

Formation of Strong Boron Lewis Acid Sites on Silica

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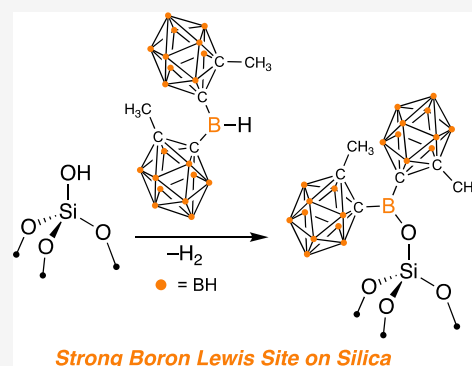


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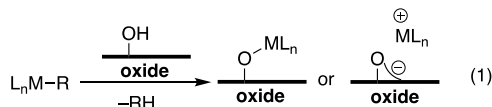
Supporting Information

ABSTRACT: Bis(1-methyl-*ortho*-carboranyl)borane ($\text{HB}^{\text{Me}}\text{oCb}_2$) is a very strong Lewis acid that reacts with the isolated silanols present on silica partially dehydroxylated at 700 °C (SiO_{2-700}) to form the well-defined Lewis site $\text{MeoCb}_2\text{B}-(\text{OSi}\equiv)$ (**1**) and H_2 . $^{11}\text{B}\{^1\text{H}\}$ magic-angle spinning (MAS) nuclear magnetic resonance (NMR) data of **1** are consistent with that of a three-coordinate boron site. Contacting **1** with $\text{O}=\text{PEt}_3$ (triethylphosphine oxide TEPO) and measuring $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectra show that **1** preserves the strong Lewis acidity of $\text{HB}^{\text{Me}}\text{oCb}_2$. Hydride ion affinity and fluoride ion affinity calculations using small molecules analogs of **1** also support the strong Lewis acidity of the boron sites in this material. Reactions of **1** with $\text{Cp}_2\text{Hf}(^{13}\text{CH}_3)_2$ show that the Lewis sites are capable of abstracting methide groups from Hf to form $[\text{Cp}_2\text{Hf}-^{13}\text{CH}_3][\text{H}_3^{13}\text{C}-\text{B}(\text{MeoCb}_2)\text{OSi}\equiv]$, but with a low overall efficiency.



INTRODUCTION

The interface of materials science and organometallic chemistry is a rich landscape for the development and application of well-defined heterogeneous catalysts for a variety of chemical transformations.¹ This field depends on the discrete understanding of surface sites present on a material, typically a high surface area oxide, and how those sites react with an organometallic. Nearly all oxides are terminated with $-\text{OH}$ sites that react with organometallics through protonolysis reactions, shown in eq 1 between a generic organometallic and



surface hydroxyl to generate either $\text{L}_n\text{M}-\text{O}_x$ or $\text{L}_n\text{M}\cdots\text{O}_x$ ion-pairs (O_x = surface oxygen). The type of surface site formed in this reaction usually depends on the acidity of the surface hydroxyl,² which is dependent on the type of oxide used and is often encountered when using less common oxide supports.³

Alumina (Al_2O_3) is a classic example, where the oversimplification shown in eq 1 breaks down. Typical $\gamma\text{-Al}_2\text{O}_3$ materials are also terminated with $-\text{OH}$ groups, but a small quantity of strong Lewis sites persists on these materials.⁴ The Lewis sites play an important role in the formation of catalytically active sites on alumina, Figure 1a. For example, Al_2O_3 dehydrated at 1000 °C reacts with $\text{Cp}^*_2\text{Th}(\text{CH}_3)_2$ (Cp^* = pentamethylcyclopentadienyl) to generate $[\text{Cp}^*_2\text{Th}-\text{CH}_3]-[\text{H}_3\text{C}-\text{AlO}_x]$ formed by methide abstraction by Lewis acidic Al-sites.⁵ Lower dehydroxylation temperatures also preserve this type of reactivity, exemplified by the reaction of Al_2O_3

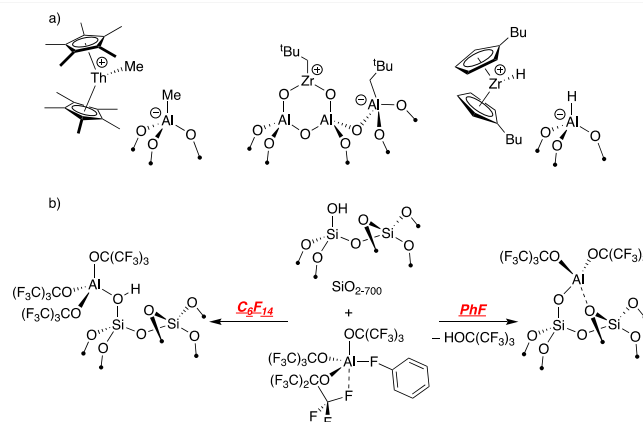


Figure 1. Representative examples of ion pairs formed on Al_2O_3 .

partially dehydroxylated at 500 °C with $\text{Zr}(\text{CH}_2^t\text{Bu})_4$ to form $[\text{Zr}(\text{CH}_2^t\text{Bu})(\text{O}_x)_2][^t\text{BuH}_2\text{C}-\text{AlO}_x]$.⁶ Both results are related to the reactivity of common olefin polymerization compositions containing metallocenes, AlR_3 , and Al_2O_3 that form $[\text{Cp}^b_2\text{Zr}-\text{H}][\text{H}-\text{AlO}_x]$ ion-pairs (Cp^b = 1-butylcyclopentadienyl).⁷

