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Borane to Boryl Hydride to Borylene Dihydride: Explicit Demonstration of Boron-to-Metal α-Hydride Migration in Aminoborane Activation

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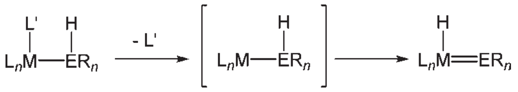
Supporting Information

ABSTRACT: The sequence of fundamental steps implicit in the conversion of a dihydroborane to a metal borylene complex have been elucidated for an $[Ir(PMe_3)_3]$ system. B−H oxidative addition has been applied for the first time to an aminodihydroborane, H_2BNR_2, leading to the generation of a rare example of a primary boryl complex, $L_n(H)M\{B(H)NR_2\}$; subsequent conversion to a borylene dihydride proceeds via a novel B-to-M α-hydride migration. The latter step is unprecedented for group 13 ligand systems, and is remarkable in offering α- substituent migration from a Lewis acidic center as a route to a two-coordinate ligand system.

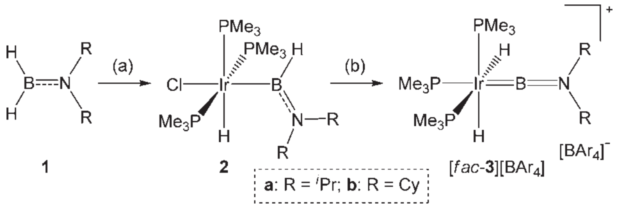
The activation of boranes by transition metal complexes is a key step in a number of important catalytic reactions, including the hydroboration of unsaturated C−E bonds,[1] the functionalization (by borylation) of unactivated C−H bonds,[2] and the dehydro-coupling of amineboranes to BN-containing polymeric materials.[3] Oxidative addition of borane B−H bonds, typically at electron-rich late transition metal centers, to give a metal boryl species is a key step in a number of these processes, and as such, has been the subject of wide-ranging and systematic study.[4] In principle, in the presence of an additional B−H bond (i.e., for primary boryl systems $L_nM\{B(H)X\}$), further ligand activation is conceivable, to generate a borylene complex, L_nMBX, in a manner analogous to the textbook syntheses of carbene and silylene systems (Scheme 1).[5,6] In practice, this E to M α-hydride migration step currently has no precedent for E = B, in part because primary boryl species of the type $L_nM\{B(H)X\}$ are very rare.[7,8]

Direct conversion of a dihydroborane to a metal borylene complex represents a new paradigm for the synthesis of a class of compound increasingly exploited in the functionalization of organic/organometallic substrates.[4d,9,10] Moreover, as has been demonstrated for related silylene systems, such dehydrogenation steps are more amenable to incorporation in catalytic cycles than other synthetic approaches.[11] However, although the viability of borylene synthesis by direct borane dehydrogenation has been demonstrated in the ground-breaking synthesis of $Ru(PCy_3)_2(H)Cl(BMes)$ from $Ru(PCy_3)_2(H)Cl(\kappa^2\text{-}H_2BMes)$,[9] mechanistic details and intermediate species have yet to be elucidated for such a transformation. With this in mind, we set out to demonstrate explicitly the sequence of fundamental steps required for the conversion of a dihydroborane to a metal borylene complex. While the initial borane activation step utilizes a precedented B−H oxidative addition methodology (albeit for a new substrate type), subsequent conversion to a borylene dihydride system relies on a completely unprecedented B-to-M α-hydride migration process.

Scheme 1. E to M α-Hydride Migration in the Synthesis of M═E Multiple Bonds (E = C, Si, B)



Scheme 2. Syntheses of Borylene Systems $[fac\text{-}3a/3b]^+$ from Aminoboranes 1a/1b via (Hydridoboryl)hydride Intermediates: α-Hydride Migration Triggered by Cl^- Abstraction[a]



[a] Key reagents: (a) $Ir(PMe_3)_3Cl(coe)$, toluene, 20 °C, 10 min, 40−50%; (b) $Na[BAr_4]$, C_6H_5F, 20 °C, 10 min, 70−80%.

