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Unprecedented B—H activation through Pd catalysed B—C_{vinyl} bond coupling on borane systems.

Pau Farràs,^[a] David Olid-Britos,^[a] Clara Viñas,^[a] Francesc Teixidor^{*[a]}

Keywords: Cobaltabisdicarbollide / Heck reaction / B-C coupling / cross-coupling / Pd catalysis.

A Pd induced cascade B—C_{vinyl} coupling that produces multiple B—C_{vinyl} bonds starting from a single B—I bond has been demonstrated. The process is most probably stimulated by the geometrical disposition of the B—H bonds confronting the B—Pd sites, along with the hydride character of the B—H units. Two and

one B—C_{vinyl} couplings on the metallacarborane substrate have been generally obtained, but formation up to six B—C_{vinyl} bonds have been observed. A theoretical reaction mechanism involving an unprecedented B—H activation is proposed to interpret the multisubstitution process.

Introduction

Transition-metal-catalyzed C—C bond coupling is a very useful reaction¹ that can be done using palladium, nickel, copper, cobalt or other metal complexes as catalysts.^[1–3] In addition, the construction of C—C bonds via palladium-catalyzed cross-coupling reactions has become a routine synthetic tool of organic synthesis by using either unactivated or organometallic reagents. Several reactions have become essential and receive the names of their pioneers, namely, Heck, Stille, Suzuki, Sonogashira, Tsuji-Trost, Negishi or Kumada reactions. More recently, a unique value inherent to Pd-catalyzed transformations has become the ability to couple them to other powerful C—C bond formation events in one reaction vessel, also named tandem or cascade reactions.^[4] This is possible due to a C—H bond activation assisted by directing groups, such as acetyl, acetamino, carboxylic acid, oxazolyl, pyridyl, and imino moieties.^[5]

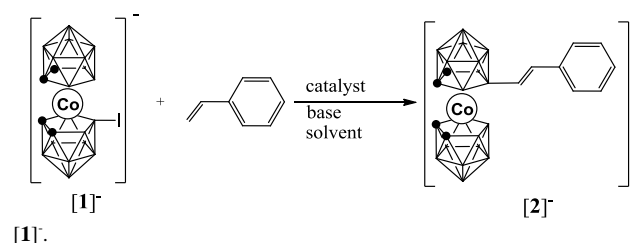
On the other hand, there are only few examples of substitution in boron clusters based on similar boron-carbon cross-coupling reactions. Reactions found in the literature are based mostly on Kumada C—C-couplings, with few examples in which the bond has been inspired by the Heck, Negishi or Suzuki-Miyaura reaction conditions. The methodology using Kumada reaction conditions was first applied to iodocarboranes by Zakharkin *et al.*^[6] and further developed by Jones,^[7] Hawthorne,^[8] Bregadze,^[9] and our group.^[10] The reaction of the anionic monoiodo derivative [8-I-3,3'-Co-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)][−], [1][−], and [B₁₂H₁₁I]^{2−} with alkyl and aryl reagents has been reported.^[10b,11] Kumada carbon-carbon reaction conditions that inspired boron-carbon bond formations have been also extended to monocarborane derivatives.^[12] Sjöberg *et al.*^[13] were successful on the substitution of iodine in 2-I-1,12-C₂B₁₀H₁₁ by various aryl groups using either Heck or Suzuki-Miyaura reaction conditions.

We were interested in the application of the Heck coupling conditions to the monoiodo derivative of the metallacarborane anion

[8-I-3,3'-Co-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)][−] [1][−]. In previous work^[10b] it was demonstrated the feasibility to react this compound with Grignard reagents in a Pd-catalyzed reaction following Kumada's conditions, and the unprecedented metal-mediated transformation of an alkyne into an alkene unit that bridges the two subclusters in [3,3'-Co-(1,2-C₂B₉H₁₁)₂][−] with Sonogashira's method.^[14] It was later reported that with a Rh catalyst, successive B-C_{alkyl} were produced in the [CB₁₁H₁₂][−] cluster.^[15] Despite all this work, no report existed on the applicability of Heck reaction in metallacarboranes.

Herein, we describe the first examples applying Heck coupling conditions on iodometallacarboranes and the unprecedented results obtained, that reveal the very distinct behaviour of boranes and arenes. In arene, only one C—C coupling occurs per C—I unit, whereas in [8-I-3,3'-Co-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)][−] two B—C_{vinyl} couplings can be generated starting from only one B—I. This implies that an unprecedented B—H activation occurs, that is observed experimentally and is supported by theoretical calculations. A possible pathway is given.

