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Article

closo-o-Carboranylmethylamine−Pyridine Associations: Synthesis, Characterization, and First Complexation Studies

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The synthesis of new pyridine-substituted carboranylmethylamines is described. The strategy involved mesylation of carboranylmethanols prior to amination reaction and is particularly adapted to the reactivity of *o*-carborane derivatives bearing a 2-pyridinyl substituent. Preparation and characterization of a corresponding *N,N*-ligand−palladium complex as well as first results in a Suzuki coupling reaction are illustrated.

Introduction

ortho-Carboranes (icosahedral *closo*-1,2-$C_2B_{10}H_{12}$) represent a class of boron clusters that have found applications in fields as diverse as material science, medicinal chemistry, selective metal ion extraction, polymers, or supramolecular chemistry.[1] These icosahedral *closo-o*-carboranes may be functionalized at one or both cage carbon atoms to give organophosphorus derivatives,[2] thiols, thioethers, and to a lesser extent amines, arsines, or selenols and may form a variety of mono- or bidentate coordination complexes.[3] The past decades have witnessed the emerging use of both metallacarboranes and *closo*-carborane-based coordination compounds in a wide range of transition metal catalyzed organic transformations.[4,5] For instance, *closo*-carborane frameworks bearing thioether and/or phosphine substituents at both C-vertices were recently shown to be highly effective bidentate ligands for Pd- and Rh-catalyzed organic transformations.[4] However, the association of amine-chelating groups to a *closo*-carborane unit as ligands is still scarcely reported, probably due to the well-known amine- and/or base-generated degradation of *closo*-carboranes.[6] Such carborane derivatives thus remain challenging and under-exploited from synthetic, coordination chemistry, and, consequently,

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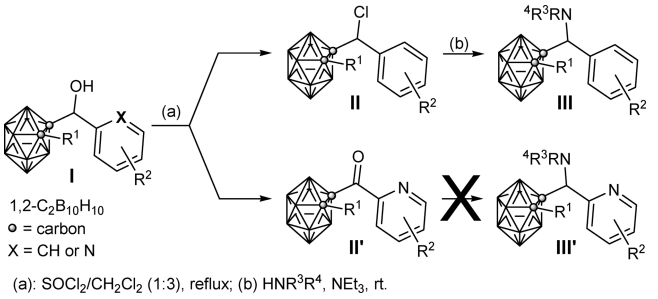
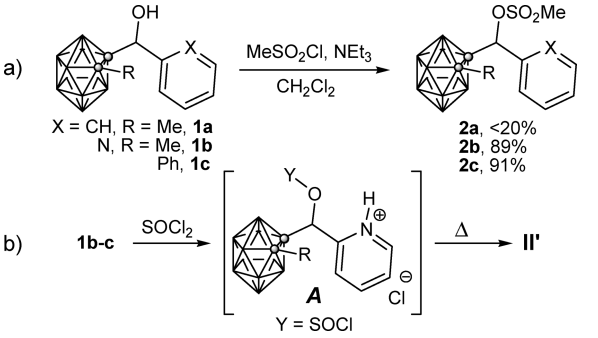
Scheme 1. Previous Results on Carboranylmethyl Alcohol Chemistry



(a): $SOCl_2/CH_2Cl_2$ (1:3), reflux; (b) HNR^3R^4, NEt_3, rt.

