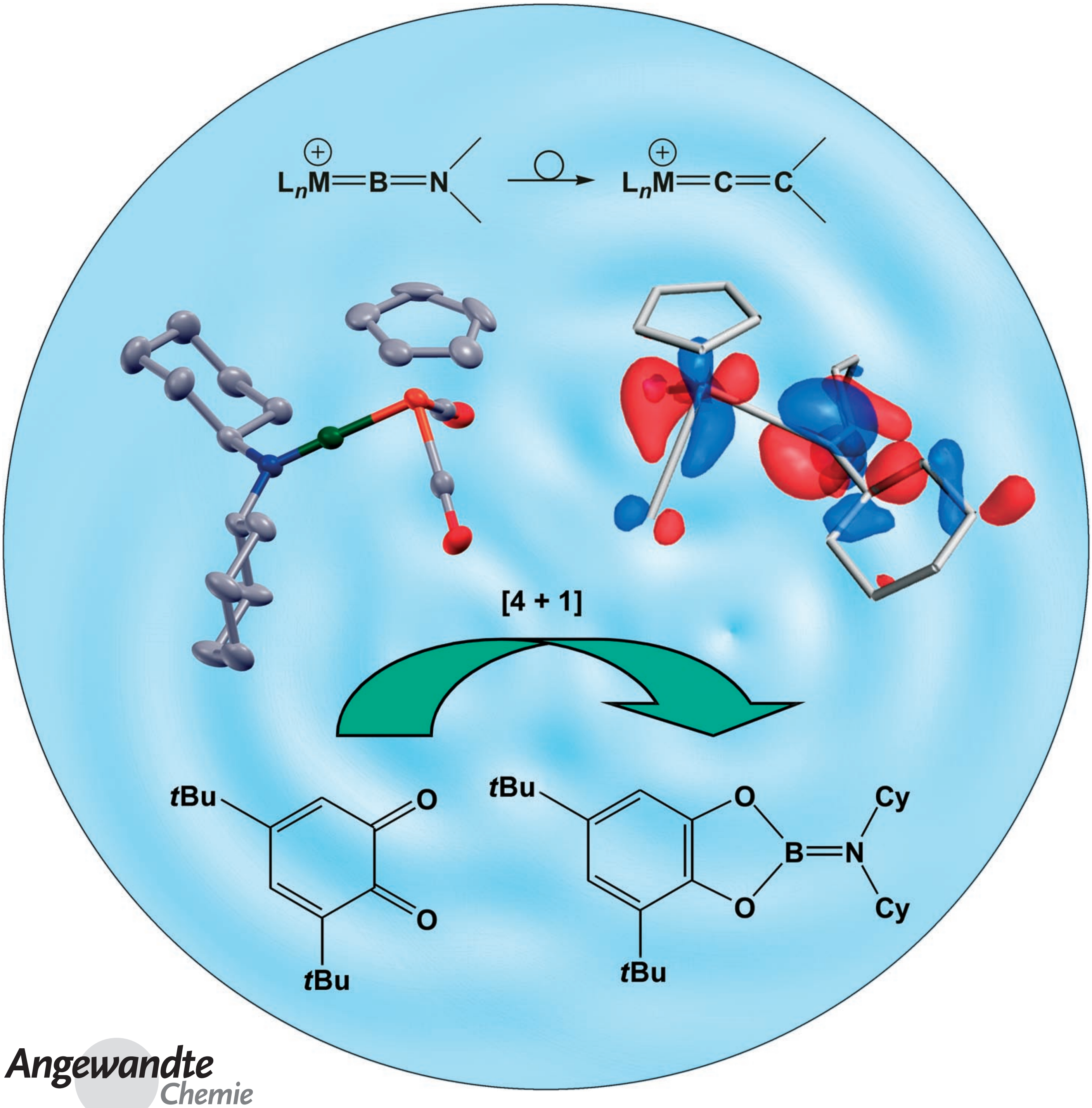
Borylene Complexes

DOI: 10.1002/ange.200602162

Cationic Terminal Borylene Complexes: Structure/Bonding Analysis and [4+1] Cycloaddition Reactivity of a BN Vinylidene Analogue**

