7-Azaindol-7-ylborate: A Novel Bidentate N^BH$_3$ Chelating Ligand

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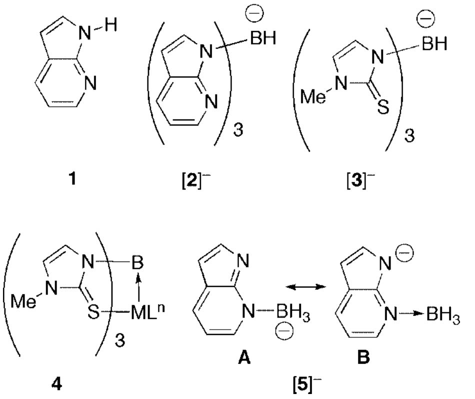
Summary: 7-Azaindole (H-azain) reacts with sodium borohydride ($NaBH_4$) to yield the sodium salt of the novel 7-azaindol-7-ylborate anion (7-azain-7)BH_3^-, two rhodium derivatives of which reveal distinct coordination modes — $[Rh\{\kappa^2N,H\text{-}H_3B(7\text{-azain-}7)\}(CO)(PPh_3)_2]$ and $[Rh\{\kappa^3N,H,H'\text{-}H_3B(7\text{-azain-}7)\}(PPh_3)_2]$—thereby demonstrating how the variable denticity of the ligand may accommodate the varying electronic requirements of the metal center.

7-Azaindole (**1**; Chart 1), first reported by Perkin in 1912[1] and first synthesized in 1945,[2] has in more recent times begun to attract attention due to the luminescence properties displayed by its derivatives; e.g., when it is complexed to zinc.[3] Various boron derivatives of 7-azaindole have also been synthesized,[4] including the scorpionate-type pro-ligand salt K[HB(7-azaindol-1-yl)$_3$] (K[**2**]).[5]

Chart 1



We have recently been concerned with the synthesis of "metallaboratranes" via the reactions of Na[HB(mt)$_3$] (Na[**3**]; mt = methimazolyl) with various organotransition-metal substrates.[6] Metallaboratranes feature a metal—boron dative bond which is housed within a tricyclo[3.3.3.0] or bicyclo[3.3.0] cage structure (**4**). The key requirement for metallaboratrane formation, via our approach, would seem to be that a suitable hydroborate ligand is capable of undergoing B—H activation to generate the M→B bond via a three-center, two-electron B—H—M interaction. This process appears to be geometrically favored when the borate also includes either two or three substituents capable of forming three-atom bridges between boron and the transition metal, hence the conspicuous absence of such transformations among the wealth of poly(pyrazolyl)borate chemistry.[7] Given that the vast majority of metallaboratranes are thus based on cages with mercaptoimidazolyl buttresses,[8–10]we were eager to establish which other bridging groups might allow metallaboratrane construction. The isolation by Ikariya of a complex featuring a three-center, two-electron Ru—H—B interaction supported by two three-atom bridges from the reaction of K[**2**] with $[Ru_4(\mu\text{-}Cl)_4(\eta\text{-}C_5Me_5)_4]$[5b] appeared to demonstrate many of the features we have come to consider prerequisite for metallaboratrane formation. We have therefore begun to investigate the coordination and organometallic chemistry of poly(azaindolyl)borates and report herein (i) the isolation of the

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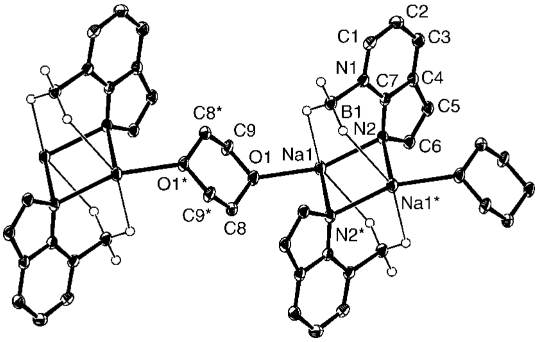
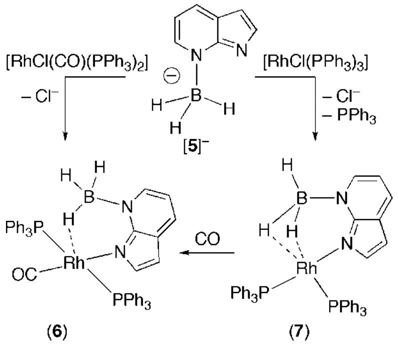


Figure 1. Molecular structure of Na[**5**]·0.5(dioxane) (ORTEP plot with 50% probability ellipsoids, C-bonded hydrogen atoms omitted for clarity). The atoms of the asymmetric unit are labeled, with selected symmetry-equivalent atoms indicated by asterisks.

