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Examining the reactivity of tris(*ortho*-carboranyl)borane with Lewis bases and application in frustrated Lewis pair Si–H bond cleavage†

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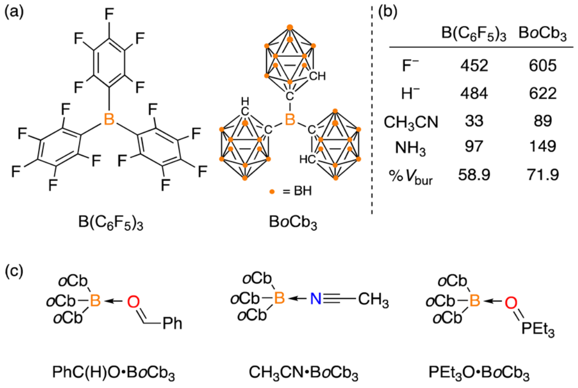
Reactions of tris(*ortho*-carboranyl)borane with Lewis bases reveals only small bases bind. The tremendous bulk and Lewis acidity is leveraged in frustrated Lewis pair Si–H cleavage with a wider range of Lewis bases and greater efficacy than $B(C_6F_5)_3$.

Introduction

Frustrated Lewis pairs (FLPs) arise from the combination of a Lewis acid and Lewis base that, due to steric demands, do not form a classical adduct.[1] The quenched reactivity can be taken advantage of to activate bonds, exemplified in the pioneering reversible metal-free activation of H_2 by Stephan with the arene bridged intramolecular FLP, $Mes_2PC_6F_4B(C_6F_5)_2$ (Mes = 2,4,6-trimethylphenyl).[2] The field has exploded with both inter- and intra-molecular systems being applied to activate a plethora of bonds and in many cases, act as catalysts.[3] While the application of FLPs is widespread, the prevalent Lewis acid reagents in these systems have been dominated by fluoroarylboranes, especially tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$.[3b,4] The compatible Lewis bases require bulk to preclude coordination and accordingly, bulky phosphines and amines have been common Lewis base partners.[5]

A bulkier Lewis acid could open the gateway to a series of smaller Lewis bases that are incompatible for FLP chemistry with fluoroarylboranes and perhaps new substrates for catalysis. Our team recently synthesized a Lewis acid candidate for FLP chemistry that uses an alternative approach to fluorine loading of aryl groups to enhance Lewis acidity, *ortho*-carboranes as large electron withdrawing substituents.[6] Tris(*ortho*-carboranyl)borane ($BoCb_3$) is accessed in one pot from three commercially available chemicals (Fig. 1a).[7] Mono- and bis-carboranylboranes have reported higher Lewis acidity than their aryl analogues but they are not as Lewis acidic as $BoCb_3$.[8,6d,9] A competition experiment reacting an equimolar amount of acetonitrile with $B(C_6F_5)_3$ and $BoCb_3$ indicates preferential binding to $BoCb_3$. Calculated fluoride and hydride affinities, as well as ammonia and acetonitrile binding affinities, exceed the values reported for fluoroarylboranes (Fig. 1b).[7,10] In addition to the greater Lewis acidity, the calculated steric profile of the fluoride adduct of $BoCb_3$ revealed greater bulk at boron than $B(C_6F_5)_3$ with a buried volume of 71.9% compared to 58.9%.[11] With the greater bulk of $BoCb_3$, a wider library of Lewis bases could be compatible for FLP chemistry which is herein investigated. In the disclosure of $BoCb_3$, acetonitrile, triethylphosphine oxide, and benzaldehyde adducts were reported (Fig. 1c).[7]



	$B(C_6F_5)_3$	$BoCb_3$
F^-	452	605
H^-	484	622
CH_3CN	33	89
NH_3	97	149
$\%V_{bur}$	58.9	71.9

Fig. 1 (a) Structures of $B(C_6F_5)_3$ and $BoCb_3$ (*o*Cb = *ortho*-carborane). (b) Calculated properties of $B(C_6F_5)_3$ and $BoCb_3$ [F^- = fluoride ion affinity, H^- = hydride ion affinity, CH_3CN = acetonitrile affinity, and NH_3 = ammonia affinity; all are in kJ mol^{-1}; $\%V_{bur}$ = % buried volume of the corresponding fluoride adducts]. (c) Known $BoCb_3$ adducts.

