**Bis(1-methyl-ortho-carboranyl)borane**


---

**Abstract:** The Lewis superacidic, bis(1-methyl-ortho-carboranyl)borane, is rapidly accessed in two steps. It is a very effective hydroboration reagent capable of B–H addition to alkenes, alkynes, and cyclopropanes. To date, this is the first Lewis superacidic secondary borane and most reactive neutral hydroboration reagent.

The hydroboration reaction, pioneered by Brown, has emerged as a powerful synthetic tool to selectively functionalize unsaturated bonds.[1] While borane (BH₃) is an effective reagent for B–H addition reactions, the remaining two B–H bonds are susceptible to further reactivity. Accordingly, secondary boranes (HBR₂) are commonly the reagent of choice for hydroboration.[2] The outcomes are highly influenced by the electronic and steric properties imparted by the two substituents on the borane. The prototypical examples are diol chelated variants but they require catalysts to enable reactivity.[3] As hydroboration emerged in synthesis,[4] research in advancing the reaction led to a quest for other reactive HBR₂ species. A breakthrough compound was developed by Piers and co-workers in the synthesis of the highly electrophilic bis(pentafluorophenyl)borane [HB(CF₃)₂], known as Piers’ borane (Figure 1).[5] This species is an extremely active hydroboration agent towards carbon-carbon multiple bonds with reactions proceeding at faster rates than other secondary boranes. It is evident that the fluorinated arenes serve as highly effective electron withdrawing groups to enhance electrophilicity and consequently, reactivity at the boron center. Parallel to the rich hydroboration chemistry, Piers’ borane has been an effective reagent in a variety of organic transformations that includes the Lewis acid component in frustrated Lewis pairs, a co-catalyst in olefin polymerization, and as a hydrogenation catalyst.[7] The widespread applications of Piers’ borane stimulated other researchers to install trifluoromethyl groups as a method of fluoride loading on arenes to alter electronics and steric[e.g. bis(3,5-bis-trifluoromethylphenyl)borane [HB(Fxy)₂][8] and bis(2,4,6-tris-trifluoromethylphenyl)borane [HB(Fmes)₂][9]] that has been an effective method for fine-tuning the electrophilicity and hydroboration activity.

Recently, tris(ortho-carboranyl)borane (BoCB₃) was reported that is substantially more Lewis acidic than the halogen-loaded aryl boranes and fits into the classification of a Lewis superacid (LSA).[10] Additionally, the steric profile of the icosahedral carborane is significantly different than an arene.[11] This led us to the hypothesis that ortho-carboranes could serve as an effective electron-withdrawing group on HBR₂ reagents and the bulk could alter selectivity or reactivity in hydroboration reactions. To date, the isolation of a Lewis superacidic secondary borane has yet to be realized.[12] Here we report a secondary borane featuring two ortho-carborane substituents that achieves Lewis superacidity and potent hydroboration activity.

Lithiation of commercially available 1-methyl-ortho-carborane (H¹⁴MeOCb) with nBuLi followed by the reaction with half an equivalent of BX₃ (X = Cl, Br) generated the haloborane XB¹⁴MeOCb₂ (yields: 31% for Cl, 33% for Br; Scheme 1). The downfield broad ¹¹B resonances at 59.7 (Cl) and 64.9 ppm (Br) are consistent with XBR₂ species.[13, 14] Treatment of both XB¹⁴MeOCb₂ intermediates with triethylsilane (HSiEt₃) accessed HB¹⁴MeOCb₂ in excellent yields (Cl: 93% and Br: 96%). The identities of Br¹⁴MeOCb₂ and HB¹⁴MeOCb₂ were confirmed by single crystal X-ray diffraction studies (Figure 2). Most known electrophilic secondary boranes are in a monomer–dimer equilibrium in solution,[15, 16] and monomers are extremely rare.[17] Interestingly, HB¹⁴MeOCb₂ is monomeric in both the solid and solution state, even at −75 °C in solution as confirmed by variable temperature ¹¹B NMR studies in toluene-d₈. The resonance for the tricoordinate boron in the ¹¹B NMR spectrum is observed at 70.9 ppm. In the ¹¹B NMR spectrum, the diagnostic resonance for the central B–H proton is a broad singlet at 5.49 ppm, downfield in comparison to the monomeric electrophilic borane HB(Fmes)₂ (3.53 ppm).[18, 19] In the corresponding ¹¹H(¹¹B) NMR spectrum, the peak sharpens (full width at half maximum = 19 Hz). Although the central boron atom is sterically encumbered, the B–C bond lengths to the central boron are 1.557(5) and 1.567(5) Å, in the typical range for an ortho-carborane bound to boron. The bulk significantly impacts the C–B–C angle as it is expanded to 128.0(3)° from the idealized trigonal plane.

