

B–H Activation

International Edition: DOI: 10.1002/anie.201511448
German Edition: DOI: 10.1002/ange.201511448Capturing HBCy₂: Using N,O-Chelated Complexes of Rhodium(I) and Iridium(I) for Chemoselective Hydroboration

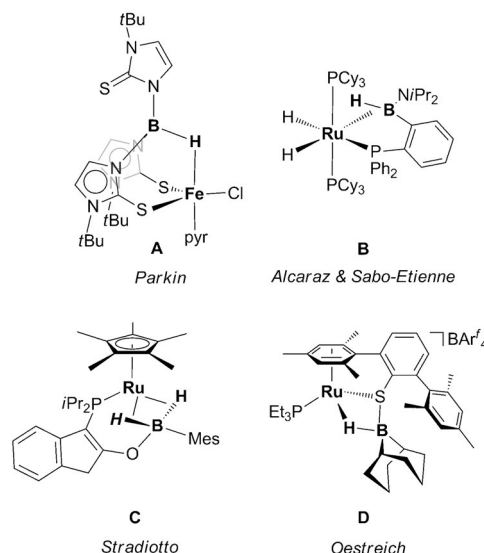
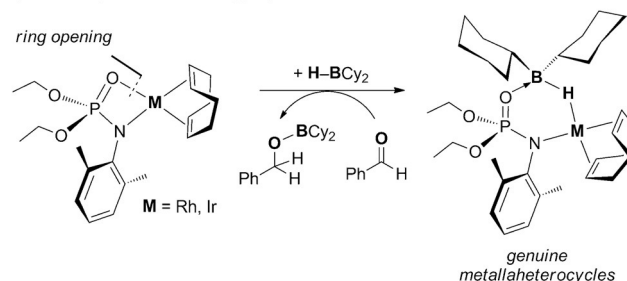
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Abstract: 1,3-N,O-chelated complexes of Rh^I and Ir^I cooperatively and reversibly stabilized the B–H bond of HBCy₂ to afford six-membered metallaheterocycles (M = Rh (**7**) or Ir (**8**)) having a δ-[M]...H–B agostic interaction. Treatment of these Shimoi-type borane adducts **7** or **8** with both an aldehyde and an alkene resulted in chemoselective aldehyde hydroboration and reformation of the 1,3-N,O-chelated starting material. The observed chemoselectivity is inverted from that of free HBCy₂, which is selective for alkene hydroboration.

The synthesis and characterization of transition-metal species having a [M]...H–B interaction (σ or agostic) has played an integral role in aiding our understanding of metal-catalyzed B–H activation processes.^[1] In this context, both base-stabilized (Shimoi-type)^[2] and base-free^[3] [M]...H–B bonding motifs have been reported. Most commonly, such interactions are encouraged by ligand design—such is the case for complexes of bis- and trispyrazolylborate and related ligands, for example (Scheme 1, type **A**).^[4] By consequence, ligand design enforces proximity between a B–H bond and metal center to encourage an interaction. For example, several classes of polyfunctional borane-containing ligands have been independently disclosed by Parkin and co-workers (Scheme 1: **A**)^[4] and Alcaraz, Sabo-Etienne, and co-workers (Scheme 1: **B**).^[5] In these studies, however, preincorporation of a B–H-containing entity was required to access the corresponding agostic [M]...H–B complex. Further, for such complexes, transfer of the boron fragment to an unsaturated organic substrate is not possible, as it is covalently tethered into the ligand framework. Alternative routes to such complexes have also been exploited with exogenous borane sources: Stradiotto and co-workers (Scheme 1: **C**)^[2c] and Oestreich and co-workers (Scheme 1: **D**)^[2d] have shown that [Ru]–X (X = O or S) bonds undergo B–H bond capture of H₂BMes (Mes = 2,4,6-trimethylphenyl) and 9-BBN (BBN = borabicyclononane), respectively.

Given our previous studies with amidate^[6] and phosphoramidate^[7] complexes of Rh^I and Ir^{III}, we reasoned that access to such a [M]...H–B motif might be realized through capture of a free borane by a hemilabile κ²-N,O-chelated metal (M = Rh^I, Ir^I) complex. As a proof of principle, our attention first

a) Previous examples of [M]...H–B agostic complexes

b) This study: hemilabile HBCy₂ capture

Scheme 1. Examples of agostic [M]...H–B complexes.

