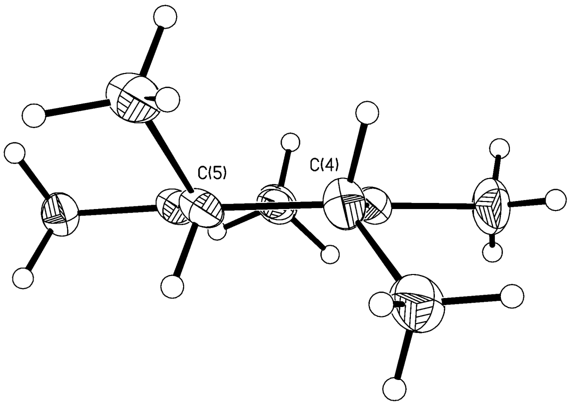


Fig. 2 Side-on view of the pentamethylcyclopentenyl cation showing the hydrogen atoms attached to C(4) and C(5) and the *trans* arrangement of CH_3 groups attached to these carbon atoms.

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† Electronic supplementary information (ESI) available: DFT calculations. See http://www.rsc.org/suppdata/cc/b2/b205081a/

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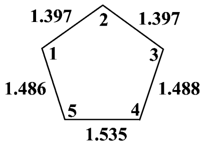

Computed structure

At this point, it is not clear (a) whether the crystal selected for X-ray crystallography by Lambert *et al.* is representative of the bulk of their product, and (b) how **1** was formed from the reaction of C_5Me_5H with $[Ph_3C][B(C_6F_5)_4]$.

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Notes and references

‡ *Crystal structure determination* of **1**: X-ray diffraction data for **1** were collected at 153 K on a Nonius-Kappa CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å; μ(Mo-Kα) = 0.182 mm^{-1}). The space group was determined to be $P2_1/c$ on the basis of systematic absences and the unit cell dimensions are a = 13.202(3), b = 13.757(3), c = 17.409(4) Å, β = 90.07(3)°, and V = 3161.8(11) Å^3. On the basis of the formula $C_{34}H_{17}BF_{20}$ and Z = 4, the calculated density for **1** is 1.715 g cm^{-3}. Data were collected to a maximum 2θ value of 55.10° and, of the total of 19057 reflections collected, 7025 were unique (R_{int} = 0.0427). The data were corrected for Lorentz and polarization effects and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically; all hydrogen atoms were located and refined. The final difference Fourier map featured a peak of 0.273 e$^-$ Å^{-3} and a hole of −0.219 e$^-$ Å^{-3}. The final R values were R_1 = 0.0512 and wR_1 = 0.0837 and GOF = 1.027. CCDC reference number 181009. See http://www.rsc.org/suppdata/cc/b2/b205081a/ for crystallographic data in CIF or other electronic format.

1 A. H. Cowley, C. L. B. Macdonald, J. S. Silverman, J. D. Gorden and A. Voigt, *Chem. Commun.*, 2001, 175.

2 J. N. Jones, A. H. Cowley and C. L. B. Macdonald, to be published.

3 (*a*) D. Loos, E. Baum, A. Ecker, H. Schnöckel and A. J. Downs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 860; (*b*) P. Jutzi, B. Neumann, G. Reumann and H.-G. Stammler, *Organometallics*, 1998, **17**, 1305.

4 (*a*) Addition of a toluene solution of $[(\text{toluene})H][B(C_6F_5)_3]$ (0.273 g, 0.344 mmol) to a solution of $[Ga(\eta^5\text{-}C_5Me_5)]_6$[3] (0.145 g, 0.118 mmol) in the same solvent at −78 °C resulted in a red–violet coloured solution from which a red solid was isolated. Recrystallization was effected by slow diffusion of hexane into a dichloromethane solution of the product at ambient temperature and afforded a small yield (~5%) of colourless crystals of **1** (mp 201–202 °C); (*b*) Reaction of a toluene solution of $[(\text{toluene})H][B(C_6F_5)_3]$ (0.141 g, 0.183 mmol) with a toluene solution of C_5Me_5H (0.025 g, 0.184 mmol) at −78 °C resulted in a wine red coloured solution from which a red solid was isolated. Recrystallization was effected by slow diffusion of hexane into a dichloromethane solution of the product at ambient temperature. The yield of colourless, crystalline **1** was 24.0%. HRMS (CI$^+$): calc. for $C_{34}H_{17}$, m/z 137.133026; found 137.133453.

5 J. B. Lambert, L. Lin and V. Rassolov, *Angew. Chem., Int. Ed.*, 2002, **41**, 1429.