Scheme 1. Cross-coupling between styrene and monoiodinated compound



[a] Dr. P. Farràs, D. Olid-Britos, Prof. Clara Viñas, Prof. F. Teixidor
Institut de Ciència de Materials de Barcelona (CSIC)
Campus de la U.A.B., E-08193 Bellaterra, Spain.
Fax: (+) 34 935805729
E-mail: teixidor@icmab.es

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Table 1. Optimization studies of cross-coupling reaction.

| entry | equiv. of styrene | catalyst | base (equiv.) | solvent | T (°C) | reaction time (h) | yield (%) ^[b] |
|------------------|-------------------|---|---------------------------------------|---------|--------|-------------------|--------------------------|
| 1 ^[a] | 2.5 | 8% PdCl ₂ (PPh ₃) ₂ 8% CuI | dry NEt ₃ (2.5) | dry DMF | 120 | 24 | 80 |
| 2 | 2.5 | 8% PdCl ₂ (PPh ₃) ₂ 8% CuI | NEt ₃ (2.5) | THF | 90 | 48 | 0 |
| 3 | 2.5 | 8% PdCl ₂ (PPh ₃) ₂ 8% CuI | Ag ₃ PO ₄ (2.5) | DMF | 120 | 24 | 60 |
| 4 | 1.5 | 8% PdCl ₂ (PPh ₃) ₂ 8% CuI | NEt ₃ (2.5) | DMF | 120 | 16 | 45 |
| 5 | 1.2 | 1% Pd Herrmann's catalyst ^[c] | Ag ₃ PO ₄ (1.5) | DMF | 120 | 6 | 45 |
| 6 | 5 | 5% PdCl ₂ (PPh ₃) ₂ 5% CuI | 2,6-Lutidine (3) | dry DMF | 140 | 16 | 45 |
| 7 | 5 | 5% PdCl ₂ (PPh ₃) ₂ 5% CuI | dry 2,6-Lutidine (3) | dry DMF | 140 | 24 | 90 |
| 8 | 2.5 | 5% Pd(PPh ₃) ₄ | 2,6-Lutidine (3) | dry DMF | 130 | 16 | 45 |
| 9 | 5 | 5% PdCl ₂ (PPh ₃) ₂ 5% CuI | 2,6-Lutidine (3) | dry DMF | 130 | 24 | 55 |

[a] Addition of 15% Pd(ac)₂. [b] Yield determined by ¹H-NMR spectroscopy comparing the relative integral areas of the C₆-H hydrogen atoms. [c] *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II).

Results and Discussion

The reaction conditions were initially screened using the parent substrate [1][−] with styrene to investigate the effects of various palladium sources, equivalents of reagents, bases, solvents and temperatures as shown in Scheme 1. It was found that 5% [PdCl₂(PPh₃)₂]/CuI in dry DMF with 3 equivalents of dry 2,6-Lutidine as base at 140 °C (Table 1, entry 7) were the optimal conditions. It was noticed that small amounts of water in either the base or the solvent led to a significant decrease in the yields. Although the influence of the temperature is important, the existence of humidity and mostly the quality of the catalyst seemed to be the key features for the reaction. The use of triethylamine as base produced lower yields due, most probably, to its low boiling point, causing its evaporation. Instead, the use of Ag₃PO₄ gave reasonable results as it could avoid the problem of evaporation. However, the increase of the yield was not significant. The reaction conditions described by Sjöberg *et al.*^[13b] were also tested, but these led to a large amount of side products. Finally, the use of a non-nucleophilic base such as 2,6-Lutidine gave the best results for the studied cases.

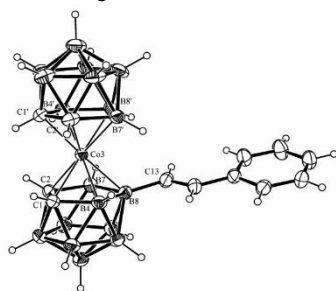



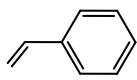
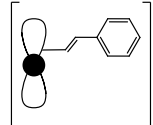

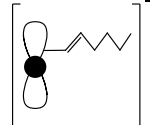
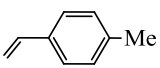
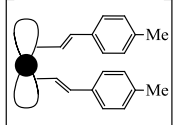

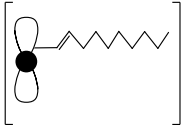
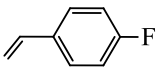
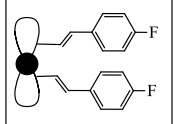

