# ORGANOMETALLICS

# Extremely Electron-Rich, Boron-Functionalized, Icosahedral **Carborane-Based Phosphinoboranes**

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# **Supporting Information**

ABSTRACT: We have prepared the first examples of B9-connected trivalent aryl and alkyl phosphinoborane species via Pd-catalyzed phosphination of 9-iodo-metacarborane. Our studies highlight the unique electronic features of the B9-connected meta-carboranyl moiety as compared to its C1-based analogue. This work suggests that the B9-functionalized meta-carboranyl substituent in these ligands exhibits more electron-releasing character than any other known carbon-based substituent, ultimately laying the foundation for a new class of phosphine ligands with extremely electron-rich character.



risubstituted phosphines (PR<sub>3</sub>) represent an important class of ligands in modern chemistry largely due to the ease with which their steric and electronic properties can be rationally tuned using various carbon-rich functional groups (R).<sup>1,2</sup> Yet, the current pool of substituents provides only a finite window for the modulation of the ligand's electronic character.<sup>3</sup> Thus, chemistry faces a fundamental challenge in identifying new and robust substituents that would overcome these limitations.

Three-dimensional aromatic icosahedral dicarba-closo-dodecaborane clusters (also referred to as carboranes, general formula  $C_2B_{10}H_{12}$ ) have been known to exhibit dramatically different electronic effects on the substituents attached to different vertices (for cluster numbering scheme, see SI).<sup>4</sup> As a consequence of a nonuniform electron distribution and electronegativity differences between boron and carbon, substituents attached at the carbon vertices usually experience a strong electron-withdrawing effect, whereas the substituents on boron atoms located furthest from the carbons experience a strong electron-donating effect. This fundamental property of carboranes was explored by Hawthorne for tuning the Lewis acidity of Hg(II) in mercurocarborand species<sup>5</sup> and later by Teixidor and Viñas, who observed that a methyl substituent attached to several boron vertices in these clusters acts as an electron-withdrawing group.<sup>6</sup> This effect has been somewhat overlooked in the past, resulting in a number of papers incorrectly generalizing the electronic properties of icosahedral carboranes as "electron-withdrawing".<sup>7</sup> A recent report suggested that icosahedral carborane substituents could enable electronic tunability of chalocogen-based ligands that is greater in magnitude than with any known carbon-based functional groups.<sup>8</sup> Specifically, by virtue of vertex differentiation one can access ligands that are sterically invariant, yet either extremely electron-poor or electron-rich.<sup>8</sup> This begs the question whether such tunability can be translated to other heteroatom-based ligands such as phosphines.

To evaluate this hypothesis, access to both C-P and B-P carboranyl-based species is required. While the chemistry of Cfunctionalized icosahedral carborane-based phosphines is well established,9 its B-functionalized counterparts are largely unknown. The only experimental evidence to support the existence of such a species was provided by Bregadze and Kabachnik in 1992,<sup>10</sup> who reported the syntheses of B9functionalized meta- and ortho-carboranyl species (C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>-PCl<sub>2</sub>) in 5% and 10% yields, respectively, upon UV photolysis of mercury carboranyl complexes and phosphorus trichloride. We envisioned that transition metal-catalyzed cross-coupling would provide a suitable route to phosphorus-functionalized Bbased phosphinocarborane derivatives. Recent work by Hawthorne, for example, utilized large, electron-rich phosphine ligands capable of supporting active Pd(0)/Pd(II) catalytic species in a facile catalytic amidation of B-iodocarboranes, wherein difficulties associated with the oxidative addition of the B-I moiety could be circumvented by judicial choice of the ligand.

In order to access B-functionalized phosphines, we utilized a modified Pd-catalyzed protocol used previously for phosphination of aryl halides.<sup>12</sup>

Upon heating 9-iodo-meta-carborane (2, Figure 1A, synthesized in a manner analogous to the one reported by the Jones and Hawthorne groups<sup>13</sup>) with diphenylphosphine in toluene at 120 °C in the presence of Pd<sub>2</sub>dba<sub>3</sub>/DIPPF (6 mol %/12 mol % ratio; dba, dibenzylideneacetone; DIPPF, 1,1'-bis(diisopropylphosphino)ferrocene) catalyst and Cs<sub>2</sub>CO<sub>3</sub>, we observed the formation of a new species via in situ<sup>31</sup>P NMR spectroscopy (Figure 1). $^{14}$ 

A broad signal resembling a quartet  $(J_{P-B} = 58 \text{ Hz})$  suggested that a B-P bond was likely formed (see SI). After prolonged heating of this reaction mixture for 36 h, complete consumption of the phosphine starting material was observed

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**Figure 1.** (A) Synthesis and (B, C) selected spectroscopic data for B9functionalized 9-*meta*-carboranyl phosphine species 3a (R = Ph). (D) Crystallographically derived molecular structure of 3a depicted with 50% thermal ellipsoid probabilities.

(<sup>31</sup>P NMR). Subsequent workup and purification of the reaction mixture yielded a crystalline substance, which was subjected to a full NMR spectroscopic analysis. In particular, the <sup>11</sup>B NMR spectrum of 3a exhibits the characteristic pattern of the B9-substituted meta-carborane cluster (Figure 1B), where the signal at ca.  $\delta$  –3 displays no coupling to the proton and integrates 1:9 to the rest of the resonances in the spectrum. A definitive structural confirmation for 3a was established using single-crystal X-ray diffraction. The solid-state structure of 3a features a trivalent phosphorus center connected to two carbon atoms on the phenyl rings and a B9 atom of the metacarboranyl moiety (Figure 1D). While considering the previously studied phosphinoboranes by Nöth and Power, we found that the B-P bond length in 3a (1.948 Å) best corresponds to the presence of a purely single-bond interaction between the B and P atoms.<sup>14</sup> This interaction is also reminiscent of the diphenylphosphineborabenzene species described by Fu,14c where delocalization of the LUMO orbital on the B atom renders  $\pi$ -donation from the P atom-centered lone electron pair unfavorable. Importantly, 3a was found to be stable both in solution and as a solid under ambient conditions for several weeks.

Drastic differences between 3a and 3a' (C1-based analogue of  $3a_i^{15}$  see SI and Figure 2) were observed upon reaction with Pt(COD)Cl<sub>2</sub> (COD, 1,4-cyclooctadiene) under similar conditions. Stirring one or two equivalents of 3a and Pt(COD)Cl<sub>2</sub> in dichloromethane resulted in a mixture of Pt(II) bisphosphine complexes 4a and 4b (Figure 2 and SI).

On the other hand, no coordination of 3a' to the Pt(II) precursor was observed (Figure 2C). Prolonged reaction times (3 days) or using an excess of 3a' (3 equiv) resulted in no conversion. Given that ligands 3a and 3a' are isosteric, the observed differences in chemical reactivity can most reasonably be attributed to the electronic influences of B9- and C1-functionalized *meta*-carboranyl moieties. Indeed, natural bond orbital analysis of the optimized structures of 3a and 3a' further corroborates the drastic differences in partial charges and lone pair energies located on the phosphorus atoms of these ligands, showing that 3a is significantly more electron-rich and therefore



Figure 2. (A, B) Comparison of the reactivity of ligands 3a and 3a' with  $Pt(COD)Cl_2$ . (C) Crystallographically derived molecular structure of 4a depicted with 50% thermal ellipsoid probabilities (H atoms omitted for clarity). (D)  ${}^{31}P{}^{1}H{}$  NMR spectrum of 4a.

reactive (see SI, Section 3). In total, these observations are consistent with recent work on carborane-based ligands featuring sulfur and selenium atoms on B9 and C1 vertices of the *meta*-carboranyl cluster (*vide supra*).

Using the developed synthetic protocol, we were able to cross-couple 2 with four electron-rich secondary phosphines, thus obtaining alkyl-based phosphinoboranes 3b-3e (Figure 3A and SI). Attempts to cross-couple <sup>t</sup>Bu<sub>2</sub>PH using these



Figure 3. (A) Synthesized alkyl-based phosphinoboranes (3b-3e). For all compounds (except for 3e), the yield is calculated based on the combination of protection/deprotection steps. (B) Syntheses of *m*-carborane-based phosphinoborane-BH<sub>3</sub> adducts and their subsequent deprotection. (C, D) Selected NMR spectroscopic data for 5d. (E) Crystallographically derived molecular structure of 5d depicted with 50% thermal ellipsoid probabilities.

conditions did not provide any phosphinoborane product. This is likely due to the size of  ${}^{t}Bu_{2}PH$ , ultimately rendering the transmetalation step ineffecient. Due to difficulties separating the DIPPF ligand from the target phosphinoboranes on silica gel, **3b–3d** mixtures were converted to their BH<sub>3</sub> adducts and purified by recrystallization, yielding pure **5b–5d**. In all cases, a characteristic shift of approximately 25–37 ppm in the <sup>31</sup>P NMR spectra was observed, consistent with the formation of borane-based adducts (Figure 3B and SI).

The <sup>11</sup>B NMR spectra of 5b-5d revealed characteristic <sup>11</sup>BH<sub>3</sub> resonances at ca.  $\delta$  38–41 (Figure 3C and SI), which integrate to a 1:10 ratio to the corresponding borane regions of the meta-carboranyl moieties. Relatively small values for coordination chemical shifts (ccs) observed from <sup>31</sup>P NMR spectra of these species compared to their free phosphine analogues (+25-37 ppm) is consistent with the ccs values reported for other bulky phosphine-BH<sub>3</sub> adducts.<sup>16</sup> Borane adducts 5b-5d were found to be bench stable both in solution and in the solid state. This observed stability is in contrast to several previously reported phosphineborane-BH<sub>3</sub> species, wherein scrambling of a BH3 and a boryl moiety via hydride transfer occurred, ultimately resulting in the decomposition of the parent species.<sup>17</sup> This further reinforces the notion that the meta-carboranyl boryl moiety serves as an innocent substituent and is chemically more stable than many previously studied boryl systems. Upon reacting 5b-5d with an excess of a weakly nucleophilic base (1,4-diazabicyclo[2.2.2]octane, DABCO) for 18 h in THF at 70 °C, we observed nearly quantitative conversion of the parent borane species to the free phosphine species 3b-3d via in situ <sup>31</sup>P NMR spectroscopy. These substances were then purified via flash column chromatography on silica gel, yielding the pure phosphines. Overall, phosphinoborane species 3b-3e were found to be stable enough to be manipulated at ambient conditions without noticeable oxidation. All other characterization data for 3b-3e are consistent with the proposed structural formulations (see SI).

Density functional theory calculations on the geometryoptimized structures of 3b-3e suggest that these species are more electron-rich than any other known alkyl-based phosphine ligands (*vide supra* and SI). To experimentally determine the electronic properties of 3a-3e, we synthesized *trans*-Rh(PR<sub>3</sub>)<sub>2</sub>(CO)Cl complexes, bearing the carbonyl (CO) ligand as a spectroscopic handle. The infrared (IR) carbonyl stretching frequency was previously shown to correlate extremely well with the electronic properties of the phosphine ligands in this type of Rh(I) complexes.<sup>18</sup> Reacting ligands 3a-**3e** with the Rh(I) precursor in CH<sub>2</sub>Cl<sub>2</sub> resulted in a quantitative formation of **6a-6e** as observed by *in situ* <sup>31</sup>P NMR spectroscopy (Figure 4).

Single crystals grown from solutions of 6a and 6b further confirmed our structural assignment for these species through X-ray diffraction studies. Notably, for 6b we observed an extremely short Rh–C bond (1.717 Å) and an elongated Rh–





Cl (2.456 Å) interaction (for comparison, in trans-Rh-(PCy<sub>3</sub>)<sub>2</sub>(CO)Cl, the Rh-C bond is 1.748 Å and Rh-Cl is 2.388 Å), <sup>18</sup> suggesting that phosphine **3b** is more electron-rich than PCy<sub>3</sub>. Finally, the IR spectroscopic data for  $\nu$ [CO] in complexes 6a-6e provide strong evidence supporting our computational analyses (Figure 4B). We found that  $\nu$ [CO] in species 6b-6e are consistently lower than in any other known trans-Rh(PR<sub>3</sub>)<sub>2</sub>(CO)Cl complexes (the lowest value reported to date is at 1943 cm<sup>-1</sup> for PCy<sub>3</sub>).<sup>18</sup> Significantly,  $\nu$ [CO] of 1981 cm<sup>-1</sup> in **6a**' indicates that ligand **3a**' is drastically less electron-rich than its B9-connected analogue, 3a. Thus crystallographic and IR spectroscopy data obtained for Rh(I) complexes bearing ligands 3b-3e suggest that these phosphinoborane species are more electron-rich than any known trivalent phosphine species containing only carbon-rich substituents.

In conclusion, we have discovered a new class of stable and extremely electron-rich phosphinoboranes featuring the B9functionalized *meta*-carboranyl substituent. Consistent with the recent study on carboranyl thioether and selenol ligands,<sup>8</sup> we observe that the B9-based *meta*-carboranyl moiety exhibits more electron-releasing character than any carbon-based substituent and thus can potentially provide chemists with a new approach to overcome the fundamental electronic property limitations associated with carbon-based substituents pertaining to ligand design. The phosphinoboranes reported herein can also be potentially interesting molecules to explore in the context of transition metal-based<sup>1</sup> and -free<sup>19</sup> catalysis.

### ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental details, crystallographic data (CIF), NMR and IR spectra, and details for computational experiments. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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