Results and discussion

To determine whether FLPs are possible with $BoCb_3$ a variety of commercially available Lewis bases were screened

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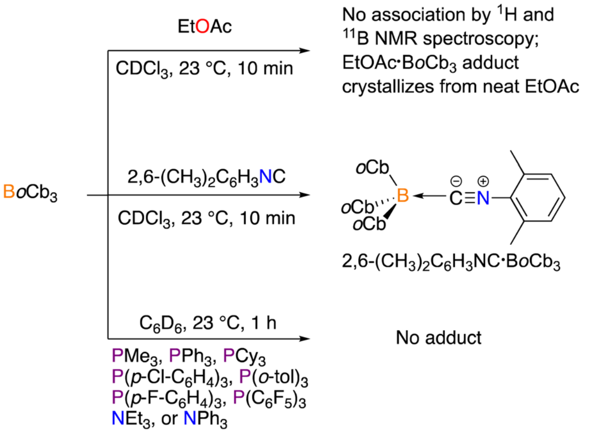


Scheme 1 Reactions of B*o*Cb$_3$ with various Lewis bases.

(Scheme 1). The reaction of B*o*Cb$_3$ with an equivalent of ethylacetate in CDCl$_3$ showed no change by ^{1}H and ^{11}B NMR spectroscopy but the adduct could be crystallized in neat ethylacetate with the structure confirmed by a single crystal X-ray diffraction study (EtOAc·B*o*Cb$_3$, Scheme 1 and Fig. 2). Dissolving the crystals in CDCl$_3$ revealed only free ethylacetate and B*o*Cb$_3$ indicating the adduct is not resilient in CDCl$_3$ solution. Reaction of B*o*Cb$_3$ with 2,6-(CH$_3$)$_2$C$_6$H$_3$NC generated the adduct, 2,6-(CH$_3$)$_2$C$_6$H$_3$NC·B*o*Cb$_3$, as confirmed by a single crystal X-ray diffraction study. In this case, the adduct remains intact in CDCl$_3$ solution as confirmed by ^{1}H NMR spectroscopy with the three *ortho* C–H resonances shifted upfield (5.02 ppm to 4.72 ppm) along with the disappearance of the tricoordinate peak at 66.9 ppm in the ^{11}B NMR spectrum. The corresponding ethylacetate and 2,6-(CH$_3$)$_2$C$_6$H$_3$NC adducts with B(C$_6$F$_5$)$_3$ have been reported and are resilient in solution.[12] Since the Lewis acidity of B*o*Cb$_3$ is higher than B(C$_6$F$_5$)$_3$ but only the ethylacetate adduct of B*o*Cb$_3$ dissociates in solution, the dissociation is presumed to occur from the larger steric profile of B*o*Cb$_3$ *versus* B(C$_6$F$_5$)$_3$. This suggests that B*o*Cb$_3$ should be a good candidate as a Lewis acid for FLP chemistry. The reactions of B*o*Cb$_3$ with an array of phosphines [PMe$_3$, PPh$_3$, PCy$_3$, P(*o*-tol)$_3$, P(*p*-Cl-C$_6$H$_4$)$_3$, P(*p*-F-C$_6$H$_4$)$_3$, and P(C$_6$F$_5$)$_3$] and amine bases (NEt$_3$ and NPh$_3$) in C$_6$D$_6$ did not result in any change in the ^{1}H and ^{31}P{^{1}H} NMR spectra from the respective starting materials, indicating adducts are not formed. It has been established that B(C$_6$F$_5$)$_3$ makes adducts with PMe$_3$, PPh$_3$, NEt$_3$, PCy$_3$, P(*p*-Cl-C$_6$H$_4$)$_3$, and P(*p*-F-C$_6$H$_4$)$_3$ but not with P(*o*-tol)$_3$ or P(C$_6$F$_5$)$_3$.[13] From this, the breadth of Lewis bases for FLP generation with B*o*Cb$_3$ is much greater than B(C$_6$F$_5$)$_3$.

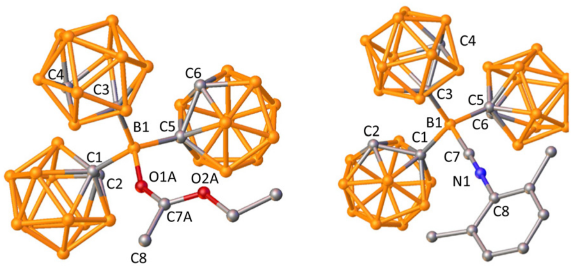


Fig. 2 Solid state structures of EtOAc·B*o*Cb$_3$ (left) and 2,6-(CH$_3$)$_2$C$_6$H$_3$NC·B*o*Cb$_3$ (right). Ellipsoids depicted at the 50% probability level and hydrogen atoms are omitted for clarity. EtOAc·B*o*Cb$_3$ is disordered and only the major occupancy component is shown. Selected bond lengths (Å) and angles (°): EtOAc·B*o*Cb$_3$: B(1)–O(1A) 1.536(3), O(1A)–C(7A) 1.260(2), B(1)–O(1A)–C(7A) 148.7(3); 2,6-(CH$_3$)$_2$C$_6$H$_3$NC·B*o*Cb$_3$: B(1)–C(7) 1.6373(15), C(7)–N(1) 1.1448(14), B(1)–C(7)–N(1) 175.74(11).