Scheme 1



first mono(azaindolyl)borates and (ii) two structurally characterized rhodium complexes of the 7-azaindolylborate ligand with distinct coordination modes that may be interconverted.

Results and Discussion

We find that under relatively mild reaction conditions (dioxane, reflux) the sodium salt of the 7-azaindol-7-ylborate anion Na[(7-azain-7)BH_3] (Na[**5**]; Chart 1) may be prepared in good yield from Na[BH_4] and 7-azaindole. Under these conditions this salt is not stable and undergoes boron-substituent redistribution to give a mixture of the anions [BH_4]$^-$, [(7-azain-7)BH_3]$^-$, [(7-azain-1)$_2BH_2$]$^-$, [**2**]$^-$, and traces of [(7-azain-1)BH_3]$^-$.[11] The intermediate precipitation of the dioxane hemisolvate of Na[**5**], however, enabled us to both selectively isolate and structurally characterize (Figure 1) this novel pro-ligand.[11]

In the solid state Na[**5**]·0.5(dioxane) has two sodium ions that are coordinated by two of the (7-azain-7)BH_3 anions via one nitrogen and two hydrogen atoms each. These dimers together with one bridging dioxane molecule, the centroid of each being situated on crystallographic centers of inversion, form infinite chains. Furthermore, these chains are held together by BH···Na bridges (not depicted in Figure 1). Both the dioxane bridging and the interchain BH···Na bridges constitute important attractive forces within this crystal structure, presumably accounting for the ready isolation of the compound Na[**5**]·0.5(dioxane) in good yield.

The striking feature of the borate anion [**5**]$^-$ itself is the B−N bond to the "pyridyl" nitrogen atom in the 7-position of the heterocycle, which not only presents a more sterically demanding environment than does the indolyl nitrogen but also is the less basic of the two azaindolide nitrogen donors. To date, 7-azaindol-7-yl boron complexes have only been reported wherein the nitrogen atom in position 1 is either protonated[4d,12] or coordinated to a second boron atom.[4a] NMR experiments with Na[**5**] in d_3-acetonitrile indicate that only one borate species is present and that the (7-azain-7)BH_3 anion remains intact. The *ultimate* appending of the BH_3 group to the pyridyl nitrogen presumably reflects a thermodynamic preference for this site, given the conditions of formation (bp of 1,4-dioxane 100–102 °C).

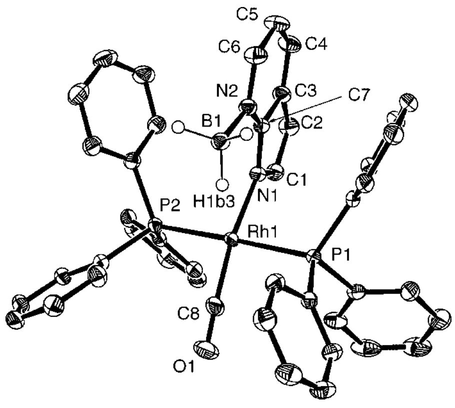


Figure 2. Molecular structure of **6** in the crystal form (ORTEP plot with 50% probability ellipsoids, C-bonded hydrogen atoms omitted for clarity).

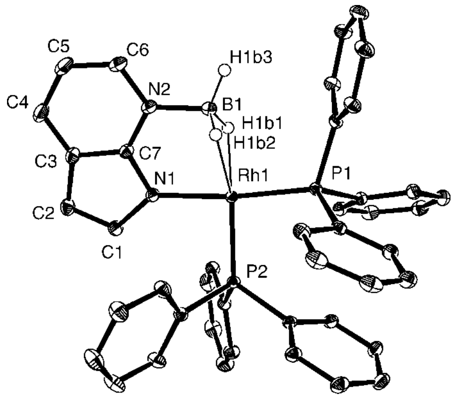


Figure 3. Molecular structure of **7** in a crystal of **7**·THF (ORTEP plot with 50% probability ellipsoids, C-bonded hydrogen atoms omitted for clarity).

