#### M=B Metathesis

### DOI: 10.1002/anie.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.<sup>[1]</sup> Such reactions are typically catalyzed by organometallic complexes that contain M=C bonds.<sup>[2]</sup> 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.<sup>[3]</sup>

Synthetic approaches that lead to the isolation of related systems with M=B bonds have been developed only recently:<sup>[4-7]</sup> for example, halide-abstraction chemistry gives access to cationic terminal borylene complexes, [L<sub>n</sub>M= BX]<sup>+.[7]</sup> 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).<sup>[4,6,7]</sup> Thus, the chemistry of [Cp\*Fe(CO)<sub>2</sub>(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.<sup>[7]</sup> In an attempt to tune the reactivity of these highly unsaturated complexes we investigated the synthesis of cationic aminoborylene systems,  $[L_n M=BNR_2]^+$ .<sup>[5]</sup> Chloride abstraction from  $[CpFe(CO)_2[B(NiPr_2)Cl]]$  (2) (Cp = cyclopentadienyl) by Na(BAr<sup>f</sup><sub>4</sub>) (Ar<sup>f</sup> =  $3,5-(CF_3)_2C_6H_3$ ) 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.

The synthesis of  $[CpFe(CO)_2(BNiPr_2)]^+(BAr_4)^-$  (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<sub>2</sub> group results in the formation of a thermally fragile borylene

 [\*] 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, CF103AT (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.



**Scheme 1.** Synthesis and reactions of **3**. a) Na[CpFe(CO)<sub>2</sub>] (1 equiv), toluene, 20 °C, 20 h.; b) Na(BAr<sup>f</sup><sub>4</sub>), (1 equiv), dichloromethane,  $-78 \rightarrow 20$  °C, 30 min.; c) ppnCl (1.67 equiv), dichloromethane, 20 °C, 30 min.; d) Ph<sub>3</sub>P=S or Ph<sub>3</sub>As=O (1 equiv), dichloromethane, 20 °C, 30 min. ppn = bis(triphenylphosphoranylidene)ammonium.

product in the subsequent halide-abstraction step,<sup>[7b,8]</sup> whereas [CpFe(CO)<sub>2</sub>{B(tmp)Cl}] (tmp = tetramethylpiperamino) was inaccessible from tmpBCl<sub>2</sub>. 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<sup>*f*</sup><sub>4</sub>) in dichloromethane results in a quantitative conversion (determined by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy) into **3**. The latter product (along with the C<sub>5</sub>H<sub>4</sub>Me 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 <sup>11</sup>B chemical shift for **3** ( $\delta_B = 93.5$  ppm) is very close to that reported by Braunschweig et al. for neutral terminal-aminoborylene systems of the type L<sub>n</sub>M=BN(SiMe<sub>3</sub>)<sub>2</sub> ( $\delta_B = 86.6$ – 98.3 ppm).<sup>[5]</sup> The downfield shift upon chloride abstraction ( $\Delta \delta_B = 38.1$  between **2** and **3**) mirrors that found for [Cp\*Fe(CO)<sub>2</sub>{B(Mes)Cl}]/[Cp\*Fe(CO)<sub>2</sub>(BMes)]<sup>+</sup> ( $\delta_B = 112.1$ and 145.0 ppm, respectively) and for [Cp\*Fe(CO)<sub>2</sub>-{B(NMe<sub>2</sub>)Cl}]/[Cp\*Fe(CO)<sub>2</sub>(BNMe<sub>2</sub>)]<sup>+</sup> ( $\delta_B = 58.6$  and 88.0 ppm, respectively).<sup>[7,8]</sup> The <sup>1</sup>H and <sup>13</sup>C NMR data are

## Communications

consistent with the presence of Cp, NiPr<sub>2</sub>, and (BAr<sup>f</sup><sub>4</sub>)<sup>-</sup> moieties in a 1:1:1 ratio, and the ES+ mass spectrum shows the presence of the  $[CpFe(CO)_2(BNiPr_2)]^+$  cation. The observation of equivalent iPr substituents is consistent with the structure of the related neutral system  $[CpV(CO)_3 =$  $BN(SiMe_3)_2$ <sup>[5c]</sup> and agrees with the results of DFT calculations for the model compounds  $[(\eta^5-C_5R_5)Fe(CO)_2(BNMe_2)]^+$ (R = H, Me), for which a minimum-energy structure close to  $C_{\rm s}$  symmetry [ < centroid-Fe-N-C  $\approx$  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.<sup>[7b,c]</sup> Furthermore, the IR spectrum of 3 shows carbonyl stretching frequencies  $(\tilde{v} = 2070, 2028 \text{ cm}^{-1})$  that are significantly blue shifted with respect to **2** ( $\tilde{v} = 2001$ , 1941 cm<sup>-1</sup>) ( $\Delta \tilde{v} \approx 50 \text{ cm}^{-1}$  for [Cp\*Fe(CO)<sub>2</sub>{B(Mes)Cl}]/[Cp\*Fe(CO)<sub>2</sub>(BMes)]<sup>+</sup>) 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 cm<sup>-1</sup>).<sup>[9]</sup> 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,<sup>[6b,7]</sup> 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  $[CpFe(CO)_{2}[B(NiPr_{2})(OPPh_{3})]^{+}(BAr_{4}^{f})^{-}$  (see below).