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Each of the examples in Figure 1a rely on the exceedingly low surface coverage of the Lewis site present on dehydrated aluminas.^{4b} Generating strong Lewis sites on oxides using the reaction shown in eq 1 with alkylaluminum^{8,9} or alkylgallium¹⁰ tends to form mixtures of surface species. $\text{Al}(\text{OC}(\text{CF}_3)_3)(\text{PhF})$,¹¹ a very strong Lewis acid, shows solvent-dependent reactivity with silica partially dehydroxylated at 700 °C (SiO_{2-700}) shown in Figure 1b. In perfluorohexane, $\text{Al}(\text{OC}(\text{CF}_3)_3)(\text{PhF})$ reacts with the isolated silanols present on SiO_{2-700} to form Brønsted acidic bridging silanols that behave as weakly coordination anions when deprotonated.¹² In fluorobenzene, $\text{Al}(\text{OC}(\text{CF}_3)_3)(\text{PhF})$ reacts with SiO_{2-700} in the more traditional manner shown in eq 1.¹³ These aluminum sites participate in similar alkyl abstraction reactions as those shown in Figure 1.^{13,14}

Access to oxides containing boron Lewis sites continues to be challenging. Common boric acid impregnation methods followed by heat treatment tend to form networks containing mixtures of 3- or 4-coordinate boron from solid-state NMR studies.^{15,16} Though lacking strong Lewis acidity, many of these materials show interesting reactivity in oxidative dehydrogenation reactions.¹⁷ BCl_3 or BF_3 also react with silica and probably form poorly defined Lewis sites.¹⁸

Reactions of trialkylboranes to generate Lewis sites are limited to the examples shown in Figure 2a. BEt_3 reacts with

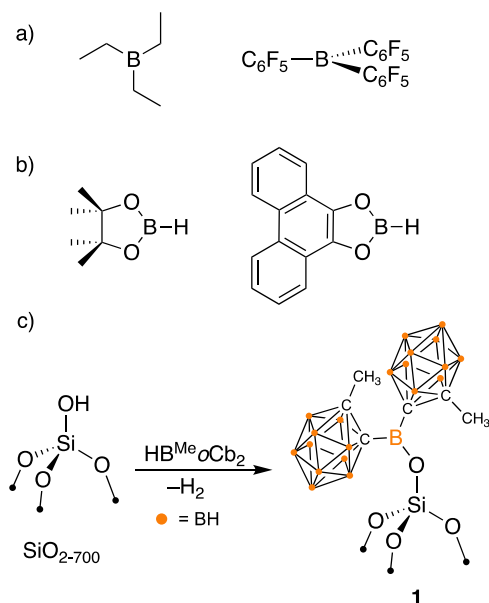


Figure 2. BR_3 (a) or HBR_2 (b) reagents used in silica functionalization reactions. The reaction of bis(1-methyl-*ortho*-carboranyl)borane ($\text{HB}^{\text{Me}}\text{oCb}_2$) with SiO_{2-700} is described in this study (c).

partially dehydroxylated silicas and is claimed to form $\text{Et}_2\text{B}-\text{OSi}\equiv$ from Fourier transform infrared (FTIR) studies.¹⁹ $\text{B}(\text{C}_6\text{F}_5)_3$, a common strong Lewis acid,²⁰ forms adducts with SiO_{2-700} that can be trapped in the presence of *N,N*-dimethylaniline to form supported anilinium sites,^{21,22} but direct protonation by surface silanols to form the Lewis acidic $(\text{C}_6\text{F}_5)_2\text{B}-\text{OSi}\equiv$ and $\text{C}_6\text{F}_5\text{H}$ was not observed. Silica dehydrated at 500 °C (SiO_{2-500}) results in the formation of pairs of Lewis sites that involves the adsorbed water on SiO_{2-500} and forms pairs of $(\text{C}_6\text{F}_5)_2\text{B}-\text{OSi}\equiv$.²³ However, these Lewis sites are not sufficiently acidic to abstract a

methide from $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$. Related species were studied in solution using isolable silsesquioxanes as models for silica surfaces.²⁴

HBR_2 tends to be more reactive toward silica.^{25,26} Pinacolborane reacts with silica to form well-defined pinacolborate species that were studied in detail by solid-state nuclear magnetic resonance (NMR) spectroscopy.²⁷ Phenantro[9,10-*d*][1,3,2]dioxaborole reacts with SiO_{2-700} either by elimination of H_2 or by protonolysis of a $\text{B}-\text{O}$ group to form well-defined surface borates.²⁸ Lewis acidity was not studied in these examples, but $\text{B}(\text{OR})_3$ species, even when containing perfluorinated alkoxy groups, are mild Lewis acids.²⁹