The salt Na[**5**]·0.5(dioxane) displays reasonable solubility in THF and may be used as a reagent in this solvent. The rhodium(I) complexes [RhCl(CO)(PPh_3)$_2$][13] and [RhCl(PPh_3)$_3$][14] react with Na[**5**] via elimination of NaCl and, in the latter case, 1 equiv of PPh_3 with the formation of the complexes **6** and **7**, respectively (Scheme 1). This leads to two completely different coordination patterns for the (7-azain-7)BH_3 ligand in these two complexes, as can be seen from their molecular structures (Figures 2 and 3).

The positions of the B-bonded hydrogen atoms were located from electron density maps, and their coordinates and isotropic thermal parameters were refined without restraints. Notwithstanding the lower precision of X-ray diffractometrically determined hydrogen atom "positions" proximal to heavy atoms, the metrical parameters of the three B-bonded hydrogen atoms

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[11] Full details of these salts will be presented elsewhere. ^{11}B NMR (CD_3CN, 25 °C):−41.4 (p, $^1J_{BH}$ = 81 Hz, [BH_4]$^-$),−16.7 (q, $^1J_{HB}$ = 92 Hz, [**5**]$^-$),−11.9 (t br, $^1J_{HB}$ not resolved [(7-azain-1)$_2BH_2$]$^-$),−6.2 (d br, $^1J_{HB}$ not resolved [**2**]$^-$),−21.9 (q, $^1J_{HB}$ = 88 Hz, [(7-azain-1)BH_3]$^-$).

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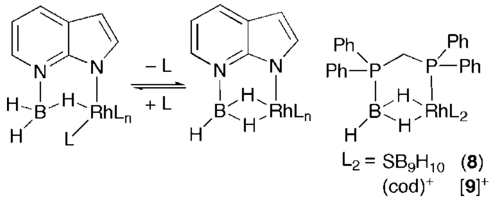
adhere to the requirements of a tetrahedral coordination sphere around the boron atom. This allows us to discuss, with some confidence, the coordination behavior of [**5**]$^-$ on the basis of the relative orientation of the B−H bonds.

In the complex **6**, the phosphine ligands are mutually trans-disposed with equivalent Rh−P distances (2.318(1), 2.319(1) Å). The indolyl nitrogen donor N1 (Rh1−N1 = 2.107(1) Å) is pseudo-trans to the carbonyl ligand (Rh1−C8 = 1.816(2) Å), with these two donors subtending an angle of 162.73(7)° (N1−Rh1−C8) so as to accommodate a three-center, two-electron B−H−Rh interaction. The bond lengths and angles associated with this interaction (Rh1−H1b3 = 2.05(2), B1−H1b3 = 1.13(2), Rh1−B1 = 3.083(2) Å; Rh1−H1b3−B1 = 151(2)°) may be compared with those reported recently for the complex [Rh(cod){$H_2B(mt)_2$}] (2.13, 1.14, 3.033 Å and 134.1°, respectively), which similarly features a B−H−Rh interaction within a six-membered rhodacycle.[15] We have previously suggested that large M−H−B angles might be taken to indicate a more electrostatic than covalent interaction[16] or what has in the field of M−H−C interactions been described as "pregostic".[17]

