

Ruthenium, Rhodium, and Iridium $Bis(\sigma-B-H)$ Diisopropylaminoborane Complexes[†]

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The coordination chemistry of diisopropylaminoborane $H_2B-N'Pr_2$ with valence isoelectronic metal fragments to form, essentially isostructural, $[MH_2(\eta^2:\eta^2-H_2B-N'Pr_2)(PCy_3)_2]^{n+}$ (M = Ru, n = 0; Rh and Ir, n = 1) has been explored by a combination of X-ray crystallography, NMR spectroscopy, and computational techniques. In the solid state and solution the aminoborane interacts with the metal centers through one four-center four-electron interaction, forming bis(σ -B-H) complexes. The structural data point to tighter interactions between both the Ru and Ir congeners compared to the Rh with significantly shorter $M \cdot \cdot B$ distances in the first two. These tighter interactions are mirrored in the spectroscopic data, with the Ru and Ir complexes showing more deshielded ¹¹B chemical shifts and ¹H M-H-B resonances that are more shielded than observed for the rhodium complex. Analysis of the bonding between metal and borane using the NBO approach is in very good agreement with the variations in the geometrical and spectroscopic parameters. There is overall a stronger interaction between the borane and the metal fragment for neutral Ru compared to cationic Rh, with cationic Ir in an intermediate situation.

Introduction

Organometallic compounds involving two identical σ -E–H (E = H, Si, B, C) bonds coordinated to one metal center are scarce.¹ For bis(σ -dihydrogen) complexes, [RuH₂(η^2 -H₂)₂-(PCy₃)₂] (**1**, Scheme 1) is the complex that has so far been shown to exhibit the most versatile properties,² and isoelectronic cationic Rh and Ir analogues also exist, although their chemistry is less well developed.³ With regard to boranes (R₂BH),⁴ bis(σ -borane) complexes have, until recently, been limited to titanium, as illustrated by the isolation of Cp₂Ti(η^2 -H–BCat)₂ **2** reported by Hartwig et al in 1996 (Cat = 1,2-O₂C₆H₄).⁵ Recently, some of us have reported compounds of general formulation [L_n-Ru(H₂BR)], with [RuH₂(η^2 : η^2 -H₂B–Mes)(PCy₃)₂] **3** (Mes =

1,3,5-Me₃C₆H₂) being the first example⁶ of a new family⁷ of stable complexes (Scheme 1) in which mesitylborane coordinates to the metal through two geminal σ -B-H bonds, leading to a four-center four-electron bonding mode. This compound was synthesized in high yield by addition of H₂BMes to [RuH₂(η^2 -H₂)₂(PCy₃)₂].

Related complexes incorporating aminoboranes, H₂B-NR₂, have very recently been reported. While studying the metalinduced dehydrogenation of amine-borane adducts, such as H₃B-NHMe₂, Alcaraz and Sabo-Etienne have reported the synthesis of the bis(σ -B–H) monomeric aminoborane ruthenium complexes $[\operatorname{RuH}_2(\eta^2:\eta^2-H_2B-\operatorname{NH}_n\operatorname{Me}_{2-n})(\operatorname{PCy}_3)_2]$ (4) (n = 0-2) by reaction of complex 1 with H₃B-NH_nMe_{3-n} (n = 1-3) under stoichiometric conditions.⁸ Independently, Weller and co-workers have reported Shimoi-type⁹ amine-borane complexes of rhodium by reaction of H₃B-NHMe₂ with $[Rh(P'Bu_3)_2][BAr^F_4]$, with the bis(σ -B-H) dimethylaminoborane rhodium complex $[RhH_2(\eta^2:\eta^2:H_2B-NMe_2)(P^iBu_3)_2]$ - $[BAr^{F}_{4}]$ { $Ar^{F} = C_{6}H_{3}(CF_{3})_{2}$ }, isoelectronic to 4, spectroscopically characterized as the final organometallic product from the catalytic dehydrogenation of H₃B-NHMe₂ using these systems.¹⁰ Replacing phosphines by N-heterocyclic carbenes,

