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Metal Complexes

Forging Unsupported Metal–Boryl Bonds with Icosahedral Carboranes

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Abstract: In contrast to the plethora of metal-catalyzed cross-coupling methods available for the installation of functional groups on aromatic hydrocarbons, a comparable variety of methods are currently not available for icosahedral carboranes, which are boron-rich three-dimensional aromatic analogues of aryl groups. Part of this is due to the limited understanding of the elementary steps for cross-coupling involving carboranes. Here, we report our efforts in isolating metal-boryl complexes to further our understanding of one of these elementary steps, oxidative addition. Structurally characterized examples of group 10 M–B bonds featuring icosahedral carboranes are completely unknown. Use of mercurocarboranes as a reagent to deliver M–B bonds saw divergent reactivity for platinum and palladium, with a Pt–B bond being isolated for the former, and a rare Pd–Hg bond being formed for the latter.

Icosahedral dicarba-*closo*-dodecaborane clusters (referred to herein as carboranes, **I** and **II**, Figure 1) of the type $C_2B_{10}H_{12}$ are robust, boron-rich molecules with unique structural and electronic properties, and are often thought of as 3D aromatic analogues of aryl groups.[1] Carboranes have been shown to be promising molecules for use as ligands in organometallic compounds, as well as important building blocks for metal-organic frameworks and molecules for the creation of well-defined self-assembly monolayer films.[1] These extremely broad areas of interest cover everything from synthetic inorganic chemistry and solid-state materials chemistry to physical and theoretical chemistry and nanoscience, and their potential for substitution at both carbon and boron vertices make them extremely attractive precursors. However, compared to traditional aromatic hydrocarbon chemistry, carborane vertex substitution is relatively underdeveloped.[2] Similar to the functionalization of aromatic hydrocarbons, an obvious choice of methods for installing functional groups on boron vertices would involve metal-catalyzed cross-coupling. Early work by Zakharkin,[3] followed by Jones,[4] Hawthorne,[5] Viñas,[6] and Beletskaya and Bregadze[7] has shown that the cross-coupling with boron-functionalized 9-B-iodocarborane coupling partners (**III** and **IV**, Figure 1) can be a powerful method for installing functional groups at the boron vertices.[8] Oxidative addition of 9-B-iodocarborane to form a M–B bond is a critical step in the cross-coupling cycle, and isolating this key intermediate could shed light on strategies to further develop this chemistry.

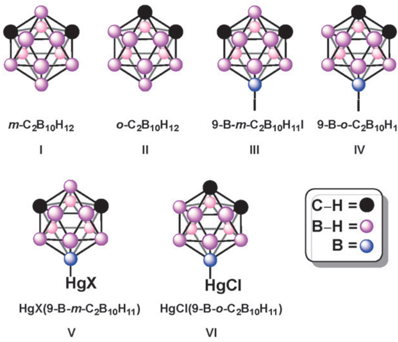

Figure 1. (**I**) and *ortho*-carborane (**II**); *meta*- (**III**) and *ortho*-iodocarborane (**IV**); *meta*-mercurocarborane (**V**, X = Cl or CO_2CF_3) and *ortho*-mercurocarborane (**VI**).

Compounds containing supported M–B bonds, in which the source of boron is carborane, can be prepared by a number of methods,[9–13] but as we are interested in the derivatization of the unfunctionalized carborane, directed B–H activation strategies are not applicable. Formation of compounds featuring an unsupported M–B bond, in which the source of boron is carborane, are rare compared to their more common boryl counterparts (of the type $M–BR_2$),[14,15] with crystallographically characterized examples in the literature limited to mercury-, tin-, and thallium-containing compounds synthesized by direct electrophilic substitution at the boron vertex.[16]

For metals relevant to cross-coupling chemistry, Grushin and co-workers[17] reported a detailed investigation into the attempted oxidative addition of 9-B-iodo-*m*-carborane (**III**, Figure 1) with Pd(0) compounds. It was found that although oxidative addition of iodocarboranes to Pd(0) precursors is fast, it is also reversible, with the equilibrium heavily favoring reformation of the reactants. Additional work carried out by Teixidor and co-workers resulted in similar conclusions.[18] Although discouraging, cited within the report by Grushin and co-workers is an intriguing paper by Zakharkin and Pisareva[19] describing the synthesis of a Pt compound in which the Hg–Cl bond in 9-B-*m*-mercurocarborane (**V**, Figure 1) was oxidatively added

