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# Borabenzene Derivatives of Main Group Elements

Xiaolai Zheng

## Abstract

The borabenzene chemistry of main group elements was systematically investigated.

Treatment of 1-chloro-3,5-dimethyl-2-trimethylsilyl-1,2-dihydroborinine with 1,3,4,5-tetramethylimidazol-2-ylidene gave the first borabenzene-carbene adduct. Reaction with  $\text{Ph}_3\text{PCH}_2$  afforded the expected ylide adduct  $3,5\text{-Me}_2\text{C}_5\text{H}_3\text{B-CH}_2\text{PPh}_3$  as well as a minor amount of the trimethylsilyl-substituted adduct  $3,5\text{-Me}_2\text{C}_5\text{H}_3\text{B-CH(SiMe}_3\text{)PPh}_3$  because of the fast proton-transfer. These new borabenzene adducts are featured with a larger charge separation as evidenced by NMR spectroscopy (solution), X-ray diffraction methods (solid state), and preliminary DFT calculations (gas phase).

Synthetic efforts on boratabenzene complexes of alkali metals made the boratabenzene ligands more readily available. Attachments of (*S*)-2-methoxymethylpyrrolidin-1-yl and 1-morpholino substituents to the *B*-exocyclic sites afforded additional pendent donors to the ligands. Five Lewis base solvates of the boratabenzene salts were determined by X-ray diffraction methods. The structural motifs comprise a contact ion-pair, a zigzag  $\mu$ -boratabenzene chain, a non-zigzag chain, a hexagonal helix, and a polymeric lithium sandwich arrangement. The highly variable structural modes reflect the predominantly ionic nature of the interactions between the boratabenzene ligands and the alkali metals.

Donor-free magnesocene analogues  $\text{Mg}(\text{C}_5\text{H}_3\text{BNMe}_2)_2$  and  $\text{Mg}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2$  were synthesized by reactions of 2-trimethylstannyldihydroborinines with  $\text{MgMe}_2$ . In the solid state,  $\text{Mg}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2$  possesses a centrosymmetric sandwich structure with the two  $\eta^6$ -boratabenzene ligands trans-arranged whereas its THF adduct  $\text{Mg}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2(\text{THF})_2$  exhibits a distorted tetrahedral  $\text{N}_2\text{O}_2$  coordination environment around the magnesium. The observation of an aminoboratabenzene that is solely  $\sigma$ -coordinated to a metal is without precedent. These results represent the first investigation on boratabenzene complexes of an alkaline earth metal.

Bis(boratabenzene) complexes  $\text{Pb}(\text{C}_5\text{H}_3\text{BMe}_2)_2$ ,  $\text{Pb}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{BNMe}_2)_2$ , and  $\text{E}[3,5\text{-Me}_2\text{C}_5\text{H}_3\text{BN}(\text{SiMe}_3)_2]_2$  ( $\text{E} = \text{Ge, Sn, Pb}$ ) were synthesized by reactions of lithium boratabenzenes with group 14 metal dihalides. Despite the presence of the 6s lone pair,  $\text{Pb}(\text{C}_5\text{H}_3\text{BMe}_2)_2$  forms Lewis base adducts with TMEDA and bipy. Structural analyses of those compounds established the facially bonding mode of the boratabenzene ligands in coordination to group 14 metals in oxidation state +2.