applications points of view.[7] On the basis of our previous experience in both carborane chemistry[8] and synthesis, complexation, and catalytic activity of benzylic amines,[9] we have been interested in the synthesis of new carboranyl amines. Our efforts to date have focused on aminobenzyl-*o*-carboranes bearing (hetero)aromatic rings (type **III** in Scheme 1). We have recently reported a convenient and general method to synthesize these compounds starting from monosubtituted carboranes and commercially available aromatic aldehydes and avoiding the cluster degradation.[8g] The key step of this methodology is a selective nucleophilic amination of the chlorides **II** as intermediates ((b) in Scheme 1). The use of mild conditions allowed minimization of partial degradation of the boron clusters by amines. Following this strategy, we sought to develop a new series of potentially interesting bidentate *N,N*-ligands incorporating both an aminomethyl-*o*-carborane cluster and a pyridine heterocycle (type **III′** in Scheme 1). If the 2-aminomethylpyridine pattern is found in many ligands recently described for coordination chemistry and/or catalysis,[10] 2-aminomethylpyridine−carborane combinations remain to our knowledge unprecedented. Unfortunately our synthetic sequence involving chlorination of carboranyl methyl alcohols followed by nucleophilic amination proved unsuccessful with pyridine-substituted substrates (Scheme 1), showing that in this case such transformation is still not trivial.[8f] In this note, we report a new easy methodology to synthesize such *N,N*-diamines that overcome the previous synthetic problems and show that this new family of ligands can form stable Pd complexes that are highly effective catalysts for Suzuki coupling reactions.

Scheme 2. Mesylation of Carboranylbenzyl Alcohols



Results and Discussion

We previously examined the mesylation of alcohol **1a**, bearing a phenyl substituent, and obtained a very poor conversion of the alcohol to the corresponding mesylate **2a** (Scheme 2a) even under harsh reaction conditions (2 equiv of $MeSO_2Cl$ in refluxing CH_2Cl_2).[8g] We hypothesized that the low reactivity of alcohol **1a** could be due to its low nucleophilicity as a result of the presence of two electron-withdrawing substituents (phenyl and *o*-carboranyl groups), in addition to the bulkiness of the cluster. For these reasons we turned our attention to the smaller $SOCl_2$ reagent, and this reacted completely to give the halogenated derivatives (type **II** in Scheme 1).[8g] However, we were puzzled by the unusual reactivity of these 2-pyridyl derivatives. In fact, in situ NMR experiments showed that the latter were far more reactive toward $SOCl_2$ than the related phenyl derivatives, regardless of the nature of the reaction product (Scheme 2b).[8f] The oxidation process affording the pyridyl-carboranyl ketone **II′** was attributed to the fast formation of plausible pyridinium-chlorosulfite intermediate ***A*** (Y = SOCl), with concomitant increase of the residual pseudo benzylic proton acidity, at the early stage of the chlorination step (Scheme 2).

Taking into account the strong analogy between intermediate ***A*** and the product resulting from mesylation of **I** (Y = SO_2Me), we were curious to test the reactivity of the 2-pyridinyl derivatives toward $MeSO_2Cl$ to see whether oxidation or mesylation would occur. Therefore two 2-pyridinyl derivatives **1b**,**c** were treated with $MeSO_2Cl$ in the presence of Et_3N at room temperature (Scheme 2a). Gratifyingly, both derivatives **1b**,**c** afforded the mesylated products **2b**,**c**, exclusively, in excellent yields, as shown in Scheme 2. These results further illustrate the particular behavior of the 2-pyridinyl-substituted carboranylmethanols **1b** and **1c** toward electrophiles[8f] and suggest the crucial intervention of the pyridine moiety in the reaction mechanism. All new compounds in this work have been fully characterized by analytical methods and ^1H, ^{11}B, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. $^{11}B\{^1H\}$ NMR spectra for all compounds are consistent with a *closo*-icosahedral geometry for the boron cage.[11] $^{13}C\{^1H\}$ NMR spectra also show characteristic peaks for the two cage-carbon vertices, pyridine ring, and benzylic CH carbons. Only relevant ^1H NMR data will be discussed later in more detail.

The successful syntheses of the mesylate derivates **2b**,**c** open new possibilities for the preparation of the desired *N,N*-diamines by nucleophilic amination. Indeed, mesylates **2b**,**c** were successfully converted into the targeted vicinal

