Tridentate Boryl Ligands

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Boryl-Based Pincer Systems: New Avenues in Boron Chemistry**

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B–H activation · boron · carboranes · aminoboranes · tridentate ligands

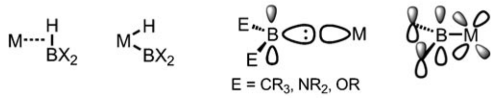
Boron chemistry has long been dominated by main-group inorganic chemistry, focusing on polyhedral boranes, borohydrides, and inorganic boranes.[1] The advent of carbaboranes (or carboranes) has significantly altered this situation, and boron has since been adopted by organic and inorganic chemists alike with much success. Carbaboranes are versatile frameworks that allow a variety of structural manipulations, mainly directed toward the carbon fragments in the skeleton.[2] These clusters exhibit a high electron-delocalizing ability, leading to very stable conjugate bases. Much recent attention was drawn to their use as very weakly coordinating anions[2c] and as building blocks for a variety of ligand structures.[2d–g] Furthermore, application of boron-based ligands has recently received much attention, with a primary focus on the various bonding modes of low-coordinate boron species.[3] For synthetic purposes, catalytic aromatic borylation and hydroboration (formally the addition of a hydrogen atom and a boryl group across a C=C bond) are widely applied in organic chemistry.

Boryl is the name for an anionic sp^2-hybridized BH_2 species and substituted derivatives thereof. Historically, metal boryl ($M{-}BE_2$; $E = OR, NR_2$, alkyl, etc.) chemistry developed much later than metal alkyl chemistry. A primary reason is the limited number of synthetic routes to boryl derivatives. For instance, stable sources of BE_2^- hardly exist,[4] whereas organolithium and Grignard reagents are commercially available. The instability of BE_2^- species is not surprising, given that boryl anions are coordinatively unsaturated. Furthermore, the B–H bond is inversely polarized compared to a typical C–H bond, that is, $B^{\delta+}{-}H^{\delta-}$ vs. $C^{\delta-}{-}H^{\delta+}$, and therefore boryl and borane species carry hydridic H atoms.

One distinct role for boron in organometallic and coordination chemistry has been as the central atom in facially coordinating tridentate ligands, so-called scorpionates.[5] However, boron has no interaction with the metal center but functions purely as bridgehead atom in these ligand scaffolds. The situation is markedly different in the recently developed metallaboratranes, in which boron acts as a neutral zero-electron donor/two-electron acceptor, also referred to as Z-type ligand.[6] However, boryl-based chelating ligands have been underdeveloped[7] and the development of boryl-centered tridentate compounds as ligands for transition metals, let alone subsequent catalysis with metal-containing species, has not been reported to date.

There has been a recent surge in the fundamental coordination chemistry of various types of low-coordinate boron-based scaffolds.[8] Notwithstanding these efforts, many boron fragments utilized in coordination chemistry and in, for example, borylation catalysis carry oxygen-linked substituents. Such compounds include pinacol derivatives $(Bpin)_2$, catecholate analogues B(cat), and boronic acids and esters utilized in cross-coupling chemistry. This situation might have limited the construction of suitable polydentate ligand structures derived from boryl units, as the divalency of oxygen severely limits side-arm functionalization. Moreover, boryl species flanked by nitrogen-based groups are stronger σ donors than their oxygen analogues.[9]

Boryl species BR_2 are very strong σ donors (and allow significant tuning by side-group modification) as a result of the electropositive nature of boron (also with respect to carbon), and therefore they exhibit a strong *trans* effect as well. This effect was studied both experimentally[10a] and theoretically[10b,c] on Pt complexes, among others. Similar to carbene ligands, boryl species have singlet ground states with an empty p orbital (Scheme 1). However, π back-donation is considered to be rather weak in most metal boryl complexes.[11] The bonding mode of a hydroborane ligand to a metal ion can vary from σ-bonded η^2-(B–H) to hydridoboryl



Scheme 1. Two limiting structures for the interaction of a hydroborane with a metal center and the two modes of boryl binding.