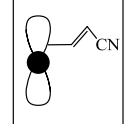
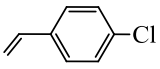
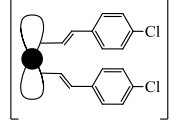
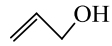
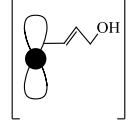
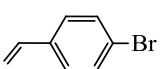
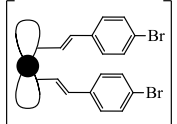
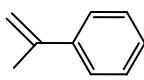
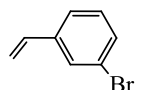
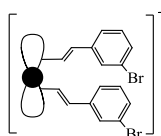
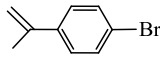
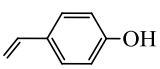
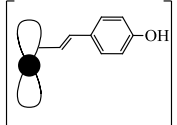

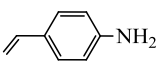
Figure 1. Molecular structure of [NMe₄][8-C₆H₇-3,3'-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], [NMe₄][2]. The displacement ellipsoids are drawn on a 30% probability level.

Compound [NMe₄][2] was obtained pure enough to get crystals from a dichloromethane/hexane mixture. The X-ray crystal structure is shown in Figure 1.

With these optimized conditions in hand, it was set out to investigate the scope of the domino process. It was begun by using substituted aryl rings (Table 2). It was found that metallocarboranes bearing a wide variety of functional groups could be synthesized. Halide (compounds [4][−], [5][−], [6][−] and [7][−]), electron donating and electron withdrawing (compounds [3][−], [8][−] and [9][−]) moieties were all well tolerated, except for [9][−] for which, under these conditions, no reaction occurred. The reaction proceeded well with vinyl substituted alkyl chains (compounds [10][−], [11][−], [12][−] and [13][−]) with the formation of the products in low to moderate yields. For the allyl alcohol [13][−], the yield is the lowest of this series. Reagents in which no hydrogen atom was present in alpha position of the double bond (compounds [14][−] and [15][−]) or that the ene group was not on a terminal position (compound [16][−]) produced no B—C_{vinyl} coupling.

The most fascinating point in these reactions was, however, the formation of the disubstituted molecules displayed in Table 2 ([3][−]–[7][−]). These disubstituted molecules are generated from the singly substituted [8-I-3,3'-Co-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)][−]. Two independent B—C_{vinyl} couplings are generated from one single B—I. To our knowledge this is the first example of a cascade set of B—C_{vinyl} couplings on the same molecule, initiated in a single B—I unit. A similar situation has never been described in C—C cross-coupling. Although disubstitution has been observed in almost every aryl substrate, the degree of substitution varies from one to another. In Table 2, yields of the major products are given, along with the ratio of mono- and di-substituted species produced. As there seen, most of the aryl derivatives produced disubstituted species whereas the alkyl ones yielded mostly monosubstituted. It has to be taken into account that the reaction conditions have been optimized to produce the monosubstituted compound [2][−] in the highest possible yield and,

Table 2. Pd-catalyzed cross-coupling reaction of [1]⁻ with vinyl groups ( = 3,3'-Co(1,2-C₂B₉H₁₀)₂).

| Compound | substrate | product | mono:di ratio | yield (%) ^a | Compound | substrate | product | mono:di ratio | yield (%) ^a |
|------------------|---|---|---------------|------------------------|-------------------|---|---|---------------|------------------------|
| [2] ⁻ |  |  | 100:0 | 90 | [10] ⁻ |  |  | 100:0 | 48 |
| [3] ⁻ |  |  | 0:100 | 77 | [11] ⁻ |  |  | 100:0 | 40 |
| [4] ⁻ |  |  | 0:100 | 84 | [12] ⁻ |  |  | 100:0 | 63 |
| [5] ⁻ |  |  | 0:100 | 55 | [13] ⁻ |  |  | 100:0 | 10 |
| [6] ⁻ |  |  | 0:100 | 25 | [14] ⁻ |  | | - | 0 |
| [7] ⁻ |  |  | 59:100 | 22 | [15] ⁻ |  | | - | 0 |
| [8] ⁻ |  |  | 100:30 | 57 | [16] ⁻ |  | | - | 0 |
| [9] ⁻ |  | | - | 0 | | | | | |

[a] Yield determined by ¹H-NMR spectroscopy comparing the relative integral areas of the C_c-H hydrogen atoms.

therefore, no screening for each compound has been done to maximize the ratio of di vs. monosubstitution. Characterization of the disubstituted molecules was done by ¹H-NMR, ¹¹B-NMR and found instead of the 2:2 pattern in monosubstituted molecules. In addition, the ¹¹B-NMR spectra did show a 2:2:8:4:2 pattern, instead of the 1:1:2:2:4:2:2:2:1:1 pattern found for the monosubstituted. This was due to the C_s symmetry of the disubstituted species, not found in monoderivatives. Besides, the MALDI-TOF mass spectrum for the isolated [2]⁻, [4]⁻, [6]⁻, [11]⁻ and [12]⁻ compounds produced the molecular mass *m/z* peaks corresponding to disubstituted, [4]⁻, and [6]⁻, and monosubstituted [2]⁻, [11]⁻ and [12]⁻, with no fragmentation. For non-purified fractions of anions [6]⁻ and [7]⁻ the MALDI-TOF-MS, both with a bromine atom in *para* and *meta* positions, revealed the formation of up to hexasubstituted derivatives (see Supporting Information for MALDI-TOF-MS spectrum of [7]⁻).