Our initial synthetic steps sought to exploit the reactions of (monomeric) dialkylaminoboranes H_2BNR_2 (**1a**/**1b**: R = ^{i}Pr/Cy) with an electron rich Ir(I) precursor with a proven track record in B−H bond activation,[12] in this case $Ir(PMe_3)_3Cl(coe)$ (Scheme 2). This strategy reflects the facts that (i) *amino*borylene complexes are typically more robust target molecules than related aryl substituted systems, (such as the BMes complex reported by Alcaraz and Sabo-Etienne);[9,13] and (ii) the reactivity of amine/aminoboranes with group 9 metals is also of interest in the formation of BN polymers.[3,14]

In the event, such chemistry proceeds smoothly to generate the corresponding hydridoiridium(hydridoboryl) complexes

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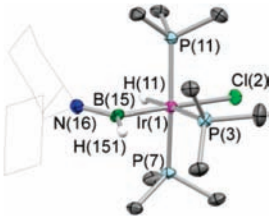


Figure 1. Molecular structure of **2b** in the solid state. H atoms [except H(11) and H(151)] omitted and Cy groups shown in wireframe format for clarity; thermal ellipsoids: 45% probability level. Key bond lengths (Å) and angles (°): Ir(1)−B(15) 2.074(4), B(15)−N(16) 1.401(5), Ir(1)−B(15)−N(16) 132.0(3), P(3)−Ir(1)−P(7) 96.8(1), P(3)−Ir(1)−P(11) 95.4(1), P(7)−Ir(1)−P(11) 167.0(1).

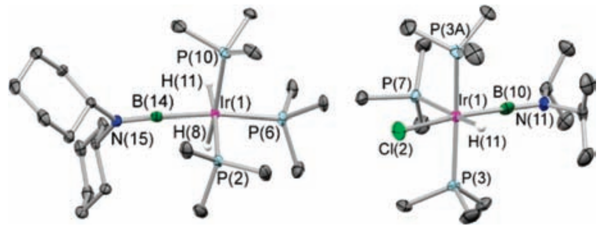
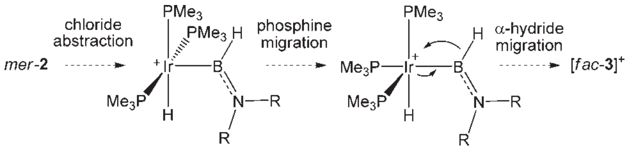


Figure 2. Molecular structures of [*fac*-**3b**]$^+$ (left) and [*mer*-**4a**]$^+$ (right) in the solid state. H atoms (except those attached to iridium) and counterions omitted for clarity; thermal ellipsoids: 45% probability level. Key bond lengths (Å) and angles (°): (for [*fac*-**3b**]$^+$) Ir(1)−B(14) 1.939(5), B(14)−N(15) 1.348(6), Ir(1)−P(2) 2.326(1), Ir(1)−P(6) 2.362(1), Ir(1)−P(10) 2.333(1), Ir(1)−B(14)−N(15) 175.9(4), P(2)−Ir(1)−P(6) 94.4(5), P(2)−Ir(1)−P(10) 101.4(1), P(6)−Ir(1)−P(10) 98.6(1); (for [*mer*-**4a**]$^+$) Ir(1)−B(10) 1.897(5), B(10)−N(11) 1.346(6), Ir(1)−B(10)−N(11) 177.2(3).

Scheme 3



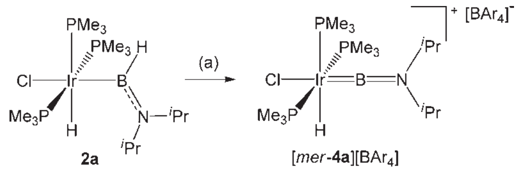
$Ir(PMe_3)_3(H)Cl\{B(H)NR_2\}$ (**2a**/**2b**) in reasonable (40−50%) isolated yield. **2a**/**2b** have been characterized by standard spectroscopic and analytical methods and (for **2b**) by X-ray crystallography. While, at a general level, B−H oxidative addition processes are well precedented, such chemistry represents the first explicit demonstration of such a process for an aminodihydroborane.[15] As such, systems of the type H_2BNR_2, which have been proposed as key intermediates in BN polymer formation, are shown explicitly to be susceptible to BH activation chemistry. Moreover, in the case of **2b**, the resulting amino(hydrido)boryl complex represents a rare structurally characterized primary boryl system.[7,8]