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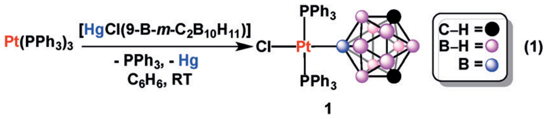
to [$Pt(PPh_3)_3$]. Subsequent extrusion of elemental mercury purportedly led to [$PtCl(PPh_3)_2$(9-B-*m*-$C_2B_{10}H_{11}$)] (**1**), [Eq. (1)], containing a Pt–B bond. However, no structural or spectroscopic evidence was provided in this or any other subsequent work. Despite this, the use of mercurocarboranes potentially provides a valuable synthetic route to compounds containing a M–B bond. In this work we assess the use of 9-B-mercurocarboranes as reagents for forming late transition metal boron-bonded complexes featuring unsupported M–B bonds to carboranes, and their subsequent reactivity.



Although Zakharkin described the synthesis of **1**, the compound itself was lightly characterized, with only melting point and elemental analysis being reported. This lack of characterization prompted us to verify the existence of the purported Pt–B bond in this compound. In order to provide a baseline, an NMR tube scale reaction of [$Pt(PPh_3)_3$] and [HgCl(9-B-*m*-$C_2B_{10}H_{11}$)] in C_6D_6 (vide supra) was carried out. The deep yellow solution produced, over time, a grey precipitate. ^{31}P NMR spectroscopy of the solution revealed a singlet resonance at 31 ppm with satellites ($^1J_{P-Pt}=3380$ Hz), consistent with the formation of a single new species with *trans*-bound phosphine ligands. Scale-up and recrystallization from a concentrated benzene solution layered with pentane produced bright yellow crystals in 84% yield (see the SI).

^{31}P NMR spectroscopy of these crystals in C_6D_6 matched that found for the NMR tube scale reaction, whilst the ^{11}B NMR spectrum featured only broad resonances, with no observable satellites associated with $^1J_{B-Hg}$ or $^1J_{B-Pt}$ coupling. An X-ray diffraction study on a single crystal obtained from this batch confirmed that the isolated compound is indeed [$PtCl(PPh_3)_2$(9-B-*m*-$C_2B_{10}H_{11}$)] (**1**, Figure 2), and features an unsupported Pt–B σ-bond, the first of its kind for an icosahedral carborane species. Compound **1** crystallizes with one molecule of benzene, and has a distorted square planar geometry,[20] with the triphenylphosphine ligands adopting a *trans* configuration. The B(9)-carboranyl ligand is bound to Pt^{II} through the apical boron of the icosahedral cluster, with a Pt–B bond length of 2.1024(17) Å.

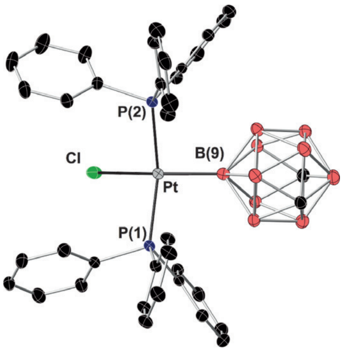


Figure 2. X-ray structure of **1** (thermal ellipsoids drawn at 50% probability). H atoms and benzene of crystallization omitted for clarity.

This length comes under the sum of respective covalent radii (2.20 Å),[21] and a survey of the Cambridge Structural Database (CSD)[22] for all compounds containing unsupported Pt–B bonds reveals that the Pt–B bond in **1** is slightly longer than the average Pt–B bond length (2.04 Å). In addition, the B(9)-carboranyl ligand can be shown to have a comparable *trans* influence to traditional boryl ligands,[23] demonstrated by the Pt–Cl bond length of 2.4166(4) Å, which is longer than the average Pt–Cl bond length (2.33 Å) but compares favorably to the average Pt–Cl bond distance (2.45 Å) when the chloride is *trans* to a boron atom.

Because **1** formally represents the product of oxidative addition of 9-B-chloro-*m*-carborane, we sought to investigate its potential reactivity towards transmetallation, thereby addressing the potential competency of **1** with respect to cross-coupling chemistry. Indeed, addition of a solution of **1** to a suspension of benzyl mercaptan and K_3PO_4 in C_6H_6 (Figure 3 A) at room temperature led, after 3 h, to complete consumption of **1** and formation of 9-B-(SCH_2Ph)-m-$C_2B_{10}H_{11}$ (**2**) as indicated by GC-MS analysis and in situ ^{11}B NMR (see the SI).[24] This suggests that both transmetallation and reductive elimination steps occurred during the reaction in a facile manner under remarkably mild conditions.

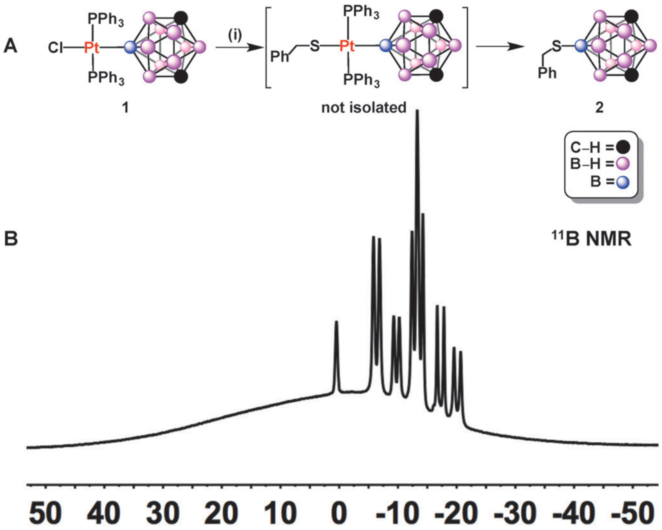


Figure 3. A: Synthesis of 9-B-(SCH_2Ph)-*m*-$C_2B_{10}H_{11}$ (**2**) mediated by **1**. Key reagents and conditions: (i) $HSCH_2Ph$, K_3PO_4, C_6H_6, R.T., 3 h. **B**: ^{11}B NMR of pure **2** in CD_2Cl_2 (see the SI).

Given that the Pd-catalyzed cross-coupling of 9-B-iodocarboranes is an established reaction manifold (vide infra) and in light of the isolation of compound **1** utilizing 9-B-*m*-mercurocarborane, it was envisaged that the same route could furnish a Pd–B compound. However, the reaction of [$Pd(PPh_3)_4$] with [HgCl(9-B-*m*-$C_2B_{10}H_{11}$)] in C_6H_6 produced no new species, with only unreacted starting materials being observed. Reaction of [$Pd(PPh_3)_4$] with the more reactive [$Hg(CO_2CF_3)$(9-B-*m*-$C_2B_{10}H_{11}$)] produced an intractable mixture. It appeared that, in our hands, PPh$_3$ was not the appropriate ligand for these studies. We therefore decided to employ a biaryl-phosphine ligand given their competence in Pd-catalyzed cross-coupling chemistry,[25,26] including that of carboranes as recently demonstrated by Hawthorne and co-workers.[27] Reaction of a model biaryl phosphine ligand XPhos with [(COD)Pd(CH$_2$SiMe$_3$)$_2$] (**VII**, Figure 4 A) in THF produces a biarylphosphine bound Pd(0) intermediate as a light yellow suspension.[28] Upon addition of [HgCl(9-B-*o*-C$_2$B$_{10}$H$_{11}$)], the suspension becomes a clear yellow solution, which upon workup produces a light yellow microcrystalline powder in 71 % yield (see the SI).

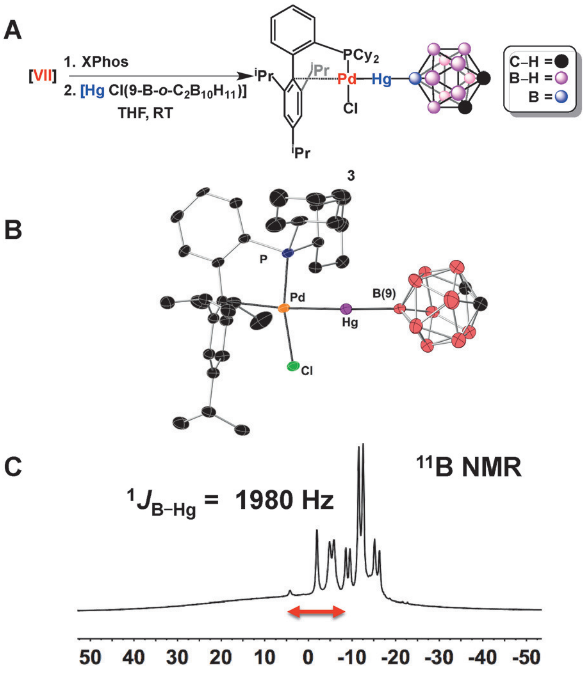
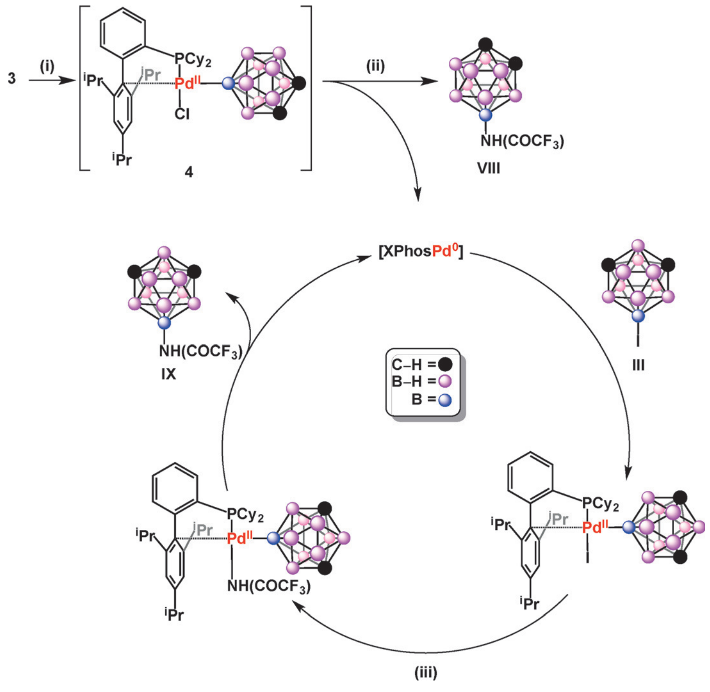


Figure 4. A: Synthesis of **3**. **B**: Single-crystal X-ray structure of **3** (thermal ellipsoids drawn at 50 % probability); H atoms, moderate disorder, THF of crystallization, and second independent structure omitted for clarity. **C**: ^{11}B NMR of **3** in CD$_2$Cl$_2$ featuring ^{199}Hg satellites (partially obscured under carborane resonances).

Multinuclear NMR analysis of the compound in CD$_2$Cl$_2$ is consistent with the formation of the product of oxidative addition of the Hg–Cl bond, [XPhosPdCl{Hg(9-B-*o*-C$_2$B$_{10}$H$_{11}$)}] (**3**), with ^{199}Hg satellites observable in the ^{11}B NMR ($^1J_{B-Hg}$ = 1980 Hz, Figure 4 C). A THF solution of **3** layered with pentane produced single crystals suitable for X-ray diffraction, which contained two independent molecules in the unit cell, but both with unsupported Pd–Hg bonds (Figure 4 B). A survey of the CSD discloses only twelve structurally characterized compounds containing a Pd–Hg interaction, with only two of the twelve containing unsupported Pd–Hg interactions, making **3** a structural rarity. The Pd–Hg bond length of 2.5435(5) Å for **3** comes under the sum of the respective covalent radii (2.71(11) Å),[21] and compares favorably with the lengths found for the unsupported interactions reported by Tanase and co-workers,[29] with **3** having the shortest observed Pd–Hg bond length to date. Compound **3** adopts a square planar geometry, with the coordination sphere around Pd^{II} completed by an *ipso* interaction of the biaryl ligand.[30] The P–Pd–Cl angle (167°) is more acute due to the chloride being bent towards the mercury, perhaps indicating some residual interaction between the atoms. The Hg–Cl length of 3.034 Å is significantly longer than the sum of the respective covalent radii (2.34 (9) Å), and longer than the average Hg–Cl bond length (2.511 Å), which makes it unlikely that a Hg–Cl σ-bond exists. DFT computational studies[31] on the geometry-optimized structure of **3** are consistent with this structural hypothesis (see the SI).



Scheme 1. Pathway for one-pot Pd-catalyzed amidation utilizing **3**. Key reagents and conditions: (i) 100 °C, Toluene, Hg; (ii) H$_2$NCOCF$_3$, K$_3$PO$_4$, KI, [XPhosPd^0] (iii) H$_2$NCOCF$_3$, K$_3$PO$_4$, KI.