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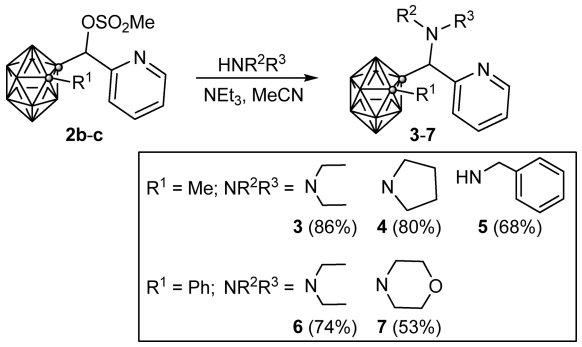
Scheme 3. Preparation of the Diamine Derivatives 3−7



diamines by their reaction with 1.5 equiv of amine at room temperature in acetonitrile (Scheme 3). The expected compounds **3**−**7** were obtained in good to excellent yields (53−86%) regardless of the nature of the nucleophile (primary or secondary, cyclic or acyclic amine). All these new compounds were fully characterized by analytical methods and NMR spectroscopy, and the molecular structures of **5** and **6** have been unequivocally established by X-ray crystallography. The molecular structures for both compounds are in agreement with the NMR data showing the vicinal disposition of the pyridine and amine nitrogens. Crystal data collection, selected bond lengths, bond angles, and torsion angles can be found in the Supporting Information.

As thought, these new aminomethyl-*o*-carboranes are characterized by the presence of two nitrogen atoms in vicinal position and can be considered as interesting *N,N*-ligands for the preparation of original transition metal complexes. In order to illustrate the potential of this family of compounds in coordination chemistry, we turned our attention to the synthesis of a palladium complex. We chose to first examine the aminomethyl-*o*-carborane **5** by virtue of two different chiral centers, one at the secondary amine nitrogen and the other at the contiguous methylene carbon. Thus, diamine **5** was treated with $Na_2[PdCl_4]$ in freshly distilled MeOH according to recent literature[12] to give the desired Pd^{II} complex **8** in nearly quantitative yield as an air-stable orange solid (Scheme 4). This complex was easily purified by simple filtration through a silica gel pad and was stable in acetone solutions for weeks. Complex **8** is to the best of our knowledge the first palladium−diamine complex incorporating an intact *closo*-boron cluster in its structure.

Complex **8** has been fully characterized by NMR spectroscopy and elemental analysis. There are two sources of chirality in this complex that would lead, in principle, to four different stereoisomers. The coordinated NH nitrogen has four different substituents leading to a chiral center that can adopt *R* and *S* configurations. The other source of chirality is the contiguous methylene carbon adopting also *R* and *S* configurations. However, only one diastereomer is observed in solution since only one set of signals was found in the ^1H, ^{11}B, and ^{13}C NMR spectra of **8**. Metal coordination to both nitrogen atoms of the ligand is confirmed by a characteristic positive shielding observed between the amine **5** and its corresponding complex **8** (Figure 1). The chemical shift differences range from 0.27 to 0.45 ppm for the pyridine

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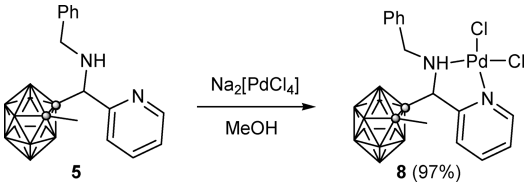
Scheme 4. Preparation of the Palladium Complex 8



protons H(a), H(b), H(c), and H(d) and from 0.37 to 0.92 ppm for the benzylic protons H(e) and H(f), respectively. As expected, the chemical shift for the NH proton is the most affected by metal coordination (δ 2.87 and 4.53 for **5** and **8**, respectively). It can be seen that an AB spin system for the diastereotopic protons of the methylene group of the benzyl fragment (H(f) in Figure 2) in ligand **5** became a well-resolved ABX spin system in complex **8** [H(f) and H(f′)]. Coupling constants between the two diastereotopic nuclei, J_{AB}, are 13.0 and 13.7 Hz for the ligand **5** and the complex **8**, respectively. Coupling of both diastereotopic nuclei with the NH proton is observed only in the complex and displays different coupling constants (9.2 and 2.2 Hz). Consequently, the NH proton appears as a broad doublet of about 8 Hz.

