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

Pau Farràs,\textsuperscript{[a]} David Olíd-Britos,\textsuperscript{[a]} Clara Viñas,\textsuperscript{[a]} Francesc Teixidor*\textsuperscript{[a]}

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

A Pd induced cascade B—C\textsubscript{vinyl} coupling that produces multiple B—C\textsubscript{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\textsubscript{vinyl} couplings on the metallacarborane substrate have been generally obtained, but formation up to six B—C\textsubscript{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 reaction\textsuperscript{1} that can be done using palladium, nickel, copper, cobalt or other metal complexes as catalysts.\textsuperscript{[2-3]} 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.\textsuperscript{[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.\textsuperscript{[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 iodoboranes by Zakharin et al.\textsuperscript{[6]a} and further developed by Jones\textsuperscript{[7]} Hawthorne,\textsuperscript{[8]} Bregadze,\textsuperscript{[9]} and our group.\textsuperscript{[10]a}

The reaction of the anionic monoiiodo derivative [8-I,3,3′-Co-(1,2-C\textsubscript{9}B\textsubscript{11}H\textsubscript{10})(1′,2′-C\textsubscript{2}B\textsubscript{2}H\textsubscript{4})]\textsuperscript{−}, [1], and [B\textsubscript{2}H\textsubscript{2}(I\textsubscript{1})\textsuperscript{2}] with alkyl and aryl reagents has been reported.\textsuperscript{[10b,11]} Kumada carbon-carbon reaction conditions that inspired boron-carbon bond formations have been also extended to monocarborane derivatives.\textsuperscript{[12]} Sjöberg et al.\textsuperscript{[13]} were successful on the substitution of iodine in 2-I-1,12-C\textsubscript{9}B\textsubscript{11}H\textsubscript{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\textsubscript{9}B\textsubscript{11}H\textsubscript{10})(1′,2′-C\textsubscript{2}B\textsubscript{2}H\textsubscript{4})]\textsuperscript{−} [1]. In previous work\textsuperscript{[10c]} 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 alken unit that bridges the two subclusters in [3,3′-Co-(1,2-C\textsubscript{9}B\textsubscript{11}H\textsubscript{10})\textsuperscript{−} with Sonogashira’s method.\textsuperscript{[14]} It was later reported that with a Rh catalyst, successive B-C\textsubscript{vinyl} were produced in the [CB\textsubscript{11}H\textsubscript{12}]\textsuperscript{2} cluster.\textsuperscript{[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-C\textsubscript{9}B\textsubscript{11}H\textsubscript{10})(1′,2′-C\textsubscript{2}B\textsubscript{2}H\textsubscript{4})] two B—C\textsubscript{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 monoiiodinated compound

[1]

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Supporting information for this article is available on the WWW under http://www.eurjic.org/ or from the author.
As there seen, molecules are generated from the singly probability level. Large amount of side products. Finally, the use of a no increase of the yield was not significant. The reaction conditions causing its evaporation. Instead, the use of Ag produced lower yields due, most probably, to its low boiling point, key features for the reaction. The use of triethylamine as base or the solvent led to a significant decrease in the yields. Although the influence of the temperature is important, the existence conditions. It was noticed that small amounts of water in either the substrate, the degree of substitution varies from one to an independent coupling. Although disubstitution has been observed in almost every couple of mono-

di-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\textsubscript{vinyl} coupling.

The most fascinating point in these reactions was, however, the formation of the disubstituted molecules displayed in Table 2 ([13]–[7]). These disubstituted molecules are generated from the singly substituted \([8-1,3,3'-Co-(1,2-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})(1',2',3'-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})]\). Two independent B—C\textsubscript{vinyl} couplings are generated from one single B—I. To our knowledge this is the first example of a cascade set of B—C\textsubscript{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 allyl 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 1. Optimization studies of cross-coupling reaction.

