M=B Metathesis

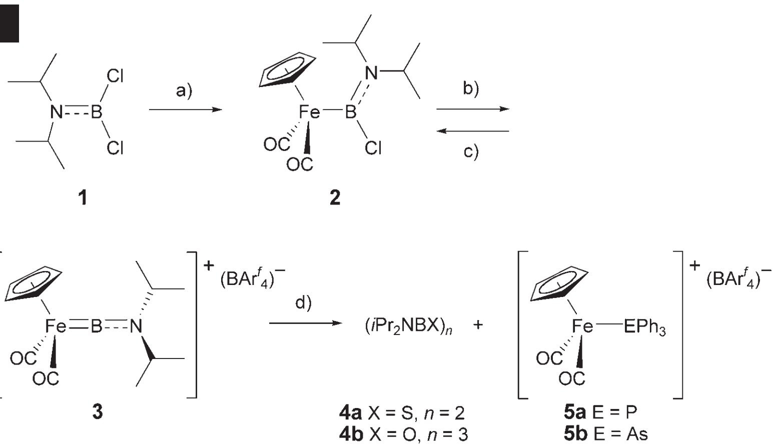
DOI: 10.1002/ange.200502343

Cationic Terminal Borylene Complexes: A Synthetic and Mechanistic Investigation of M=B Metathesis Chemistry**

*Deborah L. Kays (née Coombs), Joanna K. Day, Li-Ling Ooi, and Simon Aldridge**

Metathesis reactions constitute a key component of modern synthetic chemistry; olefin metathesis, for example, provides a versatile and widely exploited carbon–carbon bond-forming methodology.[1] Such reactions are typically catalyzed by organometallic complexes that contain M=C bonds.[2] The synthesis of analogous complexes that contain M=Si bonds, for example, has led to an in-depth investigation of their reactivity towards unsaturated substrates.[3]

Synthetic approaches that lead to the isolation of related systems with M=B bonds have been developed only recently:[4–7] for example, halide-abstraction chemistry gives access to cationic terminal borylene complexes, $[L_nM{=}BX]^+$.[7] Consequently, reports of the fundamental chemistry of M=B bonds are somewhat limited (predominantly to metal–metal transfer reactions and addition/substitution reactivity towards nucleophiles).[4,6,7] Thus, the chemistry of $[Cp^*Fe(CO)_2(BMes)]^+$ (Mes = mesityl = 2,4,6-$Me_3C_6H_2$, Cp* = pentamethylcyclopentadienyl), for example, is dominated by the electrophilic character at both the Fe and B centers.[7] In an attempt to tune the reactivity of these highly unsaturated complexes we investigated the synthesis of cationic aminoborylene systems, $[L_nM{=}BNR_2]^+$.[5] Chloride abstraction from $[CpFe(CO)_2\{B(NiPr_2)Cl\}]$ (**2**) (Cp = cyclopentadienyl) by $Na(BAr^f_4)$ (Ar^f = 3,5-$(CF_3)_2C_6H_3$) affords the thermally robust cationic B/N vinylidene analogue $[CpFe(CO)_2(BNiPr_2)]^+$, which undergoes, with E=O and E=S bonds (E = P, As), the first reported examples of M=B metathesis chemistry.



Scheme 1. Synthesis and reactions of **3**. a) $Na[CpFe(CO)_2]$ (1 equiv), toluene, 20 °C, 20 h.; b) $Na(BAr^f_4)$, (1 equiv), dichloromethane, −78→20 °C, 30 min.; c) ppnCl (1.67 equiv), dichloromethane, 20 °C, 30 min.; d) $Ph_3P{=}S$ or $Ph_3As{=}O$ (1 equiv), dichloromethane, 20 °C, 30 min. ppn = bis(triphenylphosphoranylidene)ammonium.