---

**Representative examples of fluorine loaded neutral secondary boranes (HBR₂) and targeted bis(ortho-carboranyl)borane.**

**Figure 1.** Selected examples of electrophilic secondary boranes (HBR₂) and targeted bis(ortho-carboranyl)borane.
Spectroscopy. The adduct is also resilient in solution under an N₂ environment, typically seen at room temperature.

Lewis acids. Thus, only a few carbonyl borane complexes have been detected purely on metal to ligand donation from the carbon to metal and back donation from the boron atom, unlike HB(CF₃)₂. Natural population analysis reveals the partial monomeric character. Theoretical calculations on HB(CF₃)₂ reveal 540 kJ/mol and ammonia affinity for H₂. The hydride ion affinity (HIA) for HB(CF₃)₂ is 182 kJ/mol and HB(CF₃)₂ is 120 kJ/mol, both greater than the values of HB(CF₃)₂ at 457 kJ/mol and 100 kJ/mol, respectively.

The calculated LUMO of HB(CF₃)₂ is almost entirely localized on the boron atom, unlike HB(CF₃)₂ that shows notable delocalization onto the CF₃ rings. The LUMO energy of HB(CF₃)₂ is calculated to be 0.164 eV higher than that in HB(CF₃)₂ as attributed to the delocalization. The % Lewis acid buried volume using the fluoride adducts, according to the method by Radius and co-workers, returns a value of 64% for HB(CF₃)₂, much higher than HB(CF₃)₂ at 47%, explaining the monomeric character. Natural population analysis reveals the partial charge on boron to be significantly higher in HB(CF₃)₂ (+1.25) compared to HB(CF₃)₂ (+0.57). For the hydride, the partial charges are −0.21 and −0.03, respectively. This indicates an extremely polar B-H bond in HB(CF₃)₂.

Adducts with CO, EtOAc, and OPEt₃ were prepared to experimentally evaluate the relative Lewis acidity of HB(CF₃)₂ (Scheme 2). While CO binds metals strongly, due to synergistic σ donation from the carbon to metal and back donation from the metal to ligand π* orbital, boranes cannot π back-bond and rely purely on σ donation that precludes binding, except for powerful Lewis acids. Thus, only a few carbonyl borane complexes have been detected at room temperature. Exposing a CD₃ solution of HB(CF₃)₂ to an atmosphere of CO at 25 °C formed the adduct (OC-BH(CF₃)₂) in quantitative yield based on in situ NMR spectroscopy. The adduct is also resilient in solution under an N₂ atmosphere. The carbonyl signal in the 13C{¹H} NMR spectrum is broad at 166.3 ppm. The 11B{¹H} NMR spectrum features a resonance with a significant upfield shift of the central boron atom appearing at δ = −17.5 ppm, consistent with a tetracoordinate boron center. The X-ray diffraction structure of OC-BH(CF₃)₂ reveals the boron-carbon bond length to be comparable to other electrophilic borane CO adducts [B(1)−C(1) = 1.629(8) Å c.f. OC-B(CF₃)₂ = 1.69 Å].