Simon Aldridge, Cameron Jones,* Timo Gans-Eichler, Andreas Stasch, Deborah L. Kays (née Coombs), Natalie D. Coombs, and David J. Willock*



Angewandte Chemie

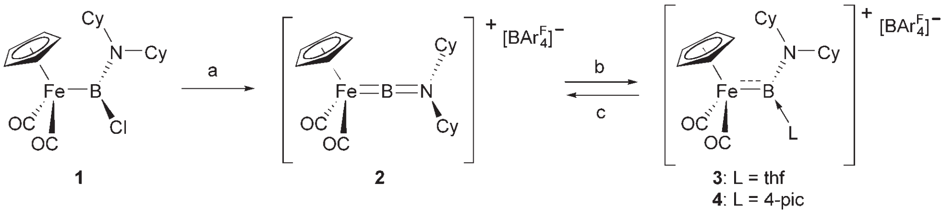
Wiley InterScience

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

The predominant routes to transition-metal borylene complexes $[(L_nM)_mBX]$ ($m = 1, 2, 3$), namely salt elimination and photolytic transfer chemistries, have been instrumental in accessing two-coordinate systems containing M−B double bonds.[1] Such compounds have excited interest not only from a desire to relate fundamental issues of geometric and electronic structure to patterns of chemical reactivity, but also as a result of obvious parallels in the classical organometallic chemistry of carbonyl, carbene, and vinylidene ligands.[2] Utilizing these synthetic approaches, four structurally authenticated species of the type $[L_nM{=}BX]$ have been reported to date.[3,4] Mirroring chemistry reported for unsaturated Group 14 ligand systems,[5] we have sought to exploit halide abstraction chemistry to access *cationic* diyl systems, $[L_nM(EX)]^+$ (E = Group 13 element), not only to broaden the range of available synthetic routes, but also to assess the influence of overall charge on the chemistry of these complexes.[6–8] This strategy has, to date, given access to the only structurally characterized example of a cationic two-coordinate borylene complex, namely $[Cp^*Fe(CO)_2(BC_6H_2Me_3\text{-}2,4,6)]^+[BAr^F_4]^-$ ($Ar^F = C_6H_3(CF_3)_2\text{-}3,5$).[6]

Given the widespread interest in transition-metal carbene and vinylidene species, for example in metathesis chemistry, and the numerous examples of systems of the type $[(\eta^5\text{-}C_5R_5)ML_n(CCR_2)]^+$,[9] we have sought to extend the halide abstraction methodology to the synthesis of the isoelectronic BN complexes $[(\eta^5\text{-}C_5R_5)ML_n(BNR_2)]^+$. Such cationic terminal aminoborylenes would not only offer insight into the CC/BN analogy, but also by comparison with neutral amino borylene and cationic aryl borylene compounds[3a,b,d,6] allow for systematic investigation of structure/bonding and reactivity on the basis of net charge and borylene substituent. As a result of these efforts, we report herein the synthesis of $[CpFe(CO)_2(BNCy_2)]^+[BAr^F_4]^-$ and an investigation of its structural and reaction chemistry.

The reaction of $[CpFe(CO)_2\{B(NCy_2)Cl\}]$ (**1**) with $Na[BAr^F_4]$ proceeds as outlined in Scheme 1 and leads to the isolation of $[CpFe(CO)_2(BNCy_2)]^+[BAr^F_4]^-$ (**2**) in 80% yield. In contrast to the analogous (diisopropylamino)borylene complex, which is an oil,[8] **2** is a crystalline solid which was characterized by standard spectroscopic and analytical techniques, and by X-ray diffraction. Revealingly, ^{11}B NMR and IR data for **2** and $[CpFe(CO)_2(BN\textit{i}Pr_2)]^+[BAr^F_4]^-$ are essentially identical ($\delta = 93.1$ and 93.5 ppm; $\tilde{\nu}(CO) = 2071$, 2028 and 2070, 2028 cm^{-1}, respectively) and fall within the ranges expected for a cationic aminoborylene complex.[8] In the case of $[CpFe(CO)_2(BN\textit{i}Pr_2)]^+[BAr^F_4]^-$ the presence of an Fe=B bond was inferred from spectroscopic, computational, and reactivity data;[8] in the case of **2** this double bond can be demonstrated explicitly by X-ray crystallography. Compound **2** therefore represents only the second structurally characterized cationic terminal borylene complex,[6] and the first such system featuring a heteroatom donor at boron. As such, it provides a unique basis for discussion of structure and bonding, both as a function of net charge (compare with the neutral analogues $[L_nM(BNR_2)]$)[3a,b,d] and borylene substituent (compare with $[Cp^*Fe(CO)_2(BC_6H_2Me_3\text{-}2,4,6)]^+$).[6] As a further aid to understanding the bonding situation in **2** we have also synthesized and structurally characterized the 4-picoline adduct $[CpFe(CO)_2\{B(NCy_2)(4\text{-pic})\}][BAr^F_4]^-$ (**4**) (see the Supporting Information for details), thus allowing for the first time direct structural comparison of otherwise identical two-coordinate and base-stabilized borylenes.



