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Cationic Terminal Aminoborylene Complexes: Controlled Stepwise Insertion into M=B and B=N Double Bonds**

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Insertion reactions of unsaturated molecules represent one of the key fundamental reaction types in organometallic chemistry, with relevance to a number of important catalytic processes (for example, alkene polymerization and hydroformylation).[1–3] Typically, such reactions occur by initial coordination of the substrate and subsequent migration of one of the metal-bound ligands (R) with accompanying formation of metal–substrate and substrate–R single bonds.[1] Thus, numerous examples exist of insertion into M−C single bonds, and the insertion of alkynes into Fischer carbene M=C linkages has also been widely reported.[4] In a similar fashion, the insertion of molecules containing C=E or C≡E functions into M−B single bonds represents a key bond-forming step in metal-catalyzed diboration chemistry.[5]

The recent development of viable synthetic approaches to transition-metal complexes containing metal–boron double bonds (for example, terminal borylene complexes [$L_nM=BX$]) has stimulated research activity aimed at mapping the fundamental modes of reactivity of such systems.[6] In part, such work reflects a desire to compare behavior with related multiply bonded ligands (for example, carbenes and silylenes) for which patterns of reactivity are not only well-known, but also widely exploited in useful chemical transformations.[7] Thus, in addition to simple substitution or addition processes dominated by the electrophilic character of the two-coordinate boron center,[8] both thermal and photolytic borylene transfer processes have been demonstrated towards transition-metal substrates.[9] Furthermore, a number of fundamental modes of reactivity with respect to unsaturated organic molecules have been demonstrated, including cycloaddition,[10] metathesis,[11] and reduction processes.[12] Herein we detail the reactivity of the cationic terminal aminoborylene complexes $[CpFe(CO)_2(BNR)_2]^+[BAr^F_4]^-$, (**1a**: R = *i*Pr; **1b**: R = Cy; Cp = C_5H_5; Ar^F = 3,5-$(CF_3)_2C_6H_3$) towards carbodiimide substrates, which proceeds by the first reported examples of insertion into a M=B double bond.

The reactions of borylene complex **1a** or **1b** with two or more equivalents of dicyclohexylcarbodiimide proceed to completion over a period of 4 h, leading to the generation in each case of a single boron-containing species, for which ^{11}B NMR data implies a highly symmetrical four-coordinate boron environment featuring no metal–boron bonds. A combination of multinuclear (^1H, ^{13}C, ^{11}B, ^{19}F) NMR and IR spectroscopies, mass spectrometry, and single-crystal X-ray diffraction data is consistent with the products of these two reactions being formulated as $[CpFe(CO)_2C(NCy)_2B(NCy)_2CNR_2]^+[BAr^F_4]^-$, (**2a**: R = *i*Pr; **2b**: R = Cy), in which two molecules of carbodiimide have been assimilated by the parent borylene by insertion into both the Fe=B and B=N double bonds (Scheme 1). The solid-state structures of **2a** (Figure 1) and **2b** (see the Supporting Information) revealed by single-crystal X-ray diffraction studies confirm the boronium cation centered spirocyclic structures implied by these insertion steps,[13,14] and contain both four-membered guanidinate and metalla-amidinate rings.

The geometries of the {$R_2NC(NCy)_2B$} fragments in **2a**,**b** are very similar to that of the only other reported boron guanidinate system, $Me_2NC(NPh)_2B(CF_3)_2$, with the caveat that the bulkier NR_2 groups (R = *i*Pr, Cy) on the ligand backbone (compare Me_2N) enforce a non-coplanar alignment of the R_2N and BN_2C planes (torsion angles 52.0 and 37.2° for **2a** and **2b**, respectively), thus resulting in minimal π overlap and significantly longer C−N bonds (for example, 1.366(2) and 1.315(3) Å for **2a** and $Me_2NC(NPh)_2B(CF_3)_2$, respectively).[15–17] The {$CpFe(CO)_2C(NCy)_2B$} moiety represents a rare example of a metalla-amidinate unit; the only other reported example, $[CpMo(CO)_3C(NCy)_2Mo(CO)_2Cp]$, is described as containing a Mo−C single bond between the {$CpMo(CO)_3$} fragment and the amidinate carbon atom.[18] However, in the case of **2a** and related systems (see below) the metal–carbon distance (1.948(2) Å for **2a**) is relatively short for a single bond between {$CpFe(CO)_2$} and sp^2-hybridized C units.[19]

To explore the likely mechanism for the formation of **2a**/**2b** from **1a**/**1b**, a series of experiments were carried out employing either 1) variable-temperature NMR monitoring of the reaction mixture or 2) substoichiometric quantities of

