

Generation of Cationic Two-Coordinate Group-13 Ligand Systems by Spontaneous Halide Ejection: Remarkably Nucleophile-Resistant (Dimethylamino)borylene Complexes

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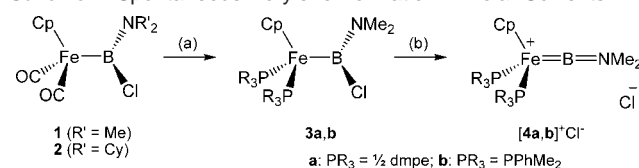
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The chemistry of compounds containing metal–boron double bonds (e.g., borylene complexes, $L_nM=B(X)$), although a relatively new field, has evolved from the stage where such systems might have been regarded merely as structural novelties to one in which their reactivity can now be exploited synthetically, in some cases in catalytic systems.¹ In part, this reflects the development of a wider range of synthetic methodologies, allowing for increased diversity (in terms of the range of compounds available) and hence for a systematic appraisal of both electronic structure and reactivity. Recent reports from the Braunschweig group implicating group-6 metal borylene complexes in the controlled functionalization of organic substrates and the catalysis of C–C bond-forming reactions² and those from Sabo-Etienne and co-workers describing the direct synthesis of a borylene complex from the corresponding borane³ hint at broader exploitation of the chemistry of this class of compounds.

Within this sphere, cationic borylene complexes, $[L_nM(BX)]^+$,^{4,5} have been implicated in the functionalization of organic substrates via a number of routes but suffer from (i) a lack of tolerance to nucleophilic or protic reagents^{4b,5d} and (ii) the inconvenience of the two-step (metathesis/halide abstraction) synthetic procedure necessitated from dihaloboranes.¹ Bearing in mind the dramatic changes in electronic structure (and enhancements in stability) brought about in related carbene and silylene systems by replacing ancillary carbonyl ligands with less π -acidic phosphines [cf. the relative stabilities of $[CpFe(CO)_2(CH_2)]^+$ and $[CpFe(dppe)(CH_2)]^+$],^{6,7} we chose to investigate the synthesis of borylene complexes of the type $[(\eta^5-C_5R_5)M(PR_3)_2(BNR_2)]^+$. As a result of this work, we report here not only the synthesis of a much more nucleophile-tolerant system but also—most surprisingly—an unprecedented boryl/borylene interconversion via spontaneous halide ejection.^{7,8} Further evidence for the remarkable electronic structure of this system includes the lack of need for steric bulk at R, in contrast to all other isolated terminal aminoborylene complexes $L_nM(BNR_2)$,¹ and (despite this minimal steric shielding) marked resistance to the coordination of strong σ donors such as pyridine at the two-coordinate boron center. $[CpFe(dmpe)(BNMe_2)]^+$ represents the first terminal borylene complex containing a simple dimethylamino substituent.

Key features associated with the syntheses of phosphine-ligated borylene complexes are outlined in Scheme 1. Introduction of the phosphine coligands is most conveniently carried out via photolytic carbonyl substitution utilizing previously reported boryl complex precursors (e.g., conversion of **1** to **3a** or **3b**).^{5c,9,10}

Scheme 1. Spontaneous Borylene Formation in Polar Solvents^a



^a Key reagents/conditions: (a) PR₃, toluene, broad-band UV irradiation, 6 h, R = Me; (b) dissolution in polar solvent (dichloromethane, chloroform), 38% isolated yield.

The success of this approach is crucially dependent on the choice of ancillary amino substituents. Thus, for (sterically bulky) NCy₂-substituted complex **2**, reaction with dmpe gives a bridged dinuclear boryl complex,^{5f} while that with excess PMe₃ gives $[CpFe(CO)(PMe_3)_2]^+Cl^-$ via borylene extrusion [see the Supporting Information (SI)]. Use of the much less bulky NMe₂ precursor **1**, however, circumvents this problem, and the corresponding dmpe-ligated species $CpFe(dmpe)_2\{B(NMe_2)Cl\}$ (**3a**) can be synthesized by photolysis in toluene solution. NMR data for this solution are consistent with the conversion of **1** to **3a** via the intermediate $CpFe(CO)(dmpe)_2\{B(NMe_2)Cl\}$. Thus, successive ¹¹B NMR resonances are observed at $\delta_B = 57, 62,$ and 66 ppm, consistent with stepwise replacement of the two carbonyl ligands by phosphine donors [cf. $\delta_B = 52, 58,$ and 60 ppm reported by Hartwig for $CpFe(CO)_2Bcat$, $CpFe(CO)(PMe_3)Bcat$, and $CpFe(PMe_3)_2Bcat$, respectively].¹¹ The ³¹P NMR data are also consistent with the initial formation of a κ^1 -dmpe ligand ($\delta_P = 53$ and -45 ppm) prior to the adoption of a chelating mode of coordination in **3a** ($\delta_P = 75$ ppm).¹²