These unprecedented experimental results employing Heck conditions encouraged us to produce a plausible mechanism for this

MALDI-TOF-MS spectroscopies. These techniques clearly evidenced the formation of these species. In the ¹H-NMR spectra only one resonance corresponding to the four C_c-H groups was reaction. Taking as a model the mechanism described by Surawatanawong *et al.* for the Heck reaction with palladium diphosphines,^[16] we evaluated the relevant parts of the catalytic cycle. For these qualitative studies, and to economize computer time, studies were conducted with propylene, on the monoiodo derivative of cobaltabisdicarbollide [1]⁻ and [Pd(PH₃)₃] catalyst with density functional theory (DFT). It has been compared for min₁ and min₂ the changes caused by the substitution of PH₃ to PPh₃. No significant changes have been observed in the geometry of the cluster-Pd moiety (see Supporting Information for further details). The studies begin with an energy profile (electronic energies are considered) for the oxidative addition, followed by the insertion of the propylene. Further steps, namely β-hydride transfer/olefin elimination of the product and the abstraction of proton by the base, are not considered.

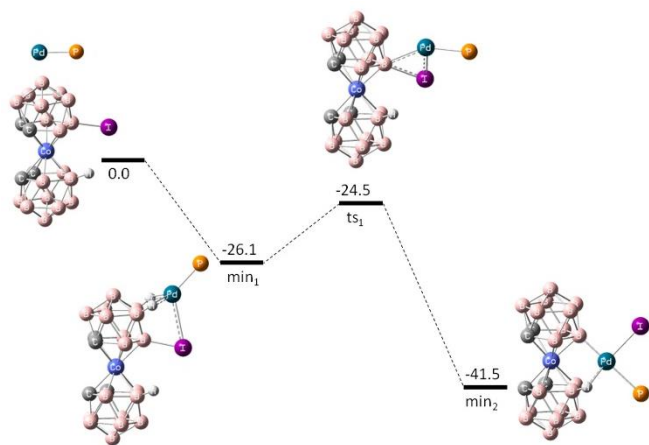


Figure 2. Energy profile for the oxidative addition to palladium phosphine complex. The relative energies are given in kcal/mol. Hydrogen atoms except for the atoms participating in the reaction have been omitted for better clarity.

Monoligated palladium species have been proposed to be important intermediates in the catalytic cycle.^[17] Therefore, for the purpose of simplicity, it was considered the use of [PdL] instead of [PdL₂] as the catalyst for the oxidative addition step. The most stable reaction pathway is shown in Figure 2. Intermediate min₂ is energetically favourable by 41.5 kcal/mol. Interestingly, in the first complex min₁ an interaction between palladium and the two most reactive B—H vertices, B(9) and B(12), is found, with B—H...Pd distances of 2.06 and 2.09 Å. This kind of interaction is recursive throughout the mechanism. The transition state ts₁ has the typical Y—Pd—I arrangement with an angle of 59° as expected for an early transition state.^[18] Bond distances are 2.61 and 2.46 Å for Pd—B and Pd—I bonds respectively. After overcoming the transition state, the system rearranges to min₂ as a T-shaped structure with a 90.4° angle between B(8)—Pd—I. In this case, the B(8)—Pd bond is shorter than in ts₁, being 2.05 Å. A closer distance Pd—B(8') at 2.02 Å is found between palladium and the most reactive B—H vertex on the non-substituted C₂B₉H₁₁ cage. This B(8')—H...Pd interaction can be explained by the position of the iodine atom in the structure, and the favourable B—H geometrical disposition of the B(8')—H in the cluster, beaming out of the centre of the originally non-substituted icosahedron. Our group reported some years ago that B—H vertices dissipate better the electron density out of an anionic cluster than C—H vertices.¹⁷ This causes that the halogen atom prefers to be *trans* to B(8')—H...Pd instead of B(8)—Pd as it is known that H⁻ is one of the strongest *trans* influence ligands.^[19]