The synthesis of $[CpFe(CO)_2(BNiPr_2)]^+(BAr^f_4)^-$ (**3**) is outlined in Scheme 1. The key precursor **2** was synthesized by the selective substitution of a chloride substituent in iPr_2NBCl_2 (**1**) by $[CpFe(CO)_2]^-$. The steric bulk of the amino substituents is a key point: the use of the smaller NMe_2 group results in the formation of a thermally fragile borylene product in the subsequent halide-abstraction step,[7b,8] whereas $[CpFe(CO)_2\{B(tmp)Cl\}]$ (tmp = tetramethylpiperamino) was inaccessible from $tmpBCl_2$. Compound **2** is a pale yellow sublimable crystalline solid, which was characterized by multinuclear NMR and IR spectroscopy, mass spectrometry, and X-ray crystallographic analysis (Figure 1).

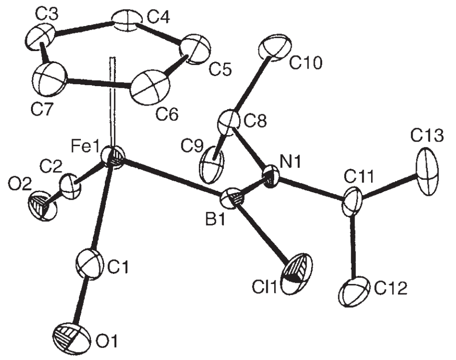


Figure 1. Structure of **2** (50% ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe(1)-B(1) 2.054(4), B(1)-Cl(1) 1.841(4), B(1)-N(1) 1.389(5); centroid-Fe(1)-B(1)-N(1) 83.7(4).

The reaction of **2** with $Na(BAr^f_4)$ in dichloromethane results in a quantitative conversion (determined by ^1H and ^{11}B NMR spectroscopy) into **3**. The latter product (along with the C_5H_4Me analogue) is a colourless oil at (or close to) room temperature, but its formulation can be definitively established from spectroscopic and reactivity data. The measured ^{11}B chemical shift for **3** (δ_B = 93.5 ppm) is very close to that reported by Braunschweig et al. for neutral terminal-aminoborylene systems of the type $L_nM{=}BN(SiMe_3)_2$ (δ_B = 86.6–98.3 ppm).[5] The downfield shift upon chloride abstraction ($\Delta\delta_B$ = 38.1 between **2** and **3**) mirrors that found for $[Cp^*Fe(CO)_2\{B(Mes)Cl\}]/[Cp^*Fe(CO)_2(BMes)]^+$ (δ_B = 112.1 and 145.0 ppm, respectively) and for $[Cp^*Fe(CO)_2\{B(NMe_2)Cl\}]/[Cp^*Fe(CO)_2(BNMe_2)]^+$ (δ_B = 58.6 and 88.0 ppm, respectively).[7,8] The ^1H and ^{13}C NMR data are

---

[*] Dr. D. L. Kays (née Coombs), J. K. Day, Dr. L.-L. Ooi, Dr. S. Aldridge
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

[**] We thank the EPSRC for funding and access to the National Mass Spectrometry facility and Prof. C. Jones (Cardiff) for help in modeling crystallographic disorder.

Supporting information for this article (crystal structure data for **2** and **6**, and data for **4a**, **4b**, **5a**, and **5b**) are available on the WWW under http://www.angewandte.org or from the author.

consistent with the presence of Cp, N*i*Pr$_2$, and $(BAr^f_4)^-$ moieties in a 1:1:1 ratio, and the ES+ mass spectrum shows the presence of the $[CpFe(CO)_2(BN\textit{i}Pr_2)]^+$ cation. The observation of equivalent *i*Pr substituents is consistent with the structure of the related neutral system $[CpV(CO)_3{=}BN(SiMe_3)_2]$[5c] and agrees with the results of DFT calculations for the model compounds $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(BNMe_2)]^+$ (R = H, Me), for which a minimum-energy structure close to C_s symmetry [< centroid-Fe-N-C ≈ 90° (84.6° for R = Me)] and a low barrier to rotation about the Fe-B-N axis ($\approx 2.2\ \text{kcal mol}^{-1}$) have been calculated.[7b,c] Furthermore, the IR spectrum of **3** shows carbonyl stretching frequencies ($\tilde{\nu} = 2070,\ 2028\ \text{cm}^{-1}$) that are significantly blue shifted with respect to **2** ($\tilde{\nu} = 2001,\ 1941\ \text{cm}^{-1}$) ($\Delta\tilde{\nu} \approx 50\ \text{cm}^{-1}$ for $[Cp^*Fe(CO)_2\{B(Mes)Cl\}]/[Cp^*Fe(CO)_2(BMes)]^+$) and are very similar to those reported for the archetypal Fischer carbene systems such as $[CpFe(CO)_2{=}CH(SPh)]^+(PF_6)^-$ ($\tilde{\nu} = 2073,\ 2034\ \text{cm}^{-1}$).[9] Further evidence for the nature of **3** was obtained: 1) from the reaction of **3** with ppnCl (see Supporting Information), which like the analogous reaction for structurally characterized cationic derivatives,[6b,7] generates a haloboryl complex (in this case **2**) by the addition of a halide at boron and 2) from the reaction of **3** with $Ph_3P{=}O$, which proceeds via the structurally characterized adduct $[CpFe(CO)_2\{B(N\textit{i}Pr_2)(OPPh_3)\}]^+(BAr^f_4)^-$ (see below).