This paper describes the reaction of bis(1-methyl-*ortho*-carboranyl)borane ($\text{HB}^{\text{Me}}\text{oCb}_2$)³⁰ with SiO_{2-700} , Figure 2c. $\text{HB}^{\text{Me}}\text{oCb}_2$ is a Lewis superacid, defined as Lewis acids having higher fluoride ion affinity (FIA) than that of SbF_5 .^{29,31} The *ortho*-carboranyl functionalities attached to the central boron act as strong electron-withdrawing groups and provide a more congested steric environment around the Lewis acidic boron compared to that of $-\text{C}_6\text{F}_5$.³² In addition, the Lewis acidic *p*-orbital on boron is highly localized on the central boron atom,³³ which is in contrast to the more delocalized lowest unoccupied molecular orbital (LUMO) in $\text{B}(\text{C}_6\text{F}_5)_3$. The data described below show that the boron sites formed in reactions with silica that generate **1** are very Lewis acidic. As an entry point to this study, we also describe the reactions that generate $\text{HO}-\text{B}^{\text{Me}}\text{oCb}_2$ (**2**) and $\text{Me}_3\text{Si}-\text{O}-\text{B}^{\text{Me}}\text{oCb}_2$ (**3**), both of which serve as rough molecular analogs of **1**.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere of dinitrogen or argon using standard Schlenk or glovebox techniques. Benzene- d_6 was purchased from Cambridge Isotope Laboratories, dried over sodium/benzophenone, degassed by consecutive freeze–pump–thaw cycles, distilled under a vacuum, and stored in an inert atmosphere glovebox. FTIR spectra were recorded in transmission mode as pressed pellets using a Bruker Alpha IR spectrometer in an argon-filled glovebox. $\text{HB}^{\text{Me}}\text{oCb}_2$ and $\text{BrB}^{\text{Me}}\text{oCb}_2$ were prepared according to literature procedures.³⁰ Multinuclear NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$) were recorded on a Bruker AVANCE III HD 400 or 600 MHz instrument. All solid-state NMR samples were packed in 4 mm zirconia rotors and sealed with a Kel-F cap under an argon or dinitrogen atmosphere in a glovebox. Solid-state NMR spectra were recorded under magic-angle spinning (MAS) or under static conditions at 14.1 T using Bruker NEO600 spectrometer. All solid-state NMR processing used Bruker Topspin. Single-crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using $\text{Mo}-\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2 . Structures were solved and refined using SHELXTL, and figures were produced using OLEX2.

Synthesis of 1. SiO_{2-700} (0.5 g, 0.13 mmol OH) and $\text{HB}^{\text{Me}}\text{oCb}_2$ (0.040 g, 0.13 mmol, 1.0 mol equiv) were transferred to one arm of a double-Schlenk flask inside an argon-filled glovebox. The flask was removed from the glovebox, connected to a high vacuum line, and evacuated for 5 min. Benzene (~6 mL) was condensed onto the solids at 77 K. The mixture warmed to room temperature and stirred for 30 min. During this time, the mixture was stirred gently to promote mixing and prevent the compacted silica from breaking into smaller fragments. After this time, the clear colorless solution was filtered away from **1** to the other side of the double Schlenk. The arm of the double Schlenk containing **1** was cooled to 0 °C, causing the benzene on the other side of the flask to condense onto the solid. The benzene was warmed to 25 °C, stirred for 5 min, and filtered back to the other

side of the double Schlenk. This procedure was repeated two more times to wash any residual $\text{HB}^{\text{Me}}\text{OCb}_2$ away from **1**. The volatiles from the reaction mixture were analyzed by gas chromatography–thermal conductivity detector (GC–TCD) (Figure S1 in the Supporting Information) resulting in 0.23 mmol of H_2/g of SiO_2 . **1** was dried under vacuum for 40 min. The white H-BSO solid was stored in an Ar glovebox freezer at -20°C . Inductively coupled plasma–optical emission spectrometry (ICP–OES) of **1** after digestion in 5% nitric acid solution gives $4.77\text{ mmol}_\text{B}\text{ g}^{-1}$. Cross-polarization MAS carbon NMR ($^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR) data: 25 ($\equiv\text{Si}-\text{O}-\text{B}(\text{MeoCb})_2$), 71, and 78 ppm ($\equiv\text{Si}-\text{O}-\text{B}(\text{MeoCb})_2$). $^{11}\text{B}\{^1\text{H}\}$ MAS NMR data: 33, 2, -6 , -8 , and -11 ppm, respectively.

Synthesis of 1*TEPO. An essentially identical procedure for **1** was used to generate **1*TEPO**. **1** (0.2 g, 0.046 mmol Lewis acidic B), triethylphosphine oxide (TEPO) (0.005 g, 0.9 equiv, 0.041 mmol), and pentane (~ 5 mL) were used in this procedure. **1*TEPO** was collected as a white solid and was stored in an Ar glovebox freezer at -20°C . $^{31}\text{P}\{^1\text{H}\}$ MAS NMR data: 78 ppm (**1*TEPO** and 54 ppm (physisorbed TEPO). $^{11}\text{B}\{^1\text{H}\}$ MAS NMR data: 2, -1.5 ($\equiv\text{Si}-\text{O}-\text{B}(\text{MeoCb})_2(\text{TEPO})$), -6 , -8 , and -11 ppm. This spectrum contains a minor signal at 33 ppm from unreacted **1**.