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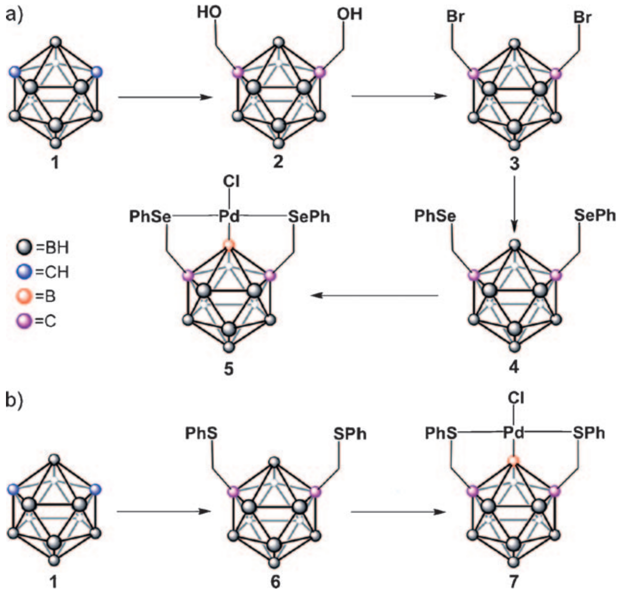
through oxidative addition of the B–H bond. The differences in reactivity for these compounds are pronounced, and recent mechanistic investigations have yielded surprising kinetic behavior for borane eliminations and activations as compared to coordination and activation of other small molecules.

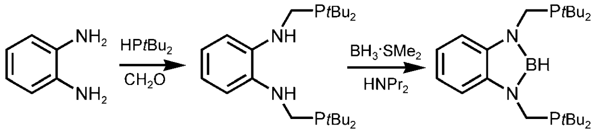
Pincer ligands have attracted long-lasting interest from a large number of research groups over the past few decades[12] and have been extensively studied for fundamental C–H, C–C, and C–N σ-bond-activation processes, transition-metal coordination chemistry, metal-mediated reactivity, and homogeneous catalysis. Some of the characteristic ligand features include rigid, tridentate binding pockets; compatibility with a large number of transition metals; high tunability at a number of key positions, intimately influencing the inner and/or outer coordination sphere of the metal ion; and incorporation of a variety of elements at the coordinating bridgehead position. Besides the archetypical carbon-based frameworks,[12,13] other novel backbones have amido,[14] silyl,[15] or phosphido[16] units to provide heterodonor functionality. Also, several neutral pincer ligands have been intensely studied in the last years, including non-innocent systems that undergo a reversible charge switch from neutral to monoanionic.[17] Strikingly absent from this overview are fragments derived from boron as the central atom.

The established chemistry of N-heterocyclic carbene frameworks incorporating low-valent main-group elements that are isoelectronic to the boryl anion (e.g. C, Si, and Ge) encouraged the application of chelating diamino substituents to stabilize the boryl anion, containing a low-valent boron(I) atom.[4] Two recent important contributions pave the way for an exploration of the chemistry of pincer ligand systems based on monoanionic boryl units as the central fragments and transition-metal homogeneous catalysis therewith.

Mirkin and co-workers initiated a new chapter in carbaborane chemistry by providing the first two ligand structures preorganized for tridentate metal coordination with a direct M–B bond.[18] The bis(selenophenyl)carbaborane (SeBSe) **4** and its bis(thiophenylether) analogue (SBS) **6** were synthesized by two separate protocols (Scheme 2). Complexation to Pd^{II} proceeded smoothly, albeit at reflux conditions to enable B–H bond cleavage, which is also typical for aryl-based Pd complexes with PCP ligands. ^{1}H-coupled ^{11}B NMR spectroscopy proved very informative to establish selective rupture of only one B–H bond to generate the tridentate ligand fragment. Pd complexes **5** and **7** were fully characterized, including by X-ray crystallography. DFT calculations provided evidence that the electronic character of Pd in these compounds is substantially different from well-known aryl-based PCP-derivatives.



Scheme 2. Preparation of a) SeBSe and b) SBS pincer ligands **4** and **6** based on a *m*-carbaborane scaffold and corresponding Pd^{II} complexes **5** and **7**. Reproduced from Ref. [18] (Copyright: American Chemical Society).