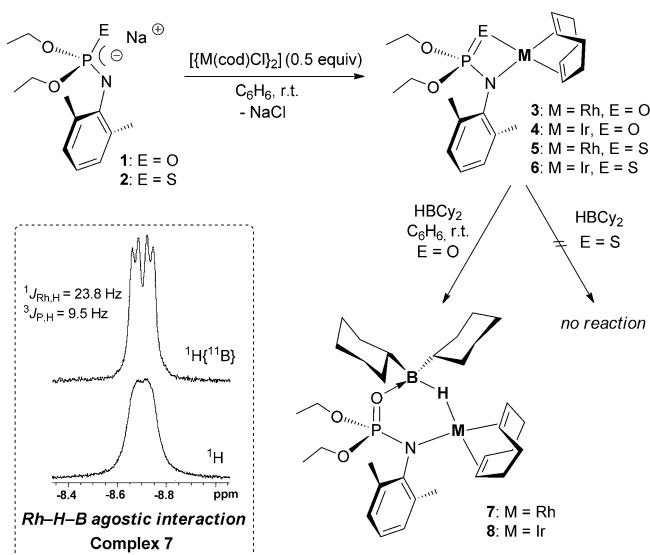
turned to the reactivity of dicyclohexylborane (HBCy₂). Amongst hindered boron hydride sources, HBCy₂ has been shown to serve as a chemoselective reagent for the hydroboration of alkenes in the presence of an aldehyde or ketone.^[8] We were particularly interested in exploring the hydroboration reactivity of HBCy₂ whilst bonded to a late-transition-metal center, with the possibility of eliciting a change in hydroboration chemoselectivity as a consequence of metal–ligand cooperation.^[9] More importantly, as a whole, this study highlights the potential inclination of 1,3-LX-type^[10] ligands, for example, amidates, amidinates, guanidates, carboxylates, and triflates, to cooperate in E–H functionalization with a late transition metal.

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Herein, we show that the resulting HBCy_2 Shimoi complexes, having a $\delta\text{-B-H}$ agostic interaction, allow for complete reversal of HBCy_2 chemoselectivity preference, thus enabling aldehyde hydroboration in the presence of an alkene, while regenerating the $\kappa^2\text{-N,O}$ -chelated starting material. To our knowledge, hemilability and joint metal-ligand cooperativity have not been used previously for both the capture and subsequent chemoselective functionalization of a borane molecule.

The reaction of $[\{\text{M}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ (0.5 equiv; $\text{M} = \text{Rh}$ or Ir ; $\text{cod} = 1,5\text{-cyclooctadiene}$) and the sodiated phosphoramidate ligand salt $\text{Na}[\text{Xyl}(\text{N})\text{P}(\text{E})(\text{OEt})_2]$ (**1**; 1 equiv)^[11] at room temperature provided the $\kappa^2\text{-N,O}$ -coordinated complexes $[\text{M}\{\kappa^2\text{-N,O-Xyl}(\text{N})\text{P}(\text{O})(\text{OEt})_2\}(\eta^4\text{-cod})]$ ($\text{M} = \text{Rh}$ (**3**), Ir (**4**)) in 80 and 65 % yield, respectively (Scheme 2). The related phosphoramidothiolate complexes **5** and **6** were also prepared by an analogous strategy in 92 and 81 % yield. These complexes were characterized by multinuclear NMR spectroscopy, mass spectrometry, X-ray diffraction, and elemental analysis. Characteristic of metallacycle formation, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a single downfield-shifted resonance, for example, at $\delta = 13.0$ ppm ($^2J_{\text{Rh,P}} = 9.7$ Hz) for **3** and $\delta = 27.7$ ppm for **4**.



Scheme 2. Synthesis of the $\delta\text{-B-H}$ agostic complexes $[\text{M}\{\kappa^2\text{-N,H-Xyl}(\text{N})\text{P}(\text{OHBCy}_2)(\text{OEt})_2\}(\eta^4\text{-cod})]$ ($\text{M} = \text{Rh}$ (**7**), Ir (**8**)), and ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra for **7** (400 MHz, C_6D_6 , 298 K).