For presumably steric reasons, the carbonyl-free product **7** obtained from [$RhCl(PPh_3)_3$] does not involve the κ^2N,H-(7-azain-7)BH_3 coordination mode found in **6**, which would require coordination of three bulky phosphine ligands. Rather, a bis(phosphine) derivative is obtained in which the 12-valence-electron "$Rh(PPh_3)_2{}^+$" fragment satisfies its electronic requirements by including *two* B−H−Rh interactions. The two phosphine ligands in **7** occupy mutually cis sites (P−Rh−P = 95.01(1)°) with essentially identical Rh−P bond lengths (Rh1−P1 = 2.232(1), Rh1−P2 = 2.233(1) Å), despite disparate trans donors, which are however much shorter than those in **6** (reflected by an increase in $^1J_{RhP}$ from 130.5 Hz in **6** to 206.4 and 153.8 Hz in **7**). The disparity in the two $^1J_{RhP}$ values for **7** might appear at odds with the equal Rh−P bond length; however, steric factors contribute to the latter, while the electronic nature of the trans ligand contributes to the former. The Rh−N bond in **7** (2.106(1) Å) is, within precision limits, identical to that in **6** (2.107(1) Å), despite the different trans ligands (CO vs PPh_3) and borate coordination mode. The most notable feature of the structure of **7** is, however, the presence of two B−H−Rh interactions (freely refined distances Rh1−H1b1 = 1.88(2), Rh1−H1b2 = 2.13(2), B1−H1b1 = 1.19(2), B1−H1b2 = 1.16(2) Å), which result in a significantly shorter separation between rhodium and boron (**6**, 3.083(2) Å; **7**, 2.378(1) Å). The effect of coordination to rhodium (cf. Na) on the geometrical parameters of the (7-azain-7)BH_3 ligand backbone are collated in Table S1 (Supporting Information) and may be summarized as follows. No statistically significant (>6 esd) differences arise between Na[**5**] and [**6**]; however, adoption of the κ^3N,H,H' coordination mode in **7** is accompanied by a contraction (ca. 12 esd) of the B−N bond in addition to the bond between this nitrogen and the adjacent ring-junction carbon (ca. 10 esd). Two canonical forms (**A**, **B**) are depicted for [**5**]$^-$ in Chart 1 with the negative charge localized on either the indolyl nitrogen (**B**) or the BH_3 group (**A**). Coordination of a Lewis acidic metal to the nitrogen or BH_2 unit might be expected to increase the contribution of **B** or **A**, respectively, with the latter attended by a decrease in the N−B bond length.

Scheme 2



Although the (7-azain-7)BH_3 chelation in **6** and **7** is unprecedented, there are parallels with the behavior of the monoborane adduct of bis(diphenylphosphino)methane (dppm-BH_3). Thus, the complex [Rh(dppm-BH_3)(SB_9H_{10})] (**8**) was shown by Barton[18] to adopt a κ^3P,H,H' coordination mode akin to the κ^3N,H,H' mode adopted by **7**. Subsequent work by Weller has extended this coordination mode to further examples based on manganese, ruthenium, and rhodium,[19] including examples where addition of an extraneous ligand to the metal center is accompanied by rearrangement to the κ^2P,H coordination mode. Most closely related to **7** are the neutral complex **8** and the cation [**9**]$^+$ (Scheme 2), which each feature a Rh(μ-H)$_2$B moiety. Specifically, for [**9**]$^+$ in the solid state it was shown that, of the two alkene donors, that trans to the Rh(μ-H)$_2$B group displays shorter Rh−C bond lengths, in concert with the observed increase in $^1J_{RhP}$ for the phosphorus trans to the Rh(μ-H)$_2$B unit in **7**; i.e., the presumably weak binding of the BH_2 group is accommodated by stronger binding of the trans ligand. Notably, the Rh···B separation for **7** (2.378(1) Å) is somewhat longer than those found in **8** and [**9**]$^+$ (2.323(2) and 2.313(3) Å, respectively); however, in contrast to the case for the planar azaindolylborate ligand, the dppe-BH_3 ligand has greater conformational flexibility due to the tetrahedral coordination at phosphorus, carbon, and boron that allows nonplanar metallacycle formation.

The ^1H NMR data for **6** and **7** call for comment inasmuch as they appear consistent with the solid-state structure for **6** but not for **7**. Thus, in the case of **6**, two very broad B−H resonances are observed in the ^1H NMR spectrum corresponding to terminal B−H (2.8–3.6 ppm, 2 H) and bridging B−H−Rh (0–1 ppm, 1 H) groups. In the case of **7**, however, a single broad resonance is observed (ca. 0.6 ppm, 3 H), indicating that exchange between terminal and bridging hydride positions is rapid. This may perhaps be rationalized by considering the two ways in which site exchange might occur. The first would involve dissociation of one (for **6**) or both (for **7**) B−H−Rh interactions, thereby allowing free rotation about the N−BH_3 bond prior to recoordination. This is plausible for the conformationally more flexible Rh(dppm-BH_3) metallacycles but would require considerable distortion of the rigid azaindolyl coordination and might therefore be a comparatively high-energy process. The alternative mechanism would involve an equilibrium between κ^2N,H and κ^3N,H,H' coordination modes, which would be a low-energy process for **7** but would violate the 18-electron rule for **6** if the latter coordination mode were transiently adopted. We therefore attribute the static and fluxional natures of **6** and **7**, respectively, to the rigidity associated with the coplanar Rh−N−C−N−B arrangement.

