Boron Ligands

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# Extending the Chain: Synthetic, Structural, and Reaction Chemistry of a BN Allenylidene Analogue**

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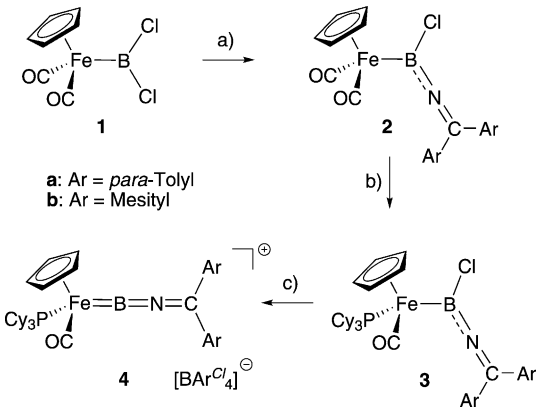
Boron donor ligands isoelectronic with classical organometallic systems are highly topical, reflecting their implication in novel stoichiometric and catalytic reaction chemistry.[1] Thus, for example, boryl complexes, $[L_xM(BX_2)_y]$, have been implicated in metal-catalyzed hydro-/diboration and C–H functionalization chemistries,[1–5] and aminoborane complexes, $[L_xM(H_2BNRR')_y]$, are relevant to the "on-metal" dehydrocoupling/polymerization of amineboranes.[6,7] As a consequence, comparative data relating to electronic structure and reactivity for isoelectronic carbon/boron donor ligand families has become available (e.g. for N-heterocyclic carbene/boryl, alkene/aminoborane, CO/BF,$BO^-$, and Cp/azaborolyl pairs).[7–12] Within this sphere, metal borylene complexes—and in particular aminoborylene systems $[L_xM(BNR_2)_y]$—represent a burgeoning area,[1,13] offering advances, e.g., in the controlled functionalization of organic/organometallic substrates, and in the catalysis of C–C bond-forming reactions.[14] However, while similarities in electronic structure between aminoborylene and classical vinylidene complexes, $[L_xM(CCR_2)_y]$, point to the possibility of synthesizing related extended-chain B donor cumulenylidene systems (with more complex patterns of reactivity), such compounds are as yet unknown.

By contrast, metal complexes featuring extended chains of unsaturated carbon centers have attracted much interest, in part due to their conjugated structures and potential applications in molecular electronics, for example, as nanoscale "molecular wires."[15] Within this sphere, allenylidene systems, $[L_xM{=}C{=}C{=}CR_2]$, have received additional attention, due to their implication in a range of synthetically valuable organic transformations (e.g. in propargylic substitution reactions and the synthesis of carbon-rich heterocycles).[16] Key to several applications is the unusual ambiphilic character of the allenylidene ligand, which displays alternating electrophilic/nucleophilic reactivity at successive carbon centers. Half-sandwich $d^6$ allenylidene complexes have been particularly thoroughly investigated, revealing nucleophilic behavior at the β-carbon center and α,γ electrophilicity.[16] Moreover, the regioselectivity of electrophilic reactivity appears to be dictated both by electronic factors (LUMO amplitudes, charge distribution) and steric considerations within the complex itself, and by the nature of the incoming nucleophile (size, hard/soft behavior).[17] With a view to establishing synthetic routes to isoelectronic BN-containing systems and probing their comparative electronic structure/reactivity, we report herein the first iminoborylene complexes, $[L_xM{=}B{=}N{=}CR_2]$.

The syntheses of the target iminoborylene complexes were carried out by the three-step procedure outlined in Scheme 1, utilizing the dichloroboryl complex $[CpFe(CO)_2BCl_2]$ (**1**; Cp = cyclopentadienyl) and $Ar_2CNLi$ (Ar = *para*-Tol, Mes) as the ultimate boron- and nitrogen-containing precursors.[18,19] Initial salt metathesis was exploited to give boryl complexes **2a**/**2b** in yields of 40–50%; **2b** can be shown spectroscopically to act as a viable source of the corresponding cationic iminoborylene complex $[CpFe(CO)_2(BNCMes_2)]^+$ through halide abstraction.[20] The lability of this system at $T > -30\,^\circ C$, however, pointed to the need to employ a more electron-rich metal fragment, for example, by the introduction of strong σ-donor phosphine co-ligands. Thus **2a**/**2b** are readily transformed into the corresponding $PCy_3$-ligated boryl systems **3a**/**3b** under photolytic conditions (in yields of 50–60%), from which iminoborylenes $[CpFe(CO)(PCy_3)(BNCAr_2)][BAr^{Cl}{}_4]$ (**4a**/**4b**) can then be accessed




