

Borinium Cations as σ -B–H Ligands in Osmium Complexes

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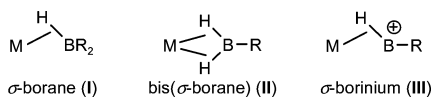
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Borinium cations are fascinating two-coordinate highly electrophilic boron species that adopt structures analogous to those observed for allenes. They are stabilized by two dual-purpose substituents that include both a sterically bulky periphery and a functional group capable of π -bonding to boron.¹ Cations of this type, in which only one substituent is capable of π -bonding, are extremely rare and require an extremely bulky group to afford added protection of the electron-deficient boron center. Thus, an alkyl- and an aryl-substituted borinium cation that are unstable at room temperature and have a tetramethylpiperidino group as the second substituent are known.²

The reactions of transition-metal complexes with boranes is a field of much current interest³ for their implications in the functionalization of organic molecules⁴ and because of their applications in the preparation of new oligomers and polymers and in the reversible dehydrocoupling of amineboranes and related compounds.⁵ Most of these processes begin with the addition of a B–H bond to the metal center. σ -Complexes are often considered as intermediates in the oxidative addition of H–E bonds (E = H, B, C, Si, etc.) and its microreverse, reductive elimination.⁶ In contrast to the large number of dihydrogen complexes and σ -silane compounds, a very limited number of M(σ -B–H) species^{6d} have been isolated and characterized. They are σ -borane (**I**) and bis(σ -borane) (**II**) derivatives (Chart 1).⁷

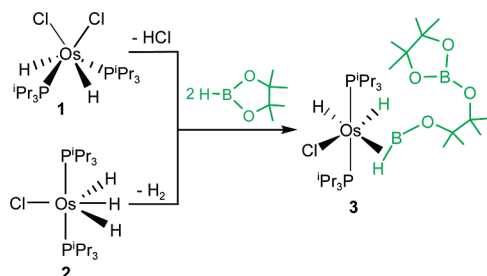
Chart 1



During our study of the chemistry of the complex $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ (**1**),⁸ we have now discovered that the 14-valence-electron metal fragment $\text{OsHCl}(\text{P}^i\text{Pr}_3)_2$ promotes hydride abstraction of boranes and amineboranes to generate monosubstituted borinium cations, which are stabilized by coordination to osmium as σ -borinium ligands (**III** in Chart 1).

Treatment of both **1** and $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**2**) with 4.4 equiv of pinacolborane in dichloromethane for 6 h at room temperature led to the σ -borinium derivative **3** (Scheme 1), which was isolated as

Scheme 1



a white solid in 78% yield. Its formation implies the dimerization of two pinacolborane molecules and hydride transfer from one of them to the osmium atom of the metal fragment $\text{OsHCl}(\text{P}^i\text{Pr}_3)_2$. The latter results from the release of HCl from **1**, which is trapped by the excess borane, and from the release of H_2 from **2**.

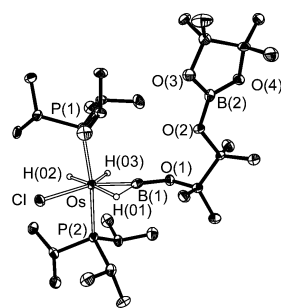
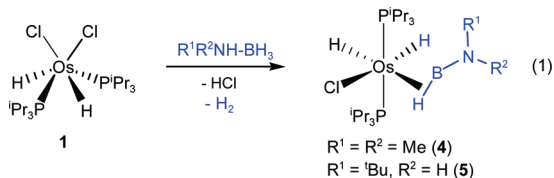


Figure 1. ORTEP drawing of complex **3**.

Complex **3** was characterized by X-ray diffraction analysis. The structure (Figure 1) proves the formation of the novel borinium cation and its stabilization by coordination of the σ -B–H bond to the transition metal. The coordination geometry around the osmium atom is the expected one for a six-coordinate osmium(II) species; i.e., it can be rationalized as a distorted octahedron with trans phosphines [$\text{P}–\text{Os}–\text{P} = 168.80(5)^\circ$]. The perpendicular plane is formed by the chloride ligand and the hydride H(02), which are mutually cis-disposed [$\text{Cl}–\text{Os}–\text{H}(02) = 90.3(17)^\circ$], the borinium cation with H(01) pointing toward the chloride ligand and trans-disposed to H(02), and the hydride H(03). The $\text{Os}–\text{B}(1)$ bond length of 1.899(7) Å is ~ 0.2 Å shorter than the separation of 2.157(5) Å between the metal and the boron atom of the η^2 -HBpin ligand in the complex $\text{RuH}[(\mu\text{-H})_2\text{Bpin}](\eta^2\text{-HBpin})(\text{PCy}_3)_2$.⁹ However, the distances between the atoms of the coordinated B–H bonds are similar in these two compounds [1.32(5) Å in **3** vs 1.35(3) Å in the ruthenium complex]. The separation between B(1) and the hydride ligand H(03) is 2.23 Å, which is ~ 0.9 Å longer than the B(1)–H(01) distance. In agreement with the structural analogy between borinium cations and allenes,¹⁰ the H(01)–B(1)–O(1) and Os–B(1)–O(1) angles of 134(2) and 164.0(5)°, respectively, are similar to the related angles in transition-metal π -allene complexes.¹¹