Scheme 1. Synthesis and simple Lewis acid/base chemistry of **2**. Reaction conditions: a) $Na[BAr^F_4]$ (1.1 equiv), CH_2Cl_2, −78 to 20°C, 6 h, 80%; b) Lewis base L (1000 equiv for **3**, 5 equiv for **4**), CH_2Cl_2, 20°C, 1 h, 52% yield of isolated product (for **4**); c) for **3**: continuous vacuum (ca. 0.1 Torr for 60 min), quantitative by ^{11}B NMR. Cy = cyclohexyl; 4-pic = 4-picoline.

The structure of **2** (Figure 1) features the linear M-B-X framework common to other base-free terminal borylene complexes (∢Fe-B-N 178.8(5)°),[3,6] with that for **4** (131.6(3)°) showing the expected narrowing upon base coordination.[10] The M−B bond length for **2** (1.859(6) Å) is much shorter than those found for *neutral* aminoborylene complexes (for example, 1.959(6) and 1.996(6) Å for $[CpV(CO)_3\{BN(SiMe_3)_2\}]$ and $[(OC)_5Cr\{BN(SiMe_3)_2\}]$, respectively),[3b,d] with this trend reflecting the expected changes in bond length as a function of metal fragment (compare the mean M−CO bond lengths of 1.816, 1.91, and 1.915 Å for $[CpFe(CO)_3]^+$, $[CpV(CO)_4]$ and $[Cr(CO)_6]$, respectively).[11] The Fe−B bond length in **2** is, however, significantly longer than that found in $[Cp^*Fe(CO)_2(BC_6H_2Me_3\text{-}2,4,6)]^+[BAr^F_4]^-$ (1.788 Å (mean)),[6] despite the reduced bulk of the cyclopentadienyl ligand. At a simplistic level this trend can be ascribed to the reduced π acidity of the boron center in the presence of the π donor amino substituent.[3b,c] Consistent with this, the B−N bond length in **2** is indicative of significant multiple-bond character (1.324(6) vs. 1.332 Å (mean) for $[R(R')N{=}B{=}NR(R')]^+$; R = *t*Bu, R′ = CH_2Ph).[12] Moreover,

---

[*] Dr. S. Aldridge, Prof. C. Jones, Dr. T. Gans-Eichler, Dr. A. Stasch, Dr. D. L. Kays (née Coombs), N. D. Coombs, Dr. D. J. Willock
Centre for Fundamental and Applied Main Group Chemistry
School of Chemistry
Cardiff University
Main Building
Park Place, Cardiff, CF10 3AT (UK)
Fax: (+44) 2920-874-030
E-mail: AldridgeS@cardiff.ac.uk
jonesca6@cardiff.ac.uk

[**] We thank the EPSRC for funding and for access to the National Mass Spectrometry facility.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