Attempts to recrystallize **3a** by removal of volatiles in vacuo and extraction of the residue into hexanes, however, revealed no hydrocarbon-soluble Fe/B-containing species (by ¹¹B NMR spectroscopy). Subsequent extraction into a polar solvent such as dichloromethane or chloroform revealed the presence of a single ¹¹B- and ³¹P-containing species giving rise to signals at $\delta_B = 88$ ppm and $\delta_P = 79$ ppm (cf. $\delta_B = 66$ and $\delta_P = 75$ ppm for **3a**). The ¹¹B chemical shift in these polar solvents is consistent with the presence of a terminal aminoborylene complex,¹ and further evidence for the formation of $[CpFe(dmpe)_2(BNMe_2)]^+Cl^-$ (i.e., **[4a]**⁺Cl⁻) comes from (i) in situ positive-ion electrospray ionization mass spectrometry (ESI-MS; Figure 1), which revealed the presence of the $[CpFe(dmpe)_2(BNMe_2)]^+$ cation, with an isotopic profile and accurate mass measurement in agreement with the calculated values; (ii) the presence in the ¹H NMR spectrum (in CD₂Cl₂) of a single NMe₂ methyl resonance [cf. the inequivalent alkyl groups found for aminoboryl complexes of the type $CpFe(L)_2\{B(NR_2)Cl\}$ in the same temperature regime;^{5a,c,9} and (iii) the essentially identical ¹H, ¹¹B, ¹³C, and ³¹P NMR spectra in CD₂Cl₂ (leaving aside the anion resonances) obtained for the crystallo-

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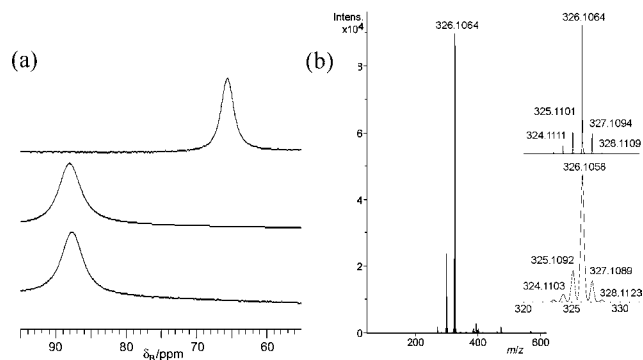


Figure 1. Spectroscopic data characterizing the autoionization of **3a** to $[4a]^+Cl^-$ in dichloromethane. (a) $^{11}B\{^1H\}$ NMR spectra in toluene (top) and dichloromethane (middle), plus the spectrum of $[4a]^+[BPh_4]^-$ in dichloromethane (bottom) for comparison. (b) Positive-ion ESI-MS data for a solution in dichloromethane. The inset shows the match of the isotopic envelope to $[CpFe(dmpe)(BNMe_2)]^+$ ($[4a]^+$).

graphically characterized $[BPh_4]^-$ and $[B(C_6H_3Cl_2-3,5)_4]^-$ salts $[4a]^+[BPh_4]^-$ and $[4a]^+[B(C_6H_3Cl_2-3,5)_4]^-$ (see below).¹³ Moreover, the implied solvent dependence of the relative stabilities of the isomeric species **3a** and $[4a]^+Cl^-$ was probed by density functional theory (DFT) methods, which revealed that ΔG is indeed strongly dependent on the dielectric constant of the medium employed (see Figure 2 and the SI). Thus, $\Delta G_{3a \rightarrow 4a} = +13.2 \text{ kcal mol}^{-1}$ in the gas phase and $+3.2 \text{ kcal mol}^{-1}$ in toluene ($\epsilon = 2.4$) but $-7.3 \text{ kcal mol}^{-1}$ in dichloromethane ($\epsilon = 9.1$), consistent with the stabilization of the solvent-separated cation/anion pair $[4a]^+Cl^-$ in the more polar medium. The role of the ancillary ligand set is also crucial, with the corresponding autoionization reaction for dicarbonyl-ligated **1** calculated to be strongly disfavored even in dichloromethane solution ($\Delta G = +22.5 \text{ kcal mol}^{-1}$), a finding consistent with experimental observations for complexes **1** and **2**. As such, the spectroscopic and computational data are consistent with the spontaneous ejection of chloride from **3a** in polar media to generate the cationic borylene complex $[4a]^+$ as the chloride salt. Similar chemistry was found for the related bis(monophosphine) systems **3b**/**4b** $^+Cl^-$ (Scheme 1). Synthetically, these transformations are without precedent in boron ligand chemistry, and they are remarkable in representing spontaneous loss of an anionic ligand from an electrophilic three-coordinate boron center.^{7,8}

