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Unprecedented B–H Activation Through Pd-Catalysed B–C_{vinyl} Bond Coupling on Borane Systems

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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 has been observed. A theoretical reaction mechanism involving an unprecedented B–H activation is proposed to interpret the multisubstitution process.

Introduction

Transition-metal-catalysed C–C bond coupling is a very useful reaction[1] which can be carried out using palladium, nickel, copper, cobalt or other metal complexes as catalysts.[1–3] In addition, the construction of C–C bonds by means of palladium-catalysed cross-coupling reactions has become a routine synthetic tool of organic synthesis by using either nonactivated 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-catalysed transformations has been recognised and this is the ability of them to be coupled 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 a 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 formed 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-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$, [**1**]$^-$, and $[B_{12}H_{11}I]^{2-}$ with alkyl and aryl reagents has been reported.[10b,11] Kumada carbon-carbon reaction conditions which inspired B–C bond formations have also been extended to monocarborane derivatives.[12] Sjöberg et al.[13] were successful in the substitution of iodine in 2-I-1,12-$C_2B_{10}H_{11}$ 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-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ [**1**]$^-$. In previous work[10b] the feasibility of the reaction between this compound and Grignard reagents in a Pd-catalysed reaction following Kumada's conditions was demonstrated as was the unprecedented metal-mediated transformation of an alkyne into an alkene unit that bridges the two subclusters in [3,3′-Co-(1,2-$C_2B_9H_{11}$)$_2$]$^-$ by means of Sonogashira's method.[14] It was later reported that with a Rh catalyst, successive B–C_{alkyl} bonds were produced in the $[CB_{11}H_{12}]^-$ cluster.[15] Despite all this work, no report existed on the applicability of the Heck reaction in metallacarboranes.

Herein, we describe the first examples of applying Heck coupling conditions to iodometallacarboranes and the unprecedented results obtained which reveal the very distinct behaviour of boranes and arenes. In arenes, only one C–C coupling occurs per C–I unit, whereas in [8-I-3,3′-Co-(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ two B–C_{vinyl} couplings can be generated starting from only one B–I bond. This implies that an unprecedented B–H activation occurs and that has been observed experimentally and is supported by theoretical calculations. A possible pathway is given.

Results and Discussion

The reaction conditions were initially screened using the parent substrate [**1**]$^-$ with styrene in order to investigate the effects of various palladium sources, equivalents of rea-

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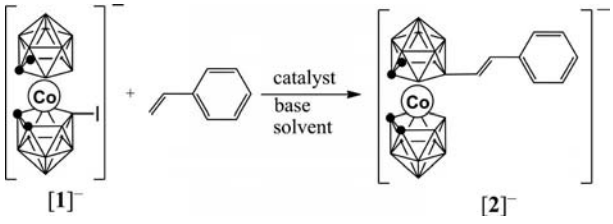
Table 1. Optimisation studies of cross-coupling reactions.

Entry	Styrene /equiv.	Catalyst	Base /equiv.	Solvent	T /°C	Reaction time /h	NMR 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_3PO_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_3PO_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] Determined by ^1H NMR spectroscopy comparing the relative integrated areas of the peaks corresponding to the C_c–H hydrogen atoms. [c] *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphanyl)benzyl]dipalladium(II).

gents, bases, solvents and temperatures as shown in Scheme 1. It was found that 5% $[PdCl_2(PPh_3)_2]$/CuI in dry DMF with 3 equiv. of dry 2,6-lutidine as a 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 which results in its evaporation. Instead, the use of Ag_3PO_4 gave reasonable results since it does not evaporate. However, the increase in the yield was not significant. The reaction conditions described by Sjöberg et al.[13b] were also tested but these led to large amounts of side products. Finally, the use of a nonnucleophilic base such as 2,6-lutidine gave the best results for the studied cases.



Scheme 1. Cross-coupling between styrene and the monoiodinated compound [**1**]⁻.

Compound $[NMe_4]$[**2**] was obtained in sufficient purity to obtain crystals from a dichloromethane/hexane mixture. The molecular structure determined by X-ray crystallography is shown in Figure 1.

