COMMUNICATION

ABSTRACT: Aminoboranes, H₂BNRR', represent the monomeric building blocks from which novel polymeric materials can be constructed via metal-mediated processes. The fundamental capabilities of these compounds to interact with metal centers have been probed through the coordination of H₂BNCy₂ at 16-electron [CpRu(PR₃)₂(H₂BNCy₂)]⁺ fragments. In contrast to the side-on binding of isoelectronic alkene donors, an alternative mono(σ-BH) mode of aminoborane ligation is established for H₂BNCy₂, with binding energies only ∼8 kcal mol⁻¹ greater than those for analogous dinitrogen variations. Complexes of these polymeric systems are known to be capable of the side-on binding of monomeric H₂BNCy₂ at 16-electron fragments of the type [CpRu(PR₃)₂(H₂BNCy₂)]⁺. While such metal systems are known to be capable of the side-on binding of alkynes, an alternative mono(σ-BH) mode of aminoborane ligation is established for H₂BNCy₂. Crystallographic studies in the solid state, together with DFT calculations and spectroscopic studies in solution, allow for the elucidation of intramolecular dehydrogenation, presumably distort the structural landscape in favor of the four-electron-donating bis(σ-BH) coordination mode over the corresponding (two-electron-donating) side-on π-bound motif. Thus, Alcaraz and Sabo-Etienne report an energetic preference of 14.3 kcal mol⁻¹ for the “end-on” bis-(σ-BH) coordination geometry of H₂BNH₂ at [L₂Ru(H)]³⁻.

With a view to investigating the intrinsic two-electron donor capabilities of aminoborane ligands, we have therefore set out to examine the coordination of monomeric H₂BNCy₂ at 16-electron fragments of the type [CpRu(PR₃)₂(H₂BNCy₂)]⁺. Despite their isoelectronic relationship with 1,1-disubstituted alkynes, the coordination chemistry of aminoboranes has only recently begun to be examined. To date, the only reported examples of such complexes feature chelating H₂BNCy₂ ligands coordinated to [L₂M(H)]³⁺ fragments via two B–H–M bridges (M = Ru, n = 0; M = Rh, n = 1; L = N-heterocyclic carbene, tertiary phosphine). Such a coordination geometry contrasts with the classical “side-on” binding mode observed for alkene donors within the same framework. However, the utilization of these 14-electron metal systems, while seemingly essential to synthetic routes which employ in situ aminoborane dehydrogenation, presumably distorts the structural landscape in favor of the four-electron-donating bis(σ-BH) coordination mode over the corresponding (two-electron-donating) side-on π-bound motif.
Scheme 1. Syntheses of κ¹-Aminoborane Complexes 5 and 6 from the Corresponding Dinitrogen Systemsa

![Scheme Image]

a key reagents/conditions: (a) Na[BAr₅]₂ (1.0 equiv), fluorobenzene, N₂ atmosphere, 10 min at 20 °C, as per ref 8; (b) H₂BNCy₂ (1.0 equiv), fluorobenzene, 5 min at 20 °C, 32% isolated yield; (c) Na[BAr₅] (1.0 equiv), fluorobenzene, N₂ atmosphere, 10 min at 20 °C, quantitative by NMR, ca. 10% isolated yield; (d) H₂BNCy₂ (1.0 equiv), fluorobenzene, 5 min at 20 °C, 24% isolated yield.

consistent with averaging of the two phosphorus environments via rapid rotation of the aminoborane ligand about the Ru—(BH centroid) axis (vide infra).