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Scheme 1. Representative $Bis(\sigma-dihydrogen)$ and $Bis(\sigma-borane)$ Metal Complexes



Scheme 2. Syntheses of $[RuH_2(\eta^2:\eta^2-H_2B-N'P_2)(PCy_3)_2]$ (7) and $[MH_2(\eta^2:\eta^2-H_2B-N'P_2)(PCy_3)_2][BAr^F_4]$ (M = Rh (8), Ir (9))



Aldridge and co-workers have isolated the corresponding $bis(\sigma$ -B-H) diisopropylaminoborane cationic rhodium and iridium complexes $[MH_2(\eta^2:\eta^2-H_2B-N^iPr_2)(IMes)_2][BAr^F_4]$ (M = Rh, Ir, IMes = 2,5-Mes₂-N₂C₃H₂) upon dehydrogenation of diisopropylamine-borane.¹¹

In this paper, we now present a straightforward route to $bis(\sigma$ -B-H) diisopropylaminoborane complexes of Ru, Rh, and Ir tricyclohexylphosphine dihydrides, by addition of preformed H₂B-NⁱPr₂ to precursor bis(dihydrogen) complexes. This leads to a unique set of isoelectronic complexes that differ only in the nature of the metal center and charge. This presents a valuable opportunity to evaluate the impact of the metal on the B-H bond coordination and activation, which we do by a combination of spectroscopic, solid-state, and computational techniques. Such studies on isoelectronic and isostructural systems involving boranes are rare.¹²

Results and Discussion

Complexes $[\operatorname{RuH}_2(\eta^{2:}\eta^{2}+\operatorname{H}_2B-\operatorname{N}^{i}\operatorname{Pr}_2)(\operatorname{PCy}_3)_2]$ (7), $[\operatorname{RhH}_2-(\eta^{2:}\eta^{2}+\operatorname{H}_2B-\operatorname{N}^{i}\operatorname{Pr}_2)(\operatorname{PCy}_3)_2][\operatorname{BAr}^F_4]$ (8), and $[\operatorname{IrH}_2(\eta^{2:}\eta^{2}+\operatorname{H}_2B-\operatorname{N}^{i}\operatorname{Pr}_2)(\operatorname{PCy}_3)_2][\operatorname{BAr}^F_4]$ (9) were synthesized by reaction of a slight excess of $\operatorname{H}_2B-\operatorname{N}^{i}\operatorname{Pr}_2$ with the corresponding bis(dihydrogen) metal complexes 1, $[\operatorname{RhH}_2(\eta^{2-}+\operatorname{H}_2)_2(\operatorname{PCy}_3)_2][\operatorname{BAr}^F_4]$ (5), and $[\operatorname{IrH}_2(\eta^{2-}+\operatorname{H}_2)_2(\operatorname{PCy}_3)_2][\operatorname{BAr}^F_4]$ (6). The latter group 9 complexes were generated *in situ* under dihydrogen pressure (Scheme 2).^{3a} The resulting bis(σ -B-H) diisopropylaminoborane complexes were fully characterized by NMR spectroscopic properties of the new complexes are similar to the data reported for $[\operatorname{RuH}_2(\eta^{2:}\eta^{2-}+\operatorname{H}_2B-\operatorname{NR}^{1}\operatorname{R}^2)(\operatorname{PCy}_3)_2](\operatorname{R}^1, \operatorname{R}^2 = H, \operatorname{Me}),^8$ $[\operatorname{MH}_2(\eta^{2:}\eta^{2-}+\operatorname{H}_2B-\operatorname{NR}^{1}\operatorname{R}^2)(\operatorname{PCy}_3)_2](\operatorname{R}^1, \operatorname{R}^2 = H, \operatorname{Me}),^8$ $[\operatorname{MH}_2(\eta^{2:}\eta^{2-}+\operatorname{H}_2B-\operatorname{NMe}_2)(\operatorname{P}^{i}\operatorname{H}_3)_2][\operatorname{BAr}^{F_4}]$.¹⁰ The ¹H NMR spectra demonstrate a $\operatorname{M}-H-\operatorname{B}$ interaction by the observation of a quadrupolar broadened relative integral 2 H signal (7: δ -6.91; 8: δ -2.30; 9: δ -6.58), and the dihydride by a sharper,