Although the reactivity of cationic aminoborylene complex **3** towards Cl^- is indicative of electrophilic character, its reactivity towards unsaturated substrates suggests a broader scope for its chemistry. Thus, the reaction of **3** with $Ph_3P{=}S$ in dichloromethane at room temperature leads to the formation of $[\textit{i}Pr_2NB(\mu\text{-}S)_2BN\textit{i}Pr_2]$ (**4a**) and $[CpFe(CO)_2(PPh_3)]^+(BAr^f_4)^-$ (**5a**) with a conversion of > 95 % (as determined by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy). The identities of the isolated products **4a** and **5a** were confirmed by comparison of NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P) and IR spectra and mass spectrometry data with those reported for authentic samples.[10a–c] The similar reactivity of **3** towards $Ph_3As{=}O$ led to the isolation of $(\textit{i}Pr_2NBO)_3$ (**4b**) and $[CpFe(CO)_2(AsPh_3)]^+(BAr^f_4)^-$ (**5b**).[10c,d]

The reactions of **3** with $Ph_3P{=}S$ and $Ph_3As{=}O$ therefore represent, to our knowledge, the first examples of net metathesis reactions for a terminal borylene complex.[11] Although metathesis chemistry has been reported for isoelectronic vinylidene systems $[CpM(CO)_2{=}C{=}CH_2]$ (M = Mn, Re),[12] no such reactivity has been reported for neutral aminoborylene complexes.[5,6] The origins of the different reactivity of **3** and an idea of the likely mechanism can be gauged by examining of the analogous reaction with $Ph_3P{=}O$. This reaction proceeds at a significantly slower rate than those of $Ph_3P{=}S$ or $Ph_3As{=}O$ which presumably reflects the greater strength of the P=O bond. In this case, however, it is possible to identify a reaction intermediate, which was characterized by NMR signals at $\delta_B = 48.9$ ppm and $\delta_P = 48.3$ ppm. The former resonance is consistent with values previously reported for base-stabilized terminal borylene complexes (e.g. $\delta_B = 51.7$–53.2 ppm for N-donor adducts of osmium aminoborylenes),[4b,c] whereas the ^{31}P chemical shift is as expected for donor/acceptor adducts of Ph_3PO with boron-centered Lewis acids ($\delta_P = 43.6$–46.7 ppm).[13] Furthermore, the observations of inequivalent *i*Pr groups by ^{1}H and ^{13}C NMR and of significantly lower carbonyl stretching frequencies ($\tilde{\nu} = 2004,\ 1949\ \text{cm}^{-1}$) are consistent with the formation of a trigonal-planar boron center by coordination of a Lewis base. Confirmation that the intermediate species is indeed the B-bound Ph_3PO adduct $[CpFe(CO)_2\{B(N\textit{i}Pr_2)(OPPh_3)\}]^+(BAr^f_4)^-$(**6**) was obtained by X-ray crystallographic analysis (Figure 2). Consistent with related complexes,[4b,c,14] the Fe–B bond length for **6** [2.057(4) Å] is more akin to that expected for a single bond than a double bond (2.054(4) and 1.792(8) Å for **2** and $[Cp^*Fe(CO)_2(BMes)]^+$, respectively).[7] Such a phenomenon has previously been ascribed to significant contributions from resonance forms that incorporate a formal M–B bond (Scheme 2),[4b,c] and a description of **6** as an amino(oxy)boryl species that features a pendant cationic phosphorus centre is probably most apt. Consistent with this, the P–O distance within **6** is significantly longer than that found in free Ph_3PO (1.540(2) vs. 1.493 Å (mean)).[15]