To determine if a B*o*Cb$_3$ adduct or FLP could induce Si–H cleavage, we first screened the adducts, CH$_3$CN·B*o*Cb$_3$, PhC(H)O·B*o*Cb$_3$, Et$_3$PO·B*o*Cb$_3$, EtOAc·B*o*Cb$_3$, and 2,6-(CH$_3$)$_2$C$_6$H$_3$NC·B*o*Cb$_3$. None of the adducts showed any sign of reaction with an equivalent of silane at 23 °C in C$_6$H$_6$. Upon screening the phosphine FLP systems, the stoichiometric reactions of B*o*Cb$_3$ and many phosphines (PR$_3$; R = Me, Ph, Cy, *p*-Cl-C$_6$H$_4$) with HSiEt$_3$ led to the ion pairs [R$_3$PSiEt$_3$][HB*o*Cb$_3$] in high yields while reactions with P(*o*-tol)$_3$ and P(*p*-F-C$_6$H$_4$)$_3$ required two equivalents of silane to consume the phosphine and B*o*Cb$_3$ starting materials. The reduced reactivity of P(*o*-tol)$_3$ is rationalized by steric bulk while P(*p*-F-C$_6$H$_4$)$_3$ is from the lower Lewis basicity from the electron withdrawing fluorine. Further corroborating this, the fully fluorinated variant, P(C$_6$F$_5$)$_3$, did not react at all with HSiEt$_3$ in the presence of B*o*Cb$_3$, even with 5 equivalents of silane. The Tolman cone angles for P(*o*-tol)$_3$ and P(C$_6$F$_5$)$_3$ are similar (~184°) which imply the electron withdrawing C$_6$F$_5$ group shuts down the reactivity.[14] Upon examining the amines, the FLP reaction of B*o*Cb$_3$, NEt$_3$, and HSiEt$_3$ formed the [Et$_3$NSiEt$_3$][HB*o*Cb$_3$] ion pair but the reaction with NPh$_3$ did not show any change in the ^{1}H NMR and ^{11}B NMR spectra. The diminished reactivity is rationalized by the weaker Lewis basicity of NPh$_3$. Comparing the reactivity with the same phosphines and B(C$_6$F$_5$)$_3$ reported in the literature, the Ph$_3$P·B(C$_6$F$_5$)$_3$ adduct required 10 equivalents of HSiEt$_3$ to achieve full conversion to the ion pair while (*p*-Cl-C$_6$H$_4$)$_3$P·B(C$_6$F$_5$)$_3$ and (*p*-F-C$_6$H$_4$)$_3$P·B(C$_6$F$_5$)$_3$ resulted in only partial conversion with ten equivalents.[13b] The Cy$_3$P·B(C$_6$F$_5$)$_3$ adduct did not react with HSiEt$_3$.[13b] The results indicate that B*o*Cb$_3$ is compatible with more Lewis bases to induce FLP Si–H cleavage.

In the literature, solution NMR spectroscopy indicates that HSiEt$_3$ interacts with B(C$_6$F$_5$)$_3$ and heating to 60 °C leads to the formation of Piers' borane, HB(C$_6$F$_5$)$_2$.[15] Contrarily, solution NMR spectroscopy does not reveal any interaction of B*o*Cb$_3$ with and heating to 120 °C did not result in any reaction.

In characterizing the ion pairs, in the phosphine reactions (Table 1), the ^{31}P{^{1}H} NMR spectra showed the resonance for the [R$_3$PSiEt$_3$] cation shift downfield from the free phosphine (R = Me −25.9 ppm *cf.* −62.0 ppm, R = Ph −2.9 ppm *cf.* −5.6 ppm, R = Cy 2.6 ppm *cf.* −9.8 ppm, R = *p*-Cl-C$_6$H$_4$ −3.1 ppm *cf.* −8.6 ppm, R = *p*-F-C$_6$H$_4$ −3.7 ppm *cf.* −9.1 ppm, R = *o*-tol 3.4 ppm *cf.* −29.7 ppm).