For the onset of the migratory insertion of propylene, two possible onsets were examined. Propylene can insert to the palladium complex (min₂) either from the substituted (min'₃) or non-substituted (min₃) cage plane as shown in Figure 3. As expected, the energy of min₃ structure is lower and propylene binds to the vacant site of min₂. Then, the B(8')—H...Pd interaction in min₂ is broken causing a migration of the iodine originated in the higher *trans* influence of the B(8)—Pd bond. Transition state ts₂ has the typical Pd- π -alkene arrangement with a Pd—C distance of 2.10 and 2.20 Å and the C=C distance on propylene is 1.45 Å, 0.03 Å longer in respect to min₃ at 1.42 Å. This distance gives indication on the relative strength of the C—C bond depending on the neighbouring atoms. For the free propylene the C—C distance is 1.36 Å, which is the same as for the isolated [8-C₃H₅-3,3'-Co-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]. Therefore, the interaction of the propylene with palladium weakens the electronic density of the

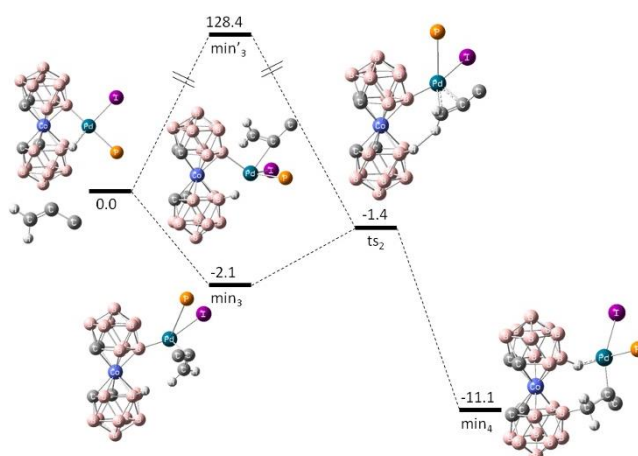


Figure 3. Energy profile for the migratory insertion of propylene. The relative energies are given in kcal/mol. Hydrogen atoms except for the atoms participating in the reaction have been omitted for better clarity.

double bond, enlarging the C—C bond distance. The relatively short dihydrogen distance between B(8')—H...H—C (2.15 Å) is remarkable causing an intramolecular reaction catalyzed by palladium that leads to the formation of min₄. It was unprecedented that the generated B—C_{vinyl} bond is formed in the initially non-substituted B(8')—H cage, instead of the B(8)—I, as one could expect for a typical Heck reaction mechanism. The hydrogen atom bonded to B(8') or one of the hydrogen atoms of the propylene has migrated to the B(8) vertex producing an agostic type B—H...Pd bond with a 109° angle, and a H...Pd distance of 1.78 Å. The iodine has moved to a *trans* position in respect to the B—C...Pd structure, indicating that the electronic connection between B(8)—H...Pd is less than for B(8')—C...Pd. At this stage it is expected that a second propylene process to produce the disubstituted species observed in the molecule interacts with the palladium complex initiating the experiments. No further calculations have been done at this stage, as it has been assumed that the same or very close mechanism occurs as for the described Heck's catalytic cycle.

Conclusion

In conclusion, a Pd induced cascade B—C_{vinyl} coupling has been found for the first time that produces multiple B—C_{vinyl} bonds starting from a single B—I bond. The process is most probably stimulated by the geometrical disposition of the B—H bonds confronting the B—Pd sites, along with the hydride character of the B—H units. Two and one B—C_{vinyl} couplings on the metallocarborane substrate have been generally observed, but MALDI-TOF-MS also indicates that further B—C_{vinyl} coupling takes place. Up to six B—C_{vinyl} bonds have been observed in the MALDI-TOF-MS, although these have been observed in few examples and in trace amounts. Further work is currently being done to explore the possibilities of the method that, initiating from a single B—I bond, can lead to mono, di and polysubstitution, a phenomenon never described in the conventional C—C cross coupling Heck conditions. To interpret this multisubstitution process a theoretical reaction mechanism is proposed (Figure 4). This transformation involves an unprecedented B—H activation that strongly supports the experimental evidence. The synthesis of π -extended systems incorporating metallocarboranes is of key importance for their application into optical systems. Therefore, the use of the methodology described in this work opens another way to obtain such molecules.

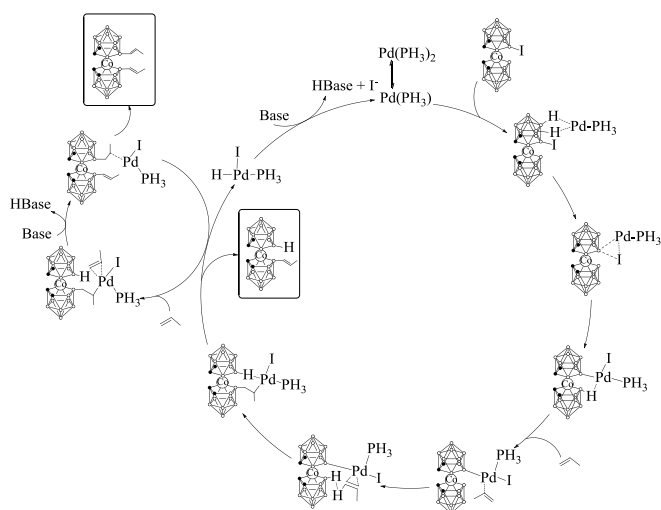


Figure 4. Suggested mechanism for the generation of B—C_{vinyl} bonds in borane systems.

Computational Details

All the calculations reported here were performed with the Gaussian 03 suite of programs.^[20] Geometries were fully optimized at the PBE/PBE/lanl2dz level of theory,^[21] as well as their thermochemical properties. All stationary points were found to be true minima (number of imaginary frequencies, $N_{\text{imag}}=0$). Calculations on the mechanism for both ground and excited states were done using the same level of theory. The potential minima are characterized by all positive frequencies and the transition states are characterized by a single imaginary frequency.

Experimental Section

General details. All carborane anions prepared are air and moisture stable; however, some reagents used are moisture-sensitive. Therefore, Schlenk and high-vacuum techniques were employed whenever necessary. The mass spectra were recorded in the negative ion mode using Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV. The ^1H , $^1\text{H}\{^{11}\text{B}\}$ -NMR (300.13 MHz), ^{11}B -NMR (96.29 MHz) and $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded from acetone- d_6 solutions at 25°C. Chemical shift values for ^{11}B -NMR spectra were referenced to external $\text{BF}_3\cdot\text{OEt}_2$, and those for ^1H , $^1\text{H}\{^{11}\text{B}\}$, and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were referenced to $\text{Si}(\text{CH}_3)_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.

General procedure: To a solution of $\text{Cs}[8\text{-I-3,3'-Co-(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ (50 mg, 1 equiv), 2,6-Lutidine (30 μL , 3 equiv), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (3.1 mg, 0.05 equiv) and CuI (1 mg, 0.05 equiv) in dry DMF (5 mL) was added the corresponding substrate (5 equiv). The mixture was then immersed in a oil bath (140 °C) for 24 h. DMF was removed by chloroform:water extraction. The organic phase was evaporated and a second extraction with a mixture $\text{Et}_2\text{O}:\text{HCl}_{\text{aq}}$ (1M) was done. The resulting solution was dried over sodium sulfate, filtrated, and concentrated under reduced pressure. The crude product was purified by column chromatography using dichloromethane:acetonitrile 70/30 as eluent and the residue was dissolved in the minimum volume of EtOH and an aqueous solution containing an excess of $[\text{NMe}_4][2]$ was added, resulting in the formation of a precipitate. This was filtered off, washed and dried in vacuo.

Data for $\text{NMe}_4[2]$: Yield: 31.7 mg (75%). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 7.35 (m, 2H, C_6H_5 , $\text{C}_o\text{-H}$), 7.22 (m, 2H, C_6H_5 , $\text{C}_m\text{-H}$), 7.10 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 7.08 (m, 1H, C_6H_5 , $\text{C}_p\text{-H}$), 6.41 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 4.35 (br s, 2H, $\text{C}_e\text{-H}$), 4.06 (br s, 2H, $\text{C}_e\text{-H}$), 3.45 (s, 12H, $\text{N}(\text{CH}_3)_4$), 2.99, 2.95, 2.89, 2.82, 2.74, 1.87, 1.64 (br s, 18H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 140.61 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 137.32 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 128.18, 125.69, 125.14 (s, C_6H_5), 55.18 (s, $\text{N}(\text{CH}_3)_4$), 53.35 (s, $\text{C}_e\text{-H}$), 50.21 (s, $\text{C}_e\text{-H}$). ^{11}B -NMR: δ = 13.09 (s, 1B, B(8)), 7.13 (d, $^1\text{J}(\text{B,H})$ = 138 Hz, 1B), 1.83 (d, $^1\text{J}(\text{B,H})$ = 141 Hz, 2B), -4.14 (d, 2B), -4.74 (d, 4B), -5.71 (d, $^1\text{J}(\text{B,H})$ = 142 Hz, 2B), -16.23 (d, $^1\text{J}(\text{B,H})$ = 132 Hz, 2B), -17.46 (d, $^1\text{J}(\text{B,H})$ = 138 Hz, 2B), -21.48 (d, $^1\text{J}(\text{B,H})$ = 152 Hz, 1B), -23.04 (d, $^1\text{J}(\text{B,H})$ = 163 Hz, 1B). MALDI-TOF MS: m/z (%): 528.41 ($\text{M}+\text{C}_8\text{H}_7$, 10%), 425.37 (M , 100%), 323.22 ($\text{M}-\text{C}_8\text{H}_7$, 8%).