<table>
<thead>
<tr>
<th>entry</th>
<th>equiv. of styrene</th>
<th>catalyst</th>
<th>base (equiv.)</th>
<th>solvent</th>
<th>T (°C)</th>
<th>reaction time (h)</th>
<th>yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1[a]</td>
<td>2.5</td>
<td>8% PdCl(_2)(PPh(_3))(_2); 8% Cul</td>
<td>dry NEt(_3) (2.5)</td>
<td>dry DMF</td>
<td>120</td>
<td>24</td>
<td>80</td>
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<tr>
<td>2</td>
<td>2.5</td>
<td>8% PdCl(_2)(PPh(_3))(_2); 8% Cul</td>
<td>NEt(_3) (2.5)</td>
<td>THF</td>
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<td>48</td>
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<td>3</td>
<td>2.5</td>
<td>8% PdCl(_2)(PPh(_3))(_2); 8% Cul</td>
<td>AgPO(_4) (2.5)</td>
<td>DMF</td>
<td>120</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>8% PdCl(_2)(PPh(_3))(_2); 8% Cul</td>
<td>NEt(_3) (2.5)</td>
<td>DMF</td>
<td>120</td>
<td>16</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>1% Pd Herrmann's catalyst[b]</td>
<td>AgPO(_4) (1.5)</td>
<td>DMF</td>
<td>120</td>
<td>6</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>5% PdCl(_2)(PPh(_3))(_2); 5% Cul</td>
<td>2,6-Lutidine (3)</td>
<td>dry DMF</td>
<td>140</td>
<td>16</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
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<td>dry 2,6-Lutidine (3)</td>
<td>dry DMF</td>
<td>140</td>
<td>24</td>
<td>90</td>
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<tr>
<td>8</td>
<td>2.5</td>
<td>5% Pd(PPh(_3))(_2)</td>
<td>2,6-Lutidine (3)</td>
<td>dry DMF</td>
<td>130</td>
<td>16</td>
<td>45</td>
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<tr>
<td>9</td>
<td>5</td>
<td>5% PdCl(_2)(PPh(_3))(_2); 5% Cul</td>
<td>2,6-Lutidine (3)</td>
<td>dry DMF</td>
<td>130</td>
<td>24</td>
<td>55</td>
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</tbody>
</table>

[a] Addition of 15% Pd(acac)\(_2\). [b] Yield determined by \(^1\)H-NMR spectroscopy comparing the relative integral areas of the C\(_2\)-H hydrogen atoms. [c] trans-di(\(\mu\)-acetato)bis([\(\mu\)-di-\(\sigma\)-tolylphosphino]benzyl)tripalladium(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% [PdCl\(_2\)(PPh\(_3\))\(_2\)]/[Cul 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 AgPO\(_4\) 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.\[1\][b] 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.

Compound [NMe\(_2\)]\(_2\)] 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 metallacarboranes 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\textsubscript{vinyl} coupling.

The most fascinating point in these reactions was, however, the formation of the disubstituted molecules displayed in Table 2 ([13]–[7]). These disubstituted molecules are generated from the singly substituted \([8-1,3,3'-Co-(1,2-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})(1',2',3'-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})]\). Two independent B—C\textsubscript{vinyl} couplings are generated from one single B—I. To our knowledge this is the first example of a cascade set of B—C\textsubscript{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 allyl 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.

![Figure 1. Molecular structure of [NMe\(_2\)]\(_2\)]\(_8\)-C\(_2\)H\(_8\)-3,3'-\((1,2-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})(1',2',3'-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11})\), [NMe\(_2\)]\(_2\)]\(_2\)]. The displacement ellipsoids are drawn on a 30% probability level.](image-url)
Table 2. Pd-catalyzed cross-coupling reaction of [1] with vinyl groups (\(\text{\textcircled{C}}\text{\textcircled{C}}\) = 3,3'-Cor(1,2-C_2B_9H_10)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substrate</th>
<th>Product</th>
<th>Mono/di ratio</th>
<th>Yield (%)</th>
<th>Compound</th>
<th>Substrate</th>
<th>Product</th>
<th>Mono/di ratio</th>
<th>Yield (%)</th>
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<tr>
<td>[9] NH_2</td>
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<td>0</td>
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</tr>
</tbody>
</table>