more shielded, resonance (a triplet for 7: $\delta - 12.37$; an apparent doublet of doublets of triplets for 8: $\delta - 15.40$; an apparent quartet for 9: $\delta - 15.5$) in a 2:2 relative integration ratio. For all compounds, the lower-field signal sharpens upon ¹¹B decoupling. For 8 and 9 selective decoupling of the M-*H*-B resonance collapses the corresponding hydride signal to a doublet of triplets for 8($J_{\text{HRh}} = 22$, $J_{\text{HP}} = 11$ Hz) and a triplet for 9($J_{\text{HP}} = 14$ Hz), demonstrating coupling (presumably *trans*) between M-*H* and M-*H*-B. The ¹¹H{³¹P} spectra reveal the remaining coupling for 8($J_{\text{HH}} = 15$ Hz) and 9($J_{\text{HH}} = 11$ Hz). In the ¹¹B{¹H} spectra of 7–9, a broad signal is observed slightly downfield shifted or similar to free diisopropylaminoborane (δ 35): 7, δ 45; 8, δ 34 (very broad); 9, δ 46.

The solid-state structures of the new complexes are shown in Figure 1 (Table 1). In the three complexes 7-9, the metal atom is in a pseudo-octahedral environment, with the tricyclohexylphosphines in axial positions and the hydrides mutually cis. The X-ray structure of 7 was determined at 110 K, and the quality of the data enables the secure location of the hydrogen atoms (the hydrides H0a and H0b and the boron-attached hydrogen atoms H1a and H1b) in the equatorial plane around the ruthenium. For the rhodium, 8, and iridium, 9, complexes the diisopropylaminoborane is disordered over two closely related sites (distributed 71.9%/28.1% for 8 and 77.5%/22.5% for 9). This disorder is slight canting of the H₂B-NⁱPr₂ ligand, i.e., M-B-N $174.9(8)^{\circ}$ (major) and $171(3)^{\circ}$ for 9, albeit with a rather large error associated with the minor component. Nevertheless the hydride ligands (M-H) in 8 and 9 were located in the final difference maps and freely refined, although the M-H-B hydrogen atoms were placed in calculated positions. In solution a $C_{2\nu}$ -symmetric structure is indicated for all three complexes. The M-B distance (see Table 1) is shorter than the sum of the covalent radii in 7 but rather similar in the case of 8 and 9 ($\sum r_{cov}(M-B) = 2.12$ Å (Ru), 2.10 Å (Ir), and 2.09 Å (Rh)).¹³ Similar $M \cdots B$ separations have been recently reported for $[MH_2(\eta^2:\eta^2-H_2B-N'Pr_2)-(IMes)_2][BAr^F_4]$ (M = Rh, Ir).¹¹ There is a correlation between the M-BH₂ distances and the observed ¹¹B and ¹H M-H-B chemical shifts in solution. The shortest distances (Ru, 7, and Ir, 9) are associated with the most deshielded ¹¹B resonances compared to free ligand and highest-field bridging hydride chemical shifts in the ¹H NMR spectra, suggesting stronger interactions between metal and borane, while complex 8 has the longest M-B distance and a ¹¹B chemical shift that is very similar to free ligand and a corresponding lower-field Rh-H-B resonance.

