

The structure of the decamethylborocenium cation: the most tightly-squeezed metallocene?

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X-Ray crystallographic analysis along with DFT calculations on the decamethylborocenium cation provide definitive structural and electronic information about this most tightly-squeezed main group metallocene—the first to adopt the elusive σ/π geometry in the solid state.

The unusual structure of beryllocene, $\text{Be}(\text{Cp})_2$ **1**, has attracted the attention of chemists for several years.¹ In both the solid and vapour states **1** adopts a ‘slip-sandwich’ structure in which the parallel Cp rings are attached to beryllium in an $\eta^1(\pi)/\eta^5$ fashion.² In solution **1** is fluxional owing to rapid changes in ring hapticities.³ The observed structure contrasts with the $\eta^1(\sigma)/\eta^5$ structure predicted on the basis of numerous theoretical calculations.^{3,4}

The borocenium cation $[\text{B}(\text{Cp})_2]^+$, which is isoelectronic with **1**, is not known and unlikely to be stable at ambient temperature. Although the decamethylborocenium cation $[\text{B}(\text{Cp}^*)_2]^+$ **2** has been characterized by ^1H and ^{11}B NMR spectroscopy,⁵ such data cannot be used to distinguish between $\eta^1(\pi)/\eta^5$ and $\eta^1(\sigma)/\eta^5$ structures. It was therefore necessary to perform an X-ray analysis of a suitable salt of **2**.

It was found that a variety of salts of **2** can be generated by treatment of $(\text{Cp}^*)_2\text{BCl}^5$ with e.g. $\text{LiB}(\text{C}_6\text{F}_5)_4$, $\text{Ga}(\text{C}_6\text{F}_5)_3$, GaCl_3 or AlCl_3 . However, from the standpoint of single crystal growth, the best reaction was that between equimolar quantities of $(\text{Cp}^*)_2\text{BCl}$ and AlCl_3 in CH_2Cl_2 – C_6D_6 solution which afforded an 86% yield of $2[\text{AlCl}_4]$ [mp ca. 60 °C (decomp.)].⁶ The solid state structure of $2[\text{AlCl}_4]$ consists of an array of two independent cations and anions.[†] There are no unusually short interionic contacts and the metrical parameters for the independent cations are very similar and hence only one set of data is discussed here. The decamethylborocenium cation **2** (Fig. 1) features one η^5 -bonded and one $\eta^1(\sigma)$ -bonded Cp^* substituent, both of which feature, within experimental error, planar C_5 rings. Such an arrangement for a main group metallocene has been predicted (*vide supra*) but never observed experimentally in the solid state. The boron–carbon distance for the η^1 -bonded Cp^* ring, $\text{B}(1)–\text{C}(1)$ [1.582(6) Å] is considerably longer than the boron– η^5 - Cp^* ring centroid distance [1.269(5) Å] and the $\text{C}(1)–\text{B}(1)–\text{Cp}^*$ ring centroid arrangement is nearly linear [177.9(5)°]. In contrast to beryllocene, which has an η^1/η^5 parallel-ring structure in the solid state,⁷ the Cp^* rings of **2** are non-parallel as indicated, for example, by the 114.4(5)° tilt angle between the $\text{B}(1)–\text{C}(1)$ bond and the least squares plane of the η^1 - Cp^* ring. A further differentiating feature is that the η^1 -attached ring of **2** exhibits a typical localized structure with average $\text{C}_\alpha–\text{C}_\beta$ and $\text{C}_\beta–\text{C}_\beta$ bond distances of 1.339(5) and 1.476(6) Å, respectively.