Data for $\text{NMe}_4[4]$: Yield: 35.0 mg (78%). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 7.41 (m, 4H, $\text{C}_6\text{H}_4\text{F}$, $\text{C}_o\text{-H}$), 7.00 (m, 4H, $\text{C}_6\text{H}_4\text{F}$, $\text{C}_m\text{-H}$), 6.81 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 2H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3\text{F}$), 6.42 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 2H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3\text{F}$), 4.29 (br s, 4H, $\text{C}_e\text{-H}$), 3.45 (s, 12H, $\text{N}(\text{CH}_3)_4$),

2.86-1.28 (br s, 16H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 139.99 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3$), 119.7 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3$), 167.21, 118.54, 131.18, 131.17 (s, C_6H_3), 55.28 (s, $\text{N}(\text{CH}_3)_4$), 53.46 (s, $\text{C}_e\text{-H}$), 51.91 (s, $\text{C}_e\text{-H}$). ^{11}B -NMR: δ = 11.10 (s, 2B, B(8,8')), 1.77 (d, $^1\text{J}(\text{B,H})$ = 118 Hz, 2B), -5.03 (d, $^1\text{J}(\text{B,H})$ = 127 Hz, 8B), -17.64 (d, $^1\text{J}(\text{B,H})$ = 137 Hz, 4B), -22.41 (d, $^1\text{J}(\text{B,H})$ = 135 Hz, 2B). MALDI-TOF MS: m/z (%): 564.44 (M , 100%), 685.47 ($\text{M}+\text{C}_8\text{H}_7\text{F}$, 12%).

Data for $\text{NMe}_4[6]$: Yield: 9.5 mg (19%). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 7.40 (m, 4H, $\text{C}_6\text{H}_4\text{Br}$, $\text{C}_o\text{-H}$), 7.34 (m, 4H, $\text{C}_6\text{H}_4\text{Br}$, $\text{C}_m\text{-H}$), 6.94 (d, $^3\text{J}(\text{H,H})$ = 15 Hz, 2H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3\text{Br}$), 6.40 (d, $^3\text{J}(\text{H,H})$ = 15 Hz, 2H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3\text{Br}$), 4.28 (br s, 4H, $\text{C}_e\text{-H}$), 3.45 (s, 12H, $\text{N}(\text{CH}_3)_4$), 2.98-1.28 (br s, 16H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 139.43 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3$), 119.17 (s, 1H, $\text{CH}=\text{CH}-\text{C}_6\text{H}_3$), 133.33, 129.28, 129.98, 127.55 (s, C_6H_3), 55.23 (s, $\text{N}(\text{CH}_3)_4$), 53.55 (s, $\text{C}_e\text{-H}$), 51.71 (s, $\text{C}_e\text{-H}$). ^{11}B -NMR: δ = 11.10 (s, 2B, B(8,8')), 1.76 (d, $^1\text{J}(\text{B,H})$ = 132 Hz, 2B), -5.03 (d, $^1\text{J}(\text{B,H})$ = 107 Hz, 8B), -17.47 (d, $^1\text{J}(\text{B,H})$ = 94 Hz, 4B), -22.71 (d, $^1\text{J}(\text{B,H})$ = 133 Hz, 2B). MALDI-TOF MS: m/z (%): 687.28 (M , 100%), 868.20 ($\text{M}+\text{C}_8\text{H}_7\text{Br}$, 13%).