While the formulations of both 5 and 6 were suggested by spectroscopic data and the bulk composition confirmed by microanalysis, unequivocal characterization was additionally reliant on crystallographic studies (Figure 1). The structures of the cationic components of these compounds feature in common (i) a three-legged piano stool geometry at ruthenium, with the non-Cp coordination environment being defined by the two phosphorus centers and the B—H centroid [〈BH centroid〉—Ru—P = 90.3, 96.3° and 90.9, 92.0° for 5 and 6, respectively], and (ii) a monodenticulate (σ-BH) aminoborane ligand characterized by a bent Ru···B···N framework [〈Ru···B···N = 130.2(3)° for 5, 133.1(4)° for 6], which contrasts with the analogous (essentially linear) fragment found for κ²-bound H₂BNCy₂ ligands (e.g., 178.4(3)° for [(IMes)₂Rh(H)₂(H₂BNCy₂)]₅). Spectroscopically, the presence of a single Ru—H—B bridging interaction is revealed by distinct RuHB and BH signals in the ¹H NMR spectra of 5 and 6 at 20 °C and is further signaled by disparate Ru—H and B—H contacts in the solid state (e.g., for 6, d[Ru(1)—H(351)] = 1.669(1), d[Ru(1)···H(352)] = 2.887 Å; d[B(35)···H(351)] = 1.244(6), d[B(35)···H(352)] = 1.150(5) Å). Moreover, the presence of only one bridging hydrogen atom is consistent with Ru···B distances [2.430(4) and 2.332(6) Å for 5 and 6, respectively] which are significantly longer than that found in (Cy₃P)₂Ru(H)₂(k²-H₂BNMe₂) [1.980(3) Å]. The finding that the Ru···B contacts for 5 and 6 are shorter than that in [CP₃Ru(NMe₃)]₂k¹-H₂·BNMe₂ [2.648(3) Å] presumably reflects the presence of a three (rather than four-) coordinate boron center and the possibility for back-bonding from ruthenium.

Three additional observations are consistent with the possibility for back-bonding from the highest occupied molecular orbital (HOMO) of the [CP₃Ru(PR₃)₂]⁺ fragment into a B—H σ* orbital of the coordinated borane in 5 and 6. First, the alignment of the coordinated B—H bond with respect to the [CP₃Ru(PR₃)₂]⁺ fragment [as manifested, for example, by a (CP centroid)—Ru—(BH centroid)—B torsion angle of 84.3° for 6] maximizes the potential for overlap between the respective orbitals (Figure 2a,b). Second, the differences in both the Ru···B [2.430(4), 2.332(6) Å] and B—H(Ru) distances [1.207(4), 1.244(6) Å] between 5 and 6 are consistent with greater back-bonding from the more electron-rich [CP₃Ru(dcyde)]⁺ fragment (cf. [CP₃Ru(PPh₃)₂]⁺), albeit with some caution attached to the interpretation of the less well defined B—H distances. Finally, the chemical shift of the RuHB bridging hydrogen is also markedly more hydridic in the case of 6 (δ̃H = 14.56, cf. 11.97 for 5). By contrast, the BN distances for the two compounds are statistically identical [1.376(4) and 1.382(7) Å], suggesting little population of the BN τ* orbital. Such an observation conflicts with that made for (Cy₃P)₂Ru(H)₂(H₂BNMe₂) but is not entirely unexpected for the current [CP₃Ru(PR₃)₂]⁺ systems, given that the BN τ* orbital in 6, for example, lies effectively orthogonal to the metal-based HOMO (Figure 2c).

Differences in the binding affinity of H₂BNCy₂ for the ruthenium center in 5 and 6 presumably also influence the fluxional behavior of these systems, as determined by variable-temperature NMR experiments. Thus, 6 is characterized by two fluxional processes relating to the dynamic behavior of the coordinated borane. At very low temperatures (T = −80 °C) in CD₂Cl₂ solution, the 3¹P(¹H) NMR spectrum of 6 shows two resonances (at δP = 79.2 and 83.1 ppm; JPP = 23 Hz) consistent with the structure of the cation determined crystallographically and with slow rotation about the Ru—(BH centroid) vector on
the NMR time scale (Scheme 2a). Coalescence of these resonances occurs at $T = -50 \degree C$, and the barrier to rotation ($\Delta G^\ddagger = 9.9 \text{ kcal mol}^{-1}$) so determined is marginally greater than the value of 7.4 kcal mol$^{-1}$ reported by Schlecht and Hartwig for a comparable process in CpMn(CO)$_2$(HBcat).$^{15}$ By contrast, the analogous fluxional process for 5 cannot be frozen out at temperatures in excess of $-90 \degree C$, suggesting that the corresponding barrier to rotation in this case is less than ca. 7 kcal mol$^{-1}$. A second fluxional process can be identified for both complexes ($T_c = 7 \degree C$, $\Delta G^\ddagger = 12.8 \text{ kcal mol}^{-1}$ for 5; $T_c = 28 \degree C$, $\Delta G^\ddagger = 14.3 \text{ kcal mol}^{-1}$ for 6) which results in coalescence of the RuHB and BH signals and of the two distinct sets of cyclohexyl methine protons. As such, these spectral changes are assigned to a process involving exchange of the bound and unbound BH hydrogens (Scheme 2b), with the markedly higher barrier associated with this process for 6 (vs 5) being consistent with the tighter binding of the borane implied crystallographically.