Although the reactivity of cationic aminoborylene complex **3** towards Cl<sup>-</sup> is indicative of electrophilic character, its reactivity towards unsaturated substrates suggests a broader scope for its chemistry. Thus, the reaction of **3** with Ph<sub>3</sub>P=S in dichloromethane at room temperature leads to the formation of  $[iPr_2NB(\mu-S)_2BNiPr_2]$  (**4a**) and  $[CpFe(CO)_2(PPh_3)]^+(BAr_4^{f})^-$  (**5a**) with a conversion of >95% (as determined by <sup>1</sup>H, <sup>11</sup>B and <sup>31</sup>P NMR spectroscopy). The identities of the isolated products **4a** and **5a** were confirmed by comparison of NMR (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P) and IR spectra and mass spectrometry data with those reported for authentic samples.<sup>[10a-c]</sup> The similar reactivity of **3** towards Ph<sub>3</sub>As=O led to the isolation of  $(iPr_2NBO)_3$  (**4b**) and  $[CpFe(CO)_2(AsPh_3)]^+(BAr_4^{f})^-$  (**5b**).<sup>[10c,d]</sup>

The reactions of 3 with Ph<sub>3</sub>P=S and Ph<sub>3</sub>As=O therefore represent, to our knowledge, the first examples of net metathesis reactions for a terminal borylene complex.<sup>[11]</sup> Although metathesis chemistry has been reported for isoelectronic vinylidene systems  $[CpM(CO)_2=C=CH_2]$  (M = Mn, Re),<sup>[12]</sup> no such reactivity has been reported for neutral aminoborylene complexes.<sup>[5,6]</sup> 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<sub>3</sub>P=O. This reaction proceeds at a significantly slower rate than those of Ph<sub>3</sub>P=S or Ph<sub>3</sub>As=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  $\delta_{\rm B} = 48.9$  ppm and  $\delta_{\rm P} = 48.3$  ppm. The former resonance is consistent with values previously reported for base-stabilized terminal borylene complexes (e.g.  $\delta_{\rm B} = 51.7 - 53.2$  ppm for N-donor adducts of osmium aminoborylenes),<sup>[4b,c]</sup> whereas the <sup>31</sup>P chemical shift is as expected for donor/acceptor adducts of Ph<sub>3</sub>PO with boroncentered Lewis acids ( $\delta_{\rm P} = 43.6 - 46.7$  ppm).<sup>[13]</sup> Furthermore, the observations of inequivalent *i*Pr groups by <sup>1</sup>H and <sup>13</sup>C NMR and of significantly lower carbonyl stretching frequencies ( $\tilde{\nu} = 2004$ , 1949 cm<sup>-1</sup>) 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<sub>3</sub>PO adduct [CpFe(CO)<sub>2</sub>{B(N*i*Pr<sub>2</sub>)-(OPPh<sub>3</sub>)}]+(BAr<sup>f</sup><sub>4</sub>)<sup>-</sup>(**6**) was obtained by X-ray crystallographic analysis (Figure 2). Consistent with related complex-



**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).

es,<sup>[4b,c,14]</sup> 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).<sup>[7]</sup> Such a phenomenon has previously been ascribed to significant contributions from resonance forms that incorporate a formal M–B bond (Scheme 2),<sup>[4b,c]</sup> 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<sub>3</sub>PO (1.540(2) vs. 1.493 Å (mean)).<sup>[15]</sup>