The $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **3** at 253 K in dichloromethane- d_2 is consistent with the structure shown in Figure 1. In accordance with the presence of three inequivalent hydrogen atoms bonded to the metal center, it contains three high-field resonances at -4.0 [H(01)], -6.9 [H(02)], and -16.3 [H(03)] ppm. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum reveals a significant cationic charge density on the boron center B(1). Thus, it shows a B(1) resonance at 55 ppm,¹² which is shifted 33 ppm downfield relative to the B(2) resonance at 22

ppm. A singlet at 37.3 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is also characteristic of **3**.



Complex **1** also generates the 14-valence-electron metal fragment $\text{OsHCl}(\text{P}^i\text{Pr}_3)_2$ in the presence of ammoniaboranes,¹³ which undergo dehydrogenation to form amineboranes. Hydride transfer from the amineborane to $\text{OsHCl}(\text{P}^i\text{Pr}_3)_2$ affords the anionic metal fragment $[\text{OsH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2]^-$, which also traps and stabilizes monosubstituted borinium cations with an alkyl- or dialkylamido substituent. Thus, the treatment of **1** with 2.0 equiv of $\text{Me}_2\text{NH-BH}_3$ in tetrahydrofuran for 2 h at room temperature afforded **4** (eq 1), which was isolated as pale-yellow crystals in 70% yield. Under the same conditions, the reaction of **1** with $^i\text{BuNH}_2\text{-BH}_3$ gave **5** as a white solid in 42% yield.

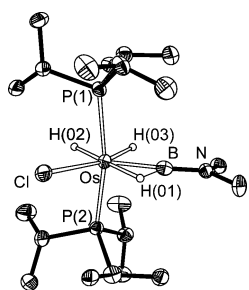


Figure 2. ORTEP drawing of complex **4**.

Complex **4** was also characterized by X-ray diffraction analysis. The structure (Figure 2) proves the formation of the amidoborinium cation and its stabilization by coordination of the B–H bond to the metal center. The geometry around the osmium atom is like that in **3** with similar structural parameters, which agree well with those obtained by density functional theory (B3PW91/LANL2DZ) calculations for the optimized structure (see the Supporting Information). Natural bond orbital (NBO)¹⁴ analysis yielded a negative charge of $-1.71e$ on the metal center and a positive charge of $+0.66e$ on the boron atom.¹⁵ The latter is significantly more positive than that on the boron center in H_2BNMe_2 ($+0.38e$). This supports the cationic character of the σ -ligand and the heterolytic cleavage of a B–H bond as the key step in the formation of this type of compound. The Os–B distance of 1.923(6) Å and the H(01)–B–N and Os–B–N angles of 139.2 and 165.2(4)°, respectively, also compare well with the corresponding parameters of **3**. In agreement with the latter and the structure shown in Figure 2, the $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of **4** and **5** contain three high-field resonances at -3.3 , -9.2 , and -16.6 ppm (**4**) and -3.3 , -9.4 , and -16.4 ppm (**5**). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra also reveal a significant cationic charge density on the boron center. The B resonances appear at even lower fields than those of **3** (66 ppm for **4** and 63 ppm for **5**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlets at 36.5 ppm (**4**) and 36.8 ppm (**5**).

In conclusion, highly electrophilic transition-metal fragments can promote hydride abstraction from alkoxyboranes and amineboranes to form σ -(BH)-borinium transition-metal complexes.

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Supporting Information Available: General experimental details; synthesis, characterization, and crystallographic data (CIF) for **3** and **4**; and computational details and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) This chemical shift is similar to those found in borinium cations with an alkyl or aryl substituent.
- (13) The generated HCl is trapped by an excess of the ammoniaborane to form $\text{R}'\text{R}''\text{NH-BH}_2\text{Cl}$ ($\text{R}' = \text{R}'' = \text{Me}$; $\text{R}' = \text{tBu}, \text{R}'' = \text{H}$) and molecular hydrogen.
- (14) NBO version 3. See: Weinhold, F.; Carpenter, J. E. In *The Structure of Small Molecules*; Naaman, R., Vager, Z., Eds.; Plenum: New York, 1988; p 227.
- (15) The positive charge on the boron atom of the free cation $[\text{HBNMe}_2]^+$ is $+1.066e$. The coordination produces a total charge transfer of $-0.40e$ from the metal center to the ligand.

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