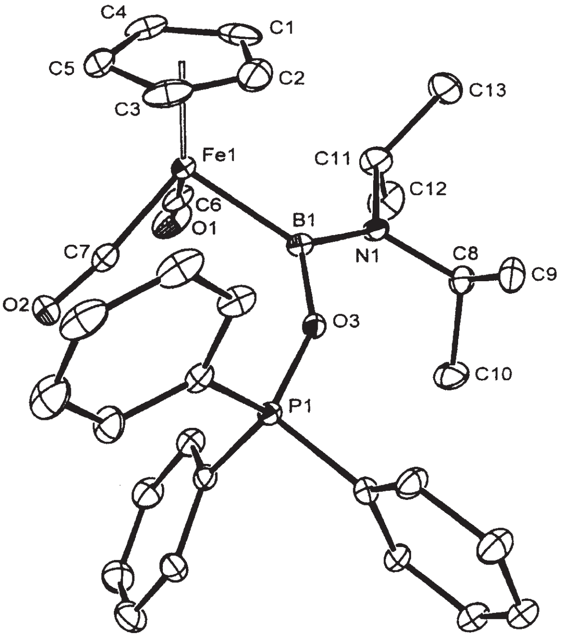
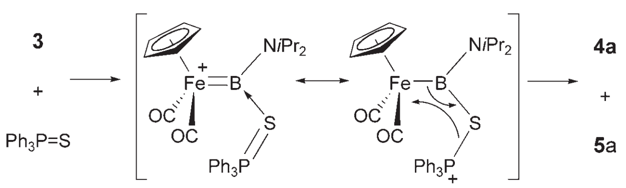


Figure 2. Structure of the cationic component of **6** (50% ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe(1)-B(1) 2.057(4), B(1)-O(3) 1.469(4), B(1)-N(1) 1.397(5), P(1)-O(3) 1.540(2); P(1)-O(1)-B(1) 148.0(2), centroid-Fe(1)-B(1)-N(1) 72.5(5).

Given the isolation of **6**, it is plausible that the first step in the reaction mechanism involves coordination of $Ph_3E{=}X$



Scheme 2. Proposed addition/substitution pathway for the metathesis reaction of **3** (exemplified by $Ph_3P{=}S$).

(E = P, As; X = O, S) at boron, and that the overall metathesis chemistry of **3** therefore occurs through a combined addition/substitution pathway (Scheme 2). Further studies aimed at better understanding the reactivity of M = B bonds towards unsaturated substrates (including C = E multiple bonds) will be reported in a full account.[17]