The molecular structure of **8** has been unequivocally confirmed by X-ray crystallography.[13] The crystal structure of the complex contains a racemic mixture of *RS*/*SR* enantiomeric pairs. The molecular structure of the N(2) *R*−C(3) *S* isomer is shown in Figure 2, and selected bond lengths, bond angles, and torsion angles are given in the Supporting Information As expected, the chelating ligand binds to the metal through a pyridyl donor N1 and secondary amine donor N2, forming a five-membered ring with an N1−Pd1−N2 angle of 81.11(10)°. The coordination sphere at Pd(1) is close to square planar, the largest deviation of Cl(2), Cl(3), N(1), and N(2) from their main plane being 0.040 Å. Whereas both Pd1−Cl bond distances are nearly identical (Pd1−Cl2, 2.2877(8) and Pd1−Cl3, 2.2887(8) Å), the Pd−N1(pyridine) bond distance of 2.030(2) Å is significantly shorter than the Pd−N2(H) distance of 2.049(3) Å. The nearly identical Pd−Cl bond distances reflect a similar *trans* influence of the pyridyl and secondary amine groups. Consequently, the difference of bond distances (Δ(Pd−N)) of 0.019 Å is probably due in part to the steric hindrance of the diamine ligand. The other possible *RR*/*SS* enantiomeric pair is not observed in the solid structure of **8**. This is not surprising because such configurations would have the benzyl group at N(2) and the carborane substituent at C(3) arranged in a *syn* fashion, with the consequent steric hindrance. Therefore, both ^1H NMR spectroscopic data in solution and crystallographic data in the solid state strongly support that the complexation reaction occurs in a diastereoselective way.

(13) Crystal data for **8**: M = 531.79, monoclinic, a = 8.9577(3) Å, b = 14.3902(3) Å, c = 18.5339(7) Å, α = 90.00°, β = 102.028(2)°, γ = 90.00°, U = 2336.63(13) Å^3, T = 120(2) K, space group $P2_1/n$, Z = 4, μ(Mo Kα) = 1.031 mm^{-1}, 27 368 reflections measured, 5352 unique reflections (R_{int} = 0.0645). The final R_1 values were 0.0392 ($I > 2\sigma(I)$). The final $wR(F_2)$ values were 0.0837 ($I > 2\sigma(I)$). The final R_1 values were 0.0574 (all data). The final $wR(F_2)$ values were 0.0910 (all data). The goodness of fit on F_2 was 1.067. Data were collected on a Bruker Nonius FR591 rotating anode equiped with a Roper CCD following standard procedures. The structure was solved and refined using the SHELX suite of programs (Sheldrick, G. M. *Acta Crystallogr. A* 2008, *A64*, 112−122). Graphics produced using CrystalMaker Software Ltd, Oxford, England.

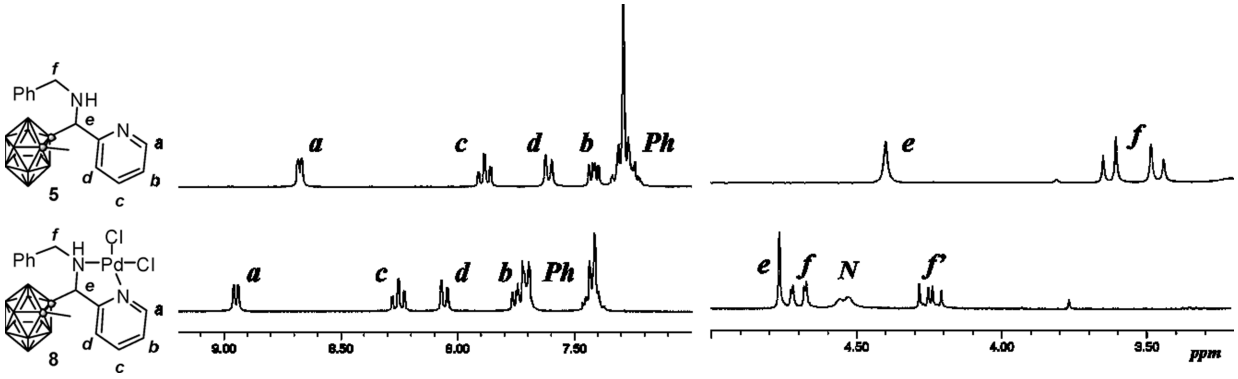


Figure 1. Comparison of the ^{1}H NMR spectra (CD_3COCD_3) of ligand **5** and its corresponding Pd complex **8**.