OC-perfluoropentaphenylborole 1.609(5) Å.[24c] The C−O bond length is within error of measurement of free CO [1.117(7) Å c.f. 1.128(1) Å][25] but the FT-IR CO stretching frequency of OC-BH(CF₃)₂ is 2207 cm⁻¹ in CδDs, higher than free CO (2143 cm⁻¹) and comparable to OC-perfluoropentaphenylborole (2195 cm⁻¹) in CH₂Cl₂ solution.[25a] Applying vacuum to the solid liberates the carbonyl to regenerate HB(CF₃)₂. Thermochemical calculations reveal OC-BH(CF₃)₂ is slightly downhill from the reagents (−28 kJ/mol).

In EtOAc-BH(CF₃)₂, the FT-IR C=O stretching frequency is 1590 cm⁻¹, indicating stronger adduct formation than B(CF₃)₂ (1648 cm⁻¹), as well as other electrophilic boranes[26] and EtOAc-AlCl₃ (1624 cm⁻¹).[24] The Et₂PO adduct enabled assessment of the Lewis acidity by the Gutmann-Beckett method.[25] The difference in δ¹P chemical shift (δ¹P) of free Et₂PO and Et₂PO-BH(CF₃)₂ is 35.8 and 30.0 ppm in CD₃ and CDCl₃, respectively. The δ¹P values are higher for HB(CF₃)₂ than the boron Lewis superacids BuOCl [δ¹P: 34.1 and 27.5 ppm in CD₃ and CDCl₃][23] and B(p-CF₃-CF₃)₂ [δ¹P: 31.9 ppm in CD₃].[26]

Scheme 1. Synthesis of HB(CF₃)₂

Theoretical calculations on HB(CF₃)₂ reveal a fluoride ion affinity (FIA) of 527 kJ/mol [BP86/SV(P)],[19] exceeding that of SbF₅ (494 kJ/mol), B(CF₃)₃ (452 kJ/mol), and HB(CF₃)₂ (429 kJ/mol). To experimentally assess the relative FIA, HB(CF₃)₂ was treated with [nBuN][SbF₅]. Based on multinuclear NMR spectroscopy (¹H, ¹¹B, ¹⁹F{¹H}), HB(CF₃)₂ was consumed within 30 minutes along with the observation of [nBuN][Sb(CF₃)₃]. As SbF₅ is the benchmark for a Lewis superacid,[17,18] HB(CF₃)₂ fits the LSA classification by computation and experiment. The hydride ion affinity (HIA) for HB(CF₃)₂ is 540 kJ/mol and ammonia affinity for HB(CF₃)₂ is 120 kJ/mol, both greater than the values of HB(CF₃)₂ at 457 kJ/mol and 100 kJ/mol, respectively.

Scheme 2. Reactions of HB(CF₃)₂ with CO, EtOAc, and OPEt₃.

The powerful Lewis acidity and highly polarized B−H bond imply that HB(CF₃)₂ might be a very active hydrometallation reagent. To assess the reactivity, HB(CF₃)₂ was reacted with styrene that led to the anti-Markovnikov product 1a in 98% yield within 10 minutes, without any polymerization (Scheme 3a). Alkenes bearing an electron-withdrawing arene (C₆F₅) and an aliphatic chain (n-butane−) also provided the anti-Markovnikov products,
1b and 1c, within 10 minutes in 94% and 98% yield, respectively. Vinyl silanes behave uniquely towards B–H reagents, often giving a mixture of α- and β-regioselectivities.\(^\text{[1b, 27]}\) The reaction of vinyl-
$\text{SiMe}_3$ with HBl\(^\text{60C}_{\text{6}}\) led to the β-isomer (1d) exclusively, in 96% yield. Internal alkenes are less reactive with trans-stilbene not reacting, even after heating at 120 °C for 36 h in m-xylene (1e). Trans-β-methylstyrlylrene required heating to 80 °C for 60 h to obtain the formal 1,3-hydroboration product 1f in 90% yield, while the expected 1,2-product 1f was not observed.