Table 1 Reactions of BoCb$_3$ and Lewis bases, with HSiEt$_3$

$$\mathrm{B}o\mathrm{Cb_3} + \mathrm{LB} + n\,\mathrm{HSiEt_3} \xrightarrow{\mathrm{C_6H_6},\ 23\ ^\circ\mathrm{C},\ 1\ \mathrm{h}} [\mathrm{LBSiEt_3}][\mathrm{HB}o\mathrm{Cb_3}]$$

LB	*n*	Product	^{31}P{^{1}H} (ppm)	Conversion[a]	Isolated yield
PMe$_3$	1	[Me$_3$PSiEt$_3$][HB*o*Cb$_3$]	−25.9	Quantitative	80%
PPh$_3$	1	[Ph$_3$PSiEt$_3$][HB*o*Cb$_3$]	−2.9	96%	96%
PCy$_3$	1	[Cy$_3$PSiEt$_3$][HB*o*Cb$_3$]	2.6	97%	87%
P(*o*-tol)$_3$	1	[(*o*-tol)$_3$PSiEt$_3$][HB*o*Cb$_3$]	3.4	52%	—
P(*o*-tol)$_3$	2	[(*o*-tol)$_3$PSiEt$_3$][HB*o*Cb$_3$]	3.4	77%	75%
P(*p*-Cl-C$_6$H$_4$)$_3$	1	[(*p*-Cl-C$_6$H$_4$)$_3$PSiEt$_3$][HB*o*Cb$_3$]	−3.1	89%	76%
P(*p*-F-C$_6$H$_4$)$_3$	1	[(*p*-F-C$_6$H$_4$)$_3$PSiEt$_3$][HB*o*Cb$_3$]	−3.7	67%	—
P(*p*-F-C$_6$H$_4$)$_3$	2	[(*p*-F-C$_6$H$_4$)$_3$PSiEt$_3$][HB*o*Cb$_3$]	−3.7	91%	76%
P(C$_6$F$_5$)$_3$	1 or 5	NR	—	0%	—
NEt$_3$	1	[Et$_3$NSiEt$_3$][HB*o*Cb$_3$]	—	Quantitative	81%
NPh$_3$	1 or 5	NR	—	0%	—

NR = no reaction. [a] Conversions determined by quantitative ^{1}H NMR spectroscopy using 0.1 mmol mesitylene as internal standard.

The ^{1}H NMR spectra revealed the hydrogens on the *ortho*-carbon atoms on the carboranes shifted upfield compared to free BoCb$_3$ (range = 4.60–4.48 ppm *cf.* 5.02 ppm).

Single crystal X-ray diffraction structures were obtained for [Me$_3$PSiEt$_3$][HB*o*Cb$_3$] and [Ph$_3$PSiEt$_3$][HB*o*Cb$_3$]. In both structures, the central B–H boron sits on a special position with a C_3-axis of symmetry. The C–B–C angles of the central boron are 114.22(12)° and 115.18(11)°, indicating significant distortion from tetrahedral due to the bulky *ortho*-carborane substituents. The B–C bond lengths from the central boron are 1.712(2) Å and 1.703(2) Å, longer than free BoCb$_3$ [range = 1.614(8)–1.627(7) Å] (Fig. 3).[7] The borohydride species with B(C$_6$F$_5$)$_3$, [HB(C$_6$F$_5$)$_3$], has a shorter B–C bond [1.641(3) Å *cf.* HBoCb$_3$ 1.712(2) Å] and less obtuse C–B–C bond angle [112.09(18)° *vs.* 114.22(12)° and 115.18(12)°] for [HB*o*Cb$_3$].[16] The longer bond and wider angle are rationalized by the larger steric bulk of *ortho*-carborane *versus* pentafluorophenyl.

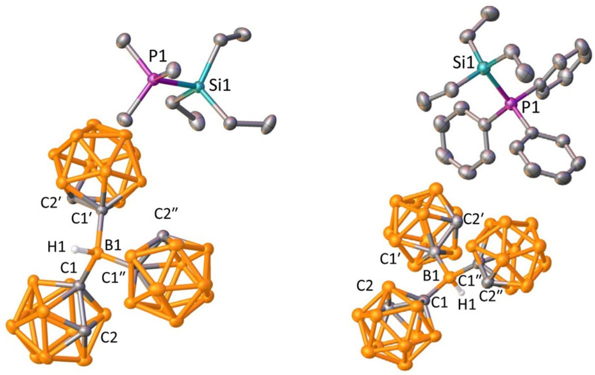
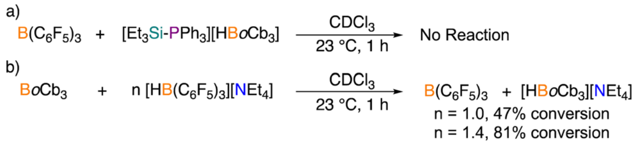


