The crystal structure of the ‘pentamethylyclopentadieny1 cation’ is that of the pentamethylyclopentenyl cation†

Jamie N. Jones, a Alan H. Cowley* and Charles L. B. Macdonald b

a Department of Chemistry, The University of Texas at Austin, Austin TX 78712, USA.
E-mail: Cowley@mail.utexas.edu

b Department of Chemistry and Biochemistry, The University of Windsor, Windsor, Ontario N9B 3P4, Canada

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The recently reported X-ray crystal structure of the 

\[ \text{[B(C_5 F_5)_4]} \text{[B(C_6 F_5)_4]} \]

salt of the ‘pentamethylyclopentadieny1 cation’ is actually that of pentamethylyclopenteny1 tetra-

kis(pentafluorophenyl)borate.

Recently, we reported \([\text{In}([\eta]^2-C_5\text{Me}_5\text{H}_2])\text{[B(C_6 F_5)_4]}\] , the first example of an inverse-sandwich main group cation.1 Originally, this species was isolated as the \([\text{[C_5 F_5]}\text{BO(H)}\text{[B(C_6 F_5)_4]}\] salt; however, more recently we have been able to prepare the corresponding \([\text{[C_5 F_5]}\text{H}]\text{[B(C_6 F_5)_4]}\). However, this experiment resulted in the isolation of a small quantity of the pentamethylyclopenteny1 salt, \([\text{C_5\text{Me}_5}\text{H}_2]\text{[B(C_6 F_5)_4]}\) (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 pentamethylyclopenteny1 salt, \([\text{C_5\text{Me}_5}\text{H}_2]\text{[B(C_6 F_5)_4]}\).5 The crystal structure of 1 is shown in Fig. 1 and a view of the pentamethylyclopenteny1 cation is presented in Fig. 2. Clearly, the most conspicuous difference between the pentamethylyclopenteny1 and pentamethylyclopentadieny1 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 hydrides were placed in idealized positions. A comparison of intra-ring C–C bond lengths (Å) is shown below:

![Diagram of C–C bond lengths](image)

The the C(4)–C(5) bond length is close to the value of 1.54 Å anticipated for a single bond between sp3 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–(C(4)–C(5)–CH3 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 cyclopenteny1 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 pentamethylyclopentadieny1 with an equimolar quantity of \([\text{[toluene]}\text{H}]\text{[B(C_5 F_5)_4]}\).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 \([\text{[toluene]}\text{H}]\text{[B(C_5 F_5)_4]}\) with \([\text{Ga}([\eta]^2-C_5\text{Me}_5\text{H}_2])\].

Calculations on the pentamethylyclopenteny1 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 CH3 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 C(4)–C(5)–C(3)–CH3 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 \([\text{C_5\text{Me}_5}\text{H}_2]\text{[B(C_6 F_5)_4]}\) (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(11)–C(15) 111.5(2), C(1)–C(2)–C(13) 108.8(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 pentamethylyclopenteny1 cation showing the hydrogen atoms attached to C(4) and C(5) and the trans arrangement of CH3 groups attached to these carbon atoms.
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 C₅Me₅H with [Ph₃C][B(C₆F₅)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; μMo-Kα = 0.182 mm⁻¹). The space group was determined to be P2₁/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) Å³. On the basis of the formula C₃₄H₁₇BF₂₀ 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 (Rint = 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 R₁ = 0.0512 and wR₁ = 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.

4 (a) Addition of a toluene solution of [(toluene)H][B(C₆F₅)₄] (0.273 g, 0.344 mmol) to a solution of [Ga(h⁵-C₅Me₅)]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 [(toluene)H][B(C₆F₅)₄] (0.141 g, 0.183 mmol) with a toluene solution of C₅Me₅H (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 C₃₄H₁₇, m/z 137.133026; found 137.133453.