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.<sup>[17]</sup>

### **Experimental Section**

2: Reaction of 1 (1.199 g, 6.6 mmol) with Na[CpFe(CO)<sub>2</sub>] (1.318 g, 6.6 mmol) in toluene (40 cm<sup>3</sup>) at room temperature for 20 h, followed by filtration, removal of volatile compounds in vacuo, and extraction with hexanes ( $\approx 40 \text{ cm}^3$ ) 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%. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta =$ 1.11 (d, J = 6.7 Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub> of *i*Pr), 1.39 (d, J = 6.7 Hz, 6H;  $CH(CH_3)_2$ , 3.40 (sept, J = 6.7 Hz, 1H;  $CH(CH_3)_2$ ), 4.44 (sept, J =6.7 Hz, 1 H; CH(CH<sub>3</sub>)<sub>2</sub>), 4.69 ppm (s, 5 H; Cp-H); <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ ):  $\delta = 21.2 (CH(CH_3)_2), 23.9 (CH(CH_3)_2), 47.8 (CH(CH_3)_2), 55.2$ (CH(CH<sub>3</sub>)<sub>2</sub>), 88.2 (Cp), 215.6 ppm (CO); <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 55.4 \text{ ppm. IR } (C_6 D_6 \text{ soln}); \tilde{\nu} = 2001, 1941 \text{ cm}^{-1} \nu \text{CO}; \text{MS (EI)}; m/z$ (%): 295 (65) [M-CO]<sup>+</sup>, 288 (weak) [M-Cl], 267 (10) [M-2CO]<sup>+</sup>, 223 (100)  $[M-NiPr_2]^+$ ,  $M^+$  not observed; MS: calcd for  $[M-CO]^+$ : 295.0592; found: 295.0595; calcd for [M-Cl]+: 288.0853; found 288.0856. Crystal data:  $C_{13}H_{19}BClFeNO_2$ , orthorhombic, *Pbca*, a =11.7410(4), b = 13.9170(4), c = 19.0830(7) Å, V = 3118.15(18) Å<sup>3</sup>, Z =8,  $\rho_{\text{calcd}} = 1.378 \text{ Mg m}^{-3}$ ,  $M_{\text{r}} = 323.40$ , T = 150(2) K. 22231 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/  $-0.537 \text{ e} \text{ Å}^{-3}$ .[16]

**3**: Reaction of **2** (0.259 g, 0.80 mmol) and Na(BAr $_{4}^{f}$ ) (0.710 g, 0.80 mmol) in dichloromethane (15 cm<sup>3</sup>) from  $-78 \rightarrow 20$  °C over 30 min leads to a quantitative conversion (determined by <sup>11</sup>B NMR) of 2 ( $\delta_{\rm B}$  = 55.4 ppm) to 3 ( $\delta_{\rm B}$  = 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 %. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.39$  (d, J = 6.6 Hz, 12 H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.32 (sept, J = 6.6 Hz, 2H; CH(CH<sub>3</sub>)<sub>2</sub>), 5.33 (s, 5H, Cp-H), 7.55 (s, 4H;  $BAr_{4}^{f}-H_{p}$ ), 7.70 ppm (s, 8H;  $BAr_{4}^{f}-H_{o}$ ); <sup>13</sup>C NMR (76 MHz,  $CD_2Cl_2$ ):  $\delta = 24.4$  (CH(CH\_3)<sub>2</sub>), 51.0 (CH(CH\_3)<sub>2</sub>), 87.1 (C(Cp)), 117.6 (BAr<sub>4</sub><sup>-</sup>-CH<sub>p</sub>), 124.6 (q, <sup>1</sup>J<sub>CF</sub> = 272 Hz, BAr<sub>4</sub><sup>-</sup>-CF<sub>3</sub>), 128.8 (q,  ${}^{2}J_{CF} = 34 \text{ Hz}, \text{ BAr}_{4}^{f} - \text{CH}_{m}), 134.8 \text{ (BAr}_{4}^{f} - \text{CH}_{o}), 161.8 \text{ (q, } {}^{1}J_{CB} =$ 49 Hz, BAr<sup>f</sup><sub>4</sub>-C<sub>ipso</sub>), 205.6 ppm (CO); <sup>11</sup>B NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -7.7$  (BAr<sup>f</sup><sub>4</sub>), 93.5 ppm (b, fwhm  $\approx 615$  Hz, BN*i*Pr<sub>2</sub>); <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -62.6$  ppm (CF<sub>3</sub>); IR (CD<sub>2</sub>Cl<sub>2</sub> soln):  $\tilde{\nu} =$ 2070, 2028 cm<sup>-1</sup>  $\nu$ CO; MS (ES): m/z (%):  $M^+$  288.1 (10).