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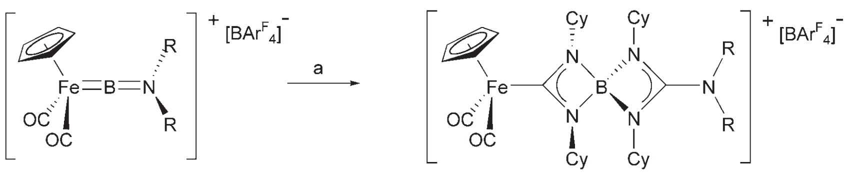


1a: R = *i*Pr
1b: R = Cy

2a: R = *i*Pr
2b: R = Cy

Scheme 1. Insertion of dicyclohexylcarbodiimide into the M=B and B=N double bonds of cationic terminal aminoborylene complexes **1a** and **1b**. Reaction conditions: a) CyN=C=NCy (2.0 equiv), dichloromethane, 4 h at 20 °C, 37–65 %.

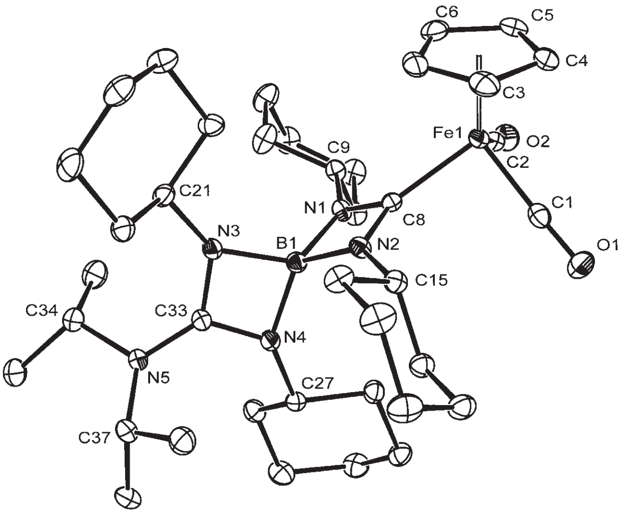
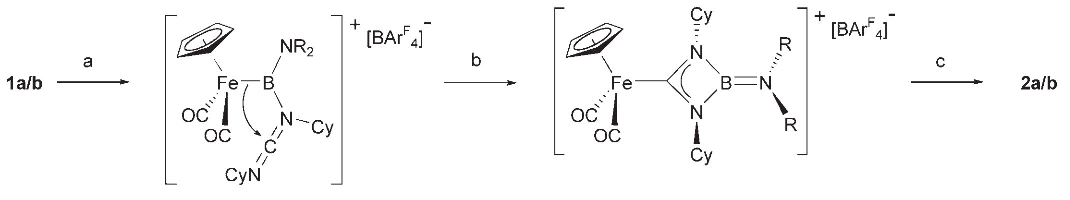


Figure 1. Structure of the cationic component of **2a**; hydrogen atoms are omitted for clarity and ORTEP ellipsoids are set at the 50% probability level. Relevant bond lengths [Å] and angles [°]: Fe1-C8 1.948(2), C8-N1 1.354(2), C8-N2 1.356(2), B1-N1 1.550(2), B1-N2 1.552(2), B1-N3 1.564(2), B1-N4 1.560(2), N3-C33 1.350(2), N4-C33 1.344(2), N5-C33 1.366(2); N1-C8-N2 98.8(1), N1-B1-N2 83.1(1), N3-B1-N4 83.2(1), N3-C33-N4 100.8(1).

dicyclohexylcarbodiimide (< 2 equiv), with the aim of probing the nature of any intermediate species. Monitoring of the reaction of **2a** with two equivalents of carbodiimide by ^{1}H and ^{11}B NMR in the temperature range −80 to 20 °C revealed the presence of two intermediate species formed sequentially at −50 °C and −30 °C, each of which gives rise to a single ^{11}B NMR resonance ($\delta_B = 71$ and 25 ppm, respectively). The first-formed (and extremely labile) intermediate is proposed to be the boron-bound carbodiimide adduct [CpFe(CO)$_2$B(N*i*Pr$_2$)(CyNCNCy)]$^+$[BAr$^F{}_4$]$^-$ (**3a**; Scheme 2) on the basis of 1) an upfield shift in the ^{11}B NMR resonance and a splitting of the ^{1}H NMR *i*Pr signals, consistent with previous studies of reactions of **2a**/**2b** towards compounds containing a C=NR functionality, which proceed by formation of N→B adducts with trigonal geometry at the boron atom (compare $\delta_B = 64.0$ and 53.9 ppm for the imine adducts [CpFe(CO)$_2$B(X)(*i*PrN=CMe$_2$)]$^+$[BAr$^F{}_4$]$^-$ (X = OC(H)Ph$_2$ and N*i*Pr$_2$, respectively)),[12] and 2) the known propensity of dicyclohexylcarbodiimide to form donor–acceptor adducts with strongly Lewis acidic boranes prior to further insertion chemistry.[20]