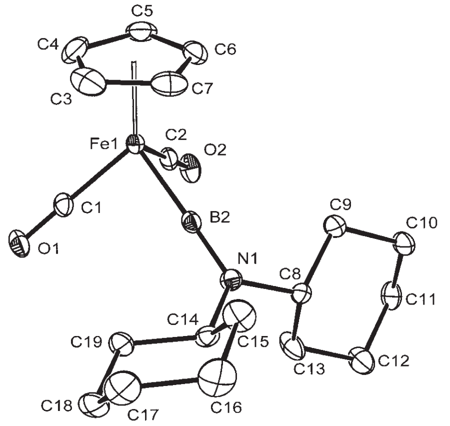


Figure 1. Structure of the cationic component of **2**·CH_2Cl_2 (ellipsoids at 50% probability; H atoms, anion, and CH_2Cl_2 molecule omitted for clarity). Relevant bond lengths [Å] and angles [°]: Fe1-B2 1.859(6), Fe1-C1 1.786(5), Fe1-Cp(centroid) 1.722(6), B2-N1 1.324(7); Fe1-B2-N1 178.8(5), B2-N1-C8 122.0(4), B2-N1-C14 121.6(4), C8-N1-C14 116.4(4); angle between least-squares planes defined by Cp(centroid)-Fe1-B2-N1 and B2-N1-C8-C14 83.3.

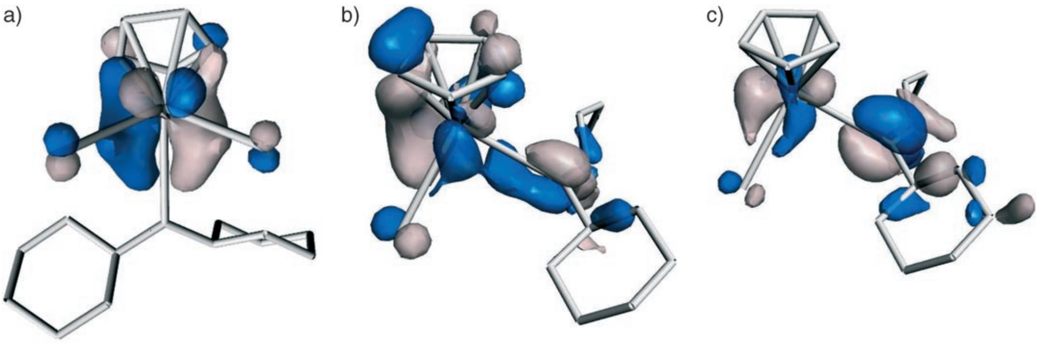


Figure 2. HOMO−2 (a), HOMO−1 (b), and HOMO (c) calculated by DFT (BLYP/TZP) for the cation $[CpFe(CO)_2(BNCy_2)]^+$ showing, respectively, Fe–B π-, Fe-B-N π-, and B–N π-bonding character. The *z*-axis is taken to be aligned with the Fe–B bond.

the shortening of both Fe–B and B–N bonds in **2** in comparison with three-coordinate systems **1** (Fe–B 2.053(3), B–N 1.396(4) Å) and **4** (Fe–B 2.049(4), B–N 1.391(5) Å) is also consistent with increased Fe–B and B–N π bonding. Indeed, the shortening of the Fe–B bond (9.4% with respect to **1**) is similar to that observed between $[Cp^*Fe(CO)_2(BC_6H_2Me_3\text{-}2,4,6)]^+$ and $[Cp^*Fe(CO)_2\{B(C_6H_2Me_3\text{-}2,4,6)Cl\}]$ (9.7%),[6] and comparable to that between archetypal alkyl and carbene systems (for example, 12.6% between $[CpFe(CO)_2(CCl_2)]^+$ and $[CpFe(CO)_2(n\text{-}C_5H_{11})]$),[13] implying a geometric basis for the presence of Fe=E bonds (E = B or C) in all three cases.