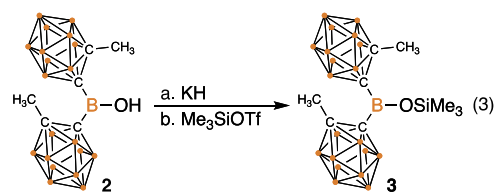
Synthesis of 1*Hf. An essentially identical procedure to that for **1** was used to generate **1*Hf**. **1** (0.100 g, 0.023 mmol Lewis acidic B), $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ (0.009 g, 1.1 equiv, 0.025 mmol), and pentane (~ 5 mL) were used in this procedure. **1*Hf** was collected as a white solid and was stored in an Ar glovebox freezer at -20°C . The volatiles from the reaction mixture were analyzed by GC resulting in 0.07 mmol of CH_4/g of SiO_2 . ICP–OES of **1** after digestion in 5% nitric acid solution gives $0.076\text{ mmol}_\text{Hf}\text{ g}^{-1}$ and $5.03\text{ mmol}_\text{B}\text{ g}^{-1}$. $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR data: 107.2 (Cp), 40.8 ($\text{Hf}-^{13}\text{CH}_3$ cation), 21.4 ($\text{Hf}-^{13}\text{CH}_3$ neutral), and 2.2 ppm ($\text{Si}-^{13}\text{CH}_3$). $^{11}\text{B}\{^1\text{H}\}$ MAS NMR data: 33 ppm ($\equiv\text{Si}-\text{O}-\text{B}(\text{MeoCb})_2$), -1 ppm ($\equiv\text{Si}-\text{O}-\text{B}(\text{CH}_3)(\text{MeoCb})_2$), -6 , -8 , and -11 ppm.

Synthesis of $\text{HO}-\text{B}^{\text{Me}}\text{OCb}_2$ (2). A solution of $\text{BrB}^{\text{Me}}\text{OCb}_2$ (1.60 mmol, 650 mg) in chloroform (10 mL) was stirred in a vial, and neat Me_3SiOH (1.60 mmol, 172.0 μL) was slowly added via micropipette at 23°C . The reaction mixture was monitored by ^1H and ^{11}B NMR spectroscopy, and after 2 h, the reaction was complete. The volatiles were removed under reduced pressure to form a white solid, which was subsequently washed with pentane (2×2 mL). The white residue was dried under vacuum to give $\text{HOB}^{\text{Me}}\text{OCb}_2$ as a white solid. Yield: 85%, 464 mg; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.52$ (s, 1H), 3.21–1.64 (m, 26H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): $\delta = 78.0$, 26.0 ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3): $\delta = 37.9$ (s), 2.6 (s), -5.0 (s), -7.3 (s), -8.4 (s), -9.8 (s), -10.5 (s) ppm; HRMS(–ESI): calcd 361.3895 for $\text{C}_6\text{H}_{26}\text{B}_{21}\text{O}$ [$\text{M} - \text{H}$] $^-$ found 361.3905.

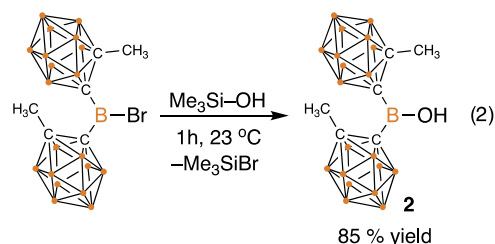
Preparation of $\text{Me}_3\text{SiOB}^{\text{Me}}\text{OCb}_2$ (3). KH (0.150 mmol, 8.0 mg) was added in one portion to a solution of $\text{HOB}^{\text{Me}}\text{OCb}_2$ (0.100 mmol, 34.2 mg) in Et_2O (1 mL). The reaction mixture was then stirred at room temperature (23°C) for 2 h. Excess solid KH was removed by filtration, and the solid was washed with Et_2O (2×2 mL). The filtrate was reduced to ~ 2 mL under vacuum, and trimethylsilyl trifluoromethanesulfonate (0.110 mmol, 20.0 μL) was added dropwise at room temperature (23°C). The reaction was stirred at 23°C for 30 min. After completion of the reaction, the volatiles were removed under vacuum, and the product was extracted using 1 mL cold toluene. The toluene was dried under vacuum to give the desired $\text{Me}_3\text{Si}-\text{O}-\text{B}^{\text{Me}}\text{OCb}_2$ as an unstable viscous liquid. Using this procedure, **3** was isolated in $\sim 95\%$ purity. Yield: 29%, 12.0 mg; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.37$ (s, 1H), 2.75–1.87 (m, 26H), 0.46 (s, 9H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): $\delta = 77.6$, 25.8, 2.3 ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3): $\delta = 32.9$ (s), 1.6 (s), -5.7 (s), -7.4 (s), -8.4 (s), -10.4 (br s) ppm.

RESULTS AND DISCUSSION

Synthesis of $\text{HO}-\text{B}^{\text{Me}}\text{OCb}_2$ (2) and Generation of $\text{Me}_3\text{Si}-\text{O}-\text{B}^{\text{Me}}\text{OCb}_2$ (3). The reaction of $\text{BrB}^{\text{Me}}\text{OCb}_2$ with $\text{Me}_3\text{Si}-\text{OH}$ forms $\text{HO}-\text{B}^{\text{Me}}\text{OCb}_2$ (**2**) in 85% yield, as shown



in eq 2. The $\text{Me}_3\text{Si}-\text{Br}$ byproduct formed was detected in the ^1H NMR spectra of reaction mixtures in CDCl_3 ($\delta = 0.59$ ppm). The ^1H NMR spectrum of analytically pure **2** in CDCl_3 solution contains signals at 2.04 ppm for the $-\text{CH}_3$ on the carborane, and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum contains a characteristic signal at 37.9 ppm for the central boron in **2**, consistent with formation of a tricoordinate boron in **2**.³⁴ The solid-state $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of **2** also contains a broad signal at 35 ppm for the tricoordinate boron.