Having established a simple protocol for access to such LX-chelated^[10] metal complexes, we next focused our attention on the capture of dicyclohexylborane (HBCy_2) by complexes **3–6**. Treatment of a solution of **3** or **4** in C_6D_6 with HBCy_2 (1 equiv) resulted in the clean formation of the four-coordinate complexes $[\text{M}\{\kappa^2\text{-N,H-Xyl}(\text{N})\text{P}(\text{OHBCy}_2)(\text{OEt})_2\}(\eta^4\text{-cod})]$ ($\text{M} = \text{Rh}$ (**7**) or Ir (**8**)), which feature six-membered chelating LX amidoborane moieties formed from hemilabile ring-opening of a $[\text{M}]\text{-O}$ bond (Scheme 2). Complexes **7** and **8** are rare examples of six-membered genuine metallaheterocycles,^[12] consisting of six unique atoms (M , H ,

B , O , P , and N , where $\text{M} = \text{Rh}$ or Ir) oriented in a near-coplanar fashion. Evidence for a significant $[\text{M}]\cdots\text{H-B}$ bonding interaction comes from a combination of solution- and solid-state techniques. In the solution state, complexes **7** and **8** show characteristic ^1H NMR resonances, in accordance with their proposed structure. Strikingly, broad upfield resonances, which sharpen on ^{11}B decoupling, at $\delta = -8.70$ ppm (dd, $^1J_{\text{Rh,H}} = 23.8$ Hz, $^3J_{\text{P,H}} = 9.5$ Hz) for **7** and $\delta = -4.89$ ppm (d, $^3J_{\text{P,H}} = 7.7$ Hz) for **8**, corroborate interaction of the metal with the B-H entity.^[13] Ring expansion of the parent four-membered metallacycles **3** and **4** is also evidenced by a change in the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift to $\delta = 22.1$ ppm ($^2J_{\text{Rh,P}} = 4.5$ Hz; $\Delta\delta = 9.1$) for **7** and $\delta = 34.3$ ppm ($\Delta\delta = 6.6$) for **8**. $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy additionally provided one broad signal attributable to an oxygen-stabilized sp^3 -hybridized boron atom at $\delta = 13.0$ ppm ($\omega_{1/2} = 573$ Hz; $\Delta\delta = -46.2$; $\delta = 59.2$ for free HBCy_2)^[14] for **7** and $\delta = 14.6$ ppm ($\omega_{1/2} = 670$ Hz; $\Delta\delta = -44.6$) for **8**. An EI MS experiment also showed a signal at m/z 645 (**7**) and 735 (**8**) with the correct isotope pattern, though $[\text{M-HBCy}_2]^+$ was identified as the base peak, thus highlighting the weak degree of stabilization provided to the borane by the phosphoramidate fragment in the gas phase. Unexpectedly, treatment of the sulfur analogues **5** or **6** with HBCy_2 (1 equiv) provided no reaction, as observable by ^1H NMR spectroscopy, thus highlighting the importance of the $\text{P=O}\cdots\text{B}$ interaction.

The solid-state structure of complexes **7** and **8** was established by single-crystal X-ray diffraction (complex **8**: Figure 1). Both complexes feature four-coordinate d^8 metal centers, supported by two olefinic groups of a 1,5-cod moiety, the phosphoramidate nitrogen atom [$\text{Rh}(1)\text{-N}(1)$ 2.118(1) and $\text{Ir}(1)\text{-N}(1)$ 2.097(2) Å], and a bridging hydride of the stabilized HBCy_2 unit [$\text{Rh}(1)\text{-H}(1)$ 1.70(2) and $\text{Ir}(1)\text{-H}(1)$ 1.63(2) Å]. It is notable that these crystals were of sufficient quality to allow for the location and free refinement of $\text{H}(1)$. As expected for a $\text{P=O}\cdots\text{B}$ interaction, the $\text{B}(1)\text{-O}(1)$ distance [1.529(2) and 1.519(2) Å for **7** and **8**] is similar to the dative B-O bond length found for a family of *ortho*-phosphine-oxide-substituted boranes (1.52–1.62 Å)^[15] and yet longer than the average B-O distance observed for four-coordinate borates [$d_{\text{avg}}(\text{B}(1)\text{-O}(1))$ (1.481 ± 0.041) Å].^[16] With regard to the OPN ligand framework, $\text{O}(1)\text{-P}(1)$ and $\text{N}(1)\text{-P}(1)$ bond lengths of 1.519(1)/1.592(1) Å for **7** and 1.515(1)/1.602(1) Å for **8** suggest P=O and P-N bonds.