***Scheme 1.*** Synthesis of iminoborylene complexes **4a/b**. Key reagents: a) $Ar_2CNLi$ (1.0 equiv), toluene, −78 °C to room temperature, 12 h, 52%/38% (**2a**/**2b**); b) $PCy_3$ (1.1 equiv), toluene, *hν*, 90 min (**3a**) or 3 h (**3b**), 60%/48% (**3a**/**3b**); c) $Na[BAr^{Cl}{}_4]$ (1.0 equiv), fluorobenzene, 5 min, 55% (**4b**); [**4a** investigated in situ].

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through the respective reactions with $Na[BAr^{Cl}_4]$ ($Ar^{Cl}$ = $C_6H_3Cl_2$-3,5).[21]

Intermediates **2a**/**2b** and **3a**/**3b** have been characterized by standard spectroscopic and analytical techniques and (in the cases of **2a**, **3a** and **3b**) by X-ray crystallography (see Figure 1 and Supporting Information). Spectroscopically, **3a**/**3b** give rise to $^{11}B$ and $^{31}P$ resonances which are not only very similar to each other ($\delta_B = 47$, 50 ppm; $\delta_P = 77.1$, 75.0 ppm), but also comparable to related aminoboryl systems.[22] Structurally, however, **3a** and **3b** diverge markedly in terms of basic ligand geometry. **3b** features a linear heteroallene-like BNC unit [∢B-N-C = 174.7(2)°] with orthogonal BN and CN π systems. As a consequence, the B–N bond is short [1.368(3) Å], reflecting substantial N→B π donation, and the Fe–B bond correspondingly fairly long [2.015(2) Å].[1,22] The structure of the less sterically encumbered *para*-tolyl system **3a**, by contrast, features a bent BNC framework [∢B-*N*-C = 144.8(2)°], implying an isolated C=N double bond, and relatively less N→B π donation. As a consequence the B–N separation [1.396(4) Å] is longer than in **3b** and the Fe–B distance concomitantly shorter [1.980(4) Å].

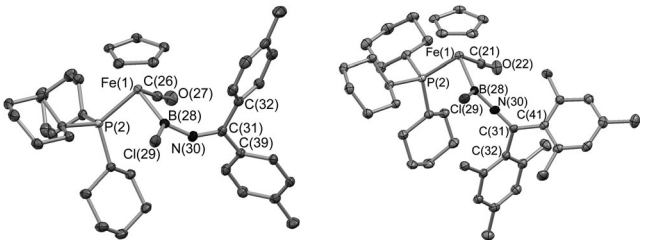
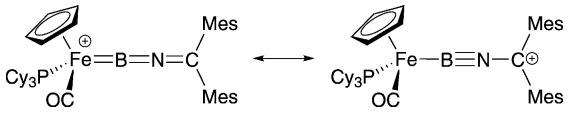



***Figure 1.*** Molecular structures of **3a** (left) and **3b** (right) in the solid state; hydrogen atoms omitted for clarity and thermal elipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: (for **3a**/**3b**) Fe(1)–B(28) 1.980(4)/2.015(2), B(28)–N(30) 1.396(4)/1.368(3), N(30)–C(31) 1.269(3)/1.263(3), B(28)-N(30)-C(31) 144.8(2)/174.7(2).

Halide abstraction from **3a**/**3b** is signaled by a well precedented downfield shift in the $^{11}B$ signal (e.g. $\delta_B = 82/85$ for **4a**/**4b**, cf. 93 for $[CpFe(CO)(PMe_3)(BNCy_2)]^+$ and 50 ppm for **3b**),[23] but also by a similar shift in the ketimino $^{13}C$ resonance (e.g. $\delta_C = 180.8/187.0$ for **4a**/**4b**, cf. 150.2 ppm for **3b**). The latter change presumably reflects mesomeric stabilization of the positive charge over the entire [FeBN-$CAr_2$] unit in **4b** (see below) in a manner characteristic of isoelectronic allenyidene systems (Scheme 2).[16] Further characterization of **4b** in solution was achieved by IR spectroscopy {$\nu$(CO) = 1969, cf. 1905 $cm^{-1}$ for **3b**; $\nu$(BNC) = 1753 $cm^{-1}$, cf. $\nu$(CCC) = 1896 $cm^{-1}$ for $[CpFe(dppe)(CCCPh_2)]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane)}[24] and by positive-ion ESI-MS which reveals the $[CpFe(CO)(PCy_3)(BNCMes_2)]^+$ cation with the expected isotopic profile and accurate mass.




