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Boron Chemistry

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BO Chemistry Comes Full Circle**

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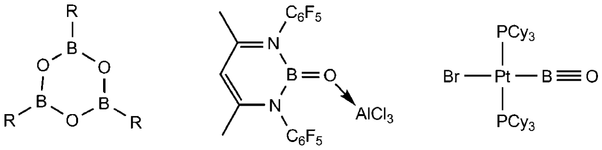
In memory of Keith Fagnou

boron · boroxines · cyclooligomerization · oxoboranes

Boron compounds have always been of significant interest to a wide range of chemists, because of the use of these compounds in organic synthesis. The discovery that organoboronic acids ($RB(OH)_2$) could be used in cross-coupling reactions is of particular importance because these compounds are relatively nontoxic and thermally, air-, and moisture-stable.[1] As such, compounds that contain three-coordinate boron atoms with electron-precise bonds are well known. Indeed, organoboron oxides, or oxoboranes, (RBO) have been known since the mid-1930s to exist as the anhydrides of boronic acids with cyclotrimeric structures assigned as $(RBO)_3$, which are generally known as boroxines (**1**, Figure 1).[2] Significant effort has been focused on trying to generate the monomeric oxoboranes RBO, where multiple bonding between the boron atom and the oxygen atom would be required to stabilize these species. However, these elusive compounds have previously only been detected in the gas phase or by low-temperature matrix isolation studies.[3] Evidence for the existence of monomeric oxoboranes suggests a strong B≡O bond that ultimately undergoes cyclooligomerization even at temperatures of approximately 50 K.[4]



1 2 3

Figure 1. Oxoborane derivatives, including the first structurally characterized transition-metal BO complex.

The first significant breakthrough in the isolation and characterization of these monomeric compounds was reported by Cowley and co-workers, who were able to circumvent the dominant cyclotrimerization reaction by coordinating a Lewis acid to an oxoborane that contains a bulky C_6F_5-substituted β-diketiminate.[5] The perfluoro aryl groups were crucial in preventing a competing insertion of the oxaborane oxygen atom into the C–H bond of the adjacent R group. The adduct $[HC(CMe)_2(NC_6F_5)_2]BO\rightarrow AlCl_3$ (**2**) was prepared by treatment of the protonated diketiminate ligand with $MeAlCl_2$ to give $[HC(CMe)_2(NC_6F_5)_2]AlCl_2$. This product undergoes a subsequent exchange–autoionization reaction with BCl_3 to afford $[\{HC(CMe)_2(NC_6F_5)_2\}BCl][AlCl_4]$, which was reacted with one equivalent of H_2O. Compound **2** was characterized by a number of analytical methods, including an X-ray diffraction study, which showed a B–O bond length of 1.304(2) Å. By comparison, the typical length of a B–O bond found in boronic acids is about 1.36 Å. DFT calculations confirm that the B–O bond in this structure has considerable double-bond character. However, drastic modifications in both the steric and the electronic components of the R group were required to isolate and stabilize this unique oxoborane derivative.

More recently, Braunschweig et al. have conducted some seminal work on the stabilization of low-coordinate boron centers by using late transition metals.[6] Although transition-metal boryl compounds (MBR_2) that contain three-coordinate boron species have been well-documented,[7] Braunschweig et al. have been able to prepare and isolate the first metal complex that contains a relatively stable BO fragment.[8] The platinum complex *trans*-$[(PCy_3)_2PtBr(BO)]$ (**3**, Cy = cyclohexyl) was prepared following the hypothesis that the anionic BO^- ligand would be a complementary isolobal analogue to the ubiquitous CO ligand. Addition of $Br_2BOSiMe_3$ to $[Pt(PCy_3)_2]$ gave **3** along with the concomitant formation of $BrSiMe_3$; the latter species was removed under high vacuum at ambient temperatures. The bis(tricyclohexylphosphine)platinum fragment is particularly well-suited for the stabilization of dicoordinate boron centers. The molecular structure of **3** was solved by X-ray diffraction and the B–O distance of 1.126(4) Å is considerably shorter than that observed in compound **2**. This observation, along with a density functional study, suggests that the BO ligand is best represented as containing a true triple bond. The most remarkable feature of **3**, however, is its impressive thermal stability as no evidence of oligomerization or decomposition was observed after heating **3** to 100 °C for 24 h or upon irradiation with a Hg/Xe arc lamp.

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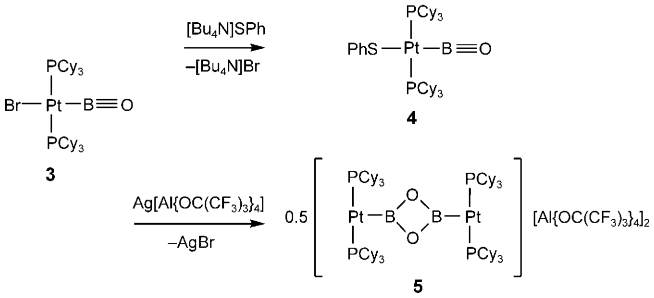

Scheme 1. Ligand substitution and cyclodimerization of platinum oxoborane complex **3**.

Initial reactivity studies showed that addition of $[Bu_4N]SPh$ to **3** gave *trans*-$[(PCy_3)_2Pt(SPh)(BO)]$ (**4**, Scheme 1), where the bromide ion has undergone a selective metathesis with the thiolate ion while leaving the BO ligand completely intact. However, bromide-ion abstraction was observed when **3** was treated with $Ag[Al\{OC(CF_3)_3\}_4]$ and instant cyclodimerization of the BO ligand gave the ionic complex $[(PCy_3)_2Pt(BO_2B)Pt(PCy_3)_2][Al\{OC(CF_3)_3\}_4]_2$ (**5**). Contrary to other platinum boryl species where the boron ligand is perpendicular to the platinum bisphosphine axis,[7b] the two platinum fragments in **5** are twisted with respect to one another by 58°, and consequently the BO_2B plane is also twisted relative to the platinum fragments to form a unique helical structure. The BO_2B ring can best be described as a rhombus within the 3σ-criterion. Rather long B−O bond lengths of 1.4 Å are believed to result from a strongly antibonding cross-ring interaction between the two electronegative oxygen atoms while a relatively short B–B distance suggests a possible electronic interaction. A similar structure has been reported for a related amino-substituted analogue that contains bulky tetramethylpiperidyl groups.[9] It will be of singular interest to see how the chemistry of the BO_2B ring in **5** is further developed.

This work discusses only the beginning of what is surely to become an exciting and prosperous area of boron chemistry. The ability to stabilize a true B≡O ligand by using a platinum bisphosphine fragment is a most remarkable discovery and bound to expand our understanding of an important family of compounds. The chemistry of boron oxides has gone full circle and the future of these compounds will undoubtedly be quite exciting!

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