

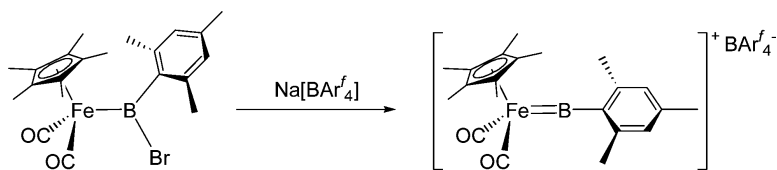
Communication

Cationic Terminal Borylenes by Halide Abstraction: Synthesis and Spectroscopic and Structural Characterization of an FeB Double Bond

Deborah L. Coombs, Simon Aldridge, Cameron Jones, and David J. Willock

J. Am. Chem. Soc., **2003**, 125 (21), 6356-6357 • DOI: 10.1021/ja0346936 • Publication Date (Web): 02 May 2003

Downloaded from <http://pubs.acs.org> on March 28, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 23 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Cationic Terminal Borylenes by Halide Abstraction: Synthesis and Spectroscopic and Structural Characterization of an Fe=B Double Bond

Deborah L. Coombs, Simon Aldridge,* Cameron Jones, and David J. Willock

Department of Chemistry, Cardiff University, P.O. Box 912, Park Place, Cardiff, CF10 3TB U.K.

Received February 17, 2003; E-mail: AldridgeS@cardiff.ac.uk

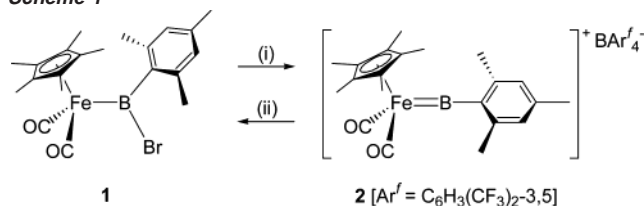
Compounds offering the potential for multiple bonding between a transition metal and a main group element have excited much recent interest, not only from a structure/bonding viewpoint but also as potential intermediates in important catalytic processes.^{1–5} In comparison to group 14 systems [e.g., alkylidenes (R₂C)¹ and silylenes (R₂Si)²], however, the synthetic, structural, and reaction chemistry of analogous compounds containing terminally bound group 13 diyl ligands (RE) is less thoroughly understood.^{3–5} Within this field, terminal borylene systems (L_nMBR) represent a very recent and numerically small addition, with the highly Lewis acidic boron center typically being stabilized by sterically bulky or π-donor R groups or by coordination of a tethered base.³

A number of structural and computational studies have sought to probe the nature of the metal–boron bond in two-coordinate borylene complexes.⁴ To this end, systematic studies have been severely hampered by the paucity of synthetic routes available and by the narrow range of compatible metal fragments (predominantly metal carbonyls). Herein we report the development of a new route to terminal borylene complexes, making use of halide abstraction to generate the first example of a cationic [L_nMBR]⁺ species.⁶ The compound so generated, [Cp*Fe(CO)₂(BMes)]⁺[BAR^f₄][−] [Ar^f = C₆H₃(CF₃)_{2-3,5}], contains the shortest M–B distance yet reported, a feature which is indicative of a novel Fe=B double bond. Comparisons of experimental and computational data with those reported for the donor/acceptor borylene Cp*B→Fe(CO)₄ are consistent with a significantly different mode of attachment of the RB ligand.^{3a} Additionally, non-heteroatom π-stabilized two-coordinate borylenes find precedent only in (OC)₅Cr=BSi(SiMe₃)₃.^{3d}

The synthesis of the necessary bromoboryl precursors (η⁵-C₅R₅)-Fe(CO)₂B(Mes)Br [R = Me (**1**) or H] has previously been reported.⁷ Treatment of **1** (46 mg, 0.1 mmol) with 1 equiv of Na[BAR^f₄] or Ag[CB₁₁H₆Br₆] in CH₂Cl₂ (20 mL) at −78 °C, followed by slow warming to room temperature, leads to complete disappearance of the ¹¹B resonance due to **1** (δ_B 113) and (in addition to resonances associated with the anion) to the appearance of a broad signal at δ_B 145 (fwhm ca. 750 Hz). In the case of the reaction with Na[BAR^f₄], filtration, layering with hexanes, and cooling to −50 °C for 1 week leads to the isolation of **2** as colorless crystals (70 mg, 56%) (Scheme 1).⁸