In order to gain more information on the borane coordination, DFT(B3PW91) geometry optimizations were carried out on the actual experimental systems, yielding 7a, 8a, and 9a for Ru, Rh, and Ir, respectively. Selected geometrical parameters are given in Table 1, and the agreement with the experimental values is very good. The calculations allow more secure location of the two hydrides H0a and H0b and of the two bridging hydrogen atoms H1a and H1b. From the calculated bond distances, there is a clear trend in the interaction between the borane $H_2B-N'Pr_2$ and the transition metal fragment $MH_2(PCy_3)_2$ (M = Ru, Rh⁺, Ir⁺). The M–B, M···H1a, and M···H1b bond distances increase along the series Ru < Ir < Rh and, concomitantly, the B-H1a and B-H1b bond distances decrease. This would tend to indicate that there is overall a stronger interaction between the borane and the metal fragment for neutral Ru compared to cationic Rh, with cationic Ir in an intermediate situation.

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Figure 1. X-ray structure of $[\text{RuH}_2(\eta^2:\eta^2:\text{H}_2\text{B}-\text{N}^i\text{Pr}_2)(\text{PCy}_3)_2]$ (7) and $[\text{MH}_2(\eta^2:\eta^2:\text{H}_2\text{B}-\text{N}^i\text{Pr}_2)(\text{PCy}_3)_2][\text{BAr}^F_4]$ (M = Rh (8), Ir (9)). The hydrogen atoms not associated with the metal center, the $[\text{BAr}^F_4]^-$ anions, and minor disordered components are omitted for clarity.

Table 1. Selected Geometrical Parameters for the Experimental (7-9) and Calculated Structures (7a-9a) and the Computed Structure of ${}^{i}Pr_{2}NBH_{2}$

	Ru		Rh^{a}		Ir ^a		
	7	7a	8	8a	9	9a	ⁱ Pr ₂ NBH ₂
M-B	1.980(3)	2.003	$2.140(13), [2.10(4)]^{b}$	2.159	$2.022(14), [2.10(5)]^c$	2.088	
M-P1	2.3051(5)	2.351	2.3335(8)	2.389	2.3380(9)	2.398	
M-P2	2.3141(5)	2.337	2.3285(7)	2.378	2.3316(8)	2.388	
B-N	1.393(3)	1.412	$1.357(13), [1.40(4)]^{b}$	1.383	$1.380(14), [1.34(5)]^c$	1.384	1.393
M-H1b	1.72(2)	1.820	d	1.895	d	1.848	
M-H1a	1.68(3)	1.805	d	1.874	d	1.832	
M-H0a	1.54(2)	1.601	1.46(3)	1.528	1.47(3)	1.571	
M-H0b	1.53(2)	1.607	1.48(3)	1.532	1.44(3)	1.576	
B-H1b	1.22(2)	1.298	d	1.252	d	1.289	1.195
B-H1a	1.25(3)	1.306	d	1.258	d	1.296	1.195
P1-M-P2	152.71(2)	152.1	156.24(3)	155.5	156.54(3)	156.3	
M-B-N	177.83(19)	178.8	$173.9(7), [170(3)]^{b}$	178.2	$174.9(8), [171(3)]^c$	178.3	

^a Numbers in brackets are for the disordered component. ^b 28.1%. ^c 22.5%. ^d Hydrogens not located.

In the framework of the Dewar-Chatt-Duncanson model, the bonding of borane to a d⁶ transition metal fragment can be described as the result of the synergistic σ donation from the $\sigma(B-H)$ density to the metal and π -backdonation from an occupied nonbonding d orbital on the metal into an accepting orbital on borane. A generic molecular orbital (MO) diagram for the interaction between the pseudo- $C_{2\nu}$ d⁶ fragment M(H)₂(PR₃)₂ (M = Ru, Rh⁺, Ir⁺) and the borane H_2BR is shown in Figure 2. The σ -donation from the B-H bonds is operative from the two highest occupied MOs of the borane ligand. In the particular case of borane, back-donation from the metal is mostly effective through donation from the d_{xz} lone pair on Ru to the vacant p AO on boron; the latter is the LUMO of the borane ligand (see Figure 2). In the present systems with aminoboranes, this scheme can be modified by considering that the empty p orbital on boron is now stabilized by donation from the nitrogen lone pair. This provides an associated higher-lying BN π^* orbital that can accept electron density from an appropriate, filled, metal orbital.