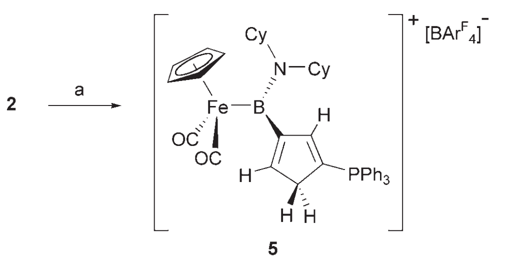
The validity of an Fe=B=N vinylidene-like bonding model for **2** was further examined by using DFT methods.[6c] Agreement between calculated (BLYP/TZP) and crystallographically determined geometric parameters is very good (see the Supporting Information), and relevant molecular orbitals are depicted in Figure 2. In addition to the HOMO−2 (−9.64 eV), which shows Fe–B π-bonding character utilizing the Fe $3d_{yz}$ and B $2p_y$ orbitals (with the LUMO+2 (−5.25 eV) having corresponding π* character), two orbitals can be identified (the HOMO−1 (−9.48 eV) and the HOMO (−9.18 eV)) which have B–N π character. The HOMO features an isolated B–N π component which has an antibonding phase relationship with the $3d_{xz}$ orbital of the iron center. The HOMO−1, by contrast, features a component which is delocalized along the entire Fe-B-N framework in the xz plane, thus providing additional Fe–B π overlap perpendicular to the HOMO−2 by utilizing the $3d_{xz}$ orbital. Partitioning of the bonding density for the Fe–B linkage in **2** yields a σ:π breakdown of 70:29,[6c] thus indicating a smaller π component than for the "isolated" Fe=B system in $[Cp^*Fe(CO)_2(BC_6H_2Me_3\text{-}2,4,6)]^+$ (38%), but a similar breakdown for the Fe–C linkage in the isoelectronic vinylidene complex $[CpFe(CO)_2(CC\mathit{i}Pr_2)]^+$ (67:33).[*] Thus, in addition to geometric arguments, quantum chemical data argue in favor of a bonding situation analogous to classical cationic Group 8 vinylidene complexes $[CpML_2({=}C{=}CR_2)]^+$.

Certain patterns of reactivity that were elucidated for **2** are also reminiscent of classical Group 8 vinylidenes, namely, addition chemistry at the α position towards C, N, and O nucleophiles.[9] Thus, 4-picoline readily coordinates at the boron center, and the weaker donor tetrahydrofuran can be shown by NMR measurements to coordinate *reversibly*. Such reactivity is consistent with significantly greater electrophilicity than typically displayed by *neutral* aminoborylenes.[14] Similar chemistry can also be exploited towards the formation of B–C bonds. Thus, reaction of **2** with triphenylphosphonium cyclopentadienide leads to the formation of $[CpFe(CO)_2\{B(NCy_2)(C_5H_4PPh_3)\}]^+[BAr^F{}_4]^-$ (**5**; Scheme 2 and Figure 3), which features a rare example of structurally authenticated σ coordination of the ylid cyclopentadienide ring,[15] in this case through the sterically less-encumbered C3 position. The crystallographically characterized product is also consistent with an additional *net* 1,3-hydrogen migration, such that C3 is trigonal planar (sum of angles: 359.0°) and there is a methylene group in the 5-position. Spectroscopic data for single crystals redissolved in CD_2Cl_2 imply the presence of a second species, which is thought to be an alternative isomer featuring the methylene group in the 4-position. The existence in solution of disubstituted cyclopentadienes of the type

---

[*] *i*Pr groups were employed for the vinylidene complex $[CpFe(CO)_2(CC\mathit{i}Pr_2)]^+$, as the corresponding Cy system failed to adequately meet all convergence criteria. For comparison, the σ:π breakdown for the strictly isoelectronic bis(isopropylamino)borylene complex $[CpFe(CO)_2(BN\mathit{i}Pr_2)]^+$ is calculated to be 70:30.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 2. Reaction of **2** with triphenylphosphonium cyclopentadienide, $Ph_3PC_5H_4$. Reaction conditions: a) $Ph_3PC_5H_4$ (1.0 equiv), CH_2Cl_2, 20 °C, 1 h, 54 %.

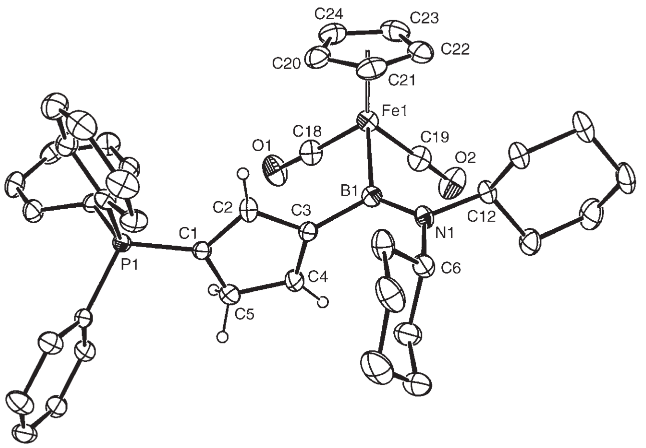
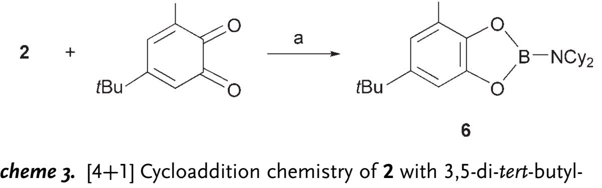