Fig. 3 Solid state structures of [Me$_3$PSiEt$_3$][HBoCb$_3$] (left) and [Ph$_3$PSiEt$_3$][HBoCb$_3$] (right). Ellipsoids depicted at the 50% probability level and hydrogen atoms are omitted for clarity. In the two structures, the cations and anions lie on three-fold symmetry sites and the remaining 2/3 of the ions are generated by symmetry. Selected bond lengths (Å) and angles (°): [Me$_3$PSiEt$_3$][HBoCb$_3$]: B(1)–C(1) 1.712(2), P(1)–Si(1) 2.295(13), C(1)–B(1)–C(1′) 114.22(12); [Ph$_3$PSiEt$_3$][HBoCb$_3$]: B(1)–C(1) 1.703(2), P(1)–Si(1) 2.359(15), C(1)–B(1)–C(1′) 115.18(11).



Scheme 2 Competition reaction between (a) [HBoCb$_3$] and B(C$_6$F$_5$)$_3$; (b) [HB(C$_6$F$_5$)$_3$] and BoCb$_3$.

To determine whether B(C$_6$F$_5$)$_3$ or BoCb$_3$ bind hydride more readily, a solution of [Ph$_3$PSiEt$_3$][HB*o*Cb$_3$] was stirred with an equivalent of B(C$_6$F$_5$)$_3$ at 23 °C for an hour. There was no indication of hydride transfer from BoCb$_3$ to B(C$_6$F$_5$)$_3$ to form [HB(C$_6$F$_5$)$_3$] based on ^{19}F{^{1}H} and ^{1}H NMR spectroscopy (Scheme 2). The equimolar reaction of [NEt$_4$][HB(C$_6$F$_5$)$_3$][17] and BoCb$_3$ in CDCl$_3$ at 23 °C resulted in partial conversion to [HB*o*Cb$_3$] and B(C$_6$F$_5$)$_3$ based on ^{19}F{^{1}H} and ^{1}H NMR spectroscopy. Adding 1.4 equivalents of [NEt$_4$][HB(C$_6$F$_5$)$_3$] resulted in full conversion of BoCb$_3$ to [NEt$_4$][HB*o*Cb$_3$]. This is in line with the higher calculated hydride affinity of BoCb$_3$ (622 kJ mol^{-1} *cf.* 484 kJ mol^{-1}).[7,10]

To investigate the versatility of the BoCb$_3$ FLP system, we attempted CO$_2$ activation. The intermolecular FLP combination of B(C$_6$F$_5$)$_3$ and P^{t}Bu$_3$ reversibly binds CO$_2$ *via* addition across a C═O which is also possible with the ethylene bridged intramolecular FLP Mes$_2$P(CH$_2$)$_2$B(C$_6$F$_5$)$_2$.[18] The exposure of a C$_6$D$_6$ solution of BoCb$_3$ and P^{t}Bu$_3$ or PMe$_3$ solution to an atmosphere of CO$_2$ at 23 °C did not result in any reaction by ^{1}H and ^{11}B NMR spectroscopy. Addition of HSiEt$_3$ to attempt the hydrosilation of CO$_2$ resulted in no reaction at 23 °C or at 80 °C.

Conclusions

This work discloses that BoCb$_3$ is resistant to forming adducts with a wide variety of bases and generates FLPs. The quenched reactivity could be applied to Si–H bond cleavage with triarylphosphines and trialkylphosphines to generate the phosphoniumsilane and tris-(*ortho*-carboranyl)borohydride ion pairs, [R_3PSiEt_3][$HBoCb_3$]. In triarylphosphines the bulk in P(*o*-tol)$_3$ and electron withdrawing nature of P(*p*-F-C_6H_4)$_3$ required an extra equivalent of silane and $P(C_6F_5)_3$ did not react at all. Notably, in prior work by Gagné, many of these did not react at all with $B(C_6F_5)_3$ and those that reacted required ten equivalents of triethylsilane. In regards to amines, NEt_3 was effective but NPh_3 did not induce any reactivity. The C–B–C bond angle in [HB*o*Cb$_3$] is more obtuse than in [$HB(C_6F_5)_3$], consistent with the steric profile. The greater hydride affinity of B*o*Cb$_3$ over $B(C_6F_5)_3$ was experimentally validated by competition studies with the respective hydride salts. These studies clearly indicate that BoCb$_3$ is bulkier and has a higher hydride affinity than $B(C_6F_5)_3$, that bodes well for FLP reactivity beyond Si–H cleavage.