To better determine the location of the bridging hydride [$\text{H}(1)$], density functional theory (DFT) calculations^[17] were performed on complexes **7** and **8**. The computed geometries are in good agreement with those observed crystallographically (see the Supporting Information), including the experimental and computed $\text{B}(1)\text{-H}(1)$ and $\text{M}(1)\text{-H}(1)$ bond lengths: 1.330/1.31(2) and 1.723/1.70(2) Å for **7** and 1.355/1.41(2) and 1.733/1.63(2) Å for **8**. The computed IR stretching frequency for the $[\text{M}]\cdots\text{H-B}$ entity is also in excellent agreement with that found experimentally: 2048/2043 cm^{-1} for **7** and 2034/2030 cm^{-1} for **8**.^[18]

In our hands, clear orange solutions of **7** or **8** in C_6D_6 became black on standing after 1 week. Analysis by ^1H NMR spectroscopy corroborated decomposition of the parent species and formation of the tetrameric metal-bridged

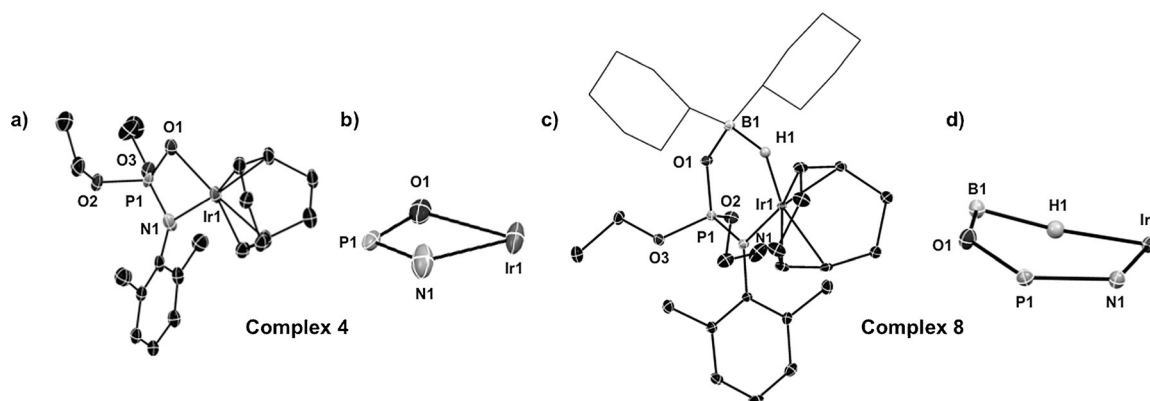
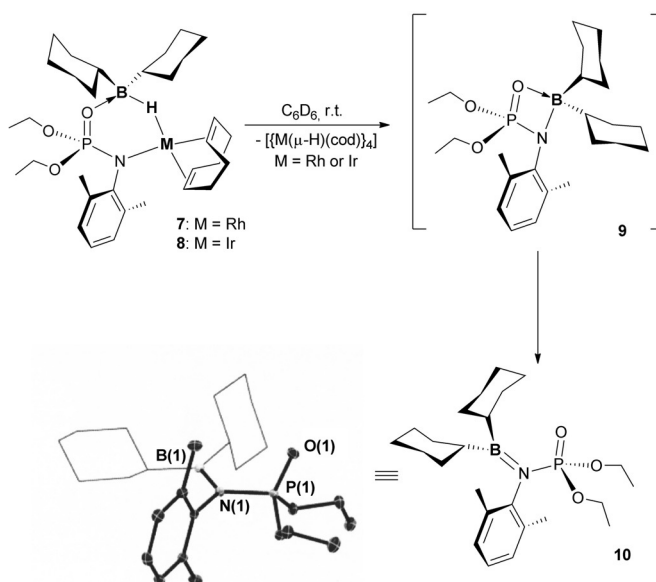