The structure of **2** also contrasts with that of the isovalent decamethylaluminocenium cation, which adopts a staggered bis(η^5 - Cp^*) ferrocene-like geometry.⁸ To provide insight into the reason(s) for this structural difference, DFT calculations were performed on $[\text{B}(\text{Cp}^*)_2]^+$, $[\text{B}(\text{Cp})_2]^+$ and $[\text{Al}(\text{Cp})_2]^+$. Geometry optimization of **2** at the BP86/A level of theory⁹ provides excellent agreement with the experimental structure. Thus, the global minimum is the observed η^1/η^5 structure with $\text{B}(1)–\text{C}(1)$ and $\text{B}(1)–\eta^5$ - Cp^* ring centroid distances of 1.593

and 1.291 Å, respectively, a $\text{C}(1)–\text{B}(1)–\text{Cp}^*$ ring centroid angle of 179°, and an η^1 - Cp^* ring tilt angle of 123°. Moreover, calculation of the ^{11}B chemical shift for this structure using the GIAO method¹⁰ (δ –43.1) is in excellent agreement with the experimental value (δ –41.5).^{5,6} The staggered bis- η^5 (D_{5d}) structure of **2** is computed to be 48.95 kcal mol^{–1} higher in energy than the η^5/η^1 structure, thus confirming that the observed geometry is not caused by crystal packing forces. Examination of space-filling models reveals the existence of pronounced steric congestion in $[(\eta^5\text{-Cp}^*)_2\text{B}]^+$ which is relieved somewhat in proceeding to the η^1/η^5 structure. However, traditional steric effects are not responsible for the observed geometry of **2** since DFT calculations on the unsubstituted borocenium cation, $[(\text{Cp})_2\text{B}]^+$ reveal that the ground state geometry is also η^1/η^5 and remarkably similar to that of **2**. More importantly, the difference in energy between the η^1/η^5 and bis- η^5 structures is essentially the same for both the Cp^* - and Cp -substituted cations (45.39 kcal mol^{–1} for the latter). Surprisingly, the D_{5d} $[(\text{Cp})_2\text{B}]^+$ structure is not even a true minimum ($N_{\text{imag}} = 4$) on the potential energy surface (PES). Conversely, no η^1/η^5 minimum is found for $[(\text{Cp})_2\text{Al}]^+$; geometry optimization on the C_s symmetry PES proceeds smoothly to the D_{5h} bis- η^5 structure instead. The difference in bonding modes is attributable to the higher electronegativity of boron and greater strength (and lower ionicity) of B–C vs. Al–C bonding. The smaller size and greater effective nuclear charge of boron is also important, especially in comparison to Cp_2Be ,

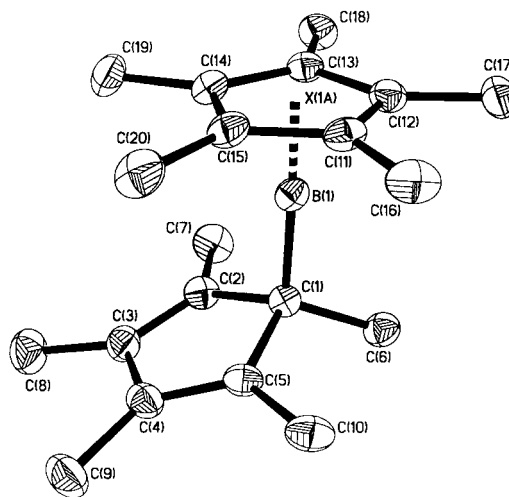


Fig. 1 ORTEP drawing of $[\text{B}(\eta^5\text{-C}_5\text{Me}_5)(\eta^1\text{-C}_5\text{Me}_5)]^+$ **2**. There are two independent cations: the bond distances (Å) and bond angles (°) for the second cation are shown in square brackets: $\text{B}(1)–\text{C}(1)$ 1.583(5) [1.586(5)], $\text{B}(1)–\text{X}(1\text{A})$ (ring centroid) 1.290(5) [1.282(5)], $\text{B}(1)–\text{C}(11)$ 1.782(6) [1.770(5)], $\text{B}(1)–\text{C}(12)$ 1.775(5) [1.769(5)], $\text{B}(1)–\text{C}(13)$ 1.782(5) [1.753(5)], $\text{B}(1)–\text{C}(14)$ 1.757(5) [1.774(5)], $\text{B}(1)–\text{C}(15)$ 1.757(5) [1.756(5)], $\text{C}(1)–\text{C}(2)$ 1.515(5) [1.520(5)], $\text{C}(2)–\text{C}(3)$ 1.343(5) [1.348(6)], $\text{C}(3)–\text{C}(4)$ 1.473(6) [1.465(6)], $\text{C}(4)–\text{C}(5)$ 1.340(5) [1.339(6)], $\text{C}(1)–\text{C}(5)$ 1.523(5) [1.521(5)], $\text{C}(1)–\text{B}(1)–\text{X}(1\text{A})$ 177.9(5) [177.2(5)], $\text{B}(1)–\text{C}(1)–\text{least-squares-plane of } (\eta^1\text{-Cp}^*)$ 114.4(5) [112.4(5)], $\text{B}(1)–\text{C}(1)–\text{C}(6)$ 112.4(3) [112.9(3)].