The emergence of two distinct binding modes for the (7-azain-7)BH_3 ligand raises the question of their interconversion. It may be surmised that the κ^3N,H,H' binding mode in **7** is preferable to

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coordination of a third (bulky) phosphine, since **7** forms in the presence of excess PPh_3. In contrast, complex **6** shows no indication (^{31}P NMR) of either phosphine or carbonyl dissociation, the latter being bound strongly (ν(CO) 1948 cm^{-1}) to the electron-rich metal center. However, subjecting a solution of **7** to carbon monoxide (1 atm, C_6D_6) leads to quantitative and irreversible formation of **6**. Weller's report of the complex $[\mathbf{9}]^+$ included a demonstration of its operation as a precatalyst for the 1,4-addition of boronic acids to α,β-unsaturated ketones. As suggested,[19] cyclooctadiene dissociation is no doubt a key precatalyst activation step; however, given our demonstration of variable hapticity for the (7-azain-7)BH_3 ligand (and presumably dppm-BH_3), it is tempting to speculate that this hemilability may well be a feature that plays a role in catalyst activity and longevity.

Experimental Section

General Procedures. All manipulations, unless otherwise stated, were carried out under an atmosphere of dinitrogen using conventional Schlenk-line and glovebox techniques. Solvents (Et_2O, THF, hexane, 1,4-dioxane) were purified by distillation under a dry and prepurified nitrogen atmosphere from sodium/potassium alloy with benzophenone ketal as indicator. All common reagents were used as obtained from commercial suppliers without further purification. The complexes $[RhCl(CO)(PPh_3)_2]$[13] and $[RhCl(PPh_3)_3]$[14] were prepared according to the indicated published procedures. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian GEMINI, MERCURY, or INOVA 300 spectrometers. ^{11}B NMR chemical shifts are relative to external $BF_3 \cdot OEt_2$. Elemental microanalytical data were obtained from the Research School of Chemistry microanalytical service. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer.

Synthesis of Na[7-azain-7-BH$_3$]·0.5(dioxane) (Na[5]·0.5(dioxane)). Under an atmosphere of dry nitrogen, 7-azaindole (2.00 g, 16.9 mmol) and powdered $NaBH_4$ (1.50 g, 39.5 mmol) were stirred in dry 1,4-dioxane (10 mL) under reflux for 19 h. The resulting suspension was stored at room temperature overnight and then filtered and the solid extracted through a Schlenk filter with the dioxane of the filtrate until only $NaBH_4$ remained on the filter. The product, Na[**5**]·0.5(dioxane), precipitated from the hot extract upon cooling. The extract was stored at room temperature for 5 days and then filtered, and the filtrate was washed with 2 mL of hexane/dioxane (1:1) and 2 mL of hexane and dried under vacuum. Yield: 2.55 g (12.9 mmol, 76%), white crystalline powder. Anal. Found: C, 54.62; H, 5.96; N, 14.05. Calcd for $C_9H_{12}BN_2NaO$: C, 54.59; H, 6.11; N, 14.15. IR (Nujol): 2320 w ν(BH), 2285, 2250 $\nu_s/\nu_{as}(BH_2Na_2)$ cm^{-1}. NMR (CD_3CN, 25 °C): ^1H, δ_H 2.4 (q, 3 H, broad, BH_3), 6.40 (d, 1 H, $^3J_{HH} = 2.6$ Hz), 6.71 (dd, 1 H, $^3J_{HH} =$ 5.4, 7.5 Hz), 7.57 (d, 1 H, $^3J_{HH} = 2.6$ Hz), 7.93 (d, 1 H, $^3J_{HH} =$ 5.4 Hz), 7.95 (d, 1 H, $^3J_{HH} = 7.5$ Hz); $^{13}C\{^1H\}$, δ_C 99.3, 110.1, 127.6, 129.3, 137.4, 142.3, 153.8; ^{11}B, δ_B −16.8 (q, $^1J_{BH} = 95.2$ Hz). Crystal data for Na[**5**]·0.5(dioxane) (CCDC 658679): $C_9H_{12}BN_2NaO$, $M_w = 198.01$, $T = 100(2)$ K, monoclinic, $P2_1/c$ (No. 14), $a = 5.1979(2)$ Å, $b = 19.9137(10)$ Å, $c = 9.6023(5)$ Å, $\beta = 99.177(3)°$, $V = 981.21(8)$ Å^3, $Z = 4$, $D_c = 1.340$ Mg m^{-3}, μ(Mo Kα) $= 0.124$ mm^{-1}, 11 618 reflections (1721 unique, $R_{int} = 0.0879$), 136 parameters, GOF 1.095, R1 $= 0.0472$, wR2 $= 0.1160$ ($2\theta_{max} = 50°$, 1352 reflections with $I > 2\sigma(I)$), residual electron density (highest peak, deepest hole) 0.289, −0.306 e Å^{-3}.