Experimental section

General considerations

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Unilab glove box or using standard Schlenk techniques. Deuterated solvents $CDCl_3$ and C_6D_6 for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc., dried by stirring for 5 days over CaH_2, distilled, and stored over 3 Å molecular sieves. Deuterated dichloromethane CD_2Cl_2 was purchased from Cambridge Isotope Laboratories, Inc. and used as received. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 3 or 4 Å molecular sieves. Tris(*ortho*-carboranyl) borane and [NEt_4][$HB(C_6F_5)_3$] were prepared by the literature procedure.[7,17] The following reagents: *ortho*-carborane, *n*BuLi, 2,6-dimethylphenyl isocyanide, triphenylphosphine, tricyclohexylphosphine, trimethylphosphine, tris(*o*-tolyl)phosphine, tris(4-chlorophenyl)phosphine, tris(4-fluorophenyl)phosphine, tris(pentafluorophenyl)phosphine, triphenylamine, tris(pentafluorophenyl)borane, tetraethylammonium bromide, and triethylsilane were purchased from commercial sources and used without further purification. Ethyl acetate was kept over molecular sieves overnight and distilled. Triethylamine was dried over CaH_2 and distilled before use. Multinuclear NMR spectra (^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, ^{11}B, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$) were recorded on a Bruker Avance III HD 400 MHz or 600 MHz instrument. High resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Orbitrap Q-Exactive spectrometer using +ESI and −ESI. Melting points (m.p.) or decomposition points (d.p.) were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation (λ = 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[19] and figures produced using OLEX2.[20]

Crystallization of EtOAc·B*o*Cb$_3$

Single crystals of EtOAc·B*o*Cb$_3$ for X-ray diffraction studies were grown from an EtOAc (5 mL) solution of B*o*Cb$_3$ (0.20 mmol, 88.5 mg) by vapor diffusion into toluene (10 mL) at 23 °C. From the crystallization vial, excess ethyl acetate was removed *via* pipette and the solids were further dried under vacuum to collect the NMR spectroscopic data. Dissolving the crystals of EtOAc·B*o*Cb$_3$ in $CDCl_3$ and acquiring a ^1H NMR spectrum did not show a resilient adduct. Titration studies are shown in the spectra section (Fig. S1 and S2†).

Preparation of 2,6-(CH$_3$)$_2$C$_6$H$_3$NC·B*o*Cb$_3$

A chloroform solution of 2,6-dimethylphenyl isocyanide (0.21 mmol, 27.9 mg, 5 mL) was added to a chloroform solution of B*o*Cb$_3$ (0.20 mmol, 88.5 mg, 5 mL) at 23 °C. The reaction mixture was stirred for 5 min. The volatiles removed *in vacuo* and the product crystallized from chloroform/*n*-pentane (3 : 7 ratio, 10 mL) to give pure 2,6-(CH_3)$_2$$C_6H_3$NC·B*o*Cb$_3$ as white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a saturated dichloromethane solution of 2,6-(CH_3)$_2$$C_6H_3$NC·B*o*Cb$_3$ into toluene. Yield: 94%, 107.3 mg; dp: 252 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 3H), 3.12–1.75 (m, 36H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 139.4, 134.0, 130.2, 121.9, 64.0, 20.8 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 2.0 (s), −3.5 (s), −5.1 to −18.0 (m) ppm; ^{11}B NMR: δ = 1.9 (d, *J* = 122.9 Hz), −3.5 (d, *J* = 138.2 Hz), −5.1 to −19.9 (m) ppm; FT-IR (ranked intensity, cm^{-1}): 3141 (7), 2646 (8), 2591 (1), 2563 (10), 2544 (9), 1475 (12), 1131 (11), 1076 (6), 1034 (3), 987 (13), 880 (5), 775 (2), 746 (14), 726 (4), 658(15); HRMS (±ESI): a peak corresponding to the adduct was not observed.

General reactions with phosphine and amine Lewis bases (PMe_3, PPh_3, PCy_3, P(*p*-Cl-C_6H_4)$_3$, P(*o*-tol)$_3$, P(*p*-F-C_6H_4)$_3$, NEt_3, or NPh_3)

The Lewis base (0.02 mmol; in 0.2 mL C_6D_6) was added to a solution of B*o*Cb$_3$ (0.02 mmol, 8.8 mg) in C_6D_6 (0.7 mL) at 23 °C and stirred for 1 h. Analyzing the sample by ^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy did not show any shift from the starting materials.

