Carborane-Based Pincers: Synthesis and Structure of SeBSe and SBS Pd(II) Complexes

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Pincer complexes,[1] formed from tridentate ligands (the "pincer") and metals or metalloids, are an exciting class of structures with utility in catalysis,[2] molecular electronics,[3] and medicine.[4] The pincer ligand provides tailorability with respect to (1) the anchoring site on the base, the central moiety from which the arms extend,[5a] (2) metal-binding heteroatoms, which control the electronic nature of the complexed atom,[5b] and (3) the auxiliary sites on the arms,[5c] which can be modified to control the chirality of the resulting structure and the steric environment around the complexed atom. To date, the base has been made primarily from hydrocarbons, including aromatic groups such as benzene and heteroatom analogues,[6a] aliphatic groups,[6b,c] and, more recently, carbene-type moieties.[6d]

Icosahedral carboranes represent one class of structures[7] that have not been explored as base units in pincer complexes. This is surprising considering these structures are highly tailorable,[8a] exhibit extraordinary stability,[8b] and provide a wide range of accessible chemical derivatization pathways.[8c] Indeed, Hawthorne et al. have pioneered synthetic methods for preparing metallacarboranes,[9a,b] the metallocene analogues of carboranes. These studies have led to many important discoveries pertaining to the fundamental chemistry of boron-containing cage structures and to their applications in nuclear waste remediation[9c] and as potential pharmaceuticals.[9d]

Herein we report the first carborane-based pincer ligand family and the complexes of these ligands metalated with Pd. The structure formed represents a new class of compounds with a previously unobserved Pd–B σ-coordination bond pincer motif.[10] Additionally, through density functional theory (DFT) calculations we show that the electronic structure of this novel complex, derived in part from this new ligand, is substantially different from its hydrocarbon analogues. The carborane-based pincer complex **5** was synthesized in four steps starting with the commercially available *m*-carborane **1** (Scheme 1a) to form the desired pincer ligand **4**. Pincer complex **5** is made in 76% yield by reacting ligand **4** with Pd(CH$_3$CN)$_4$[BF$_4$]$_2$ in acetonitrile followed by 2 equiv of (ⁿBu)$_4$NCl. Importantly, complex **5** is stable indefinitely in air and can be chromatographed on silica. All spectroscopic data are consistent with the proposed structure for **5**. For example, the mass spectrum of **5** exhibits an [M + Cl]⁻ ion at 659 *m/z* in negative ionization mode and [2M − Cl]⁺ at 1210 *m/z* in positive mode as the highest intensity peaks, respectively. Elemental analysis (C, H, Cl) confirms the elemental ratio of the pincer complex. The ¹¹B NMR spectra of ligand **4** and its Pd(II) complex **5** are consistent with the proposed complexation of Pd (Figure 1a). Complexation results in a 10 ppm downfield shift for the ¹¹B resonance associated with the B–Pd bond. Metalation of ligand **4** breaks the C_{2v} symmetry of its parent *m*-carborane cage and results in a larger number of ¹¹B resonances as compared with the spectrum for **4**. The ¹¹B{¹H} spectrum of **5**

consists of a region of four overlapping singlet resonances (from δ −3 to −18) and an isolated resonance at δ −0.7. Integration of the area under these peaks shows a 9:1 ratio, respectively. The ¹H coupled ¹¹B NMR spectrum of complex **5** exhibits a broad multiplet in the δ −3 to −18 region of the spectrum, but the resonance at δ −0.7 remains a singlet, consistent with its assignment as the B(2) atom bound to Pd(II).[10a] This B atom is the only one not bound to a hydrogen atom and therefore remains a singlet in the proton-coupled ¹¹B NMR spectrum.

**Scheme 1.** Syntheses of **5** and **7**[a]
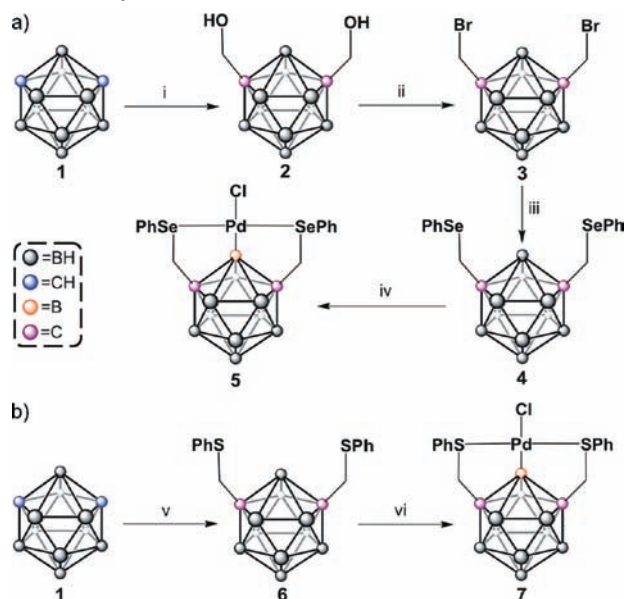
[a] (i) *n*-BuLi, ether, paraform, reflux, 85%; (ii) Br$_2$, PPh$_3$, benzene, reflux, 78%; (iii) PhSeSePh, NaBH$_4$, ethanol, reflux, 72%; (iv) Pd(CH$_3$CN)$_4$[BF$_4$]$_2$, CH$_3$CN, reflux, then (ⁿBu)$_4$NCl (2 equiv), 76%; (v) MeLi, ether, then ClCH$_2$SPh, 66%; (vi) same as (iv), 71%.