***Scheme 2.*** Limiting cationic metal iminoborylene and carbocation-functionalized iminoboryl resonance structures for **4b**.

The structure of **4b** determined crystallographically contains two closely related cation/anion pairs; each cationic component (Figure 2) reveals the expected three-legged piano-stool geometry at iron, a close-to-linear FeBNC framework, and an alignment of the $CMes_2$ fragment [∢(Cp centroid)-Fe(1)-C(30)-C(40) = 7.1°] as expected for a four-atom heterocumulene chain (cf. 6.4° for [CpFe(dppe)-$(CCCPh_2)]^+$).[24,25] In terms of bond lengths, the Fe–B distance is comparable to that found in the related aminoborylene complex $[CpFe(CO)(PMe_3)(BNCy_2)]^+$ [1.838(5) (mean) vs. 1.821(4) Å],[23] and the C–N separation [1.292(6) Å (mean)], if anything, marginally longer than that measured for precursor **3b** [1.263(3) Å]. The B–N bond, however, is noticeably shorter [at 1.314(6) Å (mean)] than those found in either $[CpFe(CO)(PMe_3)(BNCy_2)]^+$ or **3b** [1.347(5) and 1.368(3) Å, respectively].[22] Rather, this separation tends towards the distances associated with the formal B≡N triple bonds found in iminoboryl complexes, $L_xMB{\equiv}NSiMe_3$ [1.251(4)–1.265(7) Å].[26] These structural findings, together with the low-field $^{13}C$ NMR shift measured for C(30) suggest that both cationic metal iminoborylene and carbocation-functionalized iminoboryl resonance forms contribute to the electronic structure of **4b** (Scheme 2). Similar resonance structures have been proposed to account for the electronic structure of related half-sandwich iron allenylidene systems, such as $[CpFe(dppe)(CCCPh_2)]^+$.[24]

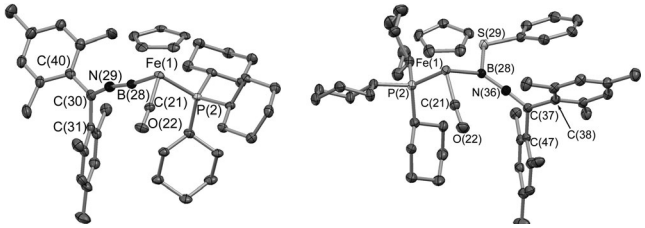



***Figure 2.*** Molecular structure of one of the cationic components of **4b** (left) and of **5b** (right); hydrogen atoms and counter-ion (for **4b**) omitted for clarity and thermal elipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: (for **4b**) Fe(1)–B(28) 1.835(6), B(28)–N(29) 1.302(8), N(29)–C(30) 1.287(7), Fe(1)-B(28)-N(29) 170.9(5), B(28)-N(29)-C(30) 166.6(5); (for **5b**) Fe(1)–B(28) 2.034(3), B(28)–N(36) 1.373(2), N(36)–C(37) 1.273(4), B(28)–S(29) 1.886(3), B(28)-N(36)-C(37) 175.3(2).

In order to put comparative discussions of electronic structure between **4b** and related allenylidene systems on a firmer basis, DFT calculations (B3LYP) were carried out on the complete $[CpFe(CO)(PCy_3)(BNCMes_2)]^+$ cation, and on the related model $CCCMes_2$ complex (see Supporting Information).[27] These reveal not only excellent agreement between the calculated and crystallographically determined geometry for **4b**, but also qualitatively similar π-bonding manifolds for the two cations. Thus, in the case of $[CpFe(CO)(PCy_3)(BNCMes_2)]^+$, for example, the HOMO–6 and HOMO–7 orbitals display orthogonal FeBN and BN π bonding character.