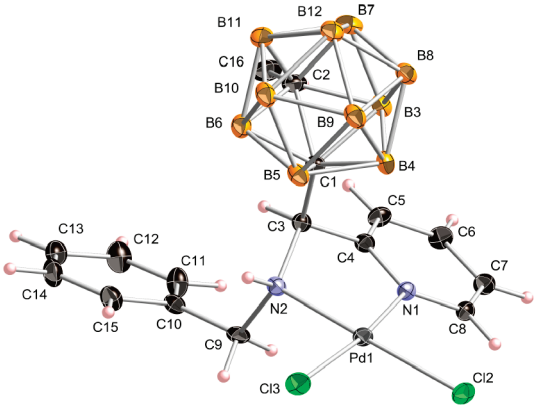


Figure 2. Molecular structure of the palladium complex **8** (thermal ellipsoids drawn at the 35% probability level, cluster hydrogens omitted for clarity).

Of the two possible diastereoisomeric couples, the *RS*/*SR* racemic mixture is the only one obtained.

To provide an initial test for the possible catalytic activity of complex **8** and whether it would resist the catalytic reaction conditions, we decided to evaluate its activity in Suzuki−Miyaura coupling reactions.[14] Preliminary results are reported in the Supporting Information (Table S1). Under classical conditions, complex **8** was shown to be promising, although it does not surpass the activities of other related catayst.[9d] Catalyst loadings as low as 1 to 0.1 mol % were sufficient to observe quantitative conversion of the starting materials into the expected biaryl products in high yields. It is also noteworthy that the carborane complex **8** was compatible with the use of water as an environmentally more friendly reaction medium and that it apparently resisted the operating temperature since Pd black was never observed after the catalytic reactions. However these results represent only preliminary data from a brief investigation, and we remain confident that such compounds have exceptional promise as catalyst precursors. Finally, this study further validates the feasibility of incorporating *closo*-*o*-carborane clusters into *N,N*-diamine ligands and their coordination to transition metals. This enables a wide spectrum of new architectures to be generated, which would not be possible with traditional ligands, as well as unique electronic properties.

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Conclusion

We have developed an efficient synthesis of novel 2-pyridinyl aminomethyl-*o*-carboranes through a new strategy adapted to the particular reactivity of *o*-carborane derivatives bearing a 2-pyridinyl substituent. Thanks to their vicinal-diamine pattern, these compounds can be considered as useful *N,N*-ligands for transition metal complexation and catalysis. To demonstrate their potential, we have prepared and fully characterized the first palladium-diamine complex containing a *closo*-*o*-carborane cluster. Its catalytic activity has been tested in Suzuki coupling reactions and proved promising. Further investigations on the properties of this new family of ligands for complexation with transition metals are currently in progress.

Experimental Section

General Comments. All manipulations were carried out in round-bottomed flasks equipped with a magnetic stirring bar, capped with a septum, and under an N_2 atmosphere. Chemicals were used as follows: THF distilled from Na/benzophenone, dichloromethane distilled from CaH_2, and MeOH distilled from Mg/I_2; all the other chemicals were commercially available and used as received. 2-Pyridinyl-*o*-carboranylmethanols were synthesized according to our previously described procedure.[8f] ^{1}H, ^{13}C, and ^{11}B spectra were recorded respectively at 300, 75, and 96 MHz and referenced to the residual solvent peak for ^{1}H and ^{13}C NMR or to $BF_3\cdot OEt_2$ as an external standard for ^{11}B NMR. All NMR spectra are measured in $CDCl_3$ unless reported. Chemical shifts are reported in ppm and coupling constants in Hz. Multiplet nomenclature is as follows: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet.