In order to quantify/contextualize the strength of the metal–ligand interaction associated with this simple monomeric BH mode of coordination of H$_2$BNCy$_2$, a series of quantum chemical calculations has been carried out on 5, 6, and related [CpRu(PR$_3$)$_2$]$_2$-containing systems (see Supporting Information). Consistent with the structural data determined in the solid state, significantly stronger binding of the aminoborane is found for 6 ($\Delta G = -26.0$ for ligand association, cf. $-15.2 \text{ kcal mol}^{-1}$ for 5). Moreover, these free energies can be put into context by the corresponding values of $-46.5$, $-19.2$, and $-17.2 \text{ kcal mol}^{-1}$ calculated for the binding of CO, $\eta^2$-C$_2$H$_4$, and N$_2$ to the same cationic [CpRu(dcype)]$^+$ fragment. Experimentally, such data are consistent with the displacement of N$_2$ by H$_2$BNCy$_2$ in the synthesis of 6, and with the (synthetically verified) reaction of 6 with CO to generate [CpRu(dcype)(CO)]$^+$ and free aminoborane (see Supporting Information). Calculations have also been carried out on 6 to shed light on the likely mechanism for the exchange process shown in Scheme 2b; a transition state can be identified (at a free energy of $+17.5 \text{ kcal mol}^{-1}$ with respect to 6) featuring a more symmetrically bound aminoborane ligand ($d[\text{Ru}−\text{H}] = 2.261$, $2.334 \text{ Å}$; $d[\text{B}−\text{H}] = 1.200$, $1.202 \text{ Å}$) and a markedly elongated Ru⋯B separation ($2.570 \text{ Å}$), consistent with a concerted nondissociative exchange process in this case.

In summary, we report the first complexes containing an aminoborane ligand coordinated to a 16-electron metal center, thereby defining the intrinsic two-electron donor capabilities of this topical ligand family. Geometric parameters for the monodentate BH-bound ground-state structures and details of dynamic fluxional processes have been probed as functions of the ancillary phosphine co-ligands. Ru(II) systems have been shown to be among the most active catalysts for the dehydrocoupling/polymerization of methylamineborane; the current study sheds light on coordination geometries and migratory pathways potentially accessible for the aminoborane monomer in catalytic systems. Further details of the reactivity of these novel systems will be reported in due course.

**ASSOCIATED CONTENT**

*Supporting Information.* Synthetic and characterization details for 4 and 5; details of all DFT-calculated structures; crystallographic data for 3–6 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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**ACKNOWLEDGMENT**

The authors thank EPSRC for funding (EP/F019181/1) and the Oxford Supercomputing Centre for computing time.

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(11) Synthesis of 6: To solution of 4 (0.24 g, 0.16 mmol) in ca. 15 mL of C6H6 was added H3BNCy2 (0.59 mL of a 0.27 M solution in C6H6, 0.16 mmol). After being stirred for 5 min, the solution was filtered and layered with hexanes (30 mL), and yellow crystals suitable for X-ray crystallography were obtained. Isolated yield, 0.08 g (32%).

(12) Crystallographic data for C32H89B2F24NP2Ru, M = 1645.13, triclinic, P1, a = 13.2296(2), b = 17.2074(3), and c = 17.6001(3) Å, α = 92.508(1), β = 103.503(1), and γ = 93.338(1)°, V = 3882.5(1) Å³, Z = 2, ρc = 1.407 Mg m⁻³, T = 150 K, λ = 0.7103 Å; 5870 refinements collected, 1802 independent [R(int) = 0.049], which were used in all calculations; R1 = 0.0566, wR2 = 0.1169 for I > 2σ(I), and R1 = 0.1072, wR2 = 0.1374 for all unique refls; max and min residual electron densities 1.42 and -1.41 e Å⁻³.

(13) A ruthenium half-sandwich complex containing a κ⁴-H3BMes ligand has also been reported, featuring a Ru–B separation of 1.921(2) Å and a Ru···B–C angle of 172.3(2)°: Hesp, K. D.; Kannemann, F. O.; Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stadliotto, M. Inorg. Chem. 2011, 50, 2431–2444.

(14) For a related example of a κ¹-bound four-coordinate amineborane, see: Kawano, Y.; Hashiba, M.; Shimo, M. Organometallics 2006, 25, 4420–4426.