General procedure for the synthesis of [LB-SiEt$_3$][HB*o*Cb$_3$] (LB = Lewis base) ion pairs

A benzene solution of the Lewis base (2 mL) was added to a benzene solution of B*o*Cb$_3$ (2 mL) followed by the addition of $HSiEt_3$ at 23 °C. The reaction mixture was stirred for 1 h. The precipitate was collected by filtration, washed with benzene (3 × 1 mL), and dried *in vacuo* to give the product as a white solid. Amounts and characterization details for each species are listed as well as any deviations from the general procedure.

[Me$_3$PSiEt$_3$][HB*o*Cb$_3$]

PMe$_3$: 0.045 mmol, 4.6 μL; B*o*Cb$_3$: 0.045 mmol, 19.9 mg; HSiEt$_3$: 0.045 mmol, 7.1 μL. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of [Me$_3$PSiEt$_3$][HB*o*Cb$_3$] by vapor diffusion into hexanes. Yield: 80%, 22.8 mg; dp: 156 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.61 (s, 3H), 2.80–1.47 (m, 39H), 1.21 (t, *J* = 8.0 Hz, 9H), 1.13 (q, *J* = 6.7 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 65.0, 8.9 (d, *J* = 37.4 Hz), 7.4, 2.0 (d, *J* = 11.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ = −1.4 (s), −4.1 (s), −5.8 to −16.6 (m) ppm; ^{11}B NMR: δ = −1.4 (d, *J* = 133.1 Hz), −4.1 (d, *J* = 149.8 Hz), −5.8 to −16.5 (m) ppm; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = −25.9 ppm; HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5771.

[Ph$_3$PSiEt$_3$][HB*o*Cb$_3$]

PPh$_3$: 0.24 mmol, 63.7 mg, in 5 mL benzene; B*o*Cb$_3$: 0.24 mmol, 106.9 mg, in 5 mL benzene; HSiEt$_3$: 0.24 mmol, 38.8 μL. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of [Ph$_3$PSiEt$_3$][HB*o*Cb$_3$] by vapor diffusion into toluene. Yield: 96%, 190.1 mg; dp: 168 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.89–7.81 (broad, m, 3H), 7.78–7.68 (m, 6H), 7.46–7.41 (m, 6H), 4.60 (s, 3H), 2.81–1.68 (m, 30H), 1.26–1.17 (m, 6H), 1.07 (t, *J* = 8.0 Hz, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 135.1 (d, *J* = 2.0 Hz), 133.5 (d, *J* = 10.1 Hz), 131.2 (d, *J* = 12.1 Hz), 65.0, 7.7 (d, *J* = 4.0 Hz), 4.8 (d, *J* = 10.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ = −1.5 (s), −4.1 (s), −5.6 to −15.7 (m) ppm; ^{11}B NMR: δ = −1.5 (d, *J* = 126.7 Hz), −4.1 (d, *J* = 134.4 Hz), −5.9 to −16.8 (m) ppm; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = −2.9 ppm; FT-IR (ranked intensity, cm^{-1}): 3131 (14), 2552 (3), 1730 (7), 1602 (10), 1439 (5), 1331 (15), 1235 (8), 1161 (12), 1112 (13), 1072 (2), 1034 (11), 885 (6), 724 (1), 682 (9), 493 (4). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5773.

[Cy$_3$PSiEt$_3$][HB*o*Cb$_3$]

PCy$_3$: 0.10 mmol, 56.1 mg; B*o*Cb$_3$: 0.10 mmol, 44.0 mg; HSiEt$_3$: 0.105 mmol, 16.7 μL. Yield: 87%, 83.6 mg; dp: 184 °C; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 4.63 (s, 3H), 2.84–1.05 (m, 78H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ = 65.3, 32.2 (d, *J* = 25.3 Hz), 29.1 (d, *J* = 3.0 Hz), 27.3 (d, *J* = 11.1 Hz), 25.7 (d, *J* = 1.0 Hz), 8.2 (d, *J* = 3.0 Hz), 6.0 (d, *J* = 8.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CD$_2$Cl$_2$): δ = −1.6 (s), −4.1 (s), −5.2 to −15.4 (m) ppm; ^{11}B NMR: δ = −1.6 (d, *J* = 140.8 Hz), −4.1 (d, *J* = 143.4 Hz), −6.2 to −16.8 (m) ppm; ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ = 2.6 ppm; FT-IR (ranked intensity, cm^{-1}): 3135 (11), 2936 (6), 2858 (14), 2550(1), 1448 (5), 1176 (13), 1119 (7), 1071 (8), 1032 (4), 890 (12), 728 (3), 710 (15), 685 (2), 519 (9), 446 (10). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5770.