Data for $\text{NMe}_4[11]$: Yield: 14.7 mg (32%). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 4.36 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{C}_8\text{H}_{17}$), 4.29 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{C}_8\text{H}_{17}$), 4.40 (br s, 2H, $\text{C}_e\text{-H}$), 4.01 (br s, 2H, $\text{C}_e\text{-H}$), 3.45 (s, 12H, $\text{N}(\text{CH}_3)_4$), 2.99-1.64 (br s, 17H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 122.31 (s, 1H, $\text{CH}=\text{CH}-\text{C}_7\text{H}_{14}$), 157.89 (s, 1H, $\text{CH}=\text{CH}-\text{C}_7\text{H}_{14}$), 37.21, 30.01, 29.81, 29.53, 23.76, 13.96 (s, C_7H_{14}), 55.26 (s, $\text{N}(\text{CH}_3)_4$), 53.48 (s, $\text{C}_e\text{-H}$), 50.98 (s, $\text{C}_e\text{-H}$). ^{11}B -NMR: δ = 12.72 (s, 1B, B(8)), 6.86 (d, $^1\text{J}(\text{B,H})$ = 150 Hz, 1B), 2.23 (d, $^1\text{J}(\text{B,H})$ = 140 Hz, 2B), -5.00 (d, $^1\text{J}(\text{B,H})$ = 107 Hz, 8B), -16.65 (d, $^1\text{J}(\text{B,H})$ = 132 Hz, 2B), -18.16 (d, $^1\text{J}(\text{B,H})$ = 138 Hz, 2B), -20.71 (d, $^1\text{J}(\text{B,H})$ = 156 Hz, 1B), -23.27 (d, $^1\text{J}(\text{B,H})$ = 173 Hz, 1B). MALDI-TOF MS: m/z : 462.45

Data for $\text{NMe}_4[12]$: Yield: 9.8 mg (26%). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 7.73 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{CN}$), 5.27 (d, $^3\text{J}(\text{H,H})$ = 18 Hz, 1H, $\text{CH}=\text{CH}-\text{CN}$), 4.08 (br s, 2H, $\text{C}_e\text{-H}$), 4.01 (br s, 2H, $\text{C}_e\text{-H}$), 3.45 (s, 12H, $\text{N}(\text{CH}_3)_4$), 2.89-1.19 (br s, 17H, B-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 148.21 (s, 1H, $\text{CH}=\text{CH}-\text{CN}$), 103.32 (s, 1H, $\text{CH}=\text{CH}-\text{CN}$), 118.19 (s, CN), 55.25 (s, $\text{N}(\text{CH}_3)_4$), 53.42 (s, $\text{C}_e\text{-H}$), 51.11 (s, $\text{C}_e\text{-H}$). ^{11}B -NMR: δ = 10.51 (s, 1B, B(8)), 6.93 (d, $^1\text{J}(\text{B,H})$ = 132 Hz, 1B), 3.91 (d, $^1\text{J}(\text{B,H})$ = 116 Hz, 2B), -1.81 (d, $^1\text{J}(\text{B,H})$ = 118 Hz, 2B), -4.34 (d, $^1\text{J}(\text{B,H})$ = 116 Hz, 4B), -5.00 (d, $^1\text{J}(\text{B,H})$ = 86 Hz, 4B), -15.71 (d, $^1\text{J}(\text{B,H})$ = 135 Hz, 2B), -17.05 (d, $^1\text{J}(\text{B,H})$ = 137 Hz, 2B), -20.62 (d, $^1\text{J}(\text{B,H})$ = 144 Hz, 1B), -22.68 (d, $^1\text{J}(\text{B,H})$ = 125 Hz, 1B). MALDI-TOF MS: m/z : 374.79 (M , 100%).

Crystal-Structure Determination.— Crystals of $\text{NMe}_4[2]$: were grown from $\text{CH}_2\text{Cl}_2/\text{Hexane}$ and used for room temperature (300(2) K) X-ray structure determination. The measurement was carried out on a *BRUKER SMART APEX CCD* diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) from an x-Ray Tube. The measurements were made in the range 1.99 to 28.36° for θ . Full-sphere data collection was carried out with ω and ϕ scans. Crystal data for $[\text{NMe}_4][2]$: Formula $\text{C}_{16}\text{H}_{40}\text{B}_{18}\text{CoN}$, M_r = 501.49, monoclinic, space group P -1, a = 13.5665(19), b = 14.409(2), c = 15.896(3), α = 89.427(3), β = 64.831(2), γ = 87.768(2), V = 2810.12 Å³, Z = 4, Reflections collected 43520, unique 13549 [$R(\text{int})$ = 0.0600]. Programs used: data collection, Smart version 5.631 (Bruker AXS 1997-02); data reduction, SAINT + version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000-2003).

The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 . The non-hydrogen atoms were refined anisotropically. The borane C-H hydrogen atoms were located in the difference map and refined with Ueq 1.2 times those of the parent atom, other parameters refined freely. The rest of hydrogens were placed in geometrically optimized positions and forced to ride on the atom to which they are attached. R indices were (all data): R_1 = 0.1160, wR_2 = 0.2430. Final R indices were ($I > 2\sigma(I)$): R_1 = 0.0793, wR_2 = 0.2249. Crystallographic data (excluding structure factors) for $[\text{NMe}_4][2]$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 783142. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): MALDI-TOF-MS for [7], effect of the PH_3 vs. PPh_3 ligand and geometry coordinates can be found.

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