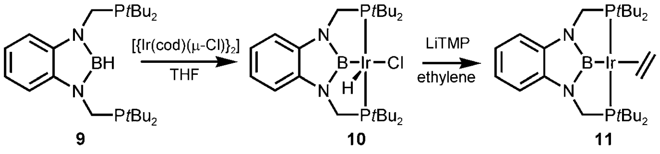
8 **9**

Scheme 3. Synthetic strategy to arrive at PBP ligand **9**.

Nozaki and co-workers, after their successful synthesis of stable boryllithium and related isolable boryl precursors,[4] now report on the elegant synthesis of a bis(phosphine)-functionalized hydro(diamino)borane species **9**.[19] *o*-Phenylenediamine is converted into the bis(*tert*-butylphosphino)methyl analogue **8** in good yield by condensation with formaldehyde and secondary phosphine (Scheme 3). Subsequent ring closure of the diamine groups using excess base-stabilized $BH_3·SMe_2$ proceeded effectively, furnishing the desired hydro(diamino)borane **9** in 78 % after deprotection of the phosphine groups, with a signal at $\delta = 26.4$ ppm in the ^{11}B NMR spectrum.

Oxidative addition of the B–H bond to an Ir^{I} complex proved facile, generating the first boryl-based pincer scaffold, coordinated to an Ir^{III} species, after stirring both precursors for only 10 min at room temperature (complex **10**). ^{11}B NMR spectroscopy showed a chemical shift difference of $\Delta\delta = +8.2$ ppm upon coordination to iridium. The hydride appeared as a triplet in the ^{1}H NMR spectrum. Coupling with the ^{11}B nucleus was absent for both hydride and phosphorus atoms owing to quadrupolar relaxation phenomena. The former indicates negligible, if any, B–H interaction originating from σ borane bond character. The $\nu_{\text{Ir–H}}$ band could be detected at 2281 cm^{-1}. X-ray crystallographic analysis confirmed the sp^{2} hybridization and established the stronger σ-bond donation of the PBP pincer versus related PCP species. The related ethylene complex **11** was made straightforwardly by chloride abstraction (Scheme 4). This species can be regarded as a model for one of the proposed intermediates during alkene borylation.

The development of tridentate scaffolds incorporating boron as a pivotal, ligating element is noteworthy from a number of perspectives. In contrast to the class of metallaboratranes, which feature an M(donor)–B(acceptor) bond, these pincer ligands contain a stable, strongly σ-donating



Scheme 4. Coordination of PBP ligand **9** in Ir complexes **10** and **11**.

boryl fragment. Side-arm functionalization can allow careful tuning of desired ligand properties. The rich carbaborane chemistry has now been expanded to include possible applications as ligands in transition-metal catalysis. These results open up new avenues in the coordination chemistry of boron as well, with possibly exciting metal-mediated reactivity.

B−H bond activation has recently been postulated in specific nitrogen-based scorpionate-like borate ligands to facilitate metallaboratrane formation concomitant with the formation of a metal hydride bond.[20] Species featuring reversible B−H bond activation could potentially serve as hydride shuttling systems for metal-mediated transformations. It should be interesting to investigate the possible non-innocent character of the novel tridentate boryl fragments described, both with respect to reversible protonation of the boron ion as well as potential redox behavior of some of these ligand scaffolds and their metal complexes.

It remains to be seen whether alternative boryl-based tridentate ligands are accessible through straightforward synthetic methodologies. With respect to complexation, the implied B−H activation might not always occur readily, hence hampering the clean preparation of metal species. Furthermore, pincer chemistry with carbaborane frameworks could find broader application if more tunable (mixed) side-arm groups could be introduced. It would be interesting to investigate the precise nature of and control over the electronic properties of boryl-based ligands. In this respect, the suggestion that Pd might be formally zero-valent in complexes **5** and **7** could have significant implications for (carba)boryl-based coordination chemistry and the resulting reactivity expected with such species.

The strongest selling point in favor of the introduction of boron as a new member in the family of heterodonor-functionalized (tridentate) ligands is fundamentally new or highly altered (e.g. more reactive) properties of the resulting metal complexes in catalytic transformations. So far these claims have not been substantiated, but the combined specific features of these EBE pincer complexes will undoubtedly inspire many new developments in the area of boron-based chemistry and catalysis.

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