Experimental Section

2: Reaction of **1** (1.199 g, 6.6 mmol) with $\mathrm{Na[CpFe(CO)_2]}$ (1.318 g, 6.6 mmol) in toluene (40 $\mathrm{cm^3}$) at room temperature for 20 h, followed by filtration, removal of volatile compounds in vacuo, and extraction with hexanes ($\approx$40 $\mathrm{cm^3}$) yielded crude **2** as an oily brown solid. Yellow crystals suitable for X-ray diffraction were obtained by sublimation under high vacuum (40 °C at 10^{-4} Torr). Yield (of sublimed material): 0.259 g, 12 %. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 1.11 (d, J = 6.7 Hz, 6 H; $\mathrm{CH(C}H_3)_2$ of *i*Pr), 1.39 (d, J = 6.7 Hz, 6 H; $\mathrm{CH(C}H_3)_2$), 3.40 (sept, J = 6.7 Hz, 1 H; $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.44 (sept, J = 6.7 Hz, 1 H; $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.69 ppm (s, 5 H; Cp-H); ^{13}C NMR (76 MHz, $\mathrm{C_6D_6}$): δ = 21.2 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 23.9 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 47.8 ($C\mathrm{H(CH_3)_2}$), 55.2 ($C\mathrm{H(CH_3)_2}$), 88.2 (Cp), 215.6 ppm (CO); ^{11}B NMR (96 MHz, $\mathrm{C_6D_6}$): δ = 55.4 ppm. IR ($\mathrm{C_6D_6}$ soln); $\tilde{\nu}$ = 2001, 1941 $\mathrm{cm^{-1}}$ νCO; MS (EI): m/z (%): 295 (65) $[M-\mathrm{CO}]^+$, 288 (weak) $[M-\mathrm{Cl}]$, 267 (10) $[M-2\,\mathrm{CO}]^+$, 223 (100) $[M-\mathrm{N}i\mathrm{Pr_2}]^+$, M^+ not observed; MS: calcd for $[M-\mathrm{CO}]^+$: 295.0592; found: 295.0595; calcd for $[M-\mathrm{Cl}]^+$: 288.0853; found 288.0856. Crystal data: $\mathrm{C_{13}H_{19}BClFeNO_2}$, orthorhombic, *Pbca*, a = 11.7410(4), b = 13.9170(4), c = 19.0830(7) Å, V = 3118.15(18) Å^3, Z = 8, ρ_{calcd} = 1.378 Mg m^{-3}, M_r = 323.40, T = 150(2) K. 22 231 reflections collected, 3175 independent (R(int) = 0.1524), which were used in all calculations. R_1 = 0.0572, wR_2 = 0.1157 for observed unique reflections ($F^2 > 2\sigma(F^2)$) and R_1 = 0.1048, wR_2 = 0.1338 for all unique reflections. Max./min. residual electron densities 0.505/−0.537 e Å^{-3}.[16]

3: Reaction of **2** (0.259 g, 0.80 mmol) and $\mathrm{Na(BAr^{\mathit{f}}_4)}$ (0.710 g, 0.80 mmol) in dichloromethane (15 $\mathrm{cm^3}$) from −78→20 °C over 30 min leads to a quantitative conversion (determined by ^{11}B NMR) of **2** (δ_{B} = 55.4 ppm) to **3** (δ_{B} = 93.5 ppm). Filtration, and recrystallization from dichloromethane/hexanes (or fluorobenzene/hexanes) at −30 °C leads to the isolation of **3** as a spectroscopically pure colourless oil. Yield of isolated material: 0.465 g, 50 %. ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 1.39 (d, J = 6.6 Hz, 12 H; $\mathrm{CH(C}H_3)_2$), 3.32 (sept, J = 6.6 Hz, 2 H; $\mathrm{C}H\mathrm{(CH_3)_2}$), 5.33 (s, 5 H, Cp-H), 7.55 (s, 4 H; $\mathrm{BAr^{\mathit{f}}_4{}^-}$-H$_p$), 7.70 ppm (s, 8 H; $\mathrm{BAr^{\mathit{f}}_4{}^-}$-H$_o$); ^{13}C NMR (76 MHz, $\mathrm{CD_2Cl_2}$): δ = 24.4 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 51.0 ($C\mathrm{H(CH_3)_2}$), 87.1 (C(Cp)), 117.6 ($\mathrm{BAr^f_4{}^-}$-CH$_p$), 124.6 (q, $^1J_{\mathrm{CF}}$ = 272 Hz, $\mathrm{BAr^f_4{}^-}$-CF$_3$), 128.8 (q, $^2J_{\mathrm{CF}}$ = 34 Hz, $\mathrm{BAr^f_4{}^-}$-CH$_m$), 134.8 ($\mathrm{BAr^f_4{}^-}$-CH$_o$), 161.8 (q, $^1J_{\mathrm{CB}}$ = 49 Hz, $\mathrm{BAr^f_4{}^-}$-C$_{ipso}$), 205.6 ppm (CO); ^{11}B NMR (96 MHz, $\mathrm{CD_2Cl_2}$): δ = −7.7 ($\mathrm{BAr^f_4{}^-}$), 93.5 ppm (b, fwhm ≈ 615 Hz, BN*i*Pr$_2$); ^{19}F NMR (283 MHz, $\mathrm{CD_2Cl_2}$): δ = −62.6 ppm (CF$_3$); IR ($\mathrm{CD_2Cl_2}$ soln): $\tilde{\nu}$ = 2070, 2028 $\mathrm{cm^{-1}}$ νCO; MS (ES): m/z (%): M^+ 288.1 (10).

Typical reaction: **3** (0.068 g, 0.06 mmol) and $\mathrm{Ph_3P{=}S}$ (1.0 equiv) were stirred together in dichloromethane for 30 min, after which the reaction was judged to be complete by ^{11}B and ^{31}P NMR (conversion of signals at δ_{B} = 93.5 ppm and δ_{P} = 43.7 ppm to δ_{B} = 35.6 ppm and δ_{P} = 60.8 ppm, respectively). Removal of volatile components in vacuo and extraction into hexanes gave *i*Pr$_2$NB(μ-S)$_2$BN*i*Pr$_2$ (**4a**), which was identified by comparison of ^{1}H, ^{13}C, and ^{11}B NMR spectroscopic and mass spectrometry data with those reported previously.[10a,b] ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR and IR spectra of the hexane-insoluble product confirmed it to be $\mathrm{[CpFe(CO)_2(PPh_3)]^+(BAr^{\mathit{f}}_4)^-}$ (**5a**).[10c] A similar procedure was adopted for the reaction of **3** with $\mathrm{Ph_3As{=}O}$.[10c,d]

6: Reaction of **3** (0.199 g, 0.17 mmol) and $\mathrm{Ph_3PO}$ (0.048 g, 0.17 mmol) in dichloromethane (5 $\mathrm{cm^3}$) at room temperature over a period of 30 min, followed by filtration and recrystallization from dichloromethane/hexanes at −30 °C led to the isolation of **6** as pale yellow crystals. Yield of isolated product: 0.105 g, 43 %. ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 1.06 (d, J = 6 Hz, 6 H; $\mathrm{CH(C}H_3)_2$), 1.20 (d, J = 6 Hz, 6 H; $\mathrm{CH(C}H_3)_2$), 3.25 (sept, J = 6 Hz, 1 H; $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.10 (sept, J = 6 Hz; $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.50 (s, 5 H; Cp-H), 7.38–7.48 (m, 9 H; Ph$_3$PO-CH_o and Ph$_3$PO-CH_p), 7.55 (s, 4 H; $\mathrm{BAr^{\mathit{f}}_4{}^-}$-H$_p$), 7.60–7.78 (m, 6 H; Ph$_3$PO-H$_m$), 7.73 ppm (s, 8 H; $\mathrm{BAr^{\mathit{f}}_4{}^-}$-H$_o$); ^{13}C NMR (76 MHz, $\mathrm{C_6D_6}$): δ = 22.4, 23.9 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 47.2 ($C\mathrm{H(CH_3)_2}$), 84.4 (C(Cp)), 117.5 ($\mathrm{BAr^f_4{}^-}$-CH$_p$), 122.6 (Ph$_3$PO-C$_{ipso}$), 124.6 (q, $^1J_{\mathrm{CF}}$ = 272 Hz; $\mathrm{BAr^f_4{}^-}$-CF$_3$), 128.9 (q, $^2J_{\mathrm{CF}}$ = 34 Hz; $\mathrm{BAr^f_4{}^-}$-C$_m$), 130.1 (Ph$_3$PO-CH$_m$), 133.5 (Ph$_3$PO-C$_o$), 134.9 ($\mathrm{BAr^f_4{}^-}$-CH$_o$), 135.9 (Ph$_3$PO-C$_p$), 161.8 (q, $^1J_{\mathrm{CB}}$ = 49 Hz; $\mathrm{BAr^f_4{}^-}$-C$_{ioso}$), 214.7 ppm (CO); ^{11}B NMR (96 MHz, $\mathrm{CD_2Cl_2}$): δ = −7.7 ($\mathrm{BAr^f_4{}^-}$), 48.9 ppm (b, fwhm ≈ 480 Hz, B-(OPPh$_3$)N*i*Pr$_2$); ^{19}F NMR (283 MHz, $\mathrm{CD_2Cl_2}$): δ = −62.7 ppm (CF$_3$); ^{31}P NMR (121 MHz, $\mathrm{CD_2Cl_2}$): δ = 48.3 ppm (Ph$_3$PO); IR ($\mathrm{CD_2Cl_2}$ soln): $\tilde{\nu}$ = 2004, 1949 $\mathrm{cm^{-1}}$ ν(CO). Crystal data: $\mathrm{C_{63}H_{46}B_2F_{24}FeNO_3P}$, triclinic, $P\bar{1}$, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, α = 68.7080(10), β = 83.7430(10), γ = 87.4800(10)°, V = 3226.47(8) Å^3, Z = 2, ρ_{calcd} = 1.471 Mg m^{-3}, M_r = 1429.45, T = 150(2) K. 51 247 reflections collected, 14 704 independent (R(int) = 0.1118) which were used in all calculations. R_1 = 0.0718, wR_2 = 1791 for observed unique reflections ($F^2 > 2\sigma(F^2)$) and R_1 = 0.1223, wR_2 = 0.1992 for all unique reflections. Max./min. residual electron densities 1.086/−0.608 e Å^{-3}.[16]