Spectroscopically, the formation of **2b**, for example, is signaled by the appearance of a broad resonance at $\delta_B = 43$ ppm (cf. 35 ppm for **1b**), by a doublet of triplets IrH resonance at $\delta_H = -8.73$ ppm ($^2J_{HP,trans} = 140.7$ Hz, $^2J_{HP,cis} = 21.3$ Hz), and by a broad BH signal at $\delta_H = 7.38$ ppm, which sharpens on ^{11}B decoupling. The presence of a planar $[Ir(PMe_3)_3H]$ unit is further implied by the $^{31}P\{^1H\}$ NMR data [doublet (int. 2), triplet (int. 1), $^2J_{PP} = 22$ Hz] and is confirmed crystallographically (Figure 1). The meridional arrangement of the PMe_3 ligands and mutually *cis* arrangement of the boryl and hydride ligands are as expected based on related chemistry reported for the oxidative addition of HBcat, and the Ir−B distance [2.074(4) Å] is also consistent with those of related compounds.[12a] The presence of boron-bound H(151) is revealed in the crystallographic difference map, and is further signaled by a (bent) IrBN unit featuring a M−B−N angle [132.0(3)°] and B−N distance [1.401(5) Å] similar to complexes containing the $B(Cl)NR_2$ ligand [e.g., 130.4(2)° and 1.396(4) Å, respectively, for $CpFe(CO)_2\{B(Cl)NCy_2\}$].[16]

To complete the conversion of **1a**/**1b** to a borylene dihydride complex, a boron-to-metal hydride migration process is necessitated. While such a transformation is hitherto without literature precedent, an generic prerequisite for α-substituent transfer is the availability of a free coordination site at the metal center.[5,17] In the case of **2a**/**2b**, this could potentially be achieved by abstraction of the ancillary chloride ligand, for example, using $Na[BAr_4]$ [$Ar = Ar^f = C_6H_3(CF_3)_2$-3,5 or $Ar^{Cl} = C_6H_3Cl_2$-3,5]. However, given the mutually *trans* disposition of the hydridoboryl and chloride substituents determined for **2b**, the generation of a vacant site *cis* to the boryl ligand would require additional migration of either a phosphine or a hydride co-ligand. In the event, the cationic complexes generated in the reactions with $Na[BAr_4]$, that is, [*fac*-$Ir(PMe_3)_3(H)_2(BNR_2)$]$^+$ ([**3a**/**3b**]$^+$), feature a facial arrangement of the three PMe_3 ligands (Scheme 3 and Figure 2), consistent with phosphine migration. Spectroscopically [**3a**/**3b**]$^+$ both give rise to two ^{31}P resonances (with relative intensities 2:1), the latter signal being significantly broadened due to the presence of a *trans* borylene ligand. Moreover, the ^1H hydride region in each case displays a second-order signal (for 2H) at δ_H ca. −12 ppm, consistent with the AA'MXX' spin system arising from the planar [*cis*-$Ir(PMe_3)_2(H)_2$] unit and additional coupling to the third unique PMe_3 ligand. Additionally, for [**3a**]$^+$, only one set of ^iPr resonances is observed (cf. two sets for boryl precursor **2a**), consistent with the formation of a two-coordinate boron center and rapid rotation about the Ir−B−N axis on the NMR time scale (as observed for $[Cp'Fe(CO)_2(BN^iPr_2)]^+$).[16] Finally, the ^{11}B NMR chemical shifts ($\delta_B = 77$ ppm for both **3a**/**3b**) are also as expected for a two-coordinate borylene ligand [cf. $\delta_B = 67$ ppm for $Cp^*Ir(CO)\{BN(SiMe_3)_2\}$],[18] and appear to rule out any appreciable interaction between the boron center and the hydride co-ligands (cf. $\delta_B = 38$ ppm for $[Ir(IMes)(IMes')(H)(BNCy_2)]^+$, featuring an Ir−H−B interaction and an Ir−B−N angle of 167.2(6)°).[14c]