The solid-state structure of **2** obtained from single-crystal X-ray diffraction data is shown in Figure 3. The sum of the bond

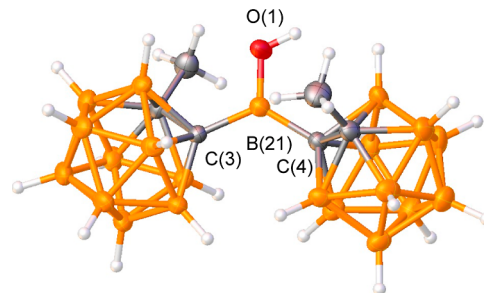


Figure 3. Solid-state structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B(21)–C(3) 1.594(2), B(21)–C(4) 1.601(2), B(21)–O(1) 1.328(1), C(3)–B(21)–C(4) 126.1(1), C(3)–B(21)–O(1) 114.0(1), and C(4)–B(21)–O(1) 119.9(1).

angles around the central boron is 360° , indicating that **3** has a planar structure, which is consistent with the solution $^{11}\text{B}\{^1\text{H}\}$ NMR chemical shift mentioned above.

The reaction in eq 1 suggests that $\text{Me}_3\text{Si}-\text{O}-\text{B}^{\text{Me}}\text{OCb}_2$ (**3**), which is a likely an intermediate in this reaction, is unstable in the presence of HBr. Preliminary results suggest that **3** is also rather unstable under standard silylation conditions. For example, **2** reacts with KH followed by $\text{Me}_3\text{Si}-\text{OTf}$ to form **3** in low yield in 95% purity as a viscous oil, eq 2. Attempts to purify **3** further were unsuccessful and yield **2** as the major product. **3** is sufficiently stable in CDCl_3 solution to record NMR spectra. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3** contains a signal at 32.9 ppm that is consistent with a planar three-coordinate Lewis acidic boron in **3**.

Reaction of $\text{HB}^{\text{Me}}\text{oCb}_2$ with SiO_{2-700} . In benzene solution, $\text{HB}^{\text{Me}}\text{oCb}_2$ reacts with SiO_{2-700} to form $\text{Me}_2\text{oCb}_2\text{B}(\text{OSi}\equiv)$ (**1**) and H_2 (0.23 mmol g^{-1}). ICP–OES of digested **1** gives $4.77 \text{ mmol}_\text{B} \text{ g}^{-1}$ (20.7 B/H_2), which is close to the expected 21:1 ratio from the amount of H_2 evolved in this reaction. Figure 4 shows the FTIR spectra of native SiO_{2-700}

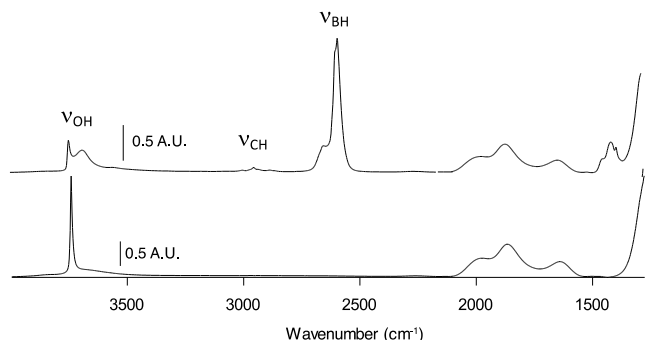


Figure 4. FTIR spectra of SiO_{2-700} (bottom) and **1** (top).

and **1**. The ν_{OH} values for isolated silanols in SiO_{2-700} decrease significantly in **1**, consistent with the reaction in Figure 2c, but unreacted silanols are present. Longer reaction times or an increase in the amount of $\text{HB}^{\text{Me}}\text{oCb}_2$ do not significantly decrease the ν_{OH} band or increase boron loading from ICP–OES measurements. The FTIR spectrum of **1** contains broad ν_{OH} at 3686 cm^{-1} , suggesting some type of hydrogen bonding interaction with residual silanols and the carborane groups. The spectrum for **1** also contains ν_{CH} at 2948 and 2878 cm^{-1} as well as ν_{BH} at 2649 and 2589 cm^{-1} .

The $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of **1** is shown in Figure 5. A broad signal at 33 ppm is assigned to the central

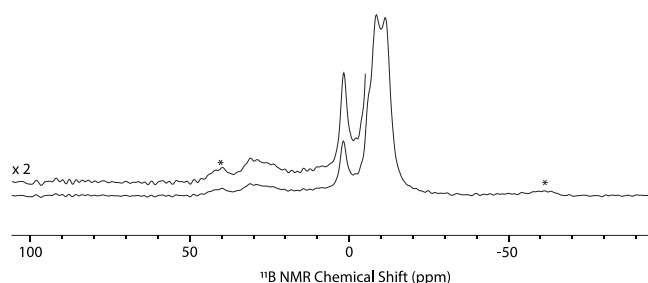
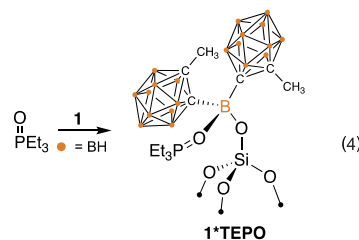


Figure 5. $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectra of **1**. $\nu_{\text{rot}} = 10 \text{ kHz}$; * = spinning sideband.