To shed more light on the electronic structure of the complexes **7a**, **8a**, and **9a**, a NBO analysis was carried out. In the Lewis-like description of the electronic structure used in the NBO analysis, the electronic transfers introduced in



Figure 2. Schematic MO diagram of the interaction between the d⁶ fragment $M(H)_2(PR_3)_2$ (M = Ru, Rh⁺, Ir⁺) and the borane H₂BR. The phosphine ligands pointing along the *z* axis have been omitted for clarity.

the above MO diagram are best described as departure from a strictly localized picture.¹⁴ The σ -donation from the B–H bond to the metal is effective through an interaction between the occupied σ (B–H) bond and the vacant σ^* (M–H) bond in *trans* position. The magnitude of the interaction is best

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Table 2. Composition of the NLMO $\sigma_{nlmo}(B-H)$ and LP_{nlmo}(M) Resulting from the Delocalization of the Parent NBO ($\sigma(BH)$ and LP(M)) into the Accepting NBO $\sigma^*(MH)$ and $\pi^*(BN)$, Respectively

	7a: M = Ru	$8a: M = Rh^+$	9a: $M = Ir^+$
$\sigma_{nlmo}(B-H)$	$0.934 \sigma(BH) + 0.319 \sigma^{*}(MH)$	$0.955 \sigma(BH) + 0.266 \sigma^{*}(MH)$	$\begin{array}{l} 0.937 \ \sigma(\mathrm{BH}) + 0.318 \ \sigma^{*}(\mathrm{MH}) \\ 0.964 \ \mathrm{LP}(\mathrm{M}) + 0.223 \ \pi^{*}(\mathrm{BN}) \end{array}$
LP _{nlmo} (M)	$0.938 LP(M) + 0.297 \pi^{*}(BN)$	$0.976 LP(M) + 0.176 \pi^{*}(BN)$	

illustrated by the relative weight of the two components in the resulting natural localized molecular orbital (NLMO, Table 2). Due to the cationic nature of the rhodium complex **8a**, the valence orbitals of the $MH_2(PCy_3)_2$ fragment are lower in energy for $M = Rh^+$ than for M = Ru. Consequently larger σ -donation from the borane should have been observed, contrary to the results presented in Table 2, where the composition of the $\sigma(BH)$ NLMO clearly indicates that σ -donation is larger with Ru. However the orbitals of the cationic rhodium complex are also more contracted than those of the neutral ruthenium complex, and this is detrimental to an effective overlap between the interacting orbitals in the σ -donation process. A third-row transition metal such as iridium has more diffuse valence orbitals, and the composition of the $\sigma(BH)$ NLMO is very similar to that of the neutral ruthenium analogue.

The Lewis structure for the three complexes **7a**, **8a**, and **9a** features a B=N π -bond as the result of the interaction of the nitrogen lone pair with the empty p AO on boron. Nevertheless, back-donation in the $\pi^*(BN)$ orbital from the metal nonbonding d_{xz} AO, acting as a lone pair (LP), is still possible. Table 2 gives the expression of the corresponding NLMO, and it is clear that back-donation varies according to Ru > Ir⁺ > Rh⁺. The lower energy of the valence orbitals for the cationic fragment results in less efficient interaction with the vacant $\pi^*(BN)$ orbital. This reduced interaction is partly compensated for by the more diffuse character of the orbital in the case of iridium, yielding a situation intermediate between Ru and Rh. In the case of Rh, both factors, lower energy and more contracted orbitals, do not favor efficient back-donation.