IR-measured carbonyl stretching frequencies for **2** (2055 and 2013 cm^{−1}) are shifted to significantly higher wavenumber compared to those of the starting boryl complex **1** (2006 and 1961 cm^{−1}),⁷ consistent with the presence of a cationic complex containing the Cp*Fe(CO)₂ unit.⁹ ¹H and ¹³C NMR data for **2** confirm the presence of mesityl, Cp*, and carbonyl fragments, and mass spectra display peaks consistent with [M – CO]⁺ and [M – 2CO]⁺ (EI) and [BAR^f₄][−] ions (ES[−]). Additionally, the strongly downfield ¹¹B NMR shift (δ_B 145) is similar to that observed previously for iron complexes containing mesitylborylene ligands, albeit adopting a μ₂-bridging mode of coordination {cf. δ_B 158 for

Scheme 1^a



^a Reagents and conditions: (i) Na[BAR^f₄], −NaBr; CH₂Cl₂, −78 °C to room temperature. (ii) [Ph₄P]Br, −[Ph₄P][BAR^f₄]; CH₂Cl₂, room temperature.

[CpFe(CO)₂]₂BMes⁷}. ¹¹B shifts in the range δ_B 87–204 have been reported by Braunschweig for terminal borylene complexes of groups 6 and 8, with lower field values being obtained for ligands containing weakly π-donor substituents.^{3b–f} The measured ¹¹B shift for **2** is therefore consistent with a terminally bound BMes ligand, although categorical structural assignment could be made only on the basis of X-ray crystallography.

The solid-state structure of **2** (Figure 1) is based around an asymmetric unit containing two (essentially identical) [Cp*Fe(CO)₂-(BMes)]⁺ cations, two [BAR^f₄][−] anions, and a molecule of CH₂Cl₂ solvent.¹⁰ There are no short cation–anion or cation–solvent contacts. Of particular interest is the nearly linear Fe–B–C unit [∠Fe(1)–B(1)–C(1) = 178.3(6)°] and the Fe–B distance [1.792(8) Å], which is significantly shorter than any transition metal-to-boron linkage previously reported. It is also 11% shorter than that found in Cp*BFe(CO)₄ [2.010(3) Å] (a compound which contains a B→Fe donor/acceptor linkage^{3a}), 18% shorter than the σ-only single bond found in the four-coordinate boryl complex (η⁵-C₅Me₄Et)Fe(CO)₂BH₂·PMe₃ [2.195(14) Å], and 8.5% shorter than the shortest Fe–B distance found for any three-coordinate boryl complex [1.959(6) Å for CpFe(CO)₂Bcat].¹¹ By means of comparison, the Fe–C distance in [CpFe(CO)₂(=CCl₂)]⁺ [1.808(12) Å] is ca. 12% shorter than that found in typical [CpFe(CO)₂] alkyl complexes.¹² The Fe–B distance in **2** is therefore consistent with the presence of an Fe=B double bond.

Tilley has proposed that the Ru=Si double bond in the cationic silylene complex [Cp*Ru(PMe₂)₂(=SiMe₂)]⁺ is composed of a Si→Ru donor/acceptor σ-component supplemented by Ru→Si π-back-bonding into the vacant Si-based p orbital.¹³ A similar bonding arrangement for **2** would imply a significantly greater Fe→B back-bonding component than that found in Cp*BFe(CO)₄. Such an arrangement is conceivable, given the highly electrophilic nature of the boron center in **2** and the significantly higher DFT-predicted π-bonding capability of the BPh ligand compared to that of BCp.^{4c} The presence of an appreciable Fe→B back-bonding component for **2** is implied by carbonyl stretching frequencies (2055, 2013 cm^{−1}) in excess of those of {Cp*Fe(CO)₂[=CMe-(OMe)]}⁺ (2045, 1999 cm^{−1}). That these values are still short of those reported for [Cp*Fe(CO)₃]⁺ (2105, 2045 cm^{−1}^{9b}), however,

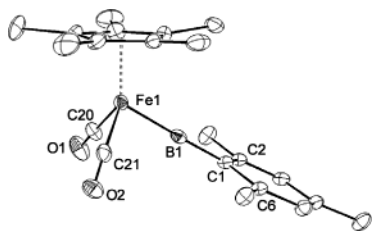


Figure 1. Structure of one of the two crystallographically independent cations in the asymmetric unit of **2**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.792(8), Fe(1)–C(20) 1.768(7), Fe(1)–Cp* centroid 1.733(7), B(1)–C(1) 1.491(10), Fe(1)–B(1)–C(1) 178.3(6), Cp* centroid–Fe(1)–C(1)–C(2) 91.3(6). Hydrogen atoms omitted for clarity.

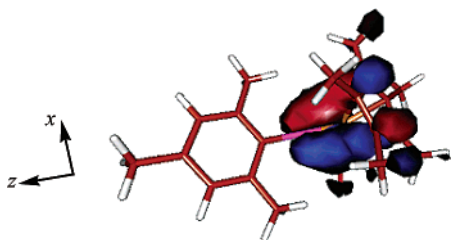


Figure 2. DFT (BLYP/TZP)-calculated HOMO-3 for $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{BMes})]^+$ showing Fe–B π -bonding character.

almost certainly reflects the stronger σ -donor nature of BR over CO, as predicted by Hoffmann and Baerends.^{4a}

The orientation of the mesityl fragment in **2** [torsion, $\angle\text{Cp}^*\text{centroid-Fe(1)-C(1)-C(2)} = 91.3(6)^\circ$] is such that an Fe→B π -interaction involving the HOMO of the $[\text{Cp}^*\text{Fe}(\text{CO})_2]^+$ fragment¹⁴ could populate one of the two perpendicular vacant p orbitals at boron, with the other being stabilized by π -interaction with the mesityl ring. Consistent with this, the distance B(1)–C(1) [1.491(10) Å] is significantly shorter than that found in **1** [1.569(3) Å]. To explore more rigorously the bonding situation in **2**, DFT calculations were carried out for the cation $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{BMes})]^+$ at the BLYP/TZP level of theory, using methods previously described.^{15c} The agreement between (fully optimized) calculated [Fe(1)–B(1) 1.843 Å, B(1)–C(1) 1.495 Å, $\angle\text{Fe(1)-B(1)-C(1)} = 177.8^\circ$, torsion = 93.7°] and measured geometric parameters is generally very good, with a 2–3% overestimate in the Fe–B bond length, mirroring previous studies.¹⁵ Based on a population analysis of the molecular orbitals at the DFT relaxed geometry, the Fe–B bond has a 62:38 σ : π breakdown of the covalent contribution to bonding [cf. 64:36 for $[\text{CpFe}(\text{CO})_2(=\text{CH}_2)]^+$ ^{15c}]. The occupied MO (HOMO-3) shown in Figure 2 shows the Fe–B π -bond formed by the overlap of B p_x and Fe d_{xz} type orbitals. Similarly, HOMO-9 shows distinct C–B π -bonding character utilizing the perpendicular B p_y orbital. These calculations therefore support a bonding model in which boron engages in π -bonding to both $[\text{Cp}^*\text{Fe}(\text{CO})_2]^+$ and Mes moieties.

Previous computational studies have predicted significant B-centered reactivity toward nucleophiles for terminal borylene complexes due to the high positive charge and LUMO amplitude at boron.⁴ On the other hand, the current study shows that, in the presence of suitable steric shielding, even complexes bearing a net positive charge can be isolated. Indeed, it seems likely that the combination of charge and steric shielding in **2** retards the dimerization process observed for the putative isoelectronic manganese system $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{BCl})]$.¹⁶ Not unexpectedly, the cationic nature of **2** appears (on first investigation) to dominate its chemistry. **2** is extremely moisture sensitive and reacts rapidly with $[\text{Ph}_4\text{P}]\text{Br}$ in CH_2Cl_2 to regenerate bromoboryl complex **1**.

Acknowledgment. We thank the EPSRC, the Royal Society, and the Nuffield Foundation for funding and Dr. A. S. Weller (University of Bath) for providing a sample of $\text{Ag}[\text{CB}_{11}\text{H}_6\text{Br}_6]$. The EPSRC mass spectrometry service is also thanked.

Supporting Information Available: Details of the X-ray crystallographic study of **2**, the DFT calculations for $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{BMes})]^+$, and the reaction of **2** with $[\text{Ph}_4\text{P}]\text{Br}$ (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) See, for example: Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.
- (2) See, for example: Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702 and references therein.
- (3) (a) Cowley, A. H.; Lomeli, V.; Voight, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401. (b) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 3179. (c) Braunschweig, H.; Colling, M.; Kollann, C.; Stammer, H. G.; Neumann, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2299. (d) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198. (e) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 205. (f) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.* **2003**, 383. (g) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 948. (h) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862.
- (4) (a) Bickelhaupt, F. M.; Radius, U.; Ehlers, A. W.; Hoffmann, R.; Baerends, E. J. *New J. Chem.* **1998**, 1. (b) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem. Eur. J.* **1998**, *4*, 210. (c) Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113. (d) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571. (e) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717. (f) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683.
- (5) See, for example: (a) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 127. (b) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70. (c) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511. (d) Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128. (e) Jutzi, P.; Neumann, B.; Reumann, G.; Stammer, H.-G. *Organometallics* **1998**, *17*, 1305. (f) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202. (g) Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammer, H.-G. *Organometallics* **1999**, *18*, 2550.
- (6) Cationic two-coordinate boron species have previously been reported only as strongly π -stabilized amino derivatives: (a) Nöth, H.; Straudigl, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 794. (b) Kölle, P.; Nöth, H. *Chem. Ber.* **1986**, *119*, 313. (c) Courtenay, S.; Mutus, J. Y.; Schurko, R. W.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 498.
- (7) (a) Coombs, D. L.; Aldridge, S.; Jones, C. *Chem. Commun.* **2002**, 856. (b) Coombs, D. L.; Aldridge, S.; Jones, C. *Dalton Trans.* **2002**, 3851.
- (8) ¹H NMR (300.53 MHz, 293 K, CD_2Cl_2): δ 2.01 (s, 15H, CH_3 of Cp*), 2.34 (s, 3H, *p*- CH_3 of Mes), 2.63 (s, 6H, *o*- CH_3 of Mes), 6.92 (s, 2H, *m*-H of Mes), 7.54 (s, 4H *p*-H of BAR_4^-), 7.70 (s, 8H, *o*-H of BAR_4^-). ¹³C NMR (75.57 MHz, 293 K, CD_2Cl_2): δ 8.7 (CH_3 of Cp*), 20.8 (*o*- CH_3 of Mes), 21.4 (*p*- CH_3 of Mes), 97.1 (quaternary C of Cp*), 116.7 (*p*-CH of BAR_4^-), 123.8 (q, ¹J_{CF} = 271 Hz, CF₃ of BAR_4^-), 125.1 (*m*-CH of Mes), 128.6 (*m*-C of BAR_4^-), 134.0 (*o*-CH of BAR_4^-), 147.9, 150.1 (quaternary C's of Mes), 160.9 (q, ¹J_{CB} = 49 Hz, *ipso*-C of BAR_4^-), 211.4 (CO) (the *ipso*-C of mesityl ligand was not observed). ¹⁹F NMR (282.78 MHz, 293 K, CD_2Cl_2): δ -62.8 (CF₃). ¹¹B NMR (96.42 MHz, 293 K, CD_2Cl_2): δ -7.6 (BAR_4^-), 145 (BMes). IR (CH_2Cl_2 solution): $\nu_{\text{CO}} = 2055, 2013 \text{ cm}^{-1}$. EI-MS: *m/z* (relative intensity) $[\text{M} - \text{CO}]^+ = 349$ (15), $[\text{M} - 2\text{CO}]^+ 321$ (5), correct isotope distribution for 1Fe, 1B. ES-MS (negative): *m/z* (relative intensity) $[\text{BAR}_4^-] = 863$ (100).
- (9) See, for example: Nlate, S.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, *434*, 89. (b) McArdle, P.; MacHale, D.; Cunningham, D.; Manning, A. R. *J. Organomet. Chem.* **1991**, *419*, C18.
- (10) Crystal data for $2 \cdot 1/2 \text{CH}_2\text{Cl}_2$: $\text{C}_{53}\text{H}_{39}\text{B}_2\text{ClF}_2\text{FeO}_2$, monoclinic, *C*₂/c, *a* = 36.301(7), *b* = 25.675(5), and *c* = 23.956(5) Å, $\beta = 93.81(3)^\circ$, *V* = 22278(8) Å³, *Z* = 16, *D*_{calc} = 1.530 g cm⁻³, $\mu(\text{MoK}\alpha) = 0.440 \text{ mm}^{-1}$. A suitable crystal was covered in predried, precooled mineral oil and mounted on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K. A total of 19 345 unique reflections were collected ($2.9 < \theta < 25.0^\circ$). Final *R*-factor: *R*₁ = 0.088.
- (11) (a) Yasue, T.; Kawano, Y.; Shimoi, M. *Chem. Lett.* **2000**, 58. (b) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.
- (12) Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830.
- (13) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 5495.
- (14) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. *J. Am. Chem. Soc.* **1979**, *101*, 585.
- (15) (a) McCullough, E. A., Jr.; Aprà, E.; Nichols, J. J. *Phys. Chem. A* **1997**, *101*, 2502. (b) Giju, K. T.; Bickelhaupt, M.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 4776. (c) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.
- (16) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1359.

JA0346936