Figure 1. ORTEP depictions of the solid-state molecular structure of a) $[\text{Ir}\{\kappa^2\text{-N,O-Xyl}(\text{N})\text{P}(\text{O})(\text{OEt})_2\}(\eta^4\text{-cod})]$ (**4**) and b) the four-membered iridacycle of **4** (displacement ellipsoids are shown at 50% probability, hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: $\text{Ir}(1)\text{--N}(1)$ 2.050(6), $\text{Ir}(1)\text{--O}(1)$ 2.158(5), $\text{P}(1)\text{--O}(1)$ 1.508(6), $\text{P}(1)\text{--N}(1)$ 1.586(7); $\text{N}(1)\text{--Ir}(1)\text{--O}(1)$ 70.3(2), $\text{O}(1)\text{--P}(1)\text{--N}(1)$ 103.1(3)), c) $[\text{Ir}\{\kappa^2\text{-N,H-Xyl}(\text{N})\text{P}(\text{OHBCy}_2)(\text{OEt})_2\}(\eta^4\text{-cod})]$ (**8**) and d) the six-membered iridacycle of **8** (displacement ellipsoids are shown at 50% probability, hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: $\text{Ir}(1)\text{--N}(1)$ 2.097(2), $\text{Ir}(1)\text{--H}(1)$ 1.63(2), $\text{B}(1)\text{--H}(1)$ 1.41(2), $\text{B}(1)\text{--O}(1)$ 1.519(2), $\text{P}(1)\text{--O}(1)$ 1.515(1), $\text{P}(1)\text{--N}(1)$ 1.602(1); $\text{B}(1)\text{--H}(1)\text{--Ir}(1)$ 147(2)).

hydrides $[\text{M}(\mu\text{-H}(\text{cod}))_4]$ ($\text{M} = \text{Rh}$: $\delta = -11.83$ ppm; Ir : $\delta = -2.89$ ppm)^[19] as well as a single boron-containing product: $[\kappa^1\text{-N-Cy}_2\text{B}=\text{N}(\text{Xyl})\text{P}(\text{O})(\text{OEt})_2]$ (**10**). Though often implicated in boron chemistry, controlled examples of B–H activation at base-stabilized sp^3 -hybridized boron centers with clean reactivity are uncommon.^[20] We propose that complex **10** results from a 1,3-oxygen-to-nitrogen migration, presumably via a $\kappa^2\text{-N,O}$ intermediate **9**. Complex **10** can also be accessed independently by way of H_2 elimination by using HBCy_2 and protio phosphoramidate ligand (see the Supporting Information).^[21] In C_6D_6 , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **10** revealed a signal at $\delta = 5.93$ ppm consistent with a change in ligand coordination mode, whereas the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum showed a single broad signal at $\delta = 54.8$ ppm ($\omega_{1/2} = 751$ Hz). The structure of **10** was also confirmed by X-ray diffraction (Scheme 3) and features a three-coordinate boron atom bonded in a $\kappa^1\text{-N}$ fashion to the phosphoramidate ligand. The $\text{B}(1)\text{--N}(1)$ bond distance is short (1.449(2) Å), congruent with a $\text{B}=\text{N}$ bond, which is representative of donation from nitrogen to boron. Comparable distances have been observed in related aminoboranes.^[22] Although, as far as we are aware, there has been no previous example of such a 1,3-boron rearrangement, Yoder and co-workers have described analogous processes for the silicon atom of silyl-protected carboxamides.^[23]

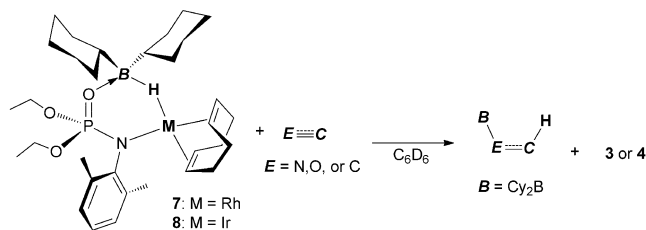
With the ultimate goal of controlling borane reactivity toward element–carbon multiple bonds, we next sought to evaluate the reactivity of complexes **7** and **8** (Table 1). Although late-transition-metal complexes bearing an agostic B–H interaction are known, only occasionally is systematic reactivity screening with element–carbon multiple bonds performed. A possible explanation lies in the inherent nature of some reported $[\text{M}] \cdots \text{H} \cdots \text{B}$ complexes, which, in contrast to the examples discussed herein, are unable to dissociate or participate in functionalization reactions.