The results from the NBO analysis are in very good agreement with the variations in the geometrical parameters observed for the calculated structures. The close values for the B-H bond distances in 7a and 9a (Table 1) agree with the description of the σ -donation as being of the same magnitude in the two complexes. The significantly lower values for 8a indicate a less efficient σ -donation from borane. Nevertheless there is transfer of electron density from B-H in all three cases, as illustrated by the lengthening of the B-H bond with respect to the value for the free borane. The trends in metal to borane back-donation discussed above are nicely illustrated by the variation of the M-B bond distance: Ru-B = 2.003 Å, Ir-B = 2.088 Å, and Rh-B = 2.159 Å. This analysis also correlates with the observed NMR data: less efficient σ -donation from the B–H bond to the metal $\sigma^*(MH)$ orbital in 8 results in a lower-field M-H-B chemical shift, whereas the M-H-B chemical shifts in 7 and 9 are essentially the same and at higher field. Likewise the ¹¹B chemical shift for the three isoelectronic complexes generally tracks the involvement of the $\pi^*(BN)$ orbital in $\mathbf{M} \cdots \mathbf{B}$ bonding: a smaller contribution leads to a smaller chemical shift change from free aminoborane.

Experimental Section

General Procedures. Manipulations were done using standard Schlenk and glovebox techniques (O_2 level < 1 ppm; Ar as inert gas). Solvents were dried using an MBraun solvent purification system. Deuterated solvents were prepared through freeze-pump-thaw

procedures and stored under argon over 4 Å molecular sieves or over potassium for d_8 -THF. C₆H₅F and 1,2-C₆H₄F₂ were dried over CaH₂, vacuum distilled, and stored over 3 Å molecular sieves. H₂BN[/]Pr₂,¹⁵ [RuH₂(η^2 -H₂)₂(PCy₃)₂],¹⁶ [RhH₂(η^2 -H₂)₂(PCy₃)₂]-[BAr^F₄],^{3a} and [IrH₂(η^2 -H₂)₂(PCy₃)₂][BAr^F₄] (see Supporting Information) were prepared by literature methods. NMR spectra were recorded on a Bruker 400 MHz Avance, a Bruker 300 MHz Avance, or a Varian Unity Plus 500 MHz spectrometer at room temperature, unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. Microanalyses were performed at the Laboratoire de Chimie de Coordination (7) or at the London Metropolitan University (**8**, **9**).

Synthesis of [**RuH**₂(η^2 : η^2 -**H**₂**B**N^{*i*}**Pr**₂)(**PCy**₃)₂] (7). At room temperature, H₂BN^{*i*}**Pr**₂ (74 μ L) was added to a toluene solution (1 mL) of RuH₂(η^2 -H₂)₂(**PCy**₃)₂ (0.0315 g, 0.0471 mmol) and the solution stirred for 15 h. Evaporation of the solvent and washing of the resulting solid with cold pentane afforded pure complex 7 as a beige solid (0.024 g, 66%). Crystals suitable for X-ray analysis were grown from a saturated pentane solution held at $-37 \,^{\circ}$ C. ³¹P{¹H} NMR (C₆D₆, 121.49 MHz): 77.8 (s). ¹H NMR (C₆D₆, 300.13 MHz): 3.55 (sept, 2H, ³J_{HH} = 6.6 Hz, 2H, CH ⁱPr), 1.16–2.38 (m, 66H, Cy), 1.35 (d, ³J_{HH} = 6.6 Hz, 12H, CH₃ ⁱPr), -6.91 (br, 2H, RuH₂B), -12.37 (t, ²J_{HP}=25.0 Hz, RuH₂). ¹³C{¹H} NMR (C₆D₆, 100.61 MHz): 47.70 (s, CH ⁱPr), 38.97, 30.79, 28.14, and 17.14 (Cy), 23.86, (s, CH₃ ⁱPr). ¹¹B{¹H} NMR (C₆D₆, 128.38 MHz): 45 (br). Anal. Calcd for C₄₂H₈₄BNP₂Ru (776.952 g·mol⁻¹): C, 64.93; H, 10.90; N, 1.80. Found: C, 65.20; H, 10.88; N, 1.61.