The second-formed intermediate is formulated as [CpFe(CO)$_2$C(NCy)$_2$BNR$_2$]$^+$[BAr$^F{}_4$]$^-$ on the basis of spectroscopic and structural data obtained for the isolated compound **4b** (R = Cy, see below). By employing 1) the dicyclohexylamino precursor **1b** and 2) careful addition of a substoichiometric amount of dicyclohexylcarbodiimide, **4b** can be synthesized free from the double-insertion product **2b**, and isolated as a crystalline solid. Most tellingly, the ^{11}B NMR chemical shift for **4b** ($\delta_B = 25$ ppm) is consistent with a product formed by insertion of carbodiimide into the Fe=B bond, thus implying the absence of any remaining direct Fe−B interaction.[21] These inferences were subsequently confirmed crystallographically (Figure 2).

From a structural perspective, the {CpFe(CO)$_2$C(NCy)$_2$} unit in **4b** resembles the {CpFe(CO)$_2$C(S)E} moieties formed by insertion of SCE (E = S or NPh) into bimetallic Fe/Zr systems, which have been reported by Gade and co-workers.[22] For the specific examples [CpFe(CO)$_2$C(S)(E)ZrL] (L = {(2-FC$_6$H$_4$)NSiMe$_2$}$_3$CH), the relatively short Fe−C bond lengths (for example, 1.934(11) Å for E = S) and low-field ^{13}C NMR shift associated with the {C(S)(E)} fragments have been ascribed to a partial carbenoid (Fe=C) character. The Fe−C bond in **4b** (1.938(3) Å) is of a similar length, and the metalla-amidinate carbon atom ($\delta_C = 251.5$ ppm) resonates at significantly lower field than is typically found for quaternary amidinate or guanidinate carbon atoms ($\delta_C \approx 160$–170 ppm).[15,16] However, on the basis of DFT calculations carried out for the Fe−C linkage in **4b** it seems likely that the overall contribution from a similar carbenoid resonance form (Scheme 3) is small.[23]



3a/b

4a/b

Scheme 2. Intermediates in the formation of **2a/b** from **1a/1b**. Reaction conditions: a) CyN=C=NCy (2.0 equiv), [D$_2$]dichloromethane, −50 °C; b) −30 °C; c) 20 °C.

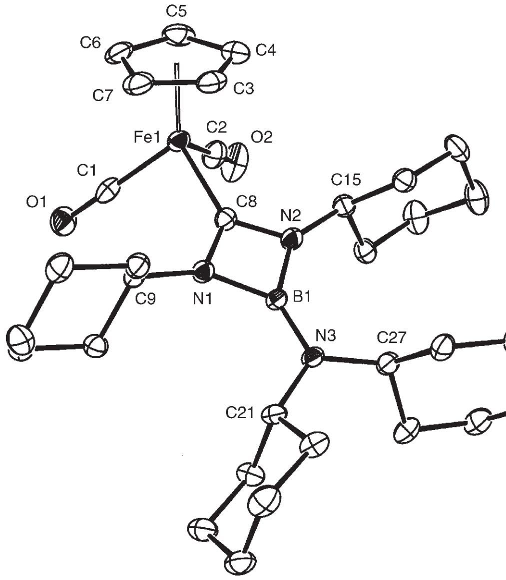
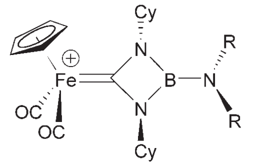


Figure 2. Structure of the cationic component of **4b**; hydrogen atoms are omitted for clarity and ORTEP ellipsoids are set at the 50% probability level. Relevant bond lengths [Å] and angles [°]: Fe1-C8 1.938(3), C8-N1 1.358(4), C8-N2 1.357(4), B1-N1 1.506(2), B1-N2 1.491(2), B1-N3 1.371(4); N1-C8-N2 98.3(2), N1-B1-N2 86.5(2).



Scheme 3. Carbenoid resonance form of **4**.

From intermediates **4a**/**4b** the second insertion step proceeds rapidly in the presence of excess carbodiimide, even at −20 °C, to yield the final product **2a**/**2b**. Insertion of carbodimides into B=N bonds has previously been reported,[15,24] Bürger and co-workers, for example, proposing a mechanism involving an initial [2+2] cycloaddition step. Additionally, the reaction of CyNCNCy with $\mathrm{Cy_2NBCl_2}$ has been shown to cleanly generate $\mathrm{Cy_2NC(NCy)_2BCl_2}$.[17]

In conclusion, we have demonstrated that insertion of unsaturated substrates is a viable fundamental reaction type for compounds containing M=B double bonds. Controlled, stepwise insertion of carbodiimide molecules into both M=B and B=N linkages of cationic aminoborylene complexes sequentially forms four-membered metalla-amidinate and guanidinate rings. Identification of intermediate species implies that 1) insertion into the M=B bond is more facile and 2) insertion into the M=B linkage is preceeded by coordination of the carbodiimide substrate at the borylene center. This latter observation implies that a mechanism may be operating which is unlike that normally observed for insertion into transition-metal–ligand bonds, that is, coordination of the substrate occurs at the ligand (rather than at the metal) and is followed by migration of the metal fragment (rather than the ligand). Cooperative reactivity of this type between linked Lewis acidic centers has previously been observed for early/late dinuclear transition-metal systems.[22] Further studies of the reactivity of M=B multiple bonds towards heteroallenes and related systems will be reported in due course.