[a] Yield determined by ^1^H-NMR spectroscopy comparing the relative integral areas of the 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 ^1^H-NMR, ^1^B-NMR and found instead of the 2:2 pattern in monosubstituted molecules. In addition, the ^1^B-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 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 ^1^H-NMR spectra only one resonance corresponding to the four C-H groups was reaction. Taking as a model the mechanism described by Surawatanawong et al. for the Heck reaction with palladium diphosphines,\(^\text{[16]}\) 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 monoiiodo derivative of cobaltabisdicarbollide [1] and [Pd(PH_3)] catalyst with density functional theory (DFT). It has been compared for min and min, the changes caused by the substitution of PH_3 to PPh_3. 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 \(\beta\)-hydride transfer/olefin elimination of the product and the abstraction of proton by the base, are not considered.
Monoligated palladium species have been proposed to be important intermediates in the catalytic cycle.\textsuperscript{[11]} Therefore, for the purpose of simplicity, it was considered the use of \([\text{PdL}]\) instead of \([\text{PdL}_2]\) as the catalyst for the oxidative addition step. The most stable reaction pathway is shown in Figure 2. Intermediate \(\text{min}_2\) is energetically favourable by 41.5 kcal/mol. Interestingly, in the first complex \(\text{min}_1\) an interaction between palladium and the two most reactive \(\text{B}−\text{H}\) vertices, \(\text{B}(9)\) and \(\text{B}(12)\), is found, with \(\text{B}−\text{H}−\cdot\cdot\cdot\text{Pd}\) distances of 2.06 and 2.09Å. This kind of interaction is recursive throughout the mechanism. The transition state \(\text{ts}_1\) has the typical \(\text{Y}−\text{Pd}−\text{I}\) arrangement with an angle of 59º as expected for an early transition state.\textsuperscript{[10]} Bond distances are 2.61 and 2.46Å for \(\text{Pd}−\text{B}\) and \(\text{Pd}−\text{I}\) bonds respectively. After overcoming the transition state, the system rearranges to \(\text{min}_3\) as a T-shaped structure with a 90.4º angle between \(\text{B}(8)−\text{Pd}−\text{I}\). In this case, the \(\text{B}(8)−\text{Pd}\) bond is shorter than in \(\text{ts}_1\), being 2.05Å. A closer distance \(\text{Pd}−\text{B}(8')\) at 2.02Å is found between palladium and the most reactive \(\text{B}−\text{H}\) vertex on the non-substituted \(\text{C}_2\text{B}_9\text{H}_{11}\) cage. This \(\text{B}(8')−\text{H}−\cdot\cdot\cdot\text{Pd}\) interaction can be explained by the position of the iodine atom in the structure, and the favourable \(\text{B}−\text{H}\) geometrical disposition of the \(\text{B}(8')−\text{H}\) in the cluster, beaming out of the centre of the originally non-substituted icosahedron. Our group reported some years ago that \(\text{B}−\text{H}\) vertices dissipate better the electron density out of an anionic cluster than \(\text{C}−\text{H}\) vertices.\textsuperscript{[12]} This causes that the halogen atom prefers to be \(\text{trans}\) to \(\text{B}(8')−\text{H}−\cdot\cdot\cdot\text{Pd}\) instead of \(\text{B}(8)−\text{Pd}\) as it is known that \(\text{H}−\cdot\cdot\cdot\text{Pd}\) is one of the strongest \(\text{trans}\) influence ligands.\textsuperscript{[19]}

For the onset of the migratory insertion of propylene, two possible pathways were examined. Propylene can insert to the palladium complex (\(\text{min}_3\)) either from the substituted (\(\text{min}'_3\)) or non-substituted (\(\text{min}_3\)) cage plane as shown in Figure 3. As expected, the energy of \(\text{min}_3\) structure is lower and propylene binds to the vacant site of \(\text{min}_3\). Then, the \(\text{B}(8')−\text{H}−\cdot\cdot\cdot\text{Pd}\) interaction in \(\text{min}_3\) is broken causing a migration of the iodine originated in the higher \(\text{trans}\) influence of the \(\text{B}(8)−\text{Pd}\) bond. Transition state \(\text{ts}_2\) has the typical \(\text{Pd}−\pi\)-alkene arrangement with a \(\text{Pd}−\text{C}\) distance of 2.10 and 2.20Å and the \(\text{C}−\text{C}\) distance on propylene is 1.45Å, 0.03Å longer in respect to \(\text{min}_3\) at 1.42Å. This distance gives indication on the relative strength of the \(\text{C}−\text{C}\) bond depending on the neighbouring atoms. For the free propylene the \(\text{C}−\text{C}\) distance is 1.36Å, which is the same as for the isolated \([\text{8-C}_2\text{H}_7\cdot\cdot\cdot\text{Co}(1,2,3-\text{C}_2\text{B}_9\text{H}_{10})(1',2',3'-\text{C}_2\text{B}_9\text{H}_{11})]\). Therefore, the interaction of the propylene with palladium weakens the electronic density of the double bond, enlarging the \(\text{C}−\text{C}\) bond distance. The relatively short dihydrogen distance between \(\text{B}(8')−\text{H}−\cdot\cdot\cdot\text{H}−\text{C}\) (2.15Å) is remarkable causing an intramolecular reaction catalyzed by palladium that leads to the formation of \(\text{min}_4\). It was unprecedented that the generated \(\text{B}−\text{C}−\text{I}\) bond is formed in the initially non-substituted \(\text{B}(8')−\text{H}\) cage, instead of the \(\text{B}(8)−\text{I}\), as one could expect for a typical Heck reaction mechanism. The hydrogen atom bonded to \(\text{B}(8')\) or one of the hydrogen atoms of the propylene has migrated to the \(\text{B}(8)\) vertex producing an agostic type \(\text{B}−\text{H}−\cdot\cdot\cdot\text{Pd}\) bond with a 109º angle, and a \(\text{H}−\cdot\cdot\cdot\text{Pd}\) distance of 1.78Å. The iodine has moved to a \(\text{trans}\) position in respect to the \(\text{B}−\text{C}−\text{Pd}\) structure, indicating that the electronic connection between \(\text{B}(8)−\text{H}−\cdot\cdot\cdot\text{Pd}\) is less than for \(\text{B}(8')−\text{C}−\cdot\cdot\cdot\text{Pd}\). 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.

\textbf{Conclusion}

In conclusion, a \(\text{Pd}\) induced cascade \(\text{B}−\text{C}_\text{vinyl}\) coupling has been found for the first time that produces multiple \(\text{B}−\text{C}_\text{vinyl}\) bonds starting from a single \(\text{B}−\text{I}\) bond. The process is most probably stimulated by the geometrical disposition of the \(\text{B}−\text{H}\) bonds confronting the \(\text{B}−\text{Pd}\) sites, along with the hydride character of the \(\text{B}−\text{H}\) units. Two and one \(\text{B}−\text{C}_\text{vinyl}\) couplings on the metallacarborane substrate have been generally observed, but MALDI-TOF-MS also indicates that further \(\text{B}−\text{C}_\text{vinyl}\) coupling takes place. Up to six \(\text{B}−\text{C}_\text{vinyl}\) 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 \(\text{B}−\text{I}\) bond, can lead to mono, di and polysubstitution, a phenomenon never described in the conventional \(\pi−\pi\) cross coupling Heck conditions. To interpret this multisubstitution process a theoretical reaction mechanism is proposed (Figure 4). This transformation involves an unprecedented \(\text{B}−\text{H}\) activation that strongly supports the experimental evidence. The synthesis of \(\pi−\pi\) extended systems incorporating metallacarboranes 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.
2.86±1.28 (br s, 16H, B-H). \( \text{[C-H]} \)-NMR: \( \delta = 139.99 \) (s, 1H, CH-CH=CH-H), 119.7 (s, 1H, CH-CH=CH-H), 167.21, 118.54, 131.18, 131.17 (s, C(=H)), 55.28 (s, N(CH3)), 53.46 (s, C(=H)), 51.91 (s, C(=H)). \( \text{13C}-\text{NMR}: \delta = 11.01 \) (2B, CH(=S)), 16.77 (s, 16H, 2B), 5.03 (d, \( J(B,H) = 127 \) Hz, 2B), -17.64 (d, \( J(B,H) = 137 \) Hz, 4B), -22.41 (d, \( J(B,H) = 135 \) Hz, 2B). MALDI-TOF MS: \( m/z \%: 564.44 \) (M+CH,F, 12%).

Data for NMe[6]: Yield: 9.5 mg (19%). \( \text{[C-H]} \)-NMR: \( \delta = 7.40 \) (m, 4H, CH2Br, C-H), 7.22 (m, 2H, CH2Br, C-H), 7.10 (d, \( J(B,H) = 18 \) Hz, 1H, CH=CH2), 7.08 (m, 7H, C6H5, C-H), 6.04 (d, \( J(H,H) = 18 \) Hz, 1H, CH=CH2), 4.35 (br s, 2H, C-H), 4.06 (br s, 2H, C-H), 3.45 (s, \( 12 \)H, N(CH3)).

Data for NMe[4]: Yield: 3.5 mg (78%). \( \text{[C-H]} \)-NMR: \( \delta = 7.41 \) (m, 4H, CH2JF, C-H), 7.00 (m, 4H, CH2JF, C-H), 6.81 (d, \( J(B,H) = 18 \) Hz, 2H, CH=CH2-CF3), 6.42 (d, \( J(B,H) = 18 \) Hz, 2H, CH=CH2-CF3), 4.29 (br s, 4H, C-H), 3.45 (s, \( 12 \)H, N(CH3)).

Figure 4. Suggested mechanism for the generation of \( \text{B-C} \)-cont bonds in borane systems.

Computational Details

All the calculations reported here were performed with the Gaussian 03 suite of programs. Geometries were fully optimized at the PBE/SVP/lanl2d level of theory, as well as their thermochromic properties. All stationary points were found to be true minima (number of imaginary frequencies, \( \text{Nimag}=0 \)). 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 carbonyl 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 \( \text{[Na, Cl]} \), \( \delta = 357 \) nm (0.5 ms pulses); voltage ion source \( 2000 \) V. The \( \text{[H]} \)-NMR (300.13 MHz), \( \text{[13C]} \)-NMR (92.29 MHz) and \( \text{[15N]} \)-NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded from acetone-\( \text{d6} \) solutions at \( 25^\circ \)C. Chemical shift values for \( \text{[13C]} \)-NMR spectra were referenced to external BF4·OEt2 and those for \( \text{[H]} \), \( \text{[1H]} \)-NMR and \( \text{[13C]} \)-[15N]-NMR spectra were referenced to Si(CH3)4. Chemical shifts are reported in units of ppm per million downfield from reference, and all coupling constants are reported in Hertz.

General procedure: to a solution of \( \text{[C(3-f-3,3'-C-O(1,2-CB6H11)(1,2-CB6H11)](50 \text{ mg}, 1 \text{ equiv})} \), 2.6-Lutidine (30 \( \mu \text{l}, 3 \text{ equiv})), [P(\text{Ph})3]2Pd(4 \text{ mg}, 0.05 \text{ equiv}) \) and Cu (1 \text{ mg}, 0.05 \text{ equiv}) in dry DMF (5 \text{ 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 residue was dissolved in the minimum volume of EtOH and an equivalent of \( \text{HCl} \) was added, resulting in the formation of a precipitate. This was filtered off, washed and dried in vacuum.

Crystal-Structure Determination. - Crystals of \text{[Me2C]} were grown from CHCl3/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 Ka radiation (\( \lambda = 0.71073 \) Å) from a 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 θ and ϕ scans. Crystal data for \text{[Me2C]}: Formula \text{C24H24Br2N2O2, M} = 501.49, monochromic, space group P - I, a = 13.5665(9), b = 14.4902(9), c = 15.8967(9), \( \alpha = 89 \) 8273, \( \beta = 89 \) 87682, \( \gamma = 152 \) 10112, \( Z = 4 \). Reflections collected 43520, unique 13549 \( R_{int} = 0.0600 \). Programs used: data collection, Small program 5.631 (Bruker AXS 1997-02); data reduction, SADABS version 2.10 (Bruker AXS 2001); structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000-03). The structure was solved by direct methods and refined by full-matrix least-squares methods on F. The non-hydrogen atoms were refined anisotropically. The boron C 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 a riding model (1.25 times those in the corresponding C-C or C-N bond) and refined with Ueq = 1.2 times those of the parent atom. The relative positions and the C-H bond distances were also restrained. R indices were all (data): R1 = 0.1160, wR2 = 0.2430. Final R indices were (I>2σ(I)): R1 = 0.0793, wR2 = 0.2249. Crystallographic data (excluding structure factors) for \text{[Me2C]} 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 CD2 1EZ, UK (fax: (+44)223-363-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): MALDI-TOF-MS for \( \text{[7]} \), effect of the PH on \( \text{[8]} \), vs. \( \text{[9]} \), ligand and geometry coordinates can be found.

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