Compound **3** is stable in air when stored below −20 °C. When heated to above 100 °C, **3** decomposes to produce Pd/Hg alloy, XPhos, and 9-B-chloro-*o*-carborane, the latter components being detected by GC-MS (see the SI). The formation of the 9-B-chloro-*o*-carborane was of interest as it implied that, upon extrusion of mercury at elevated temperatures, a transient Pd–B containing compound, [XPhosPdCl(9-B-*o*-C$_2$B$_{10}$H$_{11}$)] (**4**, Scheme 1) possibly forms. Subsequent rapid reductive elimination at the Pd center then produces 9-B-chloro-*o*-carborane. The transient nature of compound **4** can be rationalized by the observations reported by Grushin[17] for 9-B-iodo-*m*-carborane and by the generally lower stability of Pd–boryl compounds when compared to Pt.[15,32] Although the Pd–B containing compound **4** is not isolable, more convincing evidence for its existence could be obtained by utilizing compound **3** as a precatalyst for cross-coupling. We reasoned that under typical cross-coupling conditions, in situ extrusion of mercury would occur, producing the transient compound **4** as the formal product of oxidative addition that could then engage in transmetallation, followed by reductive elimination (Scheme 1).

We therefore probed the competency of **3** in the context of existing amidation cross-coupling.[27] Compound **3** was reacted with excess trifluoroacetamide in the absence of additional 9-B-halocarborane at 100 °C. A mixture of carborane-containing products was observed by GC-MS, including 9-B-chloro-*o*-carborane, and the desired product of transmetallation and reductive elimination, 9-B-(NH($COCF_3$))-*o*-$C_2B_{10}H_{11}$ (**VIII**), showing that **4** is indeed a viable intermediate. To assess the viability of compound **3** under true catalytic conditions, a one-pot reaction with 9-B-iodo-*m*-carborane (**III**, Figure 1) and a catalytic quantity (10 mol %) of compound **3** were reacted with the substrate and base at 100 °C (Scheme 1). Upon completion, GC-MS analysis showed the expected formation of **VIII** (Scheme 1) and both GC-MS and ^{11}B NMR indicated near quantitative conversion of **III** to 9-B-(NH($COCF_3$))-*m*-$C_2B_{10}H_{11}$ (**IX**, Scheme 1), thus providing excellent supporting evidence for the formation of **4**.

We have presented the isolation and full characterization of the first structurally characterized Pt^{II} B(9)-carboranyl compound featuring an unsupported M–B bond, [PtCl(PPh_3)$_2$(9-B-*m*-$C_2B_{10}H_{11}$)] (**1**), which was first reported by Zakharkin and Pisareva. It was demonstrated that compound **1** can potentially facilitate rapid installation of functional groups on the carborane in very mild conditions through substitution at the Pt^{II} center, followed by reductive elimination of the product, using benzyl mercaptan as a stoichiometric example to form 9-B-(SCH_2Ph)-m-$C_2B_{10}H_{11}$ (**2**). Attempts to isolate a similar Pd–boryl complex led to the formation of the heterobimetallic compound [XPhosPdCl{Hg(9-B-*o*-$C_2B_{10}H_{11}$)}] (**3**), featuring a rare, unsupported Pd–Hg bond. Compound **3** was shown to be able to access a transient Pd–B compound (**4**), evidenced by the stoichiometric reactivity of **3** and its competence as a precatalyst for Pd-catalyzed amidation of 9-B-iodo-*m*-carborane. Interestingly, the reported transformations are reminiscent of the scope and mechanisms of the functionalization of substrates using organomercurial species with Pd reagents documented in the early work of Heck.[33] Further work in our laboratory is ongoing to understand and exploit the facile nature of the reactivity of compounds **1** and **3** for a variety of transformations.[34]

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Keywords: boron · carboranes · cross-coupling · palladium · platinum

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[20] The extent of geometry distortion is visualized in the plot shown in the Supporting Information. Compounds of the type [PtCl(PPh$_3$)$_2$(X)] (X = any functional group) obtained from CSD[22] and their P–Pt–P and Cl–Pt–X angles are compared.

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[34] CCDC 1448227 (**1**) and 1448228 (**3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

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