While attempts to obtain single crystals of $[4a]^+Cl^-$ proved unsuccessful, salt metathesis with $Na^+[BPh_4]^-$ or $Na^+[B(C_6H_3Cl_2-3,5)_4]^-$ in fluorobenzene gave ready access to the corresponding salts $[4a]^+[BPh_4]^-$ and $[4a]^+[B(C_6H_3Cl_2-3,5)_4]^-$, both of which were structurally characterized (Figure 3 and the SI).¹⁴ The geometries of the cations are very similar in these two cases, featuring a two-coordinate boron center with no short intermolecular contacts $\{\angle Fe-B-N = 175.4(2)^\circ$ for $[4a]^+[BPh_4]^-$ and $175.2(3)$ and $176.0(3)^\circ$ for the two crystallographically distinct cations in $[4a]^+[B(C_6H_3Cl_2-3,5)_4]^-$. Moreover, consistent with the more electron-rich nature of the iron center in $[CpFe(dmpe)(BNMe_2)]^+$, the Fe–B bond lengths [1.811(3) Å and 1.807(4) and 1.801(4) Å, respectively] are significantly shorter than those found in related dicarbonyl-ligated species [e.g., 1.859(6) Å for $[CpFe(CO)_2-(BNCy_2)]^+$].^{5c} Comparison with other terminal borylene complexes reveals that the M–B distances measured for these two salts of $[4a]^+$ are among the shortest yet reported, being comparable to those measured for aryl- and alkylborylene systems [cf. 1.785(8) and 1.792(8) Å for $[Cp^*Fe(CO)_2(BMes)]^+$, 1.780(4) Å for $(C_3P)_2-Ru(Cl)H(BMes)$, and 1.809(9) Å for $CpMn(CO)_2(BtBu)$].^{3,4,15} Indeed, the values determined for $[4a]^+$ are the shortest yet measured for any aminoborylene system, reflecting a high degree

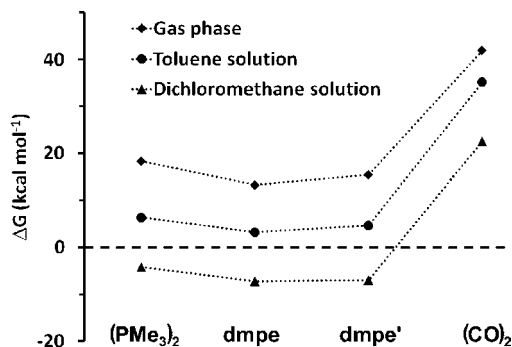


Figure 2. DFT-calculated free-energy changes for the autoionization reaction $CpFe(L)_2B(NMe_2)Cl \rightarrow [CpFe(L)_2B(NMe_2)]^+Cl^-$ as a function of reaction medium and ancillary ligand framework ($L)_2$ ($dmpe' = Me_2PCHCHPMe_2$).

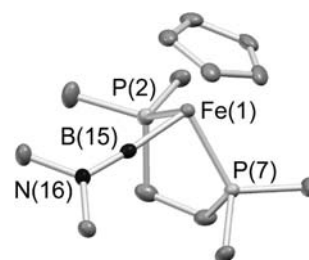


Figure 3. Molecular structure of the cationic component of $[4a]^+[BPh_4]^-$. Key bond lengths (Å) and angles (deg): Fe(1)–B(15), 1.811(3); B(15)–N(16), 1.357(3); Fe(1)–P(2), 2.157(1); Fe(1)–P(7), 2.177(1); Fe(1)–B(15)–N(16), 175.4(2).

of electronic loading at the metal center and an enhanced degree of $Fe \rightarrow B \pi$ back-bonding. Consistent with this, the DFT-calculated σ/π ratios for the Fe–B covalent bonding density in the model systems $[CpFe(PMe_3)_n(CO)_{2-n}(BNMe_2)]^+$ are 63:37, 67:33, and 71:29 for $n = 2, 1$, and 0, respectively.¹⁶

Initial studies of the reactivity of $[4a]^+Cl^-$ gave results consistent with dramatically reduced electrophilicity. Thus, in addition to resistance to nucleophilic attack by halide ions, $[4a]^+$ does not interact significantly with neutral oxygen donor Lewis bases such as thf, even when used as a solvent. This behavior contrasts with that of $[Cp^*Fe(CO)_2(BMes)]^+$ (which decomposes) and $[CpFe(CO)_2(BNCy_2)]^+$ (which binds thf reversibly) and allows the targeting of chemistry involving ether-containing solvents and/or substrates. Remarkably, on the basis of in situ NMR experiments, $[4a]^+Cl^-$ also does not appear to interact with stoichiometric pyridine, (cf. irreversible binding to give $[CpFe(CO)_2(BNCy_2 \cdot (4-pic))]^+$).^{5c} Dissolution in 6 M pyridine/dichloromethane does lead to the formation of the B-bound adduct $[4a \cdot py]^+$, albeit reversibly, and a van't Hoff analysis of the equilibrium constant data obtained over the temperature range 233–273 K (from 1H NMR measurements) yielded the thermodynamic parameters $\Delta H = -7.4 \text{ kcal mol}^{-1}$ and $\Delta S = -31.3 \text{ eu}$ for pyridine binding (Figure 4). This enthalpy change can be put into context by the significantly more exothermic data (-40.7 and $-45.6 \text{ kcal mol}^{-1}$) determined for the formation of $py \cdot BX_3$ ($X = Cl, Br$, respectively), despite the fact that $[4a]^+$ is cationic and features a two-coordinate boron center.¹⁷

With regard to protic reagents, $[4a]^+$ is unreactive toward the strong acid $[H(OEt)_2]^+[BAR^F_4]^-$ (Brookhart's acid), and the Fe–B linkage even survives intact upon exposure to water. That said, the greater functional group tolerance of $[4a]^+$ does not appear to impair its ability to act as a borylene transfer agent toward organic functional groups, as a rapid $[4 + 1]$ cycloaddition reaction with the model substrate 3,5-di-*tert*-butylbenzoquinone akin to that found

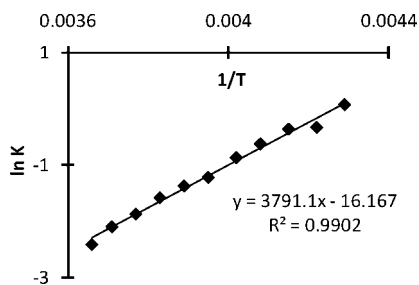


Figure 4. van't Hoff plot describing the temperature dependence of the equilibrium between $[4a]^+$ and $[4a \cdot py]^+$. The values of ΔH and ΔS quoted in the text are the means of three independent experiments.

with $[CpFe(CO)_2(BNCy_2)]^+$ was observed.^{5c} Further studies designed to exploit the borylene transfer activity and chemical robustness of $[4a]^+$ and related *chiral* bis(phosphine) systems will be reported in due course.

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Supporting Information Available: Spectroscopic data for $[4a]^+[BPh_4]^-$; spectroscopic data and crystallographic data (CIF) for $[4a]^+[B(C_6H_5Cl_2-3,5)_4]^-$; complete details of the NMR simulations for $[4a]^+Cl^-$ and the DFT calculations on **3a**, $[4a]^+Cl^-$, and related systems; and details of the crystal structure of $[CpFe(CO)(PMe_3)_2]^+Cl^-$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Syntheses of $CpFe(dmpe)\{B(NMe_2)Cl\}$ (**3a**) and $[CpFe(dmpe)(BNMe_2)]^+Cl^-$ ($[4a]^+Cl^-$): A toluene solution of $CpFe(CO)_2\{B(NMe_2)Cl\}$ (0.20 g, 0.78 mmol) and dmpe (>2 equiv) in a quartz reaction vessel was irradiated for 6 h. Periodic monitoring by ^{11}B and ^{31}P NMR spectroscopy revealed sequential formation of an intermediate postulated as $CpFe(CO)(dmpe)\{B(NMe_2)Cl\}$ ($\delta_B = 62$ ppm, $\delta_P = 53$ and -45 ppm) followed by $CpFe(dmpe)\{B(NMe_2)Cl\}$ (**3a**; $\delta_B = 66$ ppm, $\delta_P = 75$ ppm). Attempts to isolate **3a** by removal of the toluene solvent in vacuo and extraction into pentane resulted instead in the formation of $[CpFe(dmpe)(BNMe_2)]^+Cl^-$ ($[4a]^+Cl^-$). After the residue was washed with pentane and recrystallized from dichloromethane/hexanes, $[4a]^+Cl^-$ was obtained as a microcrystalline material. Isolated yield: 0.30 mmol (38%). 1H NMR (300 MHz, CD_2Cl_2) δ_H (ppm): 1.55 (m, $^2J_{P-H} = 11.0$ Hz, $^3J_{P-H} = 1.1$ Hz, 6H, PME), 1.61 (m, $^2J_{P-H} = 11.3$ Hz, $^3J_{P-H} = 0.7$ Hz, 6H, PME), 1.77 (m, $^2J_{HA-HB} = 14.4$ Hz, $^3J_{HB-HB'} = 7.6$ Hz, 2H, PCH₂), 1.97 (m, $^3J_{HA-HA'} = 9.0$ Hz, $^3J_{HB-HB'} = 7.4$ Hz, 2H, PCH₂), 2.69 (s, 6H, NMe₂), 4.61 (t, $^4J_{P-H} = 1.3$ Hz, 5H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C (ppm): 20.3 (m, $^1J_{P-C} = 25.4$ Hz, $^4J_{P-C} = 4.4$ Hz, PME), 24.7 (m, $^1J_{P-C} = 38.4$ Hz, $^4J_{P-C} = 0.6$ Hz, PME), 29.7 (m, $^1J_{P-C} = 36.7$ Hz, $^2J_{P-C} = 10.6$ Hz, PCH₂), 33.1 (NMe₂), 78.9 (Cp). ^{11}B NMR (96 MHz, CD_2Cl_2) δ_B (ppm): 88 (br, fwhm ~ 340 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ_P (ppm): 79 (m, $^2J_{P-P} = 38.3$ Hz). ESI-MS+ m/z (%): 326.1049 (100) M^+ (exact mass calcd for M^+ , 326.1049; found, 326.1058). Coupling constants were obtained for the second-order dmpe resonances in both the 1H and ^{13}C NMR spectra using gNMR (see the Supporting Information for measured and simulated spectra). The subsequent syntheses of $[4a]^+[BPh_4]^-$ and $[4a]^+[B(C_6H_5Cl_2-3,5)_4]^-$ were carried out in quantitative yield via the reactions of $[4a]^+Cl^-$ with the sodium salts of the corresponding anions in fluorobenzene over 20 min at 20 °C. Single crystals of $[4a]^+[BPh_4]^-$ and $[4a]^+[B(C_6H_5Cl_2-3,5)_4]^-$ were obtained from fluorobenzene/hexanes layering at 20 °C. Data for $[4b]^+Cl^-$: 1H NMR (300 MHz, CD_2Cl_2) δ_H (ppm): 1.44 (overlapping m, 12H, PME), 2.90 (s, 6H, NMe₂), 4.57 (br s, 5H, Cp), 7.00–7.62 (overlapping m, 10H, Ph of PPhMe₂). ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C (ppm): 24.5 (m, PME), 25.3 (m, PME), 37.0 (NMe₂), 83.4 (Cp), 129.6 (m, *o*-CH of Ph), 130.3 (m, *m*-CH of Ph), 130.5 (s, *p*-CH of Ph), 140.6 (m, *ipso*-C of Ph). ^{11}B NMR (96 MHz, CD_2Cl_2) δ_B (ppm): 92 (v br, fwhm ~ 800 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ_P (ppm): 42. ESI-MS+ m/z (%): 452.1 (100) M^+ (exact mass calcd for M^+ , 452.1530; found, 452.1541).
- (14) Crystallographic data for $[4a]^+[BPh_4]^-$: $C_{37}H_{47}B_2FeNP_2$, *M*, 645.20; monoclinic; $P2_1/c$; $a = 16.3137(2)$ Å, $b = 11.8160(1)$ Å, $c = 19.2319(2)$ Å, $\beta = 109.689(1)^\circ$; $V = 3490.5(1)$ Å³; $Z = 4$; $\rho_c = 1.228$ Mg m⁻³; $T = 150$ K; $\lambda = 0.71073$ Å; 39887 reflns collected, 7918 independent reflns ($R_{int} = 0.049$), which were used in all calculations; $R_1 = 0.0429$, $wR_2 = 0.0968$ for observed unique reflns [$I > 2\sigma(I)$]; $R_1 = 0.0660$, $wR_2 = 0.1068$ for all unique reflns; max/min residual electron densities 0.59/−0.47 e Å⁻³; CSD reference 758957.
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