Typical reaction: **3** (0.068 g, 0.06 mmol) and Ph<sub>3</sub>P=S (1.0 equiv) were stirred together in dichloromethane for 30 min, after which the reaction was judged to be complete by <sup>11</sup>B and <sup>31</sup>P NMR (conversion of signals at  $\delta_B = 93.5$  ppm and  $\delta_P = 43.7$  ppm to  $\delta_B = 35.6$  ppm and  $\delta_P = 60.8$  ppm, respectively). Removal of volatile components in vacuo and extraction into hexanes gave  $iPr_2NB(\mu$ -S)<sub>2</sub>BN*i*Pr<sub>2</sub> (**4a**), which was identified by comparison of <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopic and mass spectrometry data with those reported previously.<sup>[10a,b]</sup> <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>19</sup>F, and <sup>31</sup>P NMR and IR spectra of the hexane-insoluble product confirmed it to be [CpFe(CO)<sub>2</sub>(PPh<sub>3</sub>)]<sup>+</sup>(BAr<sup>f</sup><sub>4</sub>)<sup>-</sup> (**5a**).<sup>[10c,d]</sup>

**6**: Reaction of **3** (0.199 g, 0.17 mmol) and Ph<sub>3</sub>PO (0.048 g, 0.17 mmol) in dichloromethane (5 cm<sup>3</sup>) 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

vellow crystals. Yield of isolated product: 0.105 g, 43%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.06$  (d, J = 6 Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, J = 6 Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.25 (sept, J = 6 Hz, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 4.10 (sept, J=6 Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 4.50 (s, 5H; Cp-H), 7.38–7.48 (m, 9H; Ph<sub>3</sub>PO-CH<sub>o</sub> and Ph<sub>3</sub>PO-CH<sub>p</sub>), 7.55 (s, 4H; BAr<sup>f</sup><sub>4</sub><sup>-</sup>-H<sub>p</sub>), 7.60–7.78 (m, 6H; Ph<sub>3</sub>PO-H<sub>m</sub>), 7.73 ppm (s, 8H; BAr<sup>f</sup><sub>4</sub>--H<sub>o</sub>); <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ ):  $\delta = 22.4$ , 23.9 (CH(CH\_3)<sub>2</sub>), 47.2 (CH(CH\_3)<sub>2</sub>), 84.4 (C(Cp)), 117.5 (BAr<sup>f</sup><sub>4</sub> --CH<sub>p</sub>), 122.6 (Ph<sub>3</sub>PO-C<sub>*ipso*</sub>), 124.6 (q,  ${}^{1}J_{CF} = 272$  Hz;  $BAr_{4}^{f}$ -CF<sub>3</sub>), 128.9 (q,  ${}^{2}J_{CF}$  = 34 Hz;  $BAr_{4}^{f}$ -C<sub>m</sub>), 130.1 (Ph<sub>3</sub>PO-CH<sub>m</sub>), 133.5 (Ph<sub>3</sub>PO-C<sub>o</sub>), 134.9 (BAr<sup>f</sup><sub>4</sub><sup>-</sup>-CH<sub>o</sub>), 135.9 (Ph<sub>3</sub>PO-C<sub>p</sub>), 161.8 (q,  ${}^{1}J_{CB} = 49 \text{ Hz}; \text{ BAr}_{4}^{f} - C_{ioso}), 214.7 \text{ ppm} (CO); {}^{11}B \text{ NMR} (96 \text{ MHz},$ CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -7.7$  (BAr<sup>f</sup><sub>4</sub>), 48.9 ppm (b, fwhm  $\approx$  480 Hz, B- $(OPPh_3)NiPr_2$ ; <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -62.7$  ppm (CF<sub>3</sub>); <sup>31</sup>P NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 48.3$  ppm (Ph<sub>3</sub>PO); IR (CD<sub>2</sub>Cl<sub>2</sub>) soln):  $\tilde{\nu} = 2004$ , 1949 cm<sup>-1</sup>  $\nu$ (CO). Crystal data: C<sub>63</sub>H<sub>46</sub>B<sub>2</sub>F<sub>24</sub>FeNO<sub>3</sub>P, triclinic,  $P\bar{1}$ , a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), b = 13.9949(2), c = 19.1002(3) Å, a = 13.0324(2), a = 13.0324(68.7080(10),  $\beta = 83.7430(10)$ ,  $\gamma = 87.4800(10)^{\circ}$ ,  $V = 3226.47(8) \text{ Å}^3$ ,  $Z = 2, \rho_{\text{calcd}} = 1.471 \text{ Mg m}^{-3}, M_{\text{r}} = 1429.45, T = 150(2) \text{ K}. 51247 \text{ reflec-}$ tions collected, 14704 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/  $-0.608 \text{ e} \text{ Å}^{-3}$ .<sup>[16]</sup>

Received: July 5, 2005 Published online: October 17, 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, 11236– 11243.
- [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.

# Communications

- [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).



<sup>© 2005</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim