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Net Heterolytic Cleavage of B−H and B−B Bonds Across the N−Pd Bond in a Cationic (PNP)Pd Fragment

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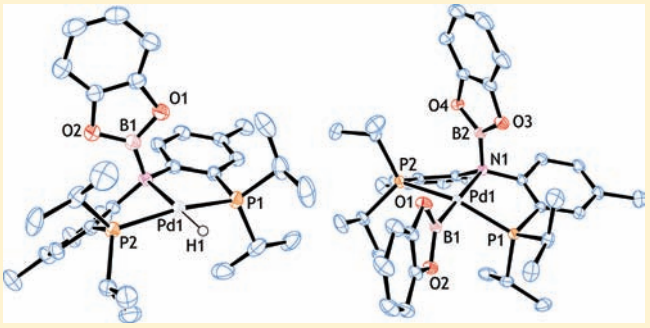
Supporting Information

ABSTRACT: The use of weakly coordinating anions $BAr^F{}_4$ (where Ar^F = 3,5-$(CF_3)_2C_6H_3$) and $CB_{11}H_{12}$ allows one to access clean reactions of the $[(PNP)Pd]^+$ fragment (PNP = bis(2-^{i}Pr$_2$P4-Me-phenyl)amido) with the B−H bond in catecholborane (CatBH) and catecholdiboron (CatBBCat). In both cases, a net heterolytic cleavage of B−H or B−B takes place, with the nitrogen atom of PNP being a recipient of a boryl fragment. The resultant products $[(PN(BCat)P)PdH]^+$ (**2**) and $[(PN(BCat)P)PdBCat]^+$ (**3**) were isolated as either $BAr^F{}_4$ or $CB_{11}H_{12}$ salts and fully characterized. They are susceptible to hydrolysis, with the B−N bond hydrolyzing selectively and rapidly at RT to give $[(PN(H)P)PdH]^+$ (**1**) and $[(PN(H)P)$-$PdBCat]^+$ (**4**). Notably, **4** and **2** are isomers, but they do not interconvert even under thermolysis at 90 °C. The Pd−B bond in **4** can be further hydrolyzed more slowly, to give **1**. On the other hand, a Pd−B bond was formed from the Pd−H bond in **2** by reaction with excess CatBH (and evolution of H_2), producing **3**.



INTRODUCTION

The activation of B−H and B−B bonds by transition-metal complexes to give boryls is of great interest to chemists because of its direct relevance to homogeneous catalysis. Transition-metal boryl complexes are important as intermediates in transition-metal-catalyzed hydroboration with boranes, diboration with diboron reagents, and borylation of alkanes and arenes.[1−10] Metal−boryl complexes are typically generated through oxidative addition (OA)[11] of boranes or diboron substrates. For example, Marder et al. have reported examples of oxidative addition of borane/diboron compounds to Pt(0),[12] and oxidative addition of B−H and B−B bonds to Rh(I) and Ir (I) is also well-known.[8,13]

Classical OA of an X−Y bond (such as B−H or B−B) to the metal center can be contrasted with and complemented by 1, 2-addition of an X−Y bond across a metal ligand bond (Scheme 1). Both cases necessitate the presence of a filled and of an empty orbital in the metal complex to rupture the X−Y bond and form new bonds to X and Y. For the classical OA, both orbitals are metal-based, whereas for the 1,2-addition, the ligand orbital contributes a lone pair and the metal an empty orbital. We have recently reported[14] 1,2-addition of H−H, alkynyl C−H, and thiolic S−H bonds cross the Pd−N moiety in a cationic, three-coordinate $[(PNP)Pd]^+$ fragment where PNP[15−17] is a diarylamido/bis(phosphine) pincer ligand (Scheme 2). This 1,2-addition can be viewed as heterolysis of the corresponding H−X bonds.[18] In contrast to most other common examples of complexes undergoing 1,2-addition of nonpolar or weakly polar bonds,[19−22] there is no π bond in the $[(PNP)Pd]^+$ fragment because the empty and the filled orbitals are orthogonal to each other and dimerization is presumably unfavorable on steric grounds. In this sense, $[(PNP)Pd]^+$ resembles the so-called frustrated Lewis pairs (FLPs) recently popularized by Stephan et al.[23]

In the present paper, we report our investigation of the 1, 2-addition of the B−H bond in catecholborane (CatBH) and the B−B bond in bis(catecholate)diboron (CatB-BCat) across the Pd−N moiety in $[(PNP)Pd]^+$. In contrast to our previous report (Scheme 2) on the net heterolytic cleavage of H−X by $[(PNP)$-$Pd]^+$,[14] here, the nitrogen atom is the recipient of X (boron) in the net heterolytic cleavage of H−X, not of hydrogen. Addition of B−H and B−B bonds across metal−oxygen functionalities is rather common. 1,2-Addition of B−H across the metal−oxygen bond in oxo-rhenium complexes and peroxo-rhodium complexes has been reported.[24,25] Addition of B−B bonds across late metal alkoxides with the release of free alkoxyboron molecules has been used for the synthesis of a variety of late metal boryls.[26−29] Another closely related precedent is the very recent report by Clark et al.[30] describing the net heterolytic cleavage of B−B (and B−H) bonds by a ruthenium center and a pendant oxygen in a Shvo-type[31] system, albeit that does not constitute 1,2-addition. On the other hand, addition of B−B bonds across a metal−nitrogen

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moiety remains unusual. It is also worth noting that relatively few palladium boryl complexes are known, mainly prepared by oxidative addition of a boron−halogen bond to a Pd center.[32]

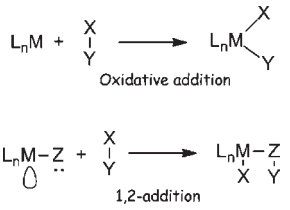
RESULTS AND DISCUSSION

Synthesis of [(PNP)Pd]$^+$ Synthons B and C. In our previously reported work on the net heterolytic cleavage of H−X bonds in thiols, H_2, or an alkyne, (PNP)PdOTf (**A**) functioned well as a synthon for $[(PNP)Pd]^+$ (Scheme 2).[14] Unfortunately, this convenient precursor did not work well in the reaction with the CatB-H substrate, which produced a mixture of unidentified species. Thus, we were prompted to turn to more weakly coordinating anions $[BAr^F{}_4]^-$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$)[33,34] and monocarba-*closo*-dodecaborate $[CB_{11}H_{12}]^-$ (also known as "carborane")[35] in place of triflate. Reaction of **A** with $Na[BAr^F{}_4]$ in THF furnished $[(PNP)Pd(THF)]BAr^F{}_4$ (**B**, Scheme 3) as a blue solid in 60% isolated yield. An analogous reaction of **A** with $Cs[CB_{11}H_{12}]$ in fluorobenzene yielded $(PNP)Pd(CB_{11}H_{12})$ (**C**, Scheme 3) as a solid of a different shade of blue in 83% yield. Both **B** and **C** were characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopies and elemental analysis. They display apparent C_{2v} symmetry in their room-temperature NMR spectra, as is expected of simple square-planar adducts of $[(PNP)Pd]^+$. We were not able to grow an X-ray quality crystal of **C**. However, using the same synthetic strategy, we prepared $(^FPNP)PdCB_{11}H_{12}$ (^{F}**C**, Scheme 3), a very similar compound bearing fluorine substituents on the ligand backbone and obtained its single crystal for an XRD study. The solid-state structure of ^{F}**C** (vide infra) revealed coordination of $CB_{11}H_{12}^-$ to the $[(^FPNP)Pd]^+$ fragment, and presumably that is the case for **C**, as well.

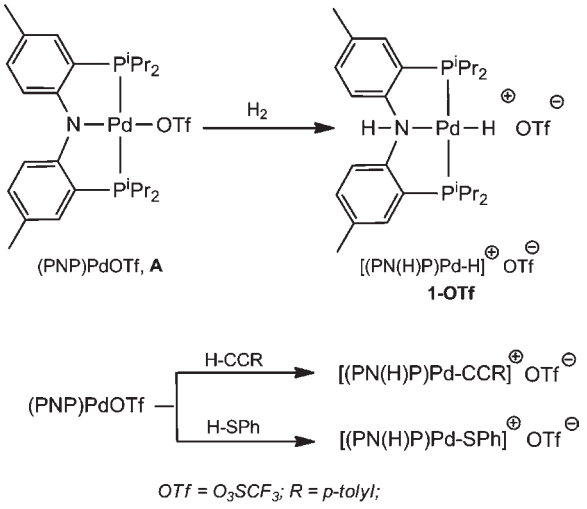
Although **B** and **C** are adducts of the authentic $[(PNP)Pd]^+$ fragment, the coordination of the THF molecule in **B** or of the carborane anion in **C** was sufficiently weak that B and C readily functioned as synthons of $[(PNP)Pd]^+$ in the reactions with B−H, B−B, and H−H bonds described below. We selected two different weakly coordinating anions in order to increase the chances of obtaining X-ray quality crystals containing the cations of interest and of obtaining analytically pure solid products. In the products of net heterolytic splitting, both $[BAr^F{}_4]^-$ and $[CB_{11}H_{12}]^-$ behave as noncoordinating anions.

Net B−H and B−B Heterolytic Splitting Reactions. Both **B** and **C** readily reacted with 1.0−1.1 equiv of CatB-H (Scheme 4), with the reaction complete in 1−3 h, as evidenced by the evolution of the blue color of **B** or **C** into yellow with the formation of the products $[(PN(BCat)P)PdH]BAr^F{}_4$ (**2-BAr$^F{}_4$**) and $[(PN(BCat)P)PdH]CB_{11}H_{12}$ (**2-CB$_{11}$H$_{12}$**). In both cases, the reaction mixtures also contained small amounts of the $[(PN(H)P)PdH]^+$ (**1-BAr$^F{}_4$** or **1-CB$_{11}$H$_{12}$**) impurities. Nonetheless, workup allowed isolation of pure **2-BAr$^F{}_4$** in ca. 60% yield, whereas **2-CB$_{11}$H$_{12}$** was characterized in the presence of **1-CB$_{11}$H$_{12}$**. ^{1}H, ^{31}P, and ^{13}C NMR spectroscopies confirmed the

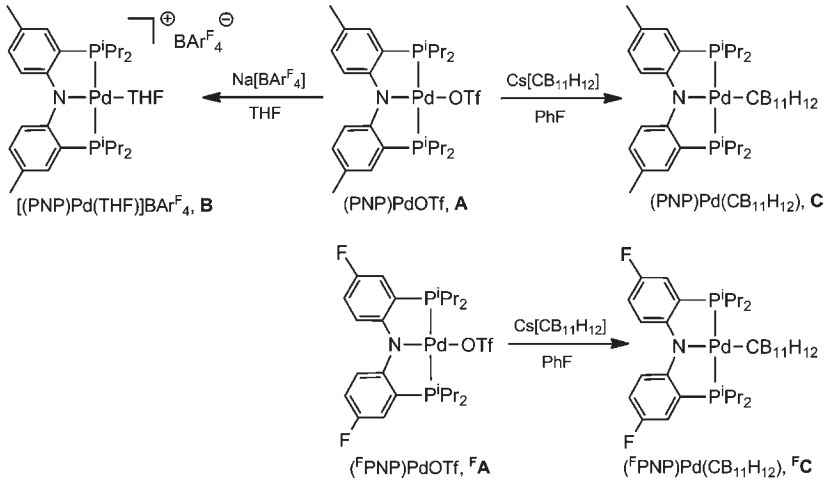
Scheme 1. Oxidative Addition to a Metal Center and the Nonoxidative 1,2-Addition



Scheme 2. Reactions of Certain H−X Substrates with (PNP)PdOTf



Scheme 3. Synthesis of Compounds B, C, and ^{F}C



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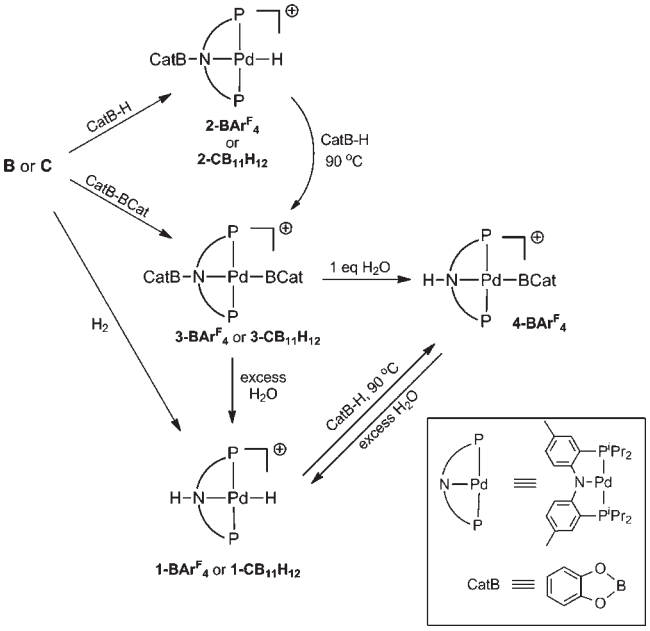
Scheme 4. Synthesis of Compounds 1−5 and Their Interconversion



structure and formulation of products **2**. Complex **2-BAr$^F_4$** was also characterized by single-crystal X-ray diffraction (vide infra) and elemental analysis. It is worth noting that the B−H bond of CatB-H added to the Pd−N bond in the opposite direction compared with the C−H and S−H substrates mentioned above;[14] that is, B added to N while H added to Pd. This is consistent with the reversal of polarity of a B−H bond versus a C−H or a S−H bond. The most telling spectroscopic evidence of this regiochemistry in salts of **2** was the Pd-H resonance at δ −12.7 (**2-BAr$^F_4$**) or −12.6 ppm (**2-CB$_{11}$H$_{12}$**) in the ^{1}H NMR spectrum.

Analogous reactions of **B** and **C** with CatB-BCat proceeded more slowly, requiring >18 h and/or mild heating for completion (Scheme 4). The products [(PN(CatB)P)PdBCat]BAr$^F_4$ (**3-BAr$^F_4$**) and [(PN(CatB)P)Pd(BCat)]CB$_{11}$H$_{12}$ (**3-CB$_{11}$H$_{12}$**) were characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopies. Like the salts of **2**, both salts of **3** possess C_s symmetry in the NMR spectra at ambient temperature. The NMR spectroscopic signatures of **3-BAr$^F_4$** and **3-CB$_{11}$H$_{12}$** were nearly identical. For example, **3-CB$_{11}$H$_{12}$** gave rise to a ^{31}P NMR resonance at δ 45.0 ppm, very similar to **3-BAr$^F_4$** (44.7 ppm). We did not observe the ^{11}B signals for **3-BAr$^F_4$** and **3-CB$_{11}$H$_{12}$** corresponding to the two different BCat groups, even upon cooling to −30 °C. This was surprising to us because the ^{11}B NMR resonances of the anions in salts of **3** were easily detected in the same experiments, and because the N-*B* resonance in **2-BAr$^F_4$** and the Pd-*B* resonance in **4-BAr$^F_4$**were also readily detected at 21.2 and 37.1 ppm, respectively, in their ^{11}B{^{1}H} NMR spectra. Presumably, the ^{11}B NMR resonances of the CatB groups in **3-BAr$^F_4$** and **3-CB$_{11}$H$_{12}$** are substantially broadened, but the origin of this broadening is unclear to us. Nonetheless, the expected ^{1}H NMR and ^{13}C NMR resonances for the two distinct CatB groups for **3-BAr$^F_4$** and **3-CB$_{11}$H$_{12}$** were observed. Compound **3-BAr$^F_4$** was found to be contaminated with **4-BAr$^F_4$**, and our best attempts at removing this impurity failed. On the other hand, compound **3-CB$_{11}$H$_{12}$** was isolated in a pure solid form, as supported by NMR spectroscopy and elemental analysis data, and it was also characterized by single-crystal X-ray diffraction (vide infra). **3-BAr$^F_4$** possesses better solubility in aromatic solvents than **3-CB$_{11}$H$_{12}$**. **3-CB$_{11}$H$_{12}$** is barely soluble in benzene, toluene, or fluorobenzene at room temperature and precipitated from the toluene reaction mixture. This low solubility is presumably responsible for the fortuitous separation of the likely impurities.

The origin of the formation of salts of **1** in the reaction of **B** and **C** with CatB-H and of **4** in reactions of B and C with CatB-BCat is not clear. It is likely the result of the protolysis of the N−B bonds in the expected products (see the Hydrolysis section below). The nature of the protic source responsible is at this point unknown. Consistent observation of apparent protolysis products after different drying precautions taken casts doubt (but does not eliminate) the possibility of adventitious water. It is also possible that the difficulty in removing B−OH impurities in CatB-H and CatB-BCat is the culprit.

Hydrolysis of B−N and Pd−B Bonds. The B−N and Pd−B bonds in complexes **3-BAr$^F_4$** as well as **3-CB$_{11}$H$_{12}$** were easily hydrolyzed (Scheme 4). The hydrolysis of the B−N bond took place more rapidly: reaction of **3-BAr$^F_4$** with 1 equiv of water produced complex **4-BAr$^F_4$**. The Pd−B bond was hydrolyzed more slowly, and excess water effected conversion of **3-BAr$^F_4$** or **3-CB$_{11}$H$_{12}$** to complex **1-BAr$^F_4$** or **1-CB$_{11}$H$_{12}$**, respectively. Thus, in the course of the hydrolysis, the N−B and Pd−B bonds were converted to the corresponding N−H and Pd−H bonds, with concomitant production of CatBOBCat (Scheme 4).[36] The ultimate hydrolysis products **1-BAr$^F_4$** and **1-CB$_{11}$H$_{12}$** were synthesized independently via reaction of **B** or **C** with H_2 and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies (and elemental analysis for **1-BAr$^F_4$**). These syntheses parallel the previously reported synthesis of **1-OTf** from (PNP)PdOTf and H_2.[14] Complexes **1-BAr$^F_4$** and **1-CB$_{11}$H$_{12}$** have the same cation as **1-OTf** and only differ in the anion. Not surprisingly, they resonated at the same chemical shift (56.3 ppm) in the ^{31}P NMR spectra and displayed the same number and symmetry of ^{1}H NMR resonances for the cation. On the other hand, the chemical shifts of the resonances in the ^{1}H NMR spectra in CD_2Cl_2 of these three compounds were quite distinct from each other, especially for the N-*H* resonances (δ 8.75, 6.96, 7.07 ppm for **1-OTf**, **1-BAr$^F_4$**, and **1-CB$_{11}$H$_{12}$**, respectively).[37] However, the chemical shifts in the ^{1}H NMR spectra in the more polar solvent acetone-d_6 were only slightly different (δ 9.15, 9.09, 9.08 ppm for the N-*H* resonances for **1-OTf**, **1-BAr$^F_4$**, and **1-CB$_{11}$H$_{12}$**, respectively). These discrepancies can be rationalized by the notion that triflate, albeit not coordinated to the metal, maintains a closer interaction with the cation in solution than [BAr$^F_4$]$^-$ or [CB$_{11}$H$_{12}$]$^-$.[38] The difference is greater in the less polar solvent (CD_2Cl_2) and nearly disappears in acetone. This notion is reinforced by the observation of hydrogen bonding between NH of the cation and the triflate anion in the solid-state structure of **1-OTf**.[14] Most likely, this is the interaction most important for the downfield shift of the NH resonance in solutions of **1-OTf** versus **1-BAr$^F_4$** or **1-CB$_{11}$H$_{12}$**.

The intermediate hydrolysis product **4-BAr$^F_4$** (Scheme 4) was isolated in 68% yield from selective reaction of **4-BAr$^F_4$** with 1 equiv of water, and we were able to obtain single crystals suitable for X-ray diffraction studies (vide infra) using this route. Alternatively, **4-BAr$^F_4$** could be prepared via thermolysis of **1-BAr$^F_4$** with excess CatB-H. Thermolysis with excess CatB-H also served to convert **2-BAr$^F_4$** to **3-BAr$^F_4$**. These reactions converted Pd−H into Pd-BCat (and H_2) but did not affect the NH bond

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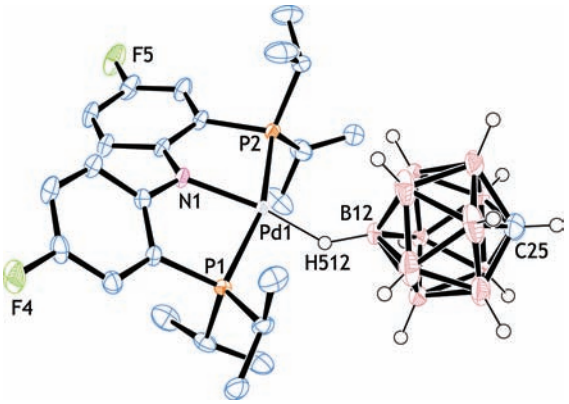

Figure 1. ORTEP drawing[48] (50% probability ellipsoids) of ^{F}**C** showing selected atom labeling. Hydrogen atoms of the ^{F}PNP ligand are omitted for clarity. Disorder of one of the ^{i}Pr groups is not shown. Selected bond distances (Å) and angles (deg) follow: Pd1−N1, 2.0072(19); Pd1−P1, 2.2969(5); Pd1−P2, 2.3449(6); Pd1−H512, 1.69(3); B12−H512, 1.22(3); P1−Pd1−P2, 161.68(2); N1−Pd1−H512, 171.0(10); B12−H512−Pd1, 133(2).

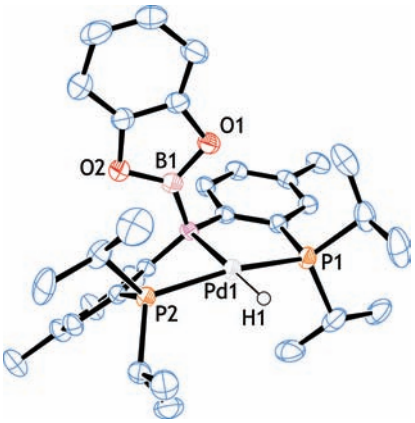

Figure 2. ORTEP drawing[48] (50% probability ellipsoids) of **2-BAr$^{F}_4$** showing selected atom labeling. Hydrogen atoms (except Pd−H) and the BAr$^{F}_4$ counterion are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Pd1−P1, 2.2624(7); Pd1−P2, 2.2838(7); Pd1−N1, 2.202(2); Pd1···B1, 2.746(3); Pd1−H1, 1.43(4); P1−Pd1−P2, 163.66(3); N1−Pd1−H1, 175.9(14).

in **4-BAr$^{F}_4$**. **4-BAr$^{F}_4$** displayed C_s symmetry in its NMR spectra and a single ^{11}B resonance for the cation (37.1 ppm).

The formation of a metal−boryl bond upon treatment of a metal hydride with boranes is not without precedent[39] Dehydrogenative borylation of C−H bonds with R_2BH reagents must also involve conversion of metal hydrides to metal boryls as part of the catalytic cycle.[40] In another study using the PNP ligand, Mindiola reported the formation of the neutral (PNP)NiBCat by treatment of (PNP)NiH with CatB-H.[41]

Select Mechanistic Considerations. Without more extensive data, it is difficult to speculate on the possible mechanism of the B−H and B−B cleavage, but several observations can be made. For the H_2 splitting,[14] we hypothesized that a likely mechanism involves intermolecular proton transfer from the dihydrogen ligand in $[(PNP)Pd(H_2)]^+$ to the N of PNP by an external base (triflate, solvent, possibly adventitious water). However, an analogous transfer of a CatB$^+$ seems a more exotic proposition,[42] especially considering the absence of triflate and the demonstrated deleterious role of water as an impurity.

It is possible that the reaction is initiated by the formation of a σ complex of a B−H or a B−B bond with $[(PNP)Pd]^+$. σ complexes of B−H bonds are well-precedented.[43] Recent computational investigations by Bo, Peris, and Fernandez argued in favor of a viable B−B σ-complex intermediate in the B−B oxidative addition to a CNC pincer-supported Pd(II) cation.[44] In our previous work with H_2 splitting,[14] we computationally investigated the possibility of H_2 oxidative addition to $[(PNP)Pd]^+$ and concluded that it was too unfavorable to play a role in the heterolytic splitting reaction. However, boryl is a more donating ligand than a hydride and it is possible that B−H or B−B OA to $[(PNP)Pd]^+$ is more accessible.

Addition of borane to the heteroatom first has been proposed for the net heterolytic splitting reaction of a Rh−peroxo complex with pinacolborane.[25] However, this pathway appears less likely with $[(PNP)Pd]^+$ because the basicity of the N site in it should be quite low, whereas the empty coordination site on Pd is clearly a very reactive moiety.

With regard to the regioselectivity of the B−H addition, **4-BAr$^{F}_4$** can be ruled out as an intermediate en route to **2-BAr$^{F}_4$**. Complexes **4-BAr$^{F}_4$** and **2-BAr$^{F}_4$** are isomers. Both can be formally viewed as products of 1,2- versus 2,1-addition of CatB-H to $[(PNP)Pd]^+$, with **2-BAr$^{F}_4$** having Pd−H and N−B bonds and **4-BAr$^{F}_4$** having Pd−B and N−H bonds. As mentioned above, only **2-BAr$^{F}_4$** could, in fact, be synthesized in this fashion. There was no conversion between these two isomers upon thermolysis of one or the other at 90 °C. Thus, we were unable to determine which is the more favorable isomer, but the lack of interconversion shows that **2-BAr$^{F}_4$** is not accessible from **4-BAr$^{F}_4$** under the reaction conditions.

Solid-State Structures of Complexes 2-BAr$^{F}_4$, 3-CB$_{11}$H$_{12}$, ^{F}C, and 4-BAr$^{F}_4$. We were able to obtain single crystals of compounds **2-BAr$^{F}_4$**, **3-CB$_{11}$H$_{12}$**, ^{F}**C**, and **4-BAr$^{F}_4$** that were suitable for X-ray diffraction studies. The ORTEP representations of the molecular structures in the solid state are given in Figures 1−4. An X-ray diffraction study for ^{F}**C** (Figure 1) found that the Pd center was four-coordinate, with the B−H unit at the 12-position of $[CB_{11}H_{12}]^-$ interacting with the metal center, and the geometry about the metal being approximately square-planar. Coordination of the $CB_{11}H_{12}^-$ anion to a metal center via the 12-H substituent has been reported by Weller et al.[45] Coordination via 12-H seems reasonable since this BH unit is the most remote from the carbon and is the most electron-rich site in the cage.[35] Complex ^{F}**C** (and presumably **C**) can be viewed as a σ-BH complex (cf. **A** in Scheme 4). It is interesting to note that it does not undergo B−H cleavage, which is probably an illustration of the different nature of the B−H bond in the $CB_{11}H_{12}^-$ cage and in CatB-H, in both the electronic and steric sense.

In the structures of **2-BAr$^{F}_4$** (Figure 2), **3-CB$_{11}$H$_{12}$** (Figure 3), and **4-BAr$^{F}_4$** (Figure 4), the Pd center adopts a slightly distorted square-planar geometry, and all three structures contain a PNP ligand with a central amine nitrogen donor. The Pd−N_{PNP} distances are notably longer in these compounds (2.202(2) Å in **2-BAr$^{F}_4$**, 2.2517(11) Å in **3-CB$_{11}$H$_{12}$**, 2.194(3) Å in **4-BAr$^{F}_4$**) than the corresponding distances in the compounds containing the PNP ligand with a central amido, sp^2-hybridized nitrogen donor (for example, 2.0072(19) Å in **5**, 2.0258(19) Å in (PNP)PdCl,[16] 2.086(4) Å in (^{F}PNP)PdH,[46] and 2.0938(15) Å in (^{F}PNP)-PdMe[46]). It is also instructive to analyze how the Pd−N bond length depends on the nature of X and Y in $[(PN(X)P)Pd-Y]^+$.

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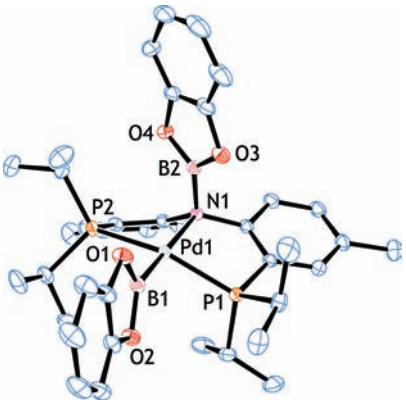

Figure 3. ORTEP drawing[48] (50% probability ellipsoids) of **3-$CB_{11}H_{12}$** showing selected atom labeling. Hydrogen atoms, the $CB_{11}H_{12}$ counterion, and the $PhCF_3$ solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Pd1−P1, 2.2753(4); Pd1−P2, 2.2880(4); Pd1−N1, 2.2517(11); Pd1−B1, 1.9879(16); P1−Pd1−P2, 156.521(13); N1−Pd1−B1, 175.16(5).

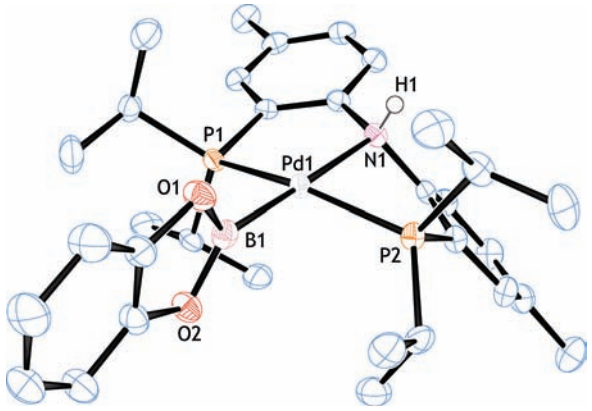

Figure 4. ORTEP drawing[48] (50% probability ellipsoids) of **4-$BAr^F{}_4$** showing selected atom labeling. Hydrogen atoms (except H1), the $BAr^F{}_4$ counterion, and the cocrystallized molecules of CH_2Cl_2 and H_2O are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Pd1−P1, 2.2635(8); Pd1−P2, 2.2859(8); Pd1−N1, 2.194(3); Pd1−B1, 1.993(4); P1−Pd1−P2, 159.94(3); N1−Pd1−B1, 178.45(13).

Table 1. Pd−N Distances (from XRD Studies, in Å) for Compounds $[(PN(X)P)Pd-Y]^+$ (1-OTf,[14] 2-$BAr^F{}_4$, 3-$CB_{11}H_{12}$, and 4-$BAr^F{}_4$

	X = CatB	X = H
Y = CatB	2.2517 (11)	2.202(2)
Y = H	2.194(3)	2.160(4)

The set of four compounds (X = CatB or H; Y = CatB or H) is completed by considering **1-OTf** (2.160(4) Å)[14] alongside **2-$BAr^F{}_4$**, **3-$CB_{11}H_{12}$**, and **4-$BAr^F{}_4$** (Table 1). It is apparent that a longer Pd−N bond length results from either X = BCat or Y = BCat. The elongation of the Pd−N bonds may be attributed to the greater trans influence of the boryl ligand than the hydride for Y = BCat,[47] and to the greater steric encumbrance of a boryl-substituted amine for X = BCat.

The boryl moieties (as defined by the O−B−O planes) attached to Pd in complexes **3-$CB_{11}H_{12}$** and **4-$BAr^F{}_4$** are oriented almost perpendicularly to the Pd coordination plane. Interestingly, the two boryl moieties (B−N and B−Pd) in **3-$CB_{11}H_{12}$** are almost perpendicular to each other, too. Both determined Pd−B bond lengths (1.9879(16) Å in **3-$CB_{11}H_{12}$** and 1.993(4) Å in **4-$BAr^F{}_4$**) are in the expected range for the palladium boryl complexes.[32] The other bond distances and angles associated with the (PNP)Pd system in **2-$BAr^F{}_4$**, **3-$CB_{11}H_{12}$**, and **4-$BAr^F{}_4$** are unremarkable. The P−Pd−P angle varies within ca. 157−164°, and the Pd−P distances in all three compounds are in the 2.26−2.29 Å range.

CONCLUSION

In conclusion, we have demonstrated that the $[(PNP)Pd]^+$ fragment is capable of net heterolytic cleavage of the B−H bond in catecholborane and the B−B bond in catecholdiboron. We have isolated and physically characterized cationic palladium hydrides and palladium boryl complexes. The activation of the B−H bond by $[(PNP)Pd]^+$ resulted in the formation of Pd−H and N−B bonds. The addition of a B−B bond across a Pd−N bond to form a palladium boryl complex is unique. It provides another route to palladium boryl complexes and to the cleavage of the B−B bond where oxidative addition of a B−B bond to the palladium center is difficult. Both the N−B and the Pd−B bonds are subject to hydrolysis, forming the corresponding N−H and Pd−H bonds.

EXPERIMENTAL SECTION

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using a standard Schlenk line or glovebox techniques. Ethyl ether, C_6D_6, and pentane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred, and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene and catecholborane (CatBH) were dried with and then distilled from CaH_2. $NaBAr^F{}_4$,[34] (^{F}PNP)PdOTf,[49] and (PNP)PdH[16] were prepared according to the published procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 300, Varian iNova 400, and Mercury 300 spectrometers. Chemical shifts are reported in δ (parts per million). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally using CF_3COOH at δ −78.5 ppm. ^{11}B NMR spectra were referenced externally using $BF_3\cdot Et_2O$ at δ 0 ppm. Elemental analyses were performed by CALI, Inc. (Parsippany, NJ).

(PNP)PdOTf (A). (PNP)PdH (216 mg, 0.40 mmol) was dissolved in 10 mL of C_6H_6, followed by the addition of MeOTf (226 μL, 2.0 mmol). The reaction mixture was allowed to stir at room temperature for 2 h. The volatiles were removed under vacuum, and the residue was recrystallized from toluene/pentane to give a pure solid. Yield: 225 mg, 85%. ^1H NMR (C_6D_6): δ 7.50 (d, 2H, J = 8 Hz, (PNP)Aryl-*H*), 6.77 (s, 2H, (PNP)Aryl-*H*), 6.60 (d, 2H, J = 8 Hz, (PNP)Aryl-*H*), 2.42 (m, 4H, C*H*Me_2), 2.02 (6H, Ar-CH_3), 1.38 (dvt, 12H, CHMe_2), 1.04 (dvt, 12H, CHMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.2 (t), 132.8, 132.7, 127.3, 117.8, 117.5, 25.2 (m), 20.8, 18.7, 18.0. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.6. ^{19}F NMR (C_6D_6): δ −79.2.

[(PNP)Pd(THF)]$BAr^F{}_4$ (B). (PNP)PdOTf (**A**) (70 mg, 0.10 mmol) was dissolved in 5 mL of cold THF, followed by the addition of $Na[BAr^F{}_4]$ (88 mg, 0.10 mmol). The reaction mixture was allowed to stir at room temperature for 1 h. All of the volatiles were removed under

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vacuum, and the residue was dissolved in PhF. The mixture was filtered off Celite, and the filtrate was pumped to dryness. The final pure product was obtained after recrystallization from PhF/pentane. Yield: 88 mg, 60%. ^{1}H NMR (CD_2Cl_2): δ 7.73 (s, 8H, BAr_4-*H*), 7.58 (s, 4H, BAr_4-*H*), 7.28 (d, 2H, J = 9 Hz, (PNP)Aryl-*H*), 6.92 (m, 4H, (PNP)Aryl-*H*), 3.95 (m, 4H, OCH_2), 2.44 (m, 4H, $CHMe_2$), 2.23 (s, 6H, Ar-CH_3), 2.02 (m, 4H, CH_2), 1.35 (dvt, 12H, $CHMe_2$), 1.26 (dvt, 12H, $CHMe_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.5 (q, J = 50 Hz), 162.1 (t), 135.4, 133.8, 132.5, 130.6, 129.6 (q, J = 234 Hz), 126.5, 123.8, 121.1, 118.1, 77.4, 25.6, 23.0, 20.5, 19.0, 18.1. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 55.5. ^{19}F NMR (CD_2Cl_2): δ −65.7. Elem. Anal. Found (calculated) for $C_{62}H_{60}BNOF_{24}P_2Pd$: C, 50.71 (50.65); H, 4.18 (4.11); N, 0.85 (0.95).

(PNP)PdCB$_{11}$H$_{12}$ (C). (PNP)PdOTf (**A**) (34.8 mg, 0.051 mmol) was dissolved in 5 mL of PhF. $CsCB_{11}H_{12}$ (17 mg, 0.062 mmol) was added to the solution. The mixture was stirred at RT overnight. The solution was then passed through Celite. The volatiles were removed under vacuum, and the resulting solid was recrystallized from PhF/pentane. Yield: 28 mg, 83%. ^{1}H NMR (CD_2Cl_2): δ 7.30 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 7.05 (br, 2H, (PNP)Aryl-*H*), 6.88 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 2.80 (m, 4H, $CHMe_2$), 2.52−1.50 (br, 12H, $CB_{11}H_{12}$), 2.21 (s, 6H, Ar-CH_3), 1.33 (app. q (dvt), J = 7.2 Hz, 12H, $CHMe_2$)), 1.26 (app. q (dvt), J = 7.2 Hz, 12H, $CHMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.1 (t, J = 9 Hz, (PNP)Aryl-*C*), 132.9 ((PNP)Aryl-*C*), 132.7 ((PNP)-Aryl-*C*), 117.9 ((PNP)Aryl-*C*), 117.6 ((PNP)Aryl-*C*), 117.3 (t, J = 6 Hz, (PNP)Aryl-*C*), 54.3, 26.0 (t, J = 11 Hz), 20.3, 20.0, 18.4. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 60.0. ^{11}B{^{1}H} NMR (C_6D_6): δ −9.4, −13.2, −15.2. Elem. Anal. Found (calculated) for $C_{27}H_{52}B_{11}NP_2Pd$: C, 47.57 (47.83); H, 7.68 (7.73); N, 2.10 (2.07).

(^{F}PNP)PdCB$_{11}$H$_{12}$ (^{F}C). (^{F}PNP)PdOTf (^{F}**A**) (55 mg, 0.079 mmol) was dissolved in 3 mL of fluorobenzene, and $CsCB_{11}H_{12}$ (27 mg, 0.097 mmol) was added with stirring. The solution immediately changed from purple to dark blue. After approximately 10 min, the solution was passed through a pad of Celite, the volatiles were removed under vacuum, and the residue was washed with pentane. The residue was dried under vacuum. Yield: 37 mg, 76%. ^{1}H NMR (C_6D_6): δ 7.22 (m, 2H, Ar-*H*), 6.86 (m, 2H, Ar-*H*), 6.75 (t, J = 8 Hz, 2H, Ar-*H*), 3.4−1.4 (br, 12H, $CB_{11}H_{12}$), 2.78 (br, 4H, $CHMe_2$), 1.20 (app. q. (dvt), 12H, Hz, CH-Me_2), 1.06 (app. q. (dvt), 12H, Hz, $CHMe_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 58.5. ^{19}F NMR (C_6D_6): δ −126.4.

[(PN(H)P)PdH]BAr$^F_4$ (1-BAr$^F_4$). Compound **B** (36 mg, 0.026 mmol) was dissolved in 0.6 mL of PhF in a J. Young NMR tube. H_2 (1 atm) was then introduced into the tube, and the mixture was allowed to stand at room temperature for 30 min until the color changed to colorless. All the volatiles were removed under vacuum. The oily residue was washed with hexanes a few times to obtain an off-white powder. The solid was dried under vacuum. Yield: 28 mg, 81%. ^{1}H NMR (CD_2Cl_2): δ 7.69 (s, 8H, BAr_4-*H*), 7.53 (s, 4H, BAr_4-*H*), 7.37 (m, 4H, (PNP)Aryl-*H*), 7.30 (d, J = 6.6 Hz, (PNP)Aryl-*H*), 6.96 (br, 1H, N-*H*), 2.53 (m, 4H, $CHMe_2$), 2.41 (s, 6H, Ar-CH_3), 1.34 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), 1.13 (app. q (dvt), J = 7.2 Hz, 12H, $CHMe_2$), 0.91 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), −12.5 (br, 1H, Pd-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.9 (q, J = 50 Hz, BAr_4-*C*), 145.5 (t, J = 8 Hz, (PNP)Aryl-*C*), 139.3 (t, J = 3 Hz, (PNP)Aryl-*C*), 135.3 (BAr_4-*C*), 134.2 ((PNP)-Aryl-*C*), 133.2 ((PNP)Aryl-*C*), 129.9 (q, J = 32 Hz, BAr_4-*C*), 125.1 (d, J = 272 Hz, BAr_4-*C*), 124.8 (t, J = 4 Hz, (PNP)Aryl-*C*), 119.7 (BAr_4-*C*), 117.9 (t, J = 4 Hz, (PNP)Aryl-*C*), 25.4 (t, J = 12 Hz), 23.3 (t, J = 13 Hz), 20.3, 19.3 (t, J = 4 Hz), 18.6 (t, J = 4 Hz), 18.4, 17.7. ^{31}P{^{1}H} NMR (C_6D_6): δ 56.4. ^{19}F{^{1}H} NMR (C_6D_6): δ −63.1. Elem. Anal. Found (calculated) for $C_{58}H_{54}BF_{24}NP_2Pd$: C, 49.67 (49.75); H, 3.95 (3.89); N, 1.71 (0.96).

[(PN(H)P)PdH]CB$_{11}$H$_{12}$ (1-CB$_{11}$H$_{12}$). Compound **A** (104 mg, 0.152 mmol) was dissolved in 6.0 mL of PhF, followed by the addition of $CsCB_{11}H_{12}$ (50.0 mg, 0.182 mmol). The reaction mixture was stirred for 4 h and ^{31}P NMR analysis indicated full conversion to compound **C**. The reaction mixture was passed through Celite, and the filtrate was transferred to a PTFE-capped flask. H_2 was introduced into the flask, and the reaction was stirred vigorously for 5 min. The initial blue color disappeared, and white precipitate was formed. The precipitate was collected by filtration and washed three times with pentane. Yield: 72 mg, 70%. ^{1}H NMR (CD_2Cl_2): δ 7.41−7.34 (m, 6H, (PNP)Aryl-*H*), 7.07 (br, 1H, N-*H*), 2.53 (m, 4H, $CHMe_2$), 2.43 (s, 6H, Ar-CH_3), 2.25−1.39 (m, 12H, $CB_{11}H_{12}$), 1.33 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), 1.17 (app. q (dvt), J = 7.2 Hz, 12H, $CHMe_2$), 0.92 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), −12.5 (br, 1H, Pd-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.3.

[(PN(BCat)P)Pd(H)]BAr$^F_4$ (2-BAr$^F_4$). Compound **B** (40 mg, 0.029 mmol) was dissolved in about 1 mL of toluene/trifluorotoluene, followed by the addition of CatB-H (3.0 μL, 0.029 mmol). The reaction mixture was allowed to stand at room temperature for 1 h, and the solution color changed to light yellow. Et_3N (1 μL, 0.007 mmol) was added to the mixture (to deprotonate and assist in the removal of the traces of **1-BAr$^F_4$** present). The volatiles were removed under vacuum, and the residue was washed with trifluorotoluene/pentane to give a white powder after drying under vacuum. Yield: 25 mg, 59%. X-ray quality crystals were obtained by crystallizing the solid in CH_2Cl_2/pentane at −35 °C. ^{1}H NMR (C_6D_5Br): δ 8.20 (s, 8H, BAr_4-*H*), 7.58 (s, 4H, BAr_4-*H*), 7.26 (m, 4H, (PNP)Aryl-*H*), 7.02 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 6.72 (br, 4H, Catechol-*H*), 2.40 (m, 2H, $CHMe_2$), 2.19 (br, 8H, Ar-CH_3 + $CHMe_2$), 1.92 (m, 2H, $CHMe_2$), 1.11 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), 0.89 (m, 12H, $CHMe_2$), 0.64 (app. q (dvt), J = 7.2 Hz, 6H, $CHMe_2$), −12.7 (t, J = 4.8 Hz, 1H, Pd-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.9 (q, J = 50 Hz, BAr_4-*C*), 147.1 (Catechol-*C*), 145.9 (t, J = 8 Hz, (PNP)Aryl-*C*), 139.7 (t, J = 3 Hz, (PNP)Aryl-*C*), 135.3 (BAr_4-*C*), 134.3 ((PNP)Aryl-*C*), 133.5 ((PNP)Aryl-*C*), 129.9 (q, J = 34 Hz, BAr_4-*C*), 125.1 (d, J = 272 Hz, BAr_4-*C*), 125.8 (t, J = 4 Hz (PNP)Aryl-*C*), 124.4 (Catechol-*C*), 119.7 (BAr_4-*C*), 117.9 (t, J = 4 Hz, (PNP)Aryl-*C*), 112.7 (Catechol-*C*), 26.4 (t, J = 12 Hz), 24.6 (t, J = 13 Hz), 20.3 (t, J = 3 Hz), 20.2, 19.5 (t, J = 4 Hz), 18.9, 18.4. ^{31}P{^{1}H} NMR (C_6D_6): δ 53.2. ^{19}F NMR (C_6D_6): δ −63.1. ^{11}B{^{1}H} NMR (C_6D_6): δ 21.2 (N-*B*), −6.3 (BAr^F_4-*B*). Elem. Anal. Found (calculated) for $C_{64}H_{57}B_2NO_2F_{24}P_2Pd$: C, 50.58 (50.64); H, 3.82 (3.78); N, 0.92 (0.92).

Thermolysis of 2-BAr$^F_4$. **2-BAr$^F_4$** (13 mg, 0.009 mmol) was dissolved in 0.6 mL of PhF in a J. Young NMR tube, and the solution was heated at 90 °C for 15 h. ^{31}P NMR spectroscopic analysis indicated no observable changes.

Reaction of 2-BAr$^F_4$ with HBCat. Compound **2-BAr$^F_4$** (10 mg, 0.0060 mmol) was dissolved in 0.6 mL of PhF in an NMR tube, followed by the addition of HBCat (4.0 μL, 0.030 mmol). The NMR tube was placed in a 95 °C oil bath. After 24 h, ^{31}P{^{1}H} NMR analysis indicated full conversion to **3-BAr$^F_4$**.

[(PN(BCat)P)Pd(H)]CB$_{11}$H$_{12}$ (2-CB$_{11}$H$_{12}$). Compound **C** (35 mg, 0.052 mmol) was dissolved in 0.6 mL of PhF, followed by the addition of CatB-H (5.5 μL, 0.052 mmol). The reaction mixture was allowed to stand at room temperature for 3 h, and the solution color changed to light yellow. ^{31}P NMR indicated that there was ∼10% of **1-CB$_{11}$H$_{12}$**, besides 90% of **2-CB$_{11}$H$_{12}$**, in the reaction mixture. White crystals were formed by carefully layering pentane on top of the PhF solution. Yield: 27 mg, 62%. However, NMR analysis indicated that these crystals still contain a mixture of both **1-CB$_{11}$H$_{12}$** and **2-CB$_{11}$H$_{12}$**. NMR data for 2-$CB_{11}H_{12}$: ^{1}H NMR (C_6D_6) (a drop of CH_2Cl_2 was added to increase solubility): δ 7.36 (m, 4H, (PNP)Aryl-*H*), 7.18 (br, 2H, (PNP)Aryl-*H*), 6.04 (br, 4H, Catechol-*H*), 2.51 (m, 2H, $CHMe_2$), 2.30 (s, 6H, Ar-CH_3), 2.25 (m, 2H, $CHMe_2$), 2.18−1.60 (br, 12H, $CB_{11}H_{12}$), 1.14 (app. q (dvt), J = 8 Hz, 6H, $CHMe_2$), 0.95 (m, 12H, $CHMe_2$), 0.68 (app. q (dvt), J = 8 Hz, 6H, $CHMe_2$), −12.6 (t, J = 5 Hz, 1H, Pd-*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.3.

[(PN(BCat)P)Pd(BCat)]BAr$^F_4$ (3-BAr$^F_4$). Compound **B** (40 mg, 0.029 mmol) was dissolved in ca. 1 mL of toluene/trifluorotoluene, followed by the addition of CatB-BCat (7.0 μL, 0.029 mmol). The

reaction mixture was allowed to stir at room temperature for overnight, and the solution changed to slightly yellow. Et_3N (1 μL, 0.007 mmol) was added to the mixture (to deprotonate and assist in the removal of the traces of **4-BAr$^F_4$** present). The volatiles were removed under vacuum, and the residue was washed with trifluorotoluene/pentane to give a white powder after drying under vacuum. However, we were not able to get **3-BAr$^F_4$** in an analytical pure form. ^{1}H NMR analysis indicated the presence of a small amount of [Et_3NH]BAr$^F_4$. Yield: 22 mg, 51%. ^{1}H NMR (C_6D_6): δ 8.27 (s, 8H, BAr_4-*H*), 7.62 (s, 4H, BAr_4-*H*), 7.10 (m, 2H, Catechol-*H*), 6.99 (br, 2H, (PNP)Aryl-*H*), 6.96 (m, 2H), 6.81−6.85 (m, 4H), 6.70 (br, 4H), 2.23 (m, 4H, C*H*Me$_2$), 2.03 (s, 6H, Ar-C*H*$_3$), 0.84 (app. q (dvt), J = 9 Hz, 6H, CH*Me*$_2$), 0.70 (app. q (dvt), J = 8 Hz, 12H, CH*Me*$_2$), 0.52 (app. q (dvt), J = 9 Hz, 6H, CH*Me*$_2$)). ^{1}H NMR (CD_2Cl_2): 7.71 (s, 8H, BAr_4-*H*), 7.55 (s, 4H, BAr_4-*H*), 7.53 (d, 2H, J = 6 Hz, (PNP)Aryl-*H*), 7.488 (br, 2H, (PNP)Aryl-*H*), 7.46 (d, 2H, J = 6 Hz, (PNP)Aryl-*H*), 7.22 (m, 2H, Catechol-*H*), 7.12 (m, 4H, Catechol-*H*), 7.06 (m, 2H, Catechol-*H*), 2.81 (m, 2H, C*H*Me$_2$), 2.72 (m, 2H, C*H*Me$_2$), 2.46 (s, 6H, Ar-C*H*$_3$), 1.11 (m, 18H, CH*Me*$_2$), 0.88 (app. q (dvt), J = 9 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.9 (q, J = 50 Hz, BAr_4-*C*), 148.3(Catechol-*C*), 147.1 (Catechol-*C*), 145.1 (t, J = 8 Hz, (PNP)Aryl-*C*), 139.7 (t, J = 3 Hz, (PNP)Aryl-*C*), 135.3 (BAr_4-*C*), 134.5 ((PNP)Aryl-*C*), 133.7 ((PNP)Aryl-*C*), 130.0 (q, J = 34 Hz, BAr_4-*C*), 123.3 (Catechol-*C*), 125.1 (d, J = 272 Hz, BAr_4-*C*), 125.8 (t, J = 4 Hz, (PNP)Aryl-*C*), 124.5 (Catechol-*C*), 119.8 (BAr_4-*C*), 117.9 (t, J = 4 Hz, (PNP)Aryl-*C*), 112.8 (Catechol-*C*), 112.3 (Catechol-*C*), 26.0 (t, J = 12 Hz), 24.5 (t, J = 13 Hz), 20.3, 19.9, 18.2, 17.5, 17.2. ^{31}P{^{1}H} NMR (C_6D_6): δ 44.7. ^{19}F NMR (C_6D_6): δ −63.2. ^{11}B{^{1}H} NMR (C_6D_6): δ −6.4 (BAr$^F_4$-*B*).

[(PN(BCat)P)Pd(BCat)]CB$_{11}$H$_{12}$ (3-CB$_{11}$H$_{12}$). Compound **C** (62 mg, 0.091 mmol) and CatB-BCat (24 mg, 0.10 mmol) were placed in a PTFE-capped flask together with 3 mL of toluene. The reaction mixture was heated at 60 °C overnight. The blue solution changed to yellow-brown the next day, and white precipitate was visible at the bottom of the flask. The white precipitate was collected on a glass frit by filtration and was dried under vacuum. Yield: 47 mg, 57%. X-ray quality crystals were obtained by slowly cooling down a hot $PhCF_3$ solution of **3-CB$_{11}$H$_{12}$**. ^{1}H NMR (C_6D_6) (a drop of CH_2Cl_2 was added to increase solubility): δ 7.19−7.16 (m, 4H, (PNP)Aryl-*H*), 7.11 (br, 2H, (PNP)Aryl-*H*), 7.04 (m, 2H, Catechol-*H*), 6.82 (m, 2H, Catechol-*H*), 6.78 (br, 4H, Catechol-*H*), 2.40 (m, 4H, C*H*Me$_2$), 2.21 (s, 6H, Ar-C*H*$_3$), 2.09−1.30 (br, 12H, CB$_{11}$*H*$_{12}$), 0.84 (m, 18H, CH*Me*$_2$), 0.61 (app. q (dvt), J = 8 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6) (a drop of CH_2Cl_2 was added to increase the solubility): δ 148.3 (Catechol-*C*), 147.2 (Catechol-*C*), 145.1 (t, J = 8 Hz, (PNP)Aryl-*C*), 139.9 ((PNP)Aryl-*C*), 134.9 ((PNP)-Aryl-*C*), 134.2 ((PNP)Aryl-*C*), 130.1 (t, J = 14 Hz, (PNP)Aryl-*C*), 126.3 (t, J = 3 Hz, (PNP)Aryl-*C*), 124.4 (Catechol-*C*), 123.0 (Catechol-*C*), 113.0 (Catechol-*C*), 112.3 (Catechol-*C*), 26.3 (t, J = 13 Hz), 24.8 (t, J = 13 Hz), 20.9, 20.3, 18.6, 18.0, 17.7, one C for $CB_{11}H_{12}$ anion is missing. ^{31}P{^{1}H} NMR (C_6D_6) (a drop of CH_2Cl_2 was added to increase solubility): δ 45.0. ^{11}B{^{1}H} NMR (C_6D_6) (a drop of CH_2Cl_2 was added to increase solubility): δ −6.6, −12.9, −15.9 ($CB_{11}H_{12}$-*B*). Elem. Anal. Found (calculated) for $C_{39}H_{60}B_{13}NO_4P_2Pd$: C, 51.27 (51.15); H, 6.69 (6.60); N, 1.64 (1.53).

Hydrolysis of 3-CB$_{11}$H$_{12}$. Compound **3-CB$_{11}$H$_{12}$** (5.0 mg, 0.0060 mmol) was dissolved in 1 mL $PhCF_3$, followed by the addition of 1 μL (excess) of degassed water. Upon addition, ^{31}P{^{1}H} NMR analysis indicated 15% of **1-CB$_{11}$H$_{12}$** and 85% of a signal at 49.7 ppm (likely **4-CB$_{11}$H$_{12}$**). The reaction mixture was fully converted to **1-CB$_{11}$H$_{12}$** after standing overnight.

[(PN(H)P)Pd(BCat)]BAr$^F_4$ (4-BAr$^F_4$). *Method A.* A solution of 0.015 mmol of **1-BAr$^F_4$** in 0.6 mL of PhF in a J. Young tube was treated with catecholborane (8.0 μL, 0.075 mmol), and the reaction mixture was allowed to sit in a 90 °C oil bath overnight. ^{31}P NMR observations revealed quantitative conversion to compound **4-BAr$^F_4$**. The mixture was passed through Celite, and the volatiles were removed under vacuum. The oily residue was washed with hexanes three times. X-ray quality crystals were obtained by recrystallizing the off-white solid from CH_2Cl_2/hexanes.

Method B. Compound **3-BAr$^F_4$** (63 mg, 0.039 mmol) was dissolved in ca. 0.6 mL of PhF and then treated with degassed water (0.70 μL, 0.039 mmol). After 40 min at room temperature, ^{31}P NMR observations revealed full conversion to compound **4-BAr$^F_4$**. Volatiles were removed under vacuum. The residue was recrystallized from CH_2Cl_2/hexanes. Yield: 40 mg, 68%. ^{1}H NMR (CD_2Cl_2): δ 7.71 (s, 8H, BAr_4-*H*), 7.54 (s, 4H, BAr_4-*H*), 7.37−7.43 (m, 6H, (PNP)Aryl-*H*), 7.23 (m, 2H, Catechol-*H*), 7.06 (m, 2H, Catechol-*H*), 6.89 (br, 1H, N-*H*), 2.71 (m, 2H, C*H*Me$_2$), 2.58 (m, 2H, C*H*Me$_2$), 2.43 (s, 6H, Ar-C*H*$_3$), 1.20−1.07 (m, 18H, CH*Me*$_2$), 0.92 (app. q (dvt), J = 7.2 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.6 (q, J = 50 Hz, BAr_4-*C*), 148.9 (Catechol-*C*), 145.2 (t, J = 8 Hz, (PNP)Aryl-*C*), 140.1 (t, J = 3 Hz, (PNP)Aryl-*C*), 135.4 (BAr_4-*C*), 135.2 ((PNP)Aryl-*C*), 134.1 ((PNP)Aryl-*C*), 129.6 (q, J = 34 Hz, BAr_4-*C*), 125.2 (d, J = 272 Hz, BAr_4-*C*), 125.7 (t, J = 4 Hz, (PNP)Aryl-*C*), 122.9 (Catechol-*C*), 121.1 (BAr_4-*C*), 118.0 (t, J = 4 Hz, (PNP)Aryl-*C*), 112.5 (Catechol-*C*), 26.1 (t, J = 12 Hz), 24.3 (t, J = 13 Hz), 21.1, 19.7, 18.5, 18.4, 17.9. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.8. ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 37.1 (br, Pd-*B*), −6.87 (s, BAr$^F_4$-*B*). Elem. Anal. Found (calculated) for $C_{64}H_{57}B_2NO_2F_{24}P_2Pd$: C, 50.31 (50.64); H, 3.59 (3.78); N, 0.93 (0.92).

Thermolysis of 4-BAr$^F_4$. **4-BAr$^F_4$** (13 mg, 0.009 mmol) was dissolved in 0.6 mL of PhF in a J. Young NMR tube, and the solution was heated at 90 °C for 15 h. ^{31}P NMR spectroscopic analysis indicated no observable changes.

Hydrolysis of 4-BAr$^F_4$. Compound **4-BAr$^F_4$** (12 mg, 0.008 mmol) was dissolved in 1 mL of toluene in an NMR tube. Degassed water (1.0 μL, excess) was added. After 4 h, ^{31}P{^{1}H} NMR analysis indicated ca. 40% conversion to compound **1-BAr$^F_4$**. It was fully converted to **1-BAr$^F_4$** after ca. 40 h.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic details for the XRD structural determinations of compounds **2-BAr$^F_4$**, **3-CB$_{11}$H$_{12}$**, **5**, and **4-BAr$^F_4$** in the form of CIF files and a pictorial ^{1}H NMR spectrum of select compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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