The structure of [**3b**][BAr^{Cl}_4] in the solid state has been determined crystallographically (Figure 2),[19] and is consistent (i) with a *fac* arrangement of the three PMe_3 ligands [the three P−Ir−P angles spanning 94.4(5)−101.4(1)°]; and (ii) with the presence of a linear two-coordinate borylene ligand [∠Ir−B−N = 175.9(4)°] within a pseudo-octahedral metal geometry. The iridium−boron distance [1.939(5) Å] is as expected for an Ir═B double bond [cf. 1.892(3) Å for $Cp^*Ir(CO)\{BN(SiMe_3)_2\}$],[18] being ca. 6.5% shorter than the corresponding single bond present in **2b**. Both of the iridium-bound hydride ligands could be located crystallographically, and their presence *trans* to P(2) and P(10) is additionally consistent (i) with the 'saw-horse' geometry defined by the remaining heavy atom skeleton; (ii) with the measured ^1H NMR spectrum; and (iii) with the positive ion ESI-MS data (obtained for a fluorobenzene solution), which reveals a molecular ion with accurate mass and isotopic composition consistent with the formulation $[Ir(PMe_3)_3(H)_2(BNCy_2)]^+$.

Scheme 4. Synthesis of [*mer*-4a]$^+$ from 2a Using an External Hydride Abstraction Agent^a



^{a} Key reagents and conditions: (a) $[Ph_3C][B(C_5F_5)_4]$, C_6H_5F, 10 min, 20 °C, ca. 70%.

The viability of 1,2-hydride migration from boron to iridium has thus been demonstrated explicitly by examining the reactivity of an isolated primary boryl complex. This chemistry is without precedent for group 13 ligand systems in general. Moreover, while it offers obvious parallels with textbook chemistry leading to carbenes/silylenes,[5,6] it is remarkable in offering α-substituent migration from a Lewis *acidic* site as a route to a two-coordinate ligand system. By means of comparison, 14-electron systems of the type $[L_2Pt\{B(hal)X\}]^+$ are known to be resistant to the analogous B-to-M α-halide migration.[17,20]

If the mechanistic proposal (Scheme 3) is correct, it should also be possible to generate a related borylene complex from **2a**/**2b** without skeletal rearrangement by employing an *external* hydride sink. Accordingly, the reaction of **2a** with $[Ph_3C][B(C_6F_5)_4]$ generates the cationic borylene system [*mer*-Ir(PMe$_3$)$_3$(H)Cl(BN^{i}Pr$_2$)]$^+$ ([*mer*-**4a**]$^+$) as the $[B(C_6F_5)_4]^-$ salt via hydride abstraction (Scheme 4).[21] The spectroscopic signatures for the *mer*-[Ir(PMe$_3$)$_3$(H)Cl] fragment closely resemble those for the analogous unit in **2a** (i.e., a doublet of triplets for the IrH signal; distinct doublet and triplet ^{31}P resonances with $^2J_{PP}$ = 21 Hz), while the ^{11}B and ^{1}H NMR signals for the boron-containing fragment (δ_B = 71 ppm; one set of ^{i}Pr signals) are consistent with the formation of a terminal borylene ligand.[16,18] These inferences were confirmed crystallographically (Figure 2) with the molecular structure revealing a *mer*-[Ir(PMe$_3$)$_3$] unit and a linear Ir—B—N framework [177.2(4)°]. The Ir—B distance [1.890(5) Å] is somewhat shorter than that found in [**3b**]$^+$ [1.939(5) Å], due to the weaker *trans* influence of the Cl$^-$ substituent retained in the *trans* position in [**4a**]$^+$ (cf. the *trans* PMe$_3$ ligand in [**3b**]$^+$).

Further studies targeting wider application of this chemistry, and the incorporation of direct borane to borylene conversion steps into catalytic processes will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Characterizing data for **2a**/**b**, [*fac*-**3a**/**b**][BAr$^f_4$] and [*mer*-**4a**][B(C$_6$F$_5$)$_4$]; CIFs for all X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) [**4a**]$^+$ is also a minor product from the (slow) reaction of [**3a**]$^+$ with CH_2Cl_2; [*mer*-**4a**][$\text{BAr}^{Cl}{}_4$] is isolated in low yield on prolonged exposure of [*fac*-**3a**][$\text{BAr}^{Cl}{}_4$] to CH_2Cl_2.