Synthesis of [Rh(CO)(PPh$_3$)$_2$(κ^2*N,H*-7-azain-7-BH$_3$)] (6). In a Schlenk flask, Na[**5**]·0.5(dioxane) (0.15 g, 0.76 mmol) and $[RhCl(CO)(PPh_3)_2]$[13] (0.52 g, 0.75 mmol) were evacuated and then stirred under a N_2 atmosphere in THF (7 mL) under reflux for 20 min and cooled. After it was stirred for 4 h at room temperature, the yellow suspension was filtered through diatomaceous earth and washed with THF (3 mL). From the filtrate the solvent was removed under vacuum, and then THF (0.5 mL) and diethyl ether (2 mL) were added. Storage at room temperature overnight provided a small amount of yellow crystals of $[RhCl(CO)(PPh_3)_2]$, which were recovered. Further diethyl ether (3 mL) was added to the clear solution, which was then stored at 4 °C overnight to yield orange crystals of **6**. The solution was decanted and the crystals washed with diethyl ether (3 mL) and dried under vacuum. Yield: 0.19 g (0.24 mmol, 32%). Anal. Found: C, 67.13; H, 5.17; N, 3.60. Calcd for $C_{44}H_{38}BN_2OP_2Rh$: C, 67.20; H, 4.87; N, 3.56. IR (Nujol): 2387 w $\nu_s(BH_2)$, 2285 w $\nu_{as}(BH_2)$, 2158 ν(BHRh), 1948 ν(CO) cm^{-1}. NMR (C_6D_6, 25 °C, two isomers): ^1H, δ_H 0–1 (d br, 1 H $^1J_{RhH}$ and $^1J_{BH}$ not resolved), 2.8−3.6 (br, 2 H, BH_2), 6.03 (d, 1 H, $^3J_{HH} = 3.0$, azain), 6.20–6.30 (m), 6.57 (d, 1 H, $^3J_{HH} = 2.7$, azain), 6.88 (d, 1 H, $^3J_{HH} = 3.0$, azain), 6.90–7.10 (m, C_6H_5), 7.28 (d, 1 H, $^3J_{HH} = 7.2$, azain), 7.4–7.9 (mm, C_6H_5 and azain), 8.04 (d, 1 H, $^3J_{HH} = 7.2$, azain); $^{13}C\{^1H\}$, δ_C [101.4/101.7, azain], [111.1/111.8, azain], 125.2 (azain), 127–129 (C_6H_5 and azain), 129.3, 129.5, 130.3, (azain), 134–135 (C_6H_5), 135.2, 135.5, 136.9 (br), [140.8/142.2, azain], [153.0/153.7, azain] (the anticipated ddd RhCO resonance was not reliably identified; bracketed pairs indicate resonances that begin to coalesce at 70 °C); ^{11}B, δ_B –15.1; $^{31}P\{^1H\}$, δ_P 47.8. Crystal data for **6** (CCDC-658680): $C_{44}H_{38}BN_2OP_2Rh$, $M_w = 786.42$, $T = 100(2)$ K, triclinic, $P\bar{1}$ (No. 2), $a = 11.6962(2)$ Å, $b = 11.7252(2)$ Å, $c = 14.5351(3)$ Å, $\alpha = 95.812(1)°$, $\beta = 94.505(1)°$, $\gamma = 106.179(1)°$, $V = 1892.63(6)$ Å^3, $Z = 2$, μ(Mo Kα) $= 0.573$ mm^{-1}, $D_c = 1.380$ Mg m^{-3}; 40 049 reflections (14 203 unique, $R_{int} = 0.0399$), 472 parameters, GOF 1.058, R1 $= 0.0367$, wR2 $= 0.0762$ ($2\theta_{max} = 66°$, 11 123 reflections with $I > 2\sigma(I)$), residual electron density (highest peak, deepest hole) 0.791, −0.761 e Å^{-3}.