Received: July 5, 2005

Keywords: boron · borylenes · halide abstraction · metathesis · vinylidene ligands

---

[1] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2002**, *35*, 18–29.

[2] a) W. A. Nugent, J. M. Mayer, *Metal Ligand Multiple Bonds*, Wiley Interscience, New York, 1988; b) J. W. Hendon, *Coord. Chem. Rev.* **2003**, *243*, 3–81.

[3] G. P. Mitchell, T. D. Tilley, *J. Am. Chem. Soc.* **1997**, *119*, 11 236–11 243.

[4] a) H. Braunschweig, M. Colling, C. Kollann, K. Merz, K. Radacki, *Angew. Chem.* **2001**, *113*, 4327–4329; *Angew. Chem. Int. Ed.* **2001**, *40*, 4198–4200; 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, K. Radacki, D. Scheschkewitz, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1685–1688; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658–1661;.

[5] For neutral aminoborylene complexes, see: 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. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215–218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205–208.

[6] 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.

[7] 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.

[8] H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465–468.

[9] C. Knors, G.-H. Kuo, J, W, Lauher, C. Eigenbrot, P. Helquist, *Organometallics* **1987**, *6*, 988–995.

[10] a) H. Nöth, W. Rattay, *J. Organomet. Chem.* **1986**, *312*, 139–148; b) W. Maringgele, A. Meller, *Z. Anorg. Allg. Chem.* **1989**, *572*, 140–144; c) H. Schumann, L. Eguren, *J. Organomet. Chem.* **1991**, *403*, 183–193; d) W. Maringgele, M. Noltemeyer, A. Meller, *Organometallics* **1997**, *16*, 2276–2284.

[11] Metathesis chemistry has been reported for C=B bonds, for example see: P. Paetzold, U. Englert, R. Finger, T. Schmitz, A. Tapper, *Z. Anorg. Allg. Chem.* **2004**, *630*, 508–518.

[12] See, for example: M. R. Terry, L. A. Mercando, C. Kelley, G. L. Geoffroy, P. Nombel, N. Lugan, R. Mathieu, R. L. Ostrander, B. E. Owens-Waltermire, A. L. Rheingold, *Organometallics* **1994**, *13*, 843–865.

[13] a) N. Burford, B. W. Royan, R. E. v. H. Spence, T. S. Cameron, A. Linden, R. D. Rogers, *J. Chem. Soc. Dalton Trans.* **1990**, 1521–1528; b) G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685–1691.

[14] H. Braunschweig, D. Rais, K. Uttinger, *Angew. Chem.* **2005**, *117*, 3829–3832; *Angew. Chem. Int. Ed.* **2005**, *44*, 3763–3766; .

[15] C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1985**, *107*, 6964–6970.

[16] Further details of the crystal structures investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-277456 (**2**) and CSD-277457 (**6**), the manes of the authors, and the journal citation.

[17] For a related article, see the following Communication in this issue: H. Braunschweig, T. Herbst, D. Rais, F. Seeler, *Angew. Chem.* **2005**, *117*, 7627–7629; *Angew. Chem. Int. Ed.* **2005**, *44*, 7461–7463 (DOI: 10-1002/anie.200502524).