General Procedure for the Mesylation of the *o*-Carboranylmethanols. MsCl (242 μL, 358 mg, 3.13 mmol, 2.5 equiv) was added dropwise to a CH_2Cl_2 solution (10 mL) containing the carboranyl alcohol (1.25 mmol) and triethylamine (527 μL, 379 mg, 3.75 mmol, 3 equiv) at 0 °C (ice/water bath), and the mixture was stirred for 18 h at room temperature. After the addition of a saturated aqueous solution of $NaHCO_3$ (25 mL) to the reaction mixture, the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic phases were dried over $MgSO_4$ and filtered. Chromatographic separation on silica gel of the residue obtained upon evaporation afforded the expected mesylate.

Mesylate 2b. The general procedure was followed starting from alcohol **1b** (332 mg, 1.25 mmol): pale yellow oil (382 mg, 1.11 mmol, 89%). ^{1}H NMR: δ 2.32 (s, 3H, $CH_3C_{cluster}$), 2.86 (s, 3H, CH_3SO_3), 5.99 (s, 1H, CHOMs), 7.37 (ddd, J = 1.1, 4.9, and 7.5, 1H, C_5H_4N), 7.55 (dd, J = 0.8 and 7.9, 1H, C_5H_4N), 7.82 (td, J = 1.6 and 7.7, 1H, C_5H_4N), 8.60 (m, 1H, C_5H_4N). ^{13}C NMR: δ 23.5, 39.2, 76.9, 77.4, 79.0, 122.3, 124.8, 137.3, 149.1,

154.3. ^{11}B NMR: δ −0.7 (d, $J_{B,H}$ = 145, 1B), −4.9 (d, $J_{B,H}$ = 151, 1B), −7.9 to −11.9 (m, 8B). IR (film): ν 3088, 3052, 3011, 2960, 2929, 2868, 2586 (BH), 1588, 1572, 1470, 1439, 1408, 1362, 1178, 1101, 1004, 963, 912, 855, 799, 671, 568, 517 cm^{-1}. MS (ESI): *m*/*z* (%) 366 (100) $[M + Na]^+$, 344 (10) $[M + H]^+$, 248 (10). HRMS (ESI): calcd for $[M + H]^+$ 344.2324; found 344.2324; calcd for $[M + H]^+$ 346.2266; found 346.2269.

General Procedure for the Synthesis of the *o*-Carboranylmethylamines. The aza-nucleophile (0.75 mmol, 1.5 equiv) and triethylamine (211 μL, 152 mg, 1.5 mmol, 3 equiv) were successively added to a MeCN solution (5 mL) of the mesylate (0.5 mmol, 1 equiv), and the mixture was stirred at room temperature until the disappearance of the starting material was observed by TLC analysis (typically 24−48 h). After the addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) to the reaction mixture, the aqueous phase was extracted with EtOAc (3 × 25 mL), and the combined organic phases were dried over $MgSO_4$ and filtered. Chromatographic separation on silica gel of the residue obtained upon evaporation of the filtered solution afforded the pure expected amine.