Temperature-dependent ⁷⁷Se NMR spectroscopy is also consistent with the proposed structure for **5**. At room temperature, ⁷⁷Se{¹H} NMR (see Supporting Information (SI), p S12) reveals three broad resonances[13] at δ 505, 535, and 543 ppm, respectively, which are assigned to the interconverting conformational forms of complex **5** in solution. Cooling the sample to −20 °C leads to resolution of the resonances and four distinct peaks. Two of these (δ 545.2 and 506.1) are assigned to the *syn* isomers, both of which have magnetically equivalent Se atoms. The remaining two, at δ 504.1 and 533.6, are assigned to the *anti* isomer, which contains magnetically inequivalent Se atoms due to the different faces of the carborane cage. Importantly, if one compares the ⁷⁷Se NMR resonance for ligand **4** (δ 354.1) with the resonances assigned to the different conformations of **5**, one finds a ∼δ 180

downfield shift, consistent with Pd(II) complexation. Fluxional behavior was also confirmed via ^{13}C NMR (see SI, p S14). ^1H NMR spectroscopy also shows a significant broadening of the **CH$_2$-arm** moiety resonances, attributed to the *syn* and *anti* isomers of **5**. A temperature dependent ^1H NMR study enabled us to estimate the activation energy for this process to be ~64 kJ/mol (see SI, p S13), based upon coalescence temperature and literature methods.[11]

Finally, the solid-state molecular structure of **5** was determined by single crystal X-ray diffraction methods. The Pd(II) center exhibits a distorted square planar coordination geometry, with two selenoether ligands coordinated in a *trans* fashion (Figure 1b) and a chloride atom ligated to Pd(II) in a *trans* fashion to B(2). The Pd−Cl bond length (2.44 Å) in **5** is slightly longer than similar motifs in aryl-based pincers (see SI, p S21, ref S5), indicating a stronger *trans* influence of the 2-boryl moiety on the *m*-carborane cage than its phenyl analogue. The Pd−B distance is one of the shortest (1.98 Å) reported to date (see SI, p S21, ref S4), based on a search performed in the Cambridge Crystallographic Data Center. To our knowledge, this structure represents the first crystallographically characterized Pd−B σ bond in carborane systems and the first metal−boron(2) bond in *m*-carborane chemistry.
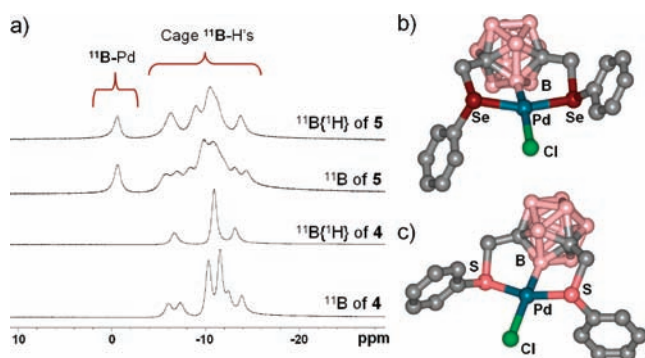
Figure 1. (a) ^{11}B NMR based structural evidence for pincer ligand **4** and its palladated complex **5**. (b and c) Crystallographically derived molecular structures of **5** and **7**, respectively (hydrogen atoms are omitted for clarity; the carbons are gray and the borons light coral).

"XBX" pincer complexes, where X is a general heteroatom, have not yet been made, and therefore, a general route to such structures is of a fundamental interest. As a demonstration of generality in accessing ligands with different heteroatom arm moieties we also synthesized and characterized the thioether, "SBS", analogue of **4**, ligand **6**, and its corresponding Pd(II) complex **7**. Pincer ligand **6** was synthesized in one step, via the dilithiation of *m*-carborane **1** and subsequent alkylation with commercially available α-chlorothioanisole (Scheme 1b). This ligand was palladated following the procedure used to prepare complex **5**. Single crystal X-ray diffraction (Figure 1c), mass spectrometry (showing a similar fragmentation pattern), and ^{11}B NMR spectroscopy (see SI, p S17) confirm that **7** is the thioether analogue of **5**. Interestingly, ^1H and ^{13}C NMR spectra of **7** (see SI, pp S19−20) suggest that only the *anti*-conformation of the complex exists at room temperature and below, unlike its "SeBSe" counterpart **5**. This is likely due to the larger *trans* effect imposed by a selenoether moiety, which weakens the Se−Pd bond and lowers the interconversion barrier.[12]

Preliminary DFT calculations (see SI, pp S5−8) provide interesting insights with respect to this unique structural motif. Based on calculated Mulliken and Löwdin charge densities, there is a net negative charge localized on the Pd atom and a relative positive charge concentrated on B(2), compared to other borons in the cage. These calculations also suggest a single bond between the Pd and B. Furthermore, the Pd−B bonds in complexes **5** and **7** exhibit strong σ-electron donation

with little π-back bonding, whereas some Pd−C analogues[1] have significant multiple bond character with both σ-electron donation and π-back bonding. Taking into consideration that the electronegativity of palladium is higher than that of boron,[13] the possibility of Pd bearing a formal oxidation state of zero in **5** and **7** cannot be dismissed at this point.

Work toward probing the stoichiometric and catalytic chemistry[14] of these complexes is currently underway. In particular, we are interested in exploring the nature of the M−B bond in carboranes, which was recently suggested to be more thermodynamically stable than the M−C analogue.[15] In addition, this is a novel type of hemilabile ligand which can be used for preparing a wide variety of supramolecular architectures, a primary focus of our current research.[16]

Supporting Information Available: Experimental and characterization for **4**−**7**. X-ray crystallographic files for **5** and **7** in CIF format. Details on DFT studies of **5**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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