10.90; N, 1.80. Found: C, 65.20; H, 10.88; N, 1.61. **Synthesis of [RhH₂(\eta^2:\eta^2-H_2BN'Pr_2)(PCy₃)₂][B**Ar^F₄] (8). A yellow solution of [RhH₂($\eta^2:\eta^2-H_2)_2$ (PCy₃)₂][**B**Ar^F₄] (0.093 mmol) in 1,2-C₆H₄F₂ (2 mL) was prepared *in situ* by hydrogenation (4 atm, 20 min) of [Rh(C₇H₈)(PCy₃)₂][**B**Ar^F₄] (0.150 g, 0.093 mmol), as previously described.^{3a} This solution was placed under an Ar atmosphere, and H₂**B**N'Pr₂ (50 μ L) was added. The resulting pale yellow solution was layered with pentane and held at 5 °C to afford the product as colorless crystals. Yield: 0.085 g (56%). ¹H NMR (C₆H₃F, 500 MHz): 8.37 (br, 8H, [BAr^F₄]⁻), 7.68 (s, 4H, [BAr^F₄]⁻), 3.45 (sept, ³J_{HH} = 6.7 Hz, 2H, CH 'Pr), 1.11–1.91 (m, 66H, Cy), 1.20 (d, ³J_{HH} = 6.6 Hz, 12H, CH₃ 'Pr), -2.30 (br, RhH₂B), -15.40 (apparent ddt, 2H, RhH₂, ¹J_{HR}h = 22, ²J_{HH} = 15, ²J_{HP} = 11 Hz, from selective decoupling experiments). ¹³C{¹H} NMR (*d*₈-THF, 126 MHz): 163.0 (q, ¹J_{BC} = 49, [BAr^F₄]⁻), 135.8 (s, [BAr^F₄]⁻), 130.2 (qq, ²J_{FC} = 32 Hz, ³J_{BC} = 3 Hz, [BAr^F₄]⁻), 125.7 (q, ¹J_{FC} = 272 Hz, [BAr^F₄]⁻), 118.3 (br, [BAr^F₄]⁻), 52.4 (s, CH 'Pr), 37.6, 31.5, 28.2, and 27.2 (Cy), 24.7 (s, CH₃ 'Pr). ¹¹B{¹H} NMR (C₆H₅F, 160 MHz): 34 (vbr, 1B, RhH₂B), -5.8 (s, 1B, [BAr^F₄]⁻). ³¹P{¹H} NMR (C₆H₅F, 202 MHz): 59.5 (d, ¹J_{RhP} = 103 Hz). Anal. Calcd for C₇₄H₉₆B₂F₂₄NP₂Rh (1642.0 g·mol⁻¹): C, 54.13; H, 5.89; N, 0.85. Found: C, 54.22; H, 5.95; N, 0.83. ESI-MS (1,2-C₆H₄F₂, 60 °C, 4.5 kV) positive ion: *m/z* 778.50 [M]⁺ (calcd 778.52).

Synthesis of $[IrH_2(\eta^2:\eta^2-H_2BN^iPr_2)(PCy_3)_2][BAr^F_4]$ (9). Complex 9 was produced in a similar manner to 8 starting from $[IrH_2(\eta^2-H_2)_2(PCy_3)_2][BAr^F_4]$, which was generated *in situ* from addition of H₂ to $[IrH\{P(\eta^2-C_6H_9)(C_6H_{11})_2\}\{P(\eta^3-C_6H_8)-(C_6H_{11})_2\}][BAr^F_4]$ (0.030 g, 0.020 mmol) (see Supporting Information for synthesis and solid-state structure). ¹H NMR (500 MHz, C₆H₅F): 8.35 (br, 8H, $[BAr^F_4]^-$), 7.67 (s, 4H, $[BAr^F_4]^-$), 3.46 (sept, ³J_{HH} = 7 Hz, 2H, CH ⁱPr), 2.05–0.95 (m, Cy), 1.21 (d, ³J_{HH} = 7 Hz, CH₃ ⁱPr), -6.58 (br, 2H, IrH₂B), -15.15 (dt,