Amine 5. The general procedure was followed starting from mesylate **2b** (172 mg, 0.5 mmol) and benzylamine (82 μL, 80 mg, 0.75 mmol): white solid (121 mg, 0.34 mmol, 68%); mp 129 °C. ^{1}H NMR: δ 1.99 (s, 3H, CH_3C$_{cluster}$), 3.36 (d, J = 13.1, 1H, CH_2NH), 3.68 (d, J = 13.1, 1H, CH_2NH), 4.13 (s, 1H, C*H*NH), 7.22−7.35 (m, 7H, C_5H_4N, C_6H_5), 7.74 (td, J = 1.9 and 7.7, 1H, C_5H_4N), 8.67 (m, 1H, C_5H_4N). ^{1}H NMR (CD_3COCD_3): δ 2.12 (s, 3H, CH_3C$_{cluster}$), 2.87 (s, 1H, N*H*), 3.45 (d, J = 13.0, 1H, CH_2NH), 3.62 (d, J = 13.0, 1H, CH_2NH), 4.39 (s, 1H, C*H*NH), 7.22−7.43 (m, 5H, C_6H_5), 7.41 (m, 1H, C_5H_4N), 7.60 (d, J = 7.7, 1H, C_5H_4N), 7.88 (td, J = 1.7 and 7.7, 1H, C_5H_4N), 8.67 (m, 1H, C_5H_4N). ^{13}C NMR: δ 22.9, 51.7, 63.4, 75.9, 81.2, 123.4, 124.0, 127.4, 128.4 (2C), 128.5 (2C), 136.4, 138.8, 149.6, 157.7. ^{11}B NMR: δ −2.1 (d, $J_{B,H}$ = 149 Hz, 1B), −4.8 (d, $J_{B,H}$ = 151 Hz, 1B), −7.0 to −13.2 (m, 8B). IR (in KBr): ν 3435, 3291, 3060, 2880, 2860, 2665, 2613 (BH), 2593 (BH), 2557 (BH), 1658, 1586, 1463, 1427, 1278, 1155, 1104, 1032, 996, 975, 883, 775, 739, 703 cm^{-1}. MS (ESI): *m*/*z* (%) 377 (100) $[M + Na]^+$, 355 (15) $[M + H]^+$. HRMS (ESI): calcd for $[M + H]^+$ 355.3180; found 355.3187; calcd for $[M + H]^+$ 353.3248; found 353.3252. $C_{16}H_{26}B_{10}N_2$ (354.50): calcd C 54.21, H 7.39, N 7.90; found C 54.45, H 7.55, N 7.81.

Preparation of the Palladium Complex 8. Na_2PdCl_4 (74 mg, 0.25 mmol) was added to a stirred solution of the amine **5** (89 mg, 0.25 mmol) in freshly distilled MeOH (5 mL). The mixture was stirred at room temperature for 16 h, and the solvent was removed by evaporation under vacuum. The residue was then filtered through a silica gel pad [first eluting with cyclohexane/EtOAc (7:3) to remove traces of free amine, then eluting with EtOAc] to give the expected palladium complex **8** as an orange solid (129 mg, 0.243 mmol, 97%). ^{1}H NMR (CD_3COCD_3): δ 1.79 (s, 3H, CH_3C$_{cluster}$), 4.23 (dd, J = 9.2 and 13.7, 1H, CH_2NH), 4.53 (d, J = 8.3, 1H, N*H*), 4.69 (dd, J = 2.2 and 13.7, 1H, CH_2NH), 4.76 (s, 1H, C*H*NH), 7.38−7.46 (m, 3H, C_6H_5), 7.68−7.76 (m, 3H, C_6H_5, C_5H_4N), 8.05 (d, J = 7.3, 1H, C_5H_4N), 8.24 (td, J = 1.7 and 7.9, 1H, C_5H_4N), 8.94 (dd, J = 1.0 and 5.6, 1H, C_5H_4N). ^{13}C NMR (CD_3COCD_3): δ 22.9, 58.7, 68.0, 78.7, 80.7, 127.3, 127.8, 130.4 (2C), 130.6, 131.8 (2C), 134.4, 141.3, 151.6, 160.5. ^{11}B NMR (CD_3COCD_3): δ −0.7 (d, $J_{B,H}$ = 146, 1B), −5.0 (d, $J_{B,H}$ = 147, 1B), −7.0 to −12.0 (m, 8B). IR (in KBr): ν 3440, 3255, 3024, 2649, 2593 (BH), 2557 (BH), 1607, 1443, 1422, 1386, 1206, 1175, 1083, 1062, 1032, 975, 775, 759, 703, 616 cm^{-1}. MS (ESI): *m*/*z* (%) 592 (30), 555 (30), 537 (100) $[M - Cl + MeCN]^+$, 496 (20) $[M - Cl]^+$, 459 (20) $[M - Cl - HCl]^+$. HRMS (ESI): calcd for $[M - Cl - HCl]^+$ 459.2057; found 459.2051; calcd for $[M - Cl - HCl]^+$ 462.2047; found 462.2046. $C_{16}H_{26}B_{10}Cl_2N_2Pd$ (531.83): calcd C 36.13, H 4.93, N 5.27; found C 36.11, H 4.92, N 5.01.

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Supporting Information Available: Experimental procedures, compound characterization and crystallographic data, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.