Experimental Section

Included here are the preparative, spectroscopic, and crystallographic data for compound **2a**; preparative, spectroscopic, and crystallographic data for **2b** and **4b** are included in the Supporting Information.

2a: A mixture of **1a** (0.115 g, 0.10 mmol) and dicyclohexylcarbodiimide (2.0 equiv) in dichloromethane (3 mL) was stirred for 4 h at room temperature, after which time the reaction was judged to be complete by ^{11}B NMR spectroscopy. Layering with hexanes and storage at −30 °C led to the formation of colorless crystals of **2a** suitable for X-ray diffraction. Yield of isolated product: 0.053 g, 37 %. ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, 20 °C): $\delta = 1.32$ (d, ^3J(H,H) = 7.0 Hz, 12 H, CH$_3$ of *i*Pr), 1.00–1.92 (m, 40 H, CH$_2$ of NCy), 3.09, (m, 2 H, CH of NCy), 3.38 (m, 2 H, CH of NCy), 3.90 (sept, ^3J(H,H) = 7.0 Hz, 2 H, CH of *i*Pr), 4.98 (s, 5 H, Cp), 7.48 (s, 4 H, *para*-H of $\mathrm{BAr^F{}_4{}^-}$), 7.64 ppm (s, 8 H; *ortho*-H of $\mathrm{BAr^F{}_4{}^-}$); ^{13}C NMR (76 MHz, [D$_2$]dichloromethane, 20 °C): $\delta = 22.4$ (CH$_3$ of *i*Pr), 25.3 (2 overlapping signals, 4-CH$_2$ of NCy), 25.4, 25.9 (3-CH$_2$ of NCy), 31.1, 34.9 (2-CH$_2$ of NCy), 50.6 (CH of *i*Pr), 53.8, 54.2 (CH of NCy), 86.1 (Cp), 117.5 (*para*-CH of $\mathrm{BAr^F{}_4{}^-}$), 124.6 (q, ^1J(C,F) = 274 Hz, CF$_3$ of $\mathrm{BAr^F{}_4{}^-}$), 128.9 (^2J(C,F) = 34 Hz, *meta*-C of $\mathrm{BAr^F{}_4{}^-}$), 134.8 (*ortho*-CH of $\mathrm{BAr^F{}_4{}^-}$), 161.8 (q, ^1J(C,B) = 50 Hz *ipso*-C of $\mathrm{BAr^F{}_4{}^-}$), 167.1 (guanidinate quaternary), 211.8 (CO), 224.0 ppm (metalla-amidinate quaternary); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 20 °C): $\delta =$ 3.4 (s, fwhm ca. 12 Hz, cation), −7.6 ppm ($\mathrm{BAr^F{}_4{}^-}$); ^{19}F NMR (283 MHz, [D$_2$]dichloromethane, 20 °C): $\delta = -62.8$ (CF$_3$); IR ([D$_2$]dichloromethane solution): $\tilde{\nu} = 2040$, 1993 cm^{-1} (CO); MS (positive-ion nanoelectrospray): *m*/*z* (%): 700.4 (55) [M^+], correct isotope pattern; MS (negative-ion nanoelectrospray): *m*/*z* (%): 863.1 (100) $[\mathrm{BAr^F{}_4}]^-$; exact mass calcd for [M^+] (^{54}Fe isotopomer) 697.4502; found: 697.4494. Crystallographic data: $\mathrm{C_{71}H_{75}B_2F_{24}FeN_5O_2}$, $M_r =$ 1563.83, monoclinic, space group $P2(1)/n$, $a = 12.973(5)$, $b =$ 27.190(5), $c = 21.590(5)$ Å, $\beta = 105.219(5)$°, $V = 7348(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.414$ Mg m^{-3}, $T = 150(2)$ K, $\lambda = 0.71069$ Å. 28 224 reflections collected, 14 381 independent [R(int) = 0.0292], which were used in all calculations. $R_1 = 0.0419$, $wR_2 = 0.1046$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0564$, $wR_2 = 0.1120$ for all unique reflections. Max./min. residual electron densities 0.312/−0.422 e Å^{-3}. CCDC-628663 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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