Our studies began by the treatment of **7** or **8** with compounds containing unsaturated C–C bonds. With styrene and 1-octene, no boron transfer was observed by ^1H and



Scheme 3. Metal-mediated B–H activation to give the phosphoramido-borane **10**. An ORTEP depiction of the solid-state molecular structure of **10** (ellipsoids at 50% probability) is also shown.

$^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy (24 h, r.t.; complexes **7** and **8** also remained unchanged). By contrast, control experiments between these substrates and free HBCy_2 resulted in rapid anti-Markovnikov hydroboration (< 5 min, r.t.), thus indicating that joint metal–ligand stabilization of HBCy_2 results in a dramatic decrease in reactivity (see the Supporting Information for full characterization of hydroborated products). The treatment of **7** or **8** with phenylacetylene once again failed to produce the hydroboration product. Given the absence of a background reaction, we suggest that these experiments provide strong evidence that HBCy_2 does not readily dissociate from the $\kappa^2\text{-N,H}$ metal chelate, thus eliminating equilibria between free and bound borane. We

Table 1: Controlled HBCy₂ reactivity with complexes **7** and **8**.

Entry	Complex	Conditions	Substrate(s)	Product(s)	Conversion ^[a]
1 (R = Ph)	7 or 8	r.t., 24 h			n.r.
2 (R = nHex)	7 or 8	r.t., 24 h			n.r.
3	7 or 8	r.t., < 5 min			n.r.
4 (R = H)	7	r.t., 24 h			> 99 %
5 (R = H)	8	r.t., < 5 min			> 99 %
6 (R = CH ₃)	8	70 °C, 1 h			> 99 %
7	8	r.t., 24 h	N≡C-Ph		60 %
8	8	r.t., < 5 min			> 99 %:0 %
9	HBCy ₂	r.t., < 5 min			66 %:33 %
10	(EtO) ₃ P-BHCy ₂	r.t., 24 h	+	+	64 %:36 %
11	8	r.t., < 5 min			> 99 %:0 %
12	HBCy ₂	r.t., < 5 min	+	+	2 %:98 %
13	8	r.t., 1 h			> 99 %:0 %
14	HBCy ₂	r.t., < 5 min	+	+	0 %:> 99 %

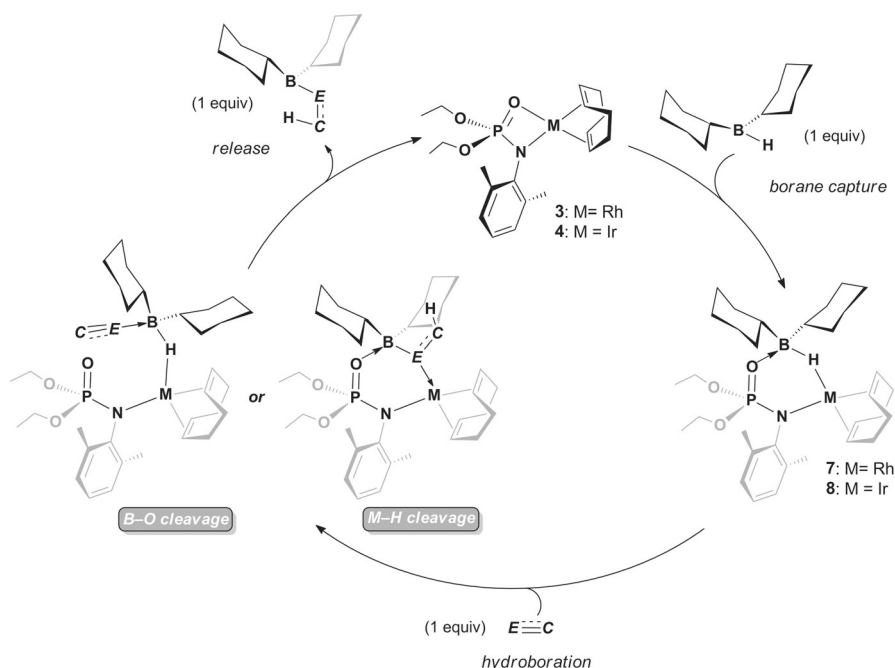
[a] Conversion was determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. n.r. = no reaction.