Synthesis of [Rh(PPh$_3$)$_2$(κ^3*N,H,H′*-7-azain-7-BH$_3$)] (7). In a Schlenk flask, Na[**5**]·0.5(dioxane) (0.13 g, 0.66 mmol) and $[RhCl(PPh_3)_3]$[14] (0.60 g, 0.65 mmol) were evacuated, stirred under a N_2 atmosphere in THF (10 mL) at 60 °C for 5 min, and then cooled. After it was stirred for 30 min at room temperature, the orange suspension was filtered through diatomaceous earth and washed with THF (2 mL). From the filtrate the product crystallized at 4 °C as the monosolvate **7**·THF. After 2 weeks the orange crystalline powder was filtered, washed with THF (1 mL), and dried under vacuum. Yield: 0.37 g (0.45 mmol, 69%). Anal. Found: C, 68.06; H, 5.32; N, 3.42. Calcd for $C_{47}H_{46}BN_2OP_2Rh$: C, 67.97; H, 5.58; N, 3.42. IR (Nujol): 2458 w ν(BH) cm^{-1}. NMR (CD_2Cl_2, 25 °C): ^1H, δ_H 0.6 (br, 3 H, BH_3), 5.96 (dd, 1 H, $^3J_{HH} = 2.9$, $^4J_{HH} = 1.2$ Hz, azain), 6.41 (d, 1 H, $^3J_{HH} = 2.9$ Hz, azain); 6.83 (dd, 1 H, $^3J_{HH} = 5.4$, 7.5 Hz, azain), 6.9–7.7 (m, 30 H, PPh_3), 7.82 (d, 1 H, $^3J_{HH} = 7.5$ Hz, azain), 7.85 (d, 1 H, $^3J_{HH} = 5.4$ Hz, azain); $^{13}C\{^1H\}$: δ_C 99.3, 111.8, 125.5, 128.5, 135.3, 142.6, 154.4 (7-azain-7), 127.4, 127.5 ($C^{3,5}$ (C_6H_5)], 129.1, 129.3 (C^4 (C_6H_5)), 134.7, 135.8 ($C^{2,6}$ (C_6H_5)), 137.1, 137.7 (C^1 (C_6H_5)); $^{11}B\{^1H\}$, δ_B −16.7 (br); $^{31}P\{^1H\}$, δ_P 46.2 (dd, $^1J_{PRh} = 206.4$, $^2J_{PP} =$ 51.2), 55.5 (dd, $^1J_{PRh} = 153.8$, $^2J_{PP} = 51.2$ Hz). Crystal data for **7**·THF (CCDC 658681): $C_{47}H_{46}BN_2OP_2Rh$, $M_w = 830.52$, $T = 100(2)$ K, triclinic, $P\bar{1}$ (No. 2), $a = 10.5388(1)$ Å, $b = 12.5141(2)$ Å, $c = 15.3891(2)$ Å, $\alpha = 95.952(1)°$, $\beta = 95.274(1)°$, $\gamma = 101.739(1)°$, $V = 1963.05(5)$ Å^3, $Z = 2$, μ(Mo Kα) $= 0.556$ mm^{-1}, $D_c = 1.405$ Mg m^{-3}, 88 279 reflections (18 500 unique, $R_{int} = 0.0515$), 499 parameters, GOF 1.061, R1 $= 0.0298$, wR2 $= 0.0704$ ($2\theta_{max} = 72°$, 15 977 reflections with $I > 2\sigma(I)$), residual electron density (highest peak, deepest hole) 0.745, −0.905 e Å^{-3}.

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Supporting Information Available: CIF files and a table giving crystallographic data for Na[**5**]·0.5(dioxane) (CCDC 658679), **6** (CCDC 658680), and **7**·THF (CCDC 658681). This material is available free of charge via the Internet at http://pubs.acs.org.

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