Figure 3. Structure of the cationic component of **5** (ellipsoids at 50% probability; H atoms, except those attached to C2, C4, and C5, and anion omitted for clarity). Relevant bond lengths [Å] and angles [°]: Fe1-B1 2.102(5), Fe1-C18 1.748(5), Fe1-Cp(centroid) 1.733(5), B1-N1 1.405(6), B1-C3 1.583(6), C1-C2 1.411(6), C2-C3 1.487(6), C3-C4 1.354(6), C4-C5 1.473(6), C1-P1 1.756(4); Fe1-B1-N1 126.7(3), Fe1-B1-C3 111.3(3), N1-B1-C3 122.0(4), B1-C3-C2 127.8(4), B1-C3-C4 125.0(4), C2-C3-C4 106.2(4).

1,3-$(Ph_3P)(X)C_5H_4$ as a mixture of isomers has previously been demonstrated.[16]

Divergent patterns of reactivity for **2** compared to other borylene systems can also be illustrated by its reaction with 3,5-di-*tert*-butyl-*ortho*-benzoquinone (Scheme 3). Although trapping of subvalent Group 14 compounds by quinone reagents has previously been demonstrated,[17,18] examples of borylene cycloaddition reactions are extremely rare.[19] Thus, the formation of **6** represents, to our knowledge, the first example of a net [4+1] cycloaddition reaction for a borylene complex.



Scheme 3. [4+1] Cycloaddition chemistry of **2** with 3,5-di-*tert*-butyl-*ortho*-benzoquinone. Reaction conditions: a) 3,5-di-*tert*-butyl-*ortho*-benzoquinone (1.0 equiv), CH_2Cl_2, 20 °C, 1 h, 81 % yield of isolated product.

In conclusion, we have reported the synthesis and structural characterization of the cationic terminal borylene complex $[CpFe(CO)_2(BNCy_2)]^+[BAr^F_4]^-$ (**2**), the first such system containing a π-donor substituent at boron. In addition, structural characterization of the picoline adduct $[CpFe(CO)_2\{B(NCy_2)(4\text{-pic})\}]^+[BAr^F_4]^-$ (**4**) allows, for the first time, comparative analysis of structural parameters for otherwise identical base-stabilized and base-free complexes. DFT and crystallographic studies are consistent with delocalized π bonding along the linear Fe-B-N framework in **2**, which incorporates significant Fe−B and B−N multiple-bond character. Compound **2** therefore represents a BN analogue of classical Group 8 cationic vinylidene systems $[(\eta^5\text{-}C_5R_5)ML_2(=C=CR_2)]^+$. In addition to reactivity characteristic of such vinylidene compounds, for example, nucleophilic addition at the α center (boron), the reactivity of **2** is also marked by the first reported example of borylene [4+1] cycloaddition. Further studies aimed at exploration of trends in structure and reactivity (including cycloaddition) for borylene systems as a function of the metal and ligand set will be reported in due course.

Experimental Section

Included here are the preparative and characterization data for compound **2**; data for **1**, **4**, **5**, and **6** are included in the Supporting Information.

2: A mixture of **1** (0.410 g, 1.02 mmol) and $Na[BAr^F_4]$ (1.1 equivalents) in CH_2Cl_2 (30 mL) was warmed from −78 to 20 °C. After stirring for a further 6 h the reaction was judged to be complete by ^{11}B NMR spectroscopy. Filtration of the mixture, concentration of the filtrate to about 5 mL, layering with hexanes (ca. 10 mL), and storage at −30 °C led to the formation of **2** as colorless crystals suitable for X-ray diffraction. Yield of isolated product: 1.00 g, 80 %; ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.17$–2.13 (m, 20 H, CH_2 of Cy), 2.87 (m, 2 H, CH of Cy), 5.24 (s, 5 H, Cp), 7.49 (s, 4 H, *para*-CH of $BAr^F_4{}^-$), 7.64 ppm (s, 8 H, *ortho*-CH of $BAr^F_4{}^-$); ^{13}C NMR (76 MHz, CD_2Cl_2): $\delta = 24.1$, 25.0, 35.5 (CH_2 of Cy), 58.6 (CH of Cy), 86.3 (Cp), 116.7 (*para*-CH of $BAr^F_4{}^-$), 123.8 (q, $^1J_{CF} = 272$ Hz, CF_3 of $BAr^F_4{}^-$), 128.0 (q, $^2J_{CF} = 31$ Hz, *meta*-C of $BAr^F_4{}^-$), 134.0 (*ortho*-CH of $BAr^F_4{}^-$), 161.0 (q, $^1J_{CB} = 50$ Hz, *ipso*-C of $BAr^F_4{}^-$), 204.8 ppm (CO); ^{11}B NMR (96 MHz, CD_2Cl_2): $\delta = -7.6$ ($BAr^F_4{}^-$), 93.1 ppm (br, frequency width at half maximum ca. 850 Hz, borylene); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta = -62.7$ ppm (CF_3); IR (CD_2Cl_2): $\tilde{\nu}(CO) = 2071$, 2028 cm^{-1}. Elemental analysis (%) calcd for **2**·CH_2Cl_2 ($C_{52}H_{41}B_2Cl_2F_{24}FeNO_2$): C 47.45, H 3.14, N 1.06; found: C 47.59, H 3.13, N 1.08; m.p. 108 °C.

Crystallographic data for **2**·CH_2Cl_2: $C_{52}H_{41}B_2Cl_2F_{24}FeNO_2$, $M_r = 1316.2$, triclinic, $P\bar{1}$, $a = 12.917(3)$, $b = 13.749(3)$, $c = 17.471(4)$ Å, $\alpha = 88.53(3)$, $\beta = 79.89(3)$, $\gamma = 74.41(3)°$, $V = 2941.5(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.486$ Mg m^{-3}, $T = 150(2)$ K, $\lambda = 0.71073$ Å. 19823 reflections collected, 10666 independent ($R(int) = 0.0313$), which were used in all calculations. $R_1 = 0.0883$, $wR_2 = 0.2492$ for observed unique reflections ($F^2 > 2\sigma(F^2)$) and $R_1 = 0.1096$, $wR_2 = 0.2668$ for all unique reflections. Max. and min. residual electron densities 1.44 and −1.25 e Å^{-3} (both near Cl2). CCDC 609044 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Received: May 31, 2006
Published online: July 25, 2006

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Keywords: boron · borylene ligands · cycloaddition · density functional calculations · iron

[1] For recent reviews of borylene chemistry, see: a) H. Braunschweig, M. Colling, *Eur. J. Inorg. Chem.* **2003**, 393–403; b) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559; c) H. Braunschweig, *Adv. Organomet. Chem.* **2004**, *51*, 163–192; d) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566–571; e) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.*, DOI: 10.1002/ange.200600506; *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200600506.

[2] See, for example: W. A. Nugent, J. M. Mayer, *Metal Ligand Multiple Bonds*, Wiley Interscience, New York, **1988**.

[3] a) H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355–3357; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179–3180; ; b) H. Braunschweig, M. Colling, C. Kollann, H. G. Stammler, B. Neumann, *Angew. Chem.* **2001**, *113*, 2359–2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298–2300; ; c) H. Braunschweig, M. Colling, C. Kollann, K. Merz, K. Radacki, *Angew. Chem.* **2001**, *113*, 4327–4329; *Angew. Chem. Int. Ed.* **2001**, *40*, 4198–4200; ; d) H. Braunschweig, M. Colling, C. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215–218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205–208.

[4] For examples of charge-neutral terminal borylene complexes featuring coordination numbers at boron of greater than two, see: a) A. H. Cowley, V. Lomeli, A. Voight, *J. Am. Chem. Soc.* **1998**, *120*, 6401–6402; b) G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Angew. Chem.* **2000**, *112*, 978–980; *Angew. Chem. Int. Ed.* **2000**, *39*, 948–950; ; c) C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Organometallics* **2002**, *21*, 4862–4872; d) H. Braunschweig, D. Rais, K. Uttinger, *Angew. Chem.* **2005**, *117*, 3829–3832; *Angew. Chem. Int. Ed.* **2005**, *44*, 3763–3766.

[5] See, for example: G. P. Mitchell, T. D. Tilley, *J. Am. Chem. Soc.* **1997**, *119*, 11236–11243.

[6] a) D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356–6357; b) D. L. Coombs, S. Aldridge, A. Rossin, C. Jones, D. J. Willock, *Organometallics* **2004**, *23*, 2911–2926; c) S. Aldridge, A. Rossin, D. L. Coombs, D. J. Willock, *Dalton Trans.* **2004**, 2649–2654.

[7] a) N. R. Bunn, S. Aldridge, D. L. Coombs, A. Rossin, D. J. Willock, C. Jones, L.-L. Ooi, *Chem. Commun.* **2004**, 1732–1733; b) N. R. Bunn, S. Aldridge, D. L. Kays, N. D. Coombs, A. Rossin, D. J. Willock, C. Jones, L.-L. Ooi, *Organometallics* **2005**, *24*, 5891–5900.

[8] D. L. Kays, J. K. Day, L.-L. Ooi, S. Aldridge, *Angew. Chem.* **2005**, *117*, 7623–7626; *Angew. Chem. Int. Ed.* **2005**, *44*, 7457–7460.

[9] For reviews on transition-metal vinylidene chemistry, see, for example: a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197–257; b) C. Bruneau, P. H. Dixneuf, *Acc. Chem. Res.* **1999**, *32*, 311–323; c) H. Katayama, F. Ozawa, *Coord. Chem. Rev.* **2004**, *248*, 1703–1715; d) H. Werner, *Coord. Chem. Rev.* **2004**, *248*, 1693–1702.

[10] For related examples of cationic base-stabilized terminal borylene complexes, see: a) H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 5796–5799; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651–5654; b) D. L. Kays, J. K. Day, S. Aldridge, R. W. Harrington, W. Clegg, *Angew. Chem.* **2006**, *118*, 3593–3596; *Angew. Chem. Int. Ed.* **2006**, *45*, 3513–3516.

[11] a) J. B. Wilford, A. Whitla, H. M. Powell, *J. Organomet. Chem.* **1967**, *8*, 491–494; b) M. E. Gress, R. A. Jacobson, *Inorg. Chem.* **1973**, *12*, 1746–1749; c) B. Rees, A. Mitschler, *J. Am. Chem. Soc.* **1976**, *98*, 7918–7924.

[12] P. Kolle, H Nöth, *Chem. Ber.* **1986**, *119*, 313–324.

[13] a) A. M. Crespi, D. F. Shriver, *Organometallics* **1985**, *4*, 1830–1835; b) R. O. Hill, C. F. Marais, J. R. Moss, K. J. Naidoo, *J. Organomet. Chem.* **1999**, *587*, 28–37.

[14] H. Braunschweig, personal communication.

[15] a) N. C. Baenziger, R. M. Flynn, D. C. Swenson, N. L. Holy, *Acta Crystallogr. Sect. B* **1978**, *34*, 2300–2301; b) R. M. G. Roberts, *Tetrahedron* **1980**, *36*, 3295–3300; c) A. J. Deeming, N. I. Powell, C. Whittaker, *J. Chem. Soc. Dalton Trans.* **1991**, 1875–1880.

[16] F. F. Pérez-Pla, S. Housseini, J. Palou, . C. D. Hall, *Int. J. Chem. Kinet.* **1997**, *29*, 561–574.

[17] See, for example: C. Laurent, S. Mazières, H. Lavayssière, P. Mazerolles, G. Doussse, *J. Organomet. Chem.* **1993**, *452*, 41–45.

[18] For an example of related reactivity of a gallium(I) diyl compound towards an α,β-unsaturated reagent, see: N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667–2679.

[19] H. Braunschweig, T. Herbst, D. Rais, F. Seeler, *Angew. Chem.* **2005**, *117*, 7627–7629; *Angew. Chem. Int. Ed.* **2005**, *44*, 7461–7463.