![Scheme 3](image)

**Scheme 3.** Hydroboration of (a) alkenes and (b) alkynes using HBl\(^\text{60C}_{\text{6}}\) with isolated yields reported. NR = no reaction. Standard reaction conditions: 0.10 mmol alkene/alkyne, 0.10 mmol HBl\(^\text{60C}_{\text{6}}\), 2 mL C\(_6\)H\(_6\), 23 °C, 10 min. Deviations from the standard reaction conditions: \(^\text{[3a]}\) xylene, 120 °C, 36 h; \(^\text{[3b]}\) 80 °C, 60 h; \(^\text{[3c]}\) 30 min. \(^\text{[3d]}\) Double hydroboration did not occur even at heating at 80 °C for 24 h in C\(_6\)H\(_6\). \(^\text{[3e]}\) No isomerization even at heating at 80 °C for 24 h in C\(_6\)H\(_6\). Complex reaction mixture.

Next, we turned our attention to alkenes (Scheme 3b). In regard to terminal alkenes, Ph, nBu, SiMe\(_3\), and Bpin substrates all gave the corresponding 1,2-hydroboration products 1g–1j in excellent yields (92–97%). Interestingly, a second hydroboration of the alkene in 1g–1i did not occur, even at elevated temperature (80 °C for 24 h in C\(_6\)D\(_6\)).\(^\text{[28]}\) This is contrary to bis(fluoroaryl)boranes that react with multiple bonds.\(^\text{[5d]}\) The unactivated internal alkene, 2-butyne, gave the hydroboration product 1k in 89% yield. To examine regioselectivity, reaction with the unsymmetric internal alkene, PhC\(_6\)Me\(_2\), gave the corresponding hydroboration product 1l in 95% yield. Compounds 1k and 1l did not isomerize to the terminal alkene even upon heating at 80 °C for 24 h. The bulky unsymmetric internal alkene PhC\(_6\)C\(_6\)Bu gives inverse regioselectivity to furnish 1m in 89% yield, indicating regioselectivity is affected by sterics. The regioselectivities were confirmed by X-ray crystallography.\(^\text{[16]}\)

Interestingly, the silane substituted internal alkynes PhC\(_6\)CSi\(_3\)Et and PhC\(_6\)CSi\(_3\)Ph gave unique 1,1-hydroboration products 1n and 1o in excellent yield (90% and 85%, respectively), where both the hydrogen atom and the B\(^{60}\)C\(_6\) group reside on the same carbon atom resulting from 1,2-Si group migration.\(^\text{[29, 20]}\) The structure of 1n is confirmed by a single crystal X-ray diffraction study (Scheme 3). Unfortunately, the tin substituted PhC\(_6\)CSnBu\(_3\) led to a complex reaction mixture (1p).

Although cyclopropanes do not have a multiple bond, the ring is an unsaturation equivalent, and the strained C–C bond could undergo a formal ring-opening 1,3-hydroboration.\(^\text{[31]}\) Unactivated cyclopropanes are the most common three-membered ring systems found in nature but methods for their selective ring-opening hydroboration are scarce.\(^\text{[32]}\) In 1971, Rickborn and co-workers described the conversion of cyclopropanes with diborane (B\(_2\)H\(_6\)) to afford alkyboranes at 100 °C, albeit with poor selectivity.\(^\text{[23]}\) Recently, Wang and co-workers showed that the super electrophilic nature of hydroborenium complexes can facilitate the α-bond metathesis of cyclopropanes to yield 1,3-hydroboration products but this reaction has yet to be realized for a neutral secondary borane.\(^\text{[32]}\) The 1:1 reaction of HBl\(^\text{60C}_{\text{6}}\) with cyclopentylborene in C\(_6\)H\(_6\) at 40 °C for 12 h led to the 1,3-hydroboration product 1l as the sole hydroboration species in 88% isolated yield with exquisite regioselectivity (Scheme 4). The reaction could be extended to 4-Br-C\(_6\)H\(_4\)- and 4-Ph-C\(_6\)H\(_4\)-substituted cyclopropanes to generate the corresponding products 2a and 2b in 90 and 94% yields, respectively. The ester functionalized variant (4-CO\(_2\)Me-C\(_6\)H\(_4\)) made adduct 2c irreversibly and did not undergo ring opening even upon heating to 120 °C for 24 h in m-xylene. The sterically crowded 1-naphthyl cyclopropane furnished the 1,3-functionalized propane in 85% yield. The aliphatic benzyl-cyclopropane led to a complex reaction mixture from unselective ring opening. The bulky disubstituted E-1,2-diphenylcyclopropane did not react with HBl\(^\text{60C}_{\text{6}}\) despite heating at 120 °C in m-xylene for 24 h (2c).

![Scheme 4](image)

**Scheme 4.** Hydroboration of cyclopropanes using HBl\(^\text{60C}_{\text{6}}\) with isolated yields reported. NR = no reaction. Standard reaction conditions: 0.10 mmol cyclopropane, 0.10 mmol HBl\(^\text{60C}_{\text{6}}\), 2 mL C\(_6\)H\(_6\), 40 °C, 12 h. \(^\text{[32c]}\) 2e was obtained, which didn’t react even after heating at 120 °C for 24 h in m-xylene. \(^\text{[2c]}\) Complex reaction mixture was observed. \(^\text{[2e]}\) Reaction kept at 120 °C for 24 h.

Given the small library of Lewis superacids boranes, we computed FIs of model systems of the hydroboration products. For the alkene and cyclopropane products, a bis[1-methyl-o-carboranyl]borane featuring a methyl group (H\(_2\)CB\(_3\)Me\(_2\)O) was used that gave a value of 524 kJ/mol. To model the alkene hydroboration products, H\(_2\)C=CB\(_3\)Me\(_2\)O was used and calculated to be 517 kJ/mol. Notably, these exceed the FIA of SB\(_3\)F\(_5\) implying that the 17 hydroboration products in this work are LSAs.

We conducted preliminary transformations of the hydroboration products to determine the potential of the B\(^{60}\)C\(_6\) moiety as a functional handle. Treating 2b with iodosobenzene, following an acid hydrolysis, led to corresponding alcohol 3a in 75% yield.\(^\text{[34]}\) The alkene can be preserved in the conversion of alkene hydroboration product 1g to the corresponding iodo-compound 3b by reaction with KO'Bu and I\(_2\), in excellent yield (83%). This exemplifies that B\(^{60}\)C\(_6\) can be transformed to other functional groups under mild conditions.
In conclusion, we prepared bis(1-methyl-ortho-carborane)borane (HBFoOCb) that is a Lewis superacids and features a very polar B–H bond. The secondary borane is an extraordinary hydroboration reagent. Notable reactions disclosed herein include the first hydroboration of a cyclopropane by a secondary borane and selective mono-hydroboration of alkynes. The steric profile is very different from the well-established bis(fluorocarbos)borane and the boron center is much more Lewis acidic. This reagent provides a facile and high yielding means to access a wide library of LSAs by the simple hydroboration reaction. This communication merely scratches the surface of the tremendous potential of this secondary borane and powerful Lewis acid.

Acknowledgements

The authors are grateful to the Welch Foundation (Grant No. AA-1846), the National Science Foundation (Award No. 1753025), and the Australian Research Council (FT16010007, DP20010013) for their generous support of this work. Allocation of computing resources from National Computational Infrastructure (NCI), Intersect, and La Trobe University are acknowledged.

Keywords: Boron • Borane • Lewis Acid • Carborane • Hydroboration


[8] 2b
2) H2O (2 equiv)
KOBu (2 equiv)
Et2O, 23 °C, 1 h

[9] Hydroboration


[11] The authors are grateful to the Welch Foundation (Grant No. AA-1846), the National Science Foundation (Award No. 1753025), and the Australian Research Council (FT16010007, DP20010013) for their generous support of this work. Allocation of computing resources from National Computational Infrastructure (NCI), Intersect, and La Trobe University are acknowledged.

Keywords: Boron • Borane • Lewis Acid • Carborane • Hydroboration


[28] Compound 1j decomposes when heated at 80 °C for 24 h in C6D6.


A Lewis superacidic secondary BH borane, bis(ortho-carboranyl)borane (HBoCb$_2$), is synthesized and its regioselective hydroboration of carbon-carbon bonds is investigated.

Institute and/or researcher Twitter usernames: @MartinGroupBU