because the putative D_{5d} structure is rendered much less stable owing to the increased repulsion between the π -clouds on the Cp ligands. Adoption of the $\eta^1(\pi)/\eta^5$ 'slipped-sandwich' structure by Cp_2Be relieves this strain sufficiently, but the closer ligand proximity in $[(\text{Cp})_2\text{B}]^+$ mandates the non-parallel, π -localized $\eta^1(\sigma)/\eta^5$ alternative. In effect, the change from Be to B^+ results in a much steeper PES which more clearly favours the $\eta^1(\sigma)/\eta^5$ structure.

In conclusion, we have elucidated the structure of, and bonding in, the first authentic example of an $\eta^1(\sigma)/\eta^5$ metallocene. Because of the small size, combined with the high effective nuclear charge of the cationic boron(III) centre, we do not anticipate the isolation of a more tightly squeezed metallocene. Investigations of the reactivity of salts of **2** are currently underway.

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Notes and references

† Crystal data for **2** $[\text{AlCl}_4]$: $\text{C}_{40}\text{H}_{60}\text{Al}_2\text{B}_2\text{Cl}_8$, $M = 900.06$ (two independent cation and anion pairs per asymmetric unit), colourless blocks, monoclinic, space group $P2_1/n$, $a = 7.133(3)$, $b = 13.611(3)$, $c = 20.493(4)$ Å, $\beta = 90.30(3)^\circ$, $V = 4779(2)$ Å³, $Z = 4$, $D_c = 1.251$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.535$ mm⁻¹. A suitable single crystal of **2** $[\text{AlCl}_4]$ was covered with mineral oil and mounted on a Nonius Kappa CCD diffractometer at 153 K. A total of 19 718 reflections were collected in the range $5.96 < 2\theta < 54.98^\circ$ using Mo-K α radiation ($\lambda = 0.71073$ Å). Of these, 10 898 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 **2** $[\text{AlCl}_4]$; $R_w = 0.2069$, $R = 0.0713$. CCDC 182/1606. See <http://www.rsc.org/suppdata/cc/b0/b001271h/> for crystallographic data in .cif format.

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- ¹H NMR (300.00 MHz, 295 K, C_6D_6): δ 1.65 (s, 15H, $\eta^5\text{-Cp}^*\text{-CH}_3$), 1.49 (s, 3H, $\eta^1\text{-Cp}^*\text{-ipso-CH}_3$), 1.63 (s, 6H, $\eta^1\text{-Cp}^*\text{-}\alpha\text{-CH}_3$), 1.69 (s, 6H, $\eta^1\text{-}\beta\text{-CH}_3$). ¹³C{¹H} NMR (75.48 MHz, 295 K, C_6D_6): δ 9.13 ($\eta^5\text{-CH}_3$), 112.93 ($\eta^5\text{-Cp}^*$ ring C), 15.48 ($\eta^1\text{-Cp}^*\text{-ipso-CH}_3$), 51.79 ($\eta^1\text{-Cp}^*\text{-ipso ring C}$), 10.63 ($\eta^1\text{-Cp}^*\text{-}\alpha\text{-CH}_3$), 136.36 ($\eta^1\text{-Cp}^*\text{-}\alpha\text{-ring C}$), 12.17 ($\eta^1\text{-Cp}^*\text{-}\beta\text{-CH}_3$), 138.10 ($\eta^1\text{-Cp}^*\text{-}\beta\text{-ring C}$). ¹¹B NMR (96.28 MHz, 295 K, C_6D_6): δ -41.5 (s). ²⁷Al NMR (78.21 MHz, C_6D_6): δ 100 (s).
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