With these optimised conditions in hand, we set out to investigate the scope of the domino process. We started by using substituted aryl rings (Table 2) and found that metallacarboranes bearing a wide variety of functional groups could be synthesised. Halide (compounds [**4**]⁻, [**5**]⁻, [**6**]⁻ and [**7**]⁻), electron-donating and -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.

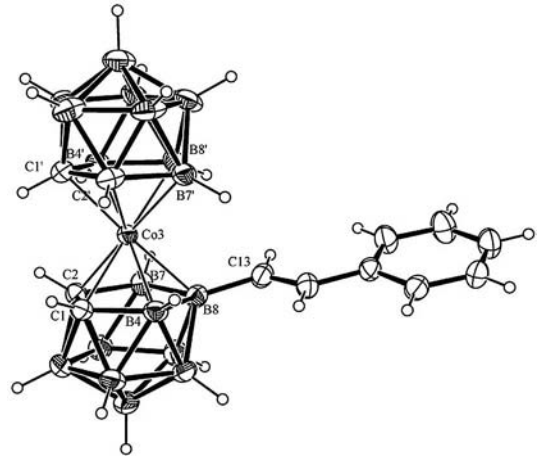
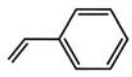
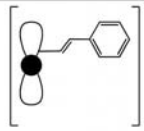
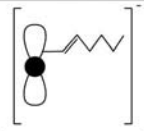
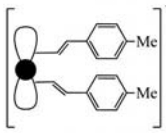
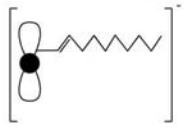
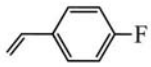
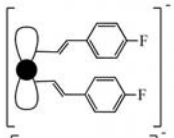
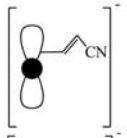
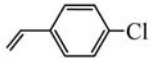
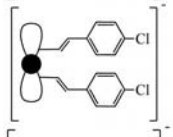
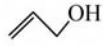
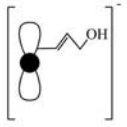
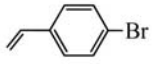
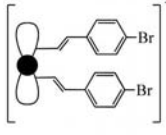
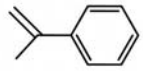
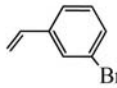
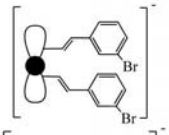
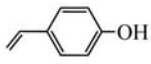
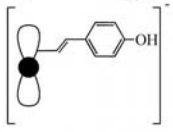


Figure 1. Molecular structure of $[NMe_4][8\text{-}C_8H_7\text{-}3,3'\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, $[NMe_4]$[**2**]. The displacement ellipsoids are shown at the 30% probability level.

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 $[8\text{-I-}3,3'\text{-Co-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$. Two independent B–$C_{vinyl}$ couplings are generated from one single B–I. To the best of our knowledge, this is the first example of a cascade set of B–

Table 2. Pd-catalysed cross-coupling reaction of [**1**]$^-$ with vinyl[a] groups.

	Substrate	Product	Mono:di ratio	Yield (%)[b]		Substrate	Product	Mono:di ratio	Yield (%)[b]
[**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] Vinyl groups:  = 3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$. [b] Yield determined by ^{1}H-NMR spectroscopy comparing the relative integral areas of the C_c-H hydrogen atoms.

C_{vinyl} couplings on the same molecule, initiated in a single B–I unit. A similar situation has never been described for 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 disubstituted species produced. As can be seen, most of the aryl derivatives produced disubstituted species whereas the alkyl ones yielded mostly monosubstituted products. It has to be taken into account that the reaction conditions have been optimised to produce the monosubstituted compound [**2**]$^-$ in the highest possible yield and, therefore, no screening for each compound has been done to maximise the ratio of di to monosubstitution. Characterisation of the disubstituted molecules was done by ^{1}H NMR, ^{11}B NMR and MALDI-TOF-MS spectroscopy. These techniques clearly evidenced the formation of these species. In the ^{1}H NMR spectra, only one resonance corresponding to the four C_c–H groups was found instead of the 2:2 pattern in monosubstituted molecules. In addition, the ^{11}B NMR spectra showed 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 products. This was due to the C_s symmetry of the disubstituted species, not found in the monosubstituted derivatives. 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 disubstitued [**4**]$^-$, and [**6**]$^-$, and monosubstituted [**2**]$^-$, [**11**]$^-$ and [**12**]$^-$, with no fragmentation. For nonpurified fractions of anions [**6**]$^-$ and [**7**]$^-$, both with a bromine atom in *para* and *meta* positions showed MALDI-TOF mass spectra indicating 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 reaction. Taking as a model the mecha-