next turned our attention to the reactions of **7** and **8** with carbonyl compounds. Satisfyingly, the reaction of these metal chelates with benzaldehyde (24 h, r.t.) gave the reduced fragment PhCH₂OBCy₂ (24 h for **7**; < 5 min for **8**) along with reformation of the parent complex **3** or **4**, as evidenced by diagnostic ³¹P{¹H} NMR spectroscopy. Given the decreased activity of complex **7**, only the Ir congener **8** was employed in the following trials. The reaction of **8** with acetophenone (24 h, r.t.) showed no conversion by NMR spectroscopy, but heating to 70 °C for 1 h gave > 95 % conversion to the borinic acid, PhCH(CH₃)OBCy₂. Finally, the scope of borane release was extended to nitriles: when complex **8** was treated with benzonitrile, the monohydroboration product was prepared with 60 % conversion (Table 1, entry 7).

To verify that carbonyl substrates do not provide free HBCy₂ in situ, we treated complex **8** with 1 equivalent each of benzaldehyde and styrene. Immediate reactivity was observed to give the aldehyde hydroboration product exclusively (Table 1, entry 8). These results differ from those of the reaction with free HBCy₂ (Table 1, entry 9). In particular, Kabalka and co-workers found that HBCy₂ can be employed as a chemoselective boron hydride source for the hydroboration of alkyl-substituted olefins (e.g. 1-octene) or alkynes in the presence of carbonyl groups.^[8,24] To ensure that the

observed change in chemoselectivity is derived from both Lewis base and metal coordination, we evaluated the hydroboration reactivity of the Lewis acid/base adduct, (EtO)₃P...BHCy₂,^[25,26] which under identical conditions showed the same selectivity as free HBCy₂ (Table 1, entry 10). This control experiment confirms that Lewis base stabilization alone cannot be solely responsible for this change in selectivity, thus confirming that the ligand and the metal are acting cooperatively. To better highlight this hydroboration chemoselectivity, when we treated complex **8** with a solution of benzaldehyde and 1-octene (1:1) in C₆D₆, the product of aldehyde hydroboration was formed selectively (Table 1, entry 11). For a reaction of decanal and 1-octene with complex **8**, a similar inversion in chemoselectivity was observed (Table 1, entry 13).

Mechanistically, these results are consistent with one of two pathways involving displacement of the [M]...H-B or P=O...B interaction through presumed carbonyl or nitrile coordination (Scheme 4). Both routes would allow for favorable transfer of the borane entity, product release, and closure of the chelate to reform complexes **3** and **4**. A similar pathway has been proposed by Lu and Williams, who used a bis(pyrazolyl)borate Ru^{II} scaffold for nitrile reduction, although substoichiometric Na[BH₄] was required for borate



Scheme 4. Proposed stepwise synthetic cycle for borane functionalization.

regeneration.^[27] Notably, given the high degree of background reactivity with HBCy_2 , catalytic turnover with this system is not possible.

In summary, phosphoramidate-ligated complexes of Rh^{I} and Ir^{I} exhibited metal–ligand cooperativity in the presence of HBCy_2 , thus leading to base-stabilized $\delta\text{-B-H}$ agostic complexes. These reagents offer complementarity in their reactivity with carbonyl groups (as compared with free HBCy_2), thus enabling chemoselective carbonyl hydroboration in the presence of an alkene. This study establishes a proof of concept for the utility of ligand–metal cooperation for tuning the chemoselectivity of a B–H bond.

Acknowledgements

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Keywords: boranes · hemilability · hydroboration · iridium · rhodium

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