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2H, IrH₂, ${}^{2}J_{HP} = 14 \text{ Hz}$, ${}^{2}J_{HH} = 11 \text{ Hz}$, from selective decoupling experiments). ${}^{11}B{}^{1}H{}$ NMR (160 MHz, C₆H₅F): 46.3 (br, BH₂), -5.9 (s, [BAr^F₄]⁻). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, C₆H₅F): 34.20 (s). Yield: 0.021 g (65%). Anal. Calcd for $C_{74}H_{96}B_2F_{24}$ -NP₂Ir (1731.3 g·mol⁻¹): C, 51.3; H, 5.59; N, 0.81. Found: C, 51.4; H, 5.75; N, 0.83. ESI-MS (C₆H₅F, 60 °C, 4.5 kV) positive ion: m/z 868.62 [M]⁺ (calcd 868.58).

X-ray Structural Analysis for 7. Data were collected at low temperature (110 K) on an Xcalibur Oxford Diffraction diffractometer using graphite-monochromated Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$ and equipped with an Oxford Instruments cooler device. The final unit cell parameters were obtained by means of a least-squares refinement. The structure was solved by direct methods using SIR92¹⁷ and refined by means of leastsquares procedures on F^2 with the aid of the program SHEL-XL97¹⁸ included in the software package WinGX version 1.63.¹⁹ The atomic scattering factors were taken from International Tables for X-ray Crystallography.²⁰ All hydrogen atoms were geometrically placed, except for the atoms H0a, H0b, H1a, and H1b, which were located by Fourier differences and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecule was performed with the program ORTEP32²¹ with 30% probability displacement ellipsoids for non-hydrogen atoms.

X-ray Structural Analysis for 8 and 9. Data were collected on an Enraf Nonius Kappa CCD diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a lowtemperature device [150(2) K];²² data were collected using COLLECT; and reduction and cell refinement was performed using DENZO/SCALEPACK.²³ The structures were solved by direct methods using SIR2004²⁴ and refined with full-matrix least-squares on F^2 using SHELXL-97.²⁵ All non-hydrogen atoms were refined anisotropically. The hydride ligands H0A and H0A were located on the Fourier difference map and freely refined; their isotropic displacement parameters were fixed to ride on the parent atoms. H1a and H1b were placed in calculated positions, with the B-H distance free to refine (AFIX 94, the restraint with identical B-H distances was applied) despite the presence of geometrically sensible Fourier peaks. All other

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hydrogen atoms were placed in calculated positions using the riding model. Disorder of the aminoborane ligand was treated by modeling it over two sites and restraining the geometry of the alkyl substituents. Disorder of the phosphine ligands was treated by modeling the appropriate substituents over two sites and restraining their geometry. Rotational disorder of the CF₃ groups of the anion in 8 and 9 was treated by modeling the fluorine atoms over two sites and restraining their geometry. Restraints to thermal parameters were applied where necessary in order to maintain sensible values. Graphical representations of the structures were made using ORTEP3.²¹

Computational Details. All the calculations have been per-formed with the Gaussian03 package²⁶ at the B3PW91 level.²⁷ The ruthenium, rhodium, and iridium atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group (16 valence electrons) and the associated basis set,²⁸ augmented by an f polarization function.²⁹ The phosphorus atom was represented by RECP from the Stuttgart group and the associated basis set,³⁰ augmented by a d polarization function ($\alpha = 0.387$).³¹ The remaining atoms (C, H, B, N) were represented by a 6-31G(d,p) basis set.³² Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima on the potential energy surface. Natural bonding orbital analysis³³ was performed with NBO version 5.0 implemented in Gaussian03.

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Supporting Information Available: Tables, text, and CIF files giving addition structural information for 7, 8, and 9. Synthesis, characterization data, and solid-state structure of [IrH{ $P(\eta^2-C_6H_9)$ - $(C_6H_{11})_2$ { $P(\eta^3-C_6H_8)(C_6H_{11})_2$ }][BAr^F₄], a full citation for ref 26, and coordinates for the calculated structures. This material is available free of charge via the Internet at http://pubs/acs/org.

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