nism described by Surawatanawong et al. for the Heck reaction with palladium diphosphanes,[16] we evaluated the relevant parts of the catalytic cycle. For these qualitative studies, and to economise on computer time, studies were conducted, using density functional theory (DFT), with propylene on the monoiodo derivative of cobaltabis(dicarbollide) $[\mathbf{1}]^-$ and a $[Pd(PH_3)]$ catalyst. By calculations it has been proven that for min_1 and min_2 the changes in the geometry of the cluster-Pd moiety caused by the substitution of PH_3 by PPh_3 are not significant (see Supporting Information for further details). The studies started with an energy profile (electronic energies were 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 were not considered.

Monoligated palladium species have been proposed as important intermediates in the catalytic cycle.[17] Therefore, for the purpose of simplicity, we considered the use of [PdL] instead of $[PdL_2]$ as the catalyst for the oxidative addition step. The most stable reaction pathway is shown in Figure 2. Intermediate min_2 is energetically favourable by 41.5 kcal mol^{-1}. Interestingly, in the first complex min_1, an interaction between palladium and the two most reactive B–H vertices, B(9) and B(12), can be 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 ts_1 has the typical Y–Pd–I arrangement with an angle of 59° as expected for an early transition state.[18] The bond lengths are 2.61 and 2.46 Å for the Pd–B and Pd–I bonds, respectively. After overcoming the transition state, the system rearranges to min_2 as a T-shaped structure with a 90.4°

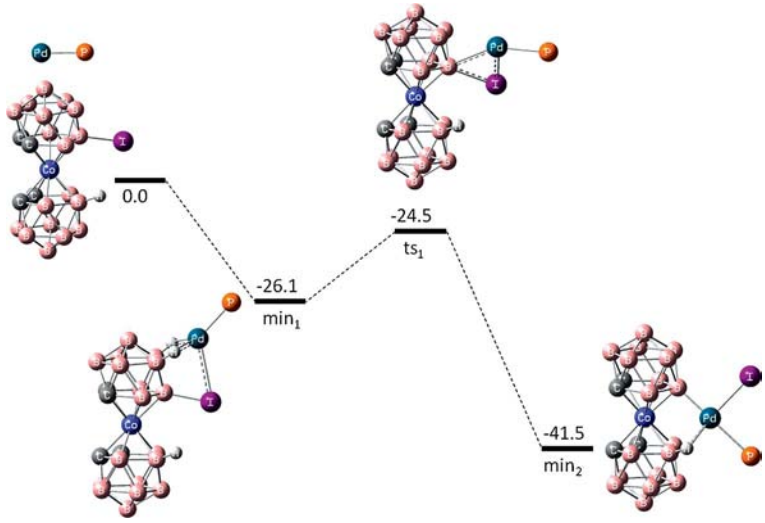


Figure 2. Energy profile for the oxidative addition to palladium phosphane complex. The relative energies are given in kcal mol^{-1}. Hydrogen atoms except for the atoms participating in the reaction have been omitted for better clarity.

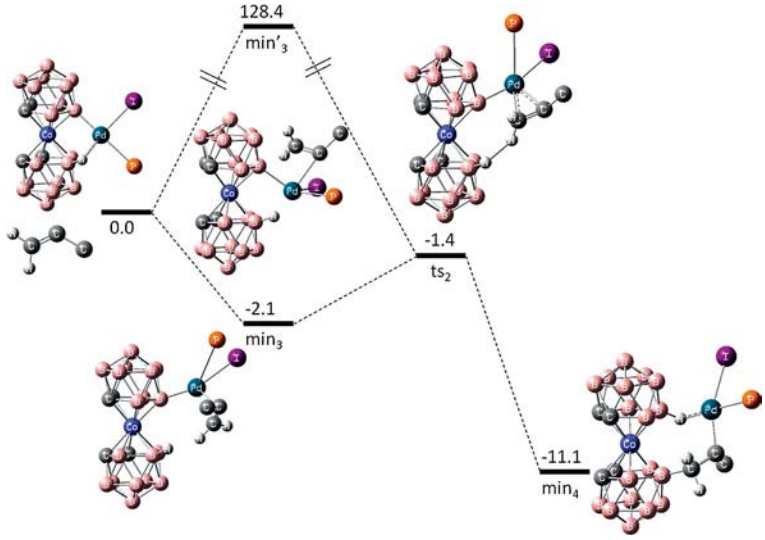


Figure 3. Energy profile for the migratory insertion of propylene. The relative energies are given in kcal mol^{-1}. Hydrogen atoms except for the atoms participating in the reaction have been omitted for better clarity.

angle across B(8)–Pd–I. In this case, the B(8)–Pd bond is shorter than in ts_1, being 2.05 Å. A closer distance Pd–B(8′), at 2.02 Å, can be found between palladium and the most reactive B–H vertex on the unsubstituted $C_2B_9H_{11}$ 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, protruding out of the centre of the originally unsubstituted icosahedron. Our group reported some years ago that B–H vertices dissipate better the electron density out of an anionic cluster than C_c–H vertices.[17] This causes that the halogen atom to prefer to be trans to B(8′)–H···Pd instead of B(8)–Pd since 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 pathways were examined. Propylene can insert to the palladium complex (min_2) either from the substituted (min'_3) or unsubstituted (min_3) cage plane as shown in Figure 3. As expected, the energy of min_3 is lower and propylene binds to the vacant site of min_2. Then, the B(8′)–H···Pd interaction in min_2 is broken causing a migration of the iodine originating from the higher *trans* influence of the B(8)–Pd bond. Transition state ts_2 has the typical Pd-π-alkene arrangement with Pd–C distances of 2.10 and 2.20 Å, and the C=C distance on the propylene is 1.45 Å, 0.03 Å longer than in min_3 at 1.42 Å. This distance gives an 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-C_3H_5-3,3′-Co-(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$. Therefore, the interaction of the propylene with palladium weakens the electronic density of the double bond, enlarging the C–C bond length.

The relatively short dihydrogen distance between B(8′)–H···H–C (2.15 Å) is remarkable and causes an intramolecular reaction catalysed by palladium that leads to the formation of min_4. The generated B–C_{vinyl} bond formed in the initially unsubstituted B(8′)–H cage, instead of the B(8)–I, as one could expect for a typical Heck reaction mechanism, is unprecedented. 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 with 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 occurs, producing the disubstituted species observed when the molecule interacts with the palladium complex initiating the experiments. No further calculations have been done at this stage because it has been assumed that the same or a very close mechanism occurs as for the described Heck catalytic cycle.

Conclusions

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

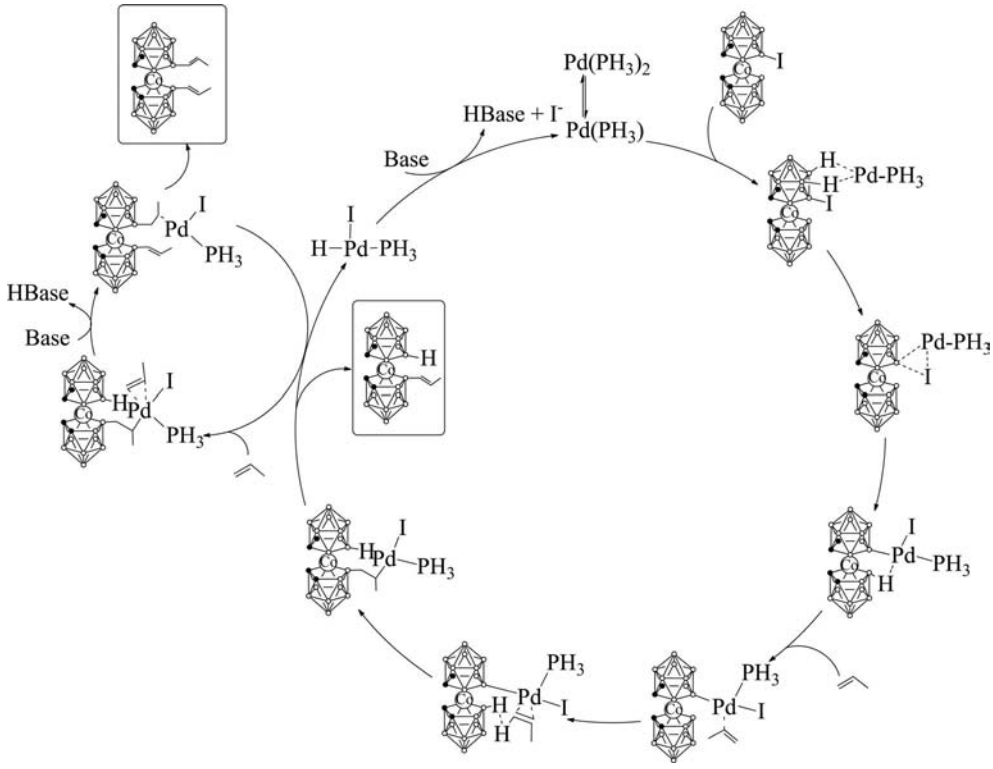


Figure 4. Suggested mechanism for the generation of B–C_{vinyl} bonds in borane systems.

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 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 been 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 reaction. To interpret this multisubstitution process a theoretical reaction mechanism has been proposed (Figure 4). This transformation involves an unprecedented B–H activation that strongly supports the experimental evidence. The synthesis of π-extended systems incorporating metallacarboranes is of key importance for their application in optical systems. Therefore, the use of the methodology described in this work opens another way to obtain such molecules.

Computational Details

All the calculations reported here were performed with the Gaussian 03 suite of programs.[20] Geometries were fully optimised at the PBEPBE/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_{imag} = 0). Calculations on the mechanism for both ground and excited states were done using the same level of theory. The potential minima are characterised by all positive frequencies and the transition states are characterised by a single imaginary frequency.

Experimental Section

General: 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 a Bruker Biflex MALDI-TOF-MS instrument [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV]. The ^{1}H, ^{1}H{^{11}B} NMR (300.13 MHz), ^{11}B NMR (96.29 MHz) and ^{13}C{^{1}H} NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded on [D_6] acetone solutions at 25 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external BF_3·OEt_2, and those for ^{1}H, ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from the reference and all coupling constants are reported in Hertz.

General Procedure: To a solution of Cs[8-I-3,3′-Co-(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (50 mg, 1 equiv.), 2,6-lutidine (30 μL, 3 equiv.), [$PdCl_2(PPh_3)_2$] (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 reaction vessel 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 Et_2O/$HCl_{aq.}$ (1 M) was carried out. The resultant solution was dried with sodium sulfate, filtered 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 [NMe_4]Cl was added resulting in the formation of a precipitate. This was filtered, washed and dried in vacuo.

Data for NMe_4[2]: Yield 31.7 mg (75%). ^{1}H{^{11}B} NMR: δ = 7.35 (m, 2 H, C_6H_5, C_o-**H**), 7.22 (m, 2 H, C_6H_5, C_m-**H**), 7.10 [d, $^3J_{H,H}$ = 18 Hz, 1 H, CH=C**H**-C_6H_5], 7.08 (m, 1 H, C_6H_5, C_p-**H**), 6.41 [d, $^3J_{H,H}$ = 18 Hz, 1 H, C**H**=CH-C_6H_5], 4.35 (br. s, 2 H, C_c-H), 4.06 (br. s, 2 H, C_c-H), 3.45 [s, 12 H, $N(CH_3)_4$], 2.99, 2.95, 2.89, 2.82, 2.74, 1.87, 1.64 (br. s, 18 H, B-H) ppm. ^{13}C{^{1}H} NMR: δ = 140.61 (s, 1 H, **C**H=CH-C_6H_5), 137.32 (s, 1 H, CH=**C**H-C_6H_5), 128.18, 125.69, 125.14 (s, C_6H_5), 55.18 [s, $N(CH_3)_4$], 53.35 (s, C_c-H), 50.21 (s, C_c-H) ppm. ^{11}B NMR: δ = 13.09 [s, 1B, B(8)], 7.13 [d, $^1J_{B,H}$ = 138 Hz, 1B], 1.83 [d, $^1J_{B,H}$ = 141 Hz, 2B], –4.14 (d, 2B), –4.74 (d, 4B), –5.71 [d, $^1J_{B,H}$ = 142 Hz, 2B], –16.23 [d, $^1J_{B,H}$ = 132 Hz, 2B], –17.46 [d, $^1J_{B,H}$ = 138 Hz, 2B], –21.48 [d, $^1J_{B,H}$ = 152 Hz, 1B], –23.04 [d, $^1J_{B,H}$ = 163 Hz, 1B] ppm. MALDI-TOF MS: *m*/*z* (%) = 528.41 (10) [M + C_8H_7], 425.37 (100) [M], 323.22 (M – C_8H_7, 8).

Data for NMe_4[4]: Yield 35.0 mg (78%). ^{1}H{^{11}B} NMR: δ = 7.41 (m, 4 H, C_6H_4F, C_o-**H**), 7.00 (m, 4 H, C_6H_4F, C_m-**H**), 6.81 [d, $^3J_{H,H}$ = 18 Hz, 2 H, CH=C**H**-C_6H_5F], 6.42 [d, $^3J_{H,H}$ = 18 Hz, 2 H, C**H**=CH-C_6H_5F], 4.29 (br. s, 4 H, C_c-H), 3.45 [s, 12 H, $N(CH_3)_4$], 2.86–1.28 (br. s, 16 H, B-H) ppm. ^{13}C{^{1}H} NMR: δ = 139.99 (s, 1 H, **C**H=CH-C_6H_5), 119.7 (s, 1 H, CH=**C**H-C_6H_5), 167.21, 118.54, 131.18, 131.17 (s, C_6H_5), 55.28 [s, $N(CH_3)_4$], 53.46 (s, C_c-H), 51.91 (s, C_c-H) ppm. ^{11}B NMR: δ = 11.10 [s, 2B, B(8,8′)], 1.77 [d, $^1J_{B,H}$ = 118 Hz, 2B], –5.03 [d, $^1J_{B,H}$ = 127 Hz, 8B], –17.64 [d, $^1J_{B,H}$ = 137 Hz, 4B], –22.41 [d, $^1J_{B,H}$ = 135 Hz, 2B] ppm. MALDI-TOF MS: *m*/*z* (%) = 564.44 (100) [M], 685.47 (M + C_8H_7F, 12).

Data for NMe_4[6]: Yield 9.5 mg (19%). ^{1}H{^{11}B} NMR: δ = 7.40 (m, 4 H, C_6H_4Br, C_o-**H**), 7.34 (m, 4 H, C_6H_4Br, C_m-**H**), 6.94 [d, $^3J_{H,H}$ = 15 Hz, 2 H, CH=C**H**-C_6H_5Br], 6.40 [d, $^3J_{H,H}$ = 15 Hz, 2 H, C**H**=CH-C_6H_5Br], 4.28 (br. s, 4 H, C_c-H), 3.45 [s, 12 H, $N(CH_3)_4$], 2.98–1.28 (br. s, 16 H, B-H) ppm. ^{13}C{^{1}H} NMR: δ = 139.43 (s, 1 H, **C**H=CH-C_6H_5), 119.17 (s, 1 H, CH=**C**H-C_6H_5), 133.33, 129.28, 129.98, 127.55 (s, C_6H_5), 55.23 [s, $N(CH_3)_4$], 53.55 (s, C_c-H), 51.71 (s, C_c-H) ppm. ^{11}B NMR: δ = 11.10 [s, 2B, B(8,8′)], 1.76 [d, $^1J_{B,H}$ = 132 Hz, 2B], –5.03 [d, $^1J_{B,H}$ = 107 Hz, 8B], –17.47 [d, $^1J_{B,H}$ = 94 Hz, 4B], –22.71 [d, $^1J_{B,H}$ = 133 Hz, 2B] ppm. MALDI-TOF MS: *m*/*z* (%) = 687.28 (100) [M], 868.20 (M + C_8H_7Br, 13).

Data for NMe_4[11]: Yield 14.7 mg (32%). ^{1}H{^{11}B} NMR: δ = 4.36 [d, ^3J(H,H) = 18 Hz, 1 H, CH=C**H**-C_8H_{17}], 4.29 [d, $^3J_{H,H}$ = 18 Hz, 1 H, C**H**=CH- C_8H_{17}], 4.40 (br. s, 2 H, C_c-H), 4.01 (br. s, 2 H, C_c-H), 3.45 [s, 12 H, $N(CH_3)_4$], 2.99–1.64 (br. s, 17 H, B-H), 1.28 (s, 14 H, CH=CH-C_7**H$_{14}$**-CH_3), 0.89 (s, 3 H, CH=CH-C_7H_{14}-C**H$_3$**) ppm. ^{13}C{^{1}H} NMR: δ = 122.31 (s, 1 H, **C**H=CH-C_7H_{14}), 157.89 (s, 1 H, CH=**C**H-C_7H_{14}), 37.21, 30.01, 29.81, 29.53, 23.76, 13.96 (s, C_7H_{14}), 55.26 [s, $N(CH_3)_4$], 53.48 (s, C_c-H), 50.98 (s, C_c-H) ppm. ^{11}B NMR: δ = 12.72 [s, 1B, B(8)], 6.86 [d, $^1J_{B,H}$ = 150 Hz, 1B], 2.23 [d, $^1J_{B,H}$ = 140 Hz, 2B], –5.00 [d, $^1J_{B,H}$ = 107 Hz, 8B], –16.65 [d, $^1J_{B,H}$ = 132 Hz, 2B], –18.16 [d, $^1J_{B,H}$ = 138 Hz, 2B], –20.71 [d, $^1J_{B,H}$ = 156 Hz, 1B], –23.27 [d, $^1J_{B,H}$ = 173 Hz, 1B] ppm. MALDI-TOF MS: *m*/*z* (%) = 462.45.

Data for NMe_4[12]: Yield 9.8 mg (26%). ^{1}H{^{11}B} NMR: δ = 7.73 [d, $^3J_{H,H}$ = 18 Hz, 1 H, CH=C**H**-CN], 5.27 [d, $^3J_{H,H}$ = 18 Hz, 1 H, C**H**=CH- CN], 4.08 (br. s, 2 H, C_c-H), 4.01 (br. s, 2 H, C_c-H), 3.45 [s, 12 H, $N(CH_3)_4$], 2.89–1.19 (br. s, 17 H, B-H) ppm. ^{13}C{^{1}H}

NMR: δ = 148.21 (s, 1 H, **C**H=CH-CN), 103.32 (s, 1 H, CH=**C**H-CN), 118.19 (s, CN), 55.25 [s, $N(CH_3)_4$], 53.42 (s, C_c-H), 51.11 (s, C_c-H) ppm. ^{11}B NMR: δ = 10.51 [s, 1B, B(8)], 6.93 [d, $^1J_{B,H}$ = 132 Hz, 1B], 3.91 [d, $^1J_{B,H}$ = 116 Hz, 2B], –1.81 [d, $^1J_{B,H}$ = 118 Hz, 2B], –4.34 [d, $^1J_{B,H}$ = 116 Hz, 4B], –5.00 [d, $^1J_{B,H}$ = 86 Hz, 4B], –15.71 [d, $^1J_{B,H}$ = 135 Hz, 2B], –17.05 [d, $^1J_{B,H}$ = 137 Hz, 2B], –20.62 [d, $^1J_{B,H}$ = 144 Hz, 1B], –22.68 [d, $^1J_{B,H}$ = 125 Hz, 1B] ppm. MALDI-TOF MS: *m*/*z* (%) = 374.79 (100) [M].

Crystal-Structure Determination. Crystals of NMe_4[**2**] were grown from CH_2Cl_2/hexane and used for room temperature [300(2) K] X-ray structure determination. The measurements were carried out on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_a 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 [NMe_4][**2**]: $C_{16}H_{40}B_{18}CoN$, M_r = 501.49, monoclinic, space group $P\bar{1}$, a = 13.5665(19), b = 14.409(2), c = 15.896(3) Å, α = 89.427(3), β = 64.831(2), γ = 87.768(2) °, V = 2810.12 Å^3, Z = 4, Reflections collected 43520, unique 13549 [R_{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 nonhydrogen atoms were refined anisotropically. The borane C–H hydrogen atoms were located in the difference map and refined with U_{eq} 1.2 times those of the parent atom, other parameters refined freely. The rest of hydrogens were placed in geometrically optimised 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.

CCDC-783142 contains the supplementary crystallographic data for [NMe_4][**2**]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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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