The idea of dual α,γ electrophilicity for both **4b** and $[CpFe(CO)(PCy_3)(CCCMes_2)]^+$ is supported by the forms of the respective LUMOs (Figure 3). Intriguingly, in the case of **4b**, the predominant orbital contribution (ca. 16%) is from

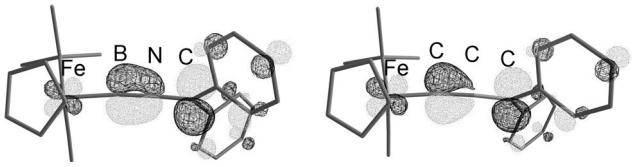
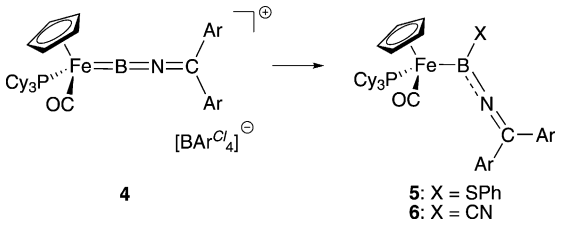



***Figure 3.*** Comparison of the LUMOs of the $[CpFe(CO)(PCy_3)(BNCMes_2)]^+$ (left) and model $[CpFe(CO)(PCy_3)(CCCMes_2)]^+$ cations (right), showing contributions from the four atoms of the heterocumulene chain (phosphine Cy and mesityl Me groups omitted for clarity).

the $2p_z$ orbital at the γ-carbon, C(30), and given the importance of frontier orbital control in reactions of allenylidene complexes with nucleophiles, we therefore set out to probe experimentally the regioselectivity of the corresponding reactivity of **4b**. In the event, reactions even of relatively soft nucleophiles such as cyanide or thiophenolate proceed exclusively by attack at the α (boron) center, as determined by spectroscopic and (in the case of $[SPh]^-$) crystallographic studies (Figure 2 and Scheme 3). While it is possible that




***Scheme 3.*** Regioselectivity in the addition of anionic nucleophiles to **4a**/**4b**: α addition of cyanide and thiophenolate.

steric factors play an important role in the observed selectivity, it is noteworthy that the corresponding reaction of the less encumbered *para*-tolyl derivative **4a** with Na[SPh] also proceeds exclusively by attack at boron. The regioselectivity of addition of thiophenolate reagents to related allenylidene complexes has been shown to be strongly dependent on the ancillary phosphine ligand set.[17e] With regard to cyanide addition, α regiochemistry is also exhibited by **4b**; this provides an interesting contrast with the γ-selectivity observed towards $CN^-$ for systems of the type $[(\eta^5\text{-}C_nH_m)Ru(PPh_3)_2(CCPh_2)]^+$ ($C_nH_m = C_5H_5$, $C_9H_7$), in which the α center is presumably more sterically protected and also less electropositive (i.e. carbon rather than boron).[28]

Further studies of the reactivity of **4b** and related extended chain BN cumulenylidene ligands towards polar unsaturated substrates are in progress and will be reported in due course.

## Experimental Section

Included here are crystallographic data for **4b**. Complete data for **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, and **6b** are included in the Supporting Information.

Crystallographic data (for **4b**): $C_{67}H_{72}B_2Cl_8FeNOP$, $M_r$ 1347.43, triclinic, $P\bar{1}$, $a = 18.0383(5)$, $b = 19.0305(5)$, $c = 23.2243(8)$ Å, $\alpha = 95.801(2)$, $\beta = 112.537(3)$, $\gamma = 109.729(2)°$, $V = 6683.4(4)$ Å$^3$, $Z = 4$, $\rho_c = 1.291$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 1.54180$ Å. 64546 reflections collected, 8788 independent [$R$(int) = 0.087], which were used in all calculations. $R_1 = 0.0941$, $wR_2 = 0.2627$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.1201$, $wR_2 = 0.2903$ for all unique reflections. Max. and min. residual electron densities 3.33 and −0.87 e Å$^{-3}$ (see CIF). CSD reference: 825825.

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[19] An alternative synthetic route to **2a**/**2b** employing Na[$CpFe(CO)_2$] and $(Cl_2BNCAr_2)_n$ was frustrated by the dimeric nature of the borane reagent for smaller Ar groups (and consequent resistance to nucleophilic attack at the four-coordinate boron center) and by the propensity of monomeric $Cl_2BNCAr_2$ to undergo substituent redistribution in vacuo to give $BCl_3$ and $B(NCAr_2)_3$ (for sterically more bulky Ar substituents).

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