tricoordinate boron. Formation of tricoordinate boron sites is relatively common in boron-oxide-type materials,¹⁵ and these signals are typically broad due to the larger quadrupolar coupling (C_Q) for tricoordinate boron compared that of to four-coordinate boron.³⁴ Available $^{11}\text{B}\{^1\text{H}\}$ MAS NMR data suggests that supported $\text{B}(\text{C}_6\text{F}_5)_3$ also adopts a tricoordinate structure.^{23,35} This is in contrast to the well-defined aluminum Lewis acid supported on silica mentioned above that forms a distorted tetrahedral aluminum site.¹³ The $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum also contains signals at 2 , -6 , -8 , and -11 ppm for the borons that are part of the carborane dodecahedron. The $^{13}\text{C}\{^1\text{H}\}$ cross-polarization MAS (CPMAS) NMR spectrum of **1** contains the expected three signals at 25 ($-\text{CH}_3$), 71 , and 78 ppm (see the Supporting Information, Figure S13).

Lewis Acidity of **1.** The change in $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of TEPO is used as a diagnostic probe to determine Lewis acidity in solution³⁶ or on solids containing Lewis acid sites.³⁷ Contacting **1** with TEPO (1 equiv/B in **1**) results in the



formation of the phosphine oxide adduct **1*TEPO**, eq 3. The $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of **1*TEPO** contains a new signal at -1.5 ppm assigned to the tetrahedral central boron. Resonances for the boron atoms of the carborane groups appear at positions identical with those in **1**. However, this spectrum also contains minor residual signal intensity for the broad tricoordinate boron signal from **1** at 33 ppm , indicating that some Lewis acidic borons in **1** do not coordinate TEPO. The $^{31}\text{P}\{^1\text{H}\}$ MAS NMR data shown in Figure 6 is consistent

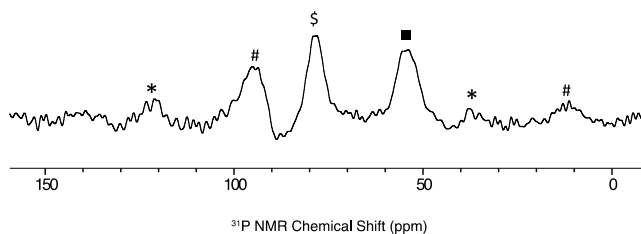


Figure 6. $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectra of **1*TEPO**. $\nu_{\text{rot}} = 10 \text{ kHz}$; \$ = **1*TEPO**; * = spinning sideband for **1*TEPO**; black square = physisorbed TEPO; # = spinning sidebands for physisorbed TEPO.

with this observation, which contains a signal at 78 ($\Delta\delta = 28 \text{ ppm}$) and 54 ppm ($\Delta\delta = 4 \text{ ppm}$), assigned to the adduct and physisorbed TEPO, respectively. Attempts to generate TEPO adducts of **2** or **3** resulted in several $^{31}\text{P}\{^1\text{H}\}$ NMR signals in solution (Figures S9 and S10).

Selected $^{31}\text{P}\{^1\text{H}\}$ NMR data for the TEPO adducts are given in Table 1. The $\Delta\delta$ values obtained for **1*TEPO** are similar to those obtained in solution for TEPO adducts of $\text{HB}^{\text{Me}}\text{oCb}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$, indicating that the accessible boron in **1** is quite Lewis acidic. These values are identical with those obtained

Table 1. Selected $\Delta\delta$ $^{31}\text{P}\{^1\text{H}\}$ NMR Data, FIA, and HIA Data for Lewis Acids in Solution or Supported on Oxides

compound	$\Delta\delta$	FIA kJ mol^{-1}	HIA kJ mol^{-1}	ref
1	28	493 ^a	480 ^a	this work
$\text{HB}^{\text{Me}}\text{oCb}_2$	35.8 (C_6D_6) 30.0 (CDCl_3)	527	540	30
$\text{B}(\text{C}_6\text{F}_5)_3$	26.6 (CD_2Cl_2)	452	484	39
$[\equiv\text{SiOAl}(\text{OR}^f)_2]$	28	528	n.d.	13
$[\text{Et}_3\text{Si}][\text{SZO}]^b$	43	n.d.	n.d.	40

^aCalculated for **4**, the DFT model of **1**. ^bSZO = sulfated zirconium oxide; n.d. = not determined.

from the TEPO adduct of $[\equiv\text{SiOAl}(\text{OR}^{\text{F}})_2(\text{O}(\text{Si}\equiv)_2)]$ but lower than the $\Delta\delta^{31}\text{P}$ for the $[\text{Et}_3\text{Si}][\text{SZO}]$. The latter surface species is a silylium-like ion, which are very strong Lewis acids that generally have large $\Delta\delta^{31}\text{P}$ values.³⁸ In solution, the Gutmann–Beckett method is unreliable for carboranyl boranes, exemplified with $\text{B}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$ being measured as less Lewis acidic than $\text{HB}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$ with ion affinities and other metrics indicating the opposite.³² This is due to the steric effects of the carborane groups.

Two other common scales to assess Lewis acidity involve comparisons of density functional theory (DFT)-calculated fluoride ion affinity (FIA) or hydride ion affinity (HIA) values.^{29,31} Calculating the FIA or HIA of **1** is complicated by the complex amorphous silica surface but can be approximated by using a DFT-generated structure of $(\text{MeO})_3\text{Si}-\text{O}-\text{B}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$ (**4**), which contains a B–O–Si linkage that is similar to **1**. The structure of **4** optimized at the BP86/SVP level of theory is shown in Figure 7. **4** contains a planar central boron, and the bond lengths and angles about the central boron are close to those obtained experimentally from the XRD structure of **2**.

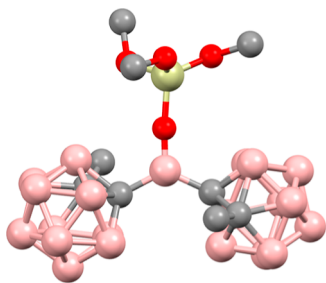


Figure 7. DFT structure of **4**. Selected bond lengths (Å) and angles (deg): B–C 1.629, B–O 1.337, Si–O 1.679, C–B–C 127.5, C–B–O 116.4, 116.1, C–Si–C 117.4, 107.5, 107.6, B–O–Si 174.5.

Values for the calculated FIA and HIA are also given in Table 1. **1** has an FIA of 493 kJ mol^{−1} and HIA of 480 kJ mol^{−1}. Compared to $\text{HB}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$ (FIA = 527 kJ mol^{−1}; HIA of 540 kJ mol^{−1}), **4** is a weaker Lewis acid. By analogy, **1** is also predicted to be a weaker Lewis acid than $\text{HB}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$, which is reflected in the smaller $\Delta\delta$ value obtained using the Guttmann–Beckett method. However, **4** is a stronger Lewis acid than $\text{B}(\text{C}_6\text{F}_5)_3$ in terms of the FIA.

Organometallic Reactivity of 1. Methide or hydride abstraction from an organometallic is a quintessential reaction of strong Lewis acid sites on oxides (Figure 1). To test if **1** is capable of any degree of methide abstraction, we treated the material with $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ (Cp = cyclopentadienyl), an organometallic known to react with well-defined aluminum Lewis acid, as shown in Figure 1b.¹⁴ This reaction results in the formation of CH_4 (0.07 mmol g^{−1}), indicating that $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ reacts with the residual silanols present on **1**. Indeed, FTIR data of **1** contacted with $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ shown in Figure 8a contains a reduced ν_{OH} band for silanols, consistent with their consumption. Also consistent with a surface reaction are the new sp^3 C–H bands in this spectrum. The ν_{BH} band in this material is unperturbed with respect to that of **1**. ICP–OES analysis of the digested material gives 0.076 mmol_{Hf} g^{−1}. This loading is surprisingly close to the amount of CH_4 formed in this reaction, indicating that the major reaction pathway between **1** and $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ involves silanols that do not

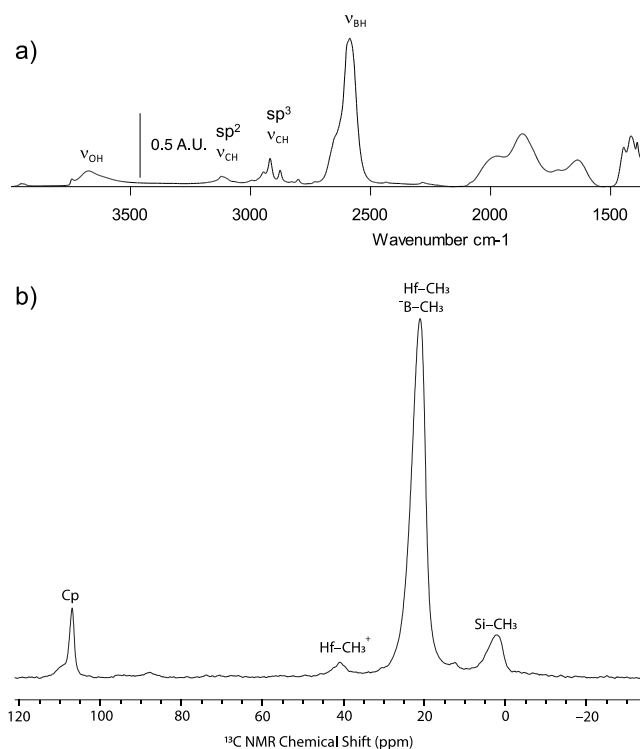
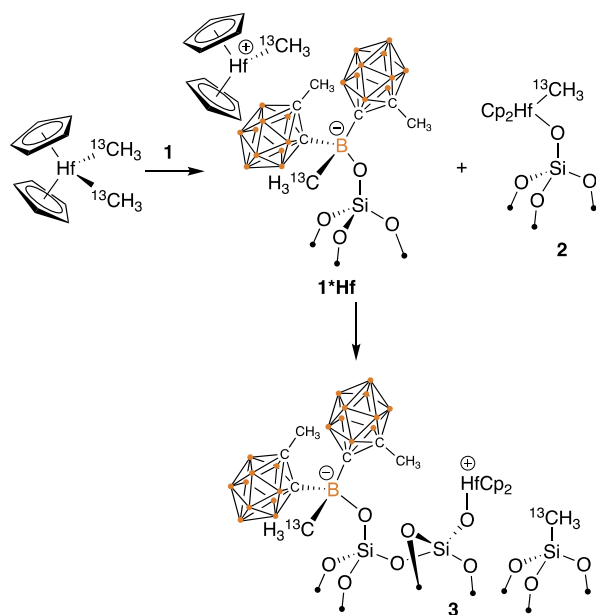


Figure 8. FTIR of $\text{Cp}_2\text{Hf}(\text{CH}_3)_2/\mathbf{1}$ (a). $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR spectrum of $\text{Cp}_2\text{Hf}(\text{CH}_3)_2/\mathbf{1}$. $\nu_{\text{rot}} = 10$ kHz (b).

react with $\text{HB}^{\text{Me}}\text{O}(\text{C}_2\text{H}_5)_2$ on SiO_{2-700} , resulting in the common protonolysis reaction shown in eq 1.

However, the $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR spectrum of **1** contacted with $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ shown in Figure 8b lends some tentative support for ionization by Lewis sites. Unsurprisingly, this spectrum contains an intense signal at 21 ppm for neutral $\text{Hf}-^{13}\text{CH}_3$ and a major Cp signal at 110 ppm. These results are consistent with the formation of $\text{Cp}_2\text{Hf}(\text{CH}_3)(\text{OSi}\equiv)$. This spectrum also contains a minor Cp signal at 113 ppm as well as a signal at 41 ppm for $\text{Hf}-^{13}\text{CH}_3^+$, consistent with the formation of small amounts of $[\text{Cp}_2\text{Hf}-^{13}\text{CH}_3][\text{H}_3^{13}\text{C}-\text{B}(\text{Me}_o\text{C}_2\text{H}_5)_2\text{OSi}\equiv]$. A signal for the $[\text{H}_3^{13}\text{C}-\text{B}(\text{Me}_o\text{C}_2\text{H}_5)_2\text{OSi}\equiv]$ was not observed, which could be due to overlap with the $\text{Hf}-\text{CH}_3$ signal in $\text{Cp}_2\text{Hf}(\text{CH}_3)(\text{OSi}\equiv)$.⁴¹ The signal at 2 ppm is from $\equiv\text{Si}-^{13}\text{CH}_3$ sites. The $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of **1** contacted with $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ contains minor additional signal intensity at −1 ppm (Figure S17). This is the expected region for a tetracoordinate boron, which was clearly observed in **1***TEPO.

The spectral data are consistent with those of the reactions in Scheme 1. $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ preferentially reacts with residual silanols present in **1** to form $\text{Cp}_2\text{Hf}(\text{CH}_3)(\text{OSi}\equiv)$ and methane. $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$ also reacts with the boron Lewis sites in **1** to form $[\text{Cp}_2\text{Hf}-^{13}\text{CH}_3][\text{H}_3^{13}\text{C}-\text{B}(\text{Me}_o\text{C}_2\text{H}_5)_2\text{OSi}\equiv]$. Reactive d⁰ organometallic cations are known to react with silica surfaces by opening of Si–O–Si bridges by transferring alkyl groups and forming $\equiv\text{Si}-^{13}\text{CH}_3$,⁴² which is consistent with the formation of **3**. However, the NMR signal intensities in both the $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR spectrum and the minimal signal intensity in the $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum for the tetrahedral $[\text{H}_3^{13}\text{C}-\text{B}(\text{Me}_o\text{C}_2\text{H}_5)_2\text{OSi}\equiv]$ anion indicate that the methide abstraction reaction in Scheme 1 is clearly a minor reaction pathway.

Scheme 1. Reaction 1 with $\text{Cp}_2\text{Hf}(\text{}^{13}\text{CH}_3)_2$ 

In a qualitative sense, the reactivity in Scheme 1 is remarkably similar to that obtained previously between $\text{Al}(\text{OC}(\text{CF}_3)_3)(\text{PhF})/\text{silica}$ and either $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ or $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$.¹⁴ However, **1** clearly forms less $\text{Hf}-\text{CH}_3^+$ than $\text{Al}(\text{OC}(\text{CF}_3)_3)(\text{PhF})/\text{silica}$. Attempts to quantify the amount of $[\text{Cp}_2\text{Hf}-\text{}^{13}\text{CH}_3][\text{H}_3\text{C}^{13}-\text{B}(\text{}^{\text{Me}}\text{oCb}_2)\text{OSi} \equiv]$ formed on **1** using vinyl chloride as an active site probe by quantification of evolved propylene⁴³ were consistent with very low surface coverage of the ion-pair (~ 0.002 mmol g^{-1} , see the Supporting Information for details). This result suggests that the sterically bulky carborane groups may restrict access to the central boron site in **1**, which results in low $\text{Hf}-\text{CH}_3^+$ surface coverage.

CONCLUSIONS

There are limited examples showing that reactions of boranes and silica (or other oxides) form well-defined products and even fewer examples that form strong Lewis sites. Monomeric $\text{HB}^{\text{Me}}\text{oCb}_2$ is a rare example, where a well-defined three-coordinate boron site forms when contacted with silica and the moderately strong Lewis acidity is preserved. This promising result suggests that other bulky secondary boranes may also react with oxides to form well-defined Lewis acid sites on the oxides. Tuning the steric environment in related boranes should result in a more efficient methide abstraction chemistry. However, this comes with the caveat that Lewis acidic boranes that would produce a more sterically open boron site often engage in monomer–dimer equilibria,⁴⁴ which may affect the products obtained during surface functionalization chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c04121>.

Coordinates of **4** used for DFT calculations (XYZ)

Experimental methods, solid-state NMR spectra, and gas chromatograph traces (PDF)

Accession Codes

CCDC 2330796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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