[(*p*-Cl-C$_6$H$_4$)$_3$PSiEt$_3$][HB*o*Cb$_3$]

P(*p*-Cl-C$_6$H$_4$)$_3$: 0.05 mmol, 18.3 mg; B*o*Cb$_3$: 0.05 mmol, 22.0 mg; HSiEt$_3$: 0.053 mmol, 8.5 μL. Yield: 76%, 35.0 mg; d.p: 148 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.62 (d, *J* = 8.0 Hz, 6H), 7.24–7.08 (m, 6H), 4.48 (s, 3H), 2.74–1.38 (m, 30H), 1.11–0.90 (m, 15H), ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 143.0 (d, *J* = 4.0 Hz), 134.4 (d, *J* = 12.1 Hz), 132.0 (d, *J* = 13.1 Hz), 116.5 (d, *J* = 62.6 Hz), 64.9, 7.8 (d, *J* = 4.0 Hz), 4.9 (d, *J* = 10.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ = −1.6 (s), −4.1 (s), −5.4 to −18.4 (m) ppm; ^{11}B NMR: δ = −1.6 (d, *J* = 133.1 Hz), −4.1 (d, *J* = 133.1 Hz), −5.8 to −18.7 (m) ppm; ^{31}P{^{1}H} (162 MHz, CDCl$_3$): δ = −3.1 ppm; FT-IR (ranked intensity, cm^{-1}): 2558 (4), 1577 (7), 1481 (10), 1392 (8), 1118 (15), 1089 (1), 1013 (11), 890 (9), 815 (3), 757 (13), 727 (2), 682 (14), 576 (6), 530 (12), 491 (5). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5767.

[(*o*-tol)$_3$PSiEt$_3$][HB*o*Cb$_3$]

P(*o*-tol)$_3$: 0.05 mmol, 15.2 mg; B*o*Cb$_3$: 0.05 mmol, 22.0 mg; HSiEt$_3$: 0.105 mmol, 16.8 μL. Washing with *n*-pentane (2 × 2 mL) and drying the solid *in vacuo* afforded the product as a white powder. Yield: 75%, 32.2 mg; d.p: 158 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.74 (t, *J* = 8.0 Hz, 3H), 7.58 (t, *J* = 6.0 Hz, 3H), 7.44 (t, *J* = 8.0 Hz, 3H), 7.03 (q, *J* = 8.0 Hz, 3H), 4.60 (s, 3H), 2.87–1.68 (m, 39H), 1.20–1.10 (m, 15H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 142.6 (d, *J* = 10.1 Hz), 135.0 (d, *J* = 11.1 Hz), 134.9 (d, *J* = 3.0 Hz), 133.7 (d, *J* = 10.1 Hz), 128.6 (d, *J* = 12.1 Hz), 117.5 (d, *J* = 58.6 Hz), 65.0, 23.7 (d, *J* = 6.1 Hz), 8.4 (d, *J* = 5.1 Hz), 5.8 (d, *J* = 10.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ = −1.6 (s), −4.2 (s), −5.8 to −16.4 (m) ppm; ^{11}B NMR: δ = −1.6 (d, *J* = 143.4 Hz), −4.0 (d, *J* = 135.7 Hz), −5.8 to −16.3 (m) ppm; ^{31}P{^{1}H} (162 MHz, CDCl$_3$): δ = 3.4 ppm; FT-IR (ranked intensity, cm^{-1}): 3136 (12), 2954 (13), 2559 (1), 1592 (14), 1453 (7), 1286 (15), 1118 (9), 1070 (3), 1032 (10), 904 (6), 804 (11), 749 (2), 558 (5), 501 (8), 461 (4). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5766.

[(*p*-F-C$_6$H$_4$)$_3$PSiEt$_3$][HB*o*Cb$_3$]

P(*p*-F-C$_6$H$_4$)$_3$: 0.05 mmol, 15.8 mg; B*o*Cb$_3$: 0.05 mmol, 22.0 mg; HSiEt$_3$: 0.105 mmol, 16.8 μL. The solid was washed with *n*-pentane (2 × 2 mL). The volatiles were evaporated *in vacuo* to provide the product as a white powder. Yield: 76%, 33.0 mg; d.p: 176 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.48–7.40 (m, 12H), 4.58 (s, 3H), 2.74–1.57 (m, 30H), 1.20 (q, *J* = 6.7 Hz, 6H), 1.10 (t, *J* = 6.0 Hz, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 135.9 (dd, *J* = 9.1 Hz, 12.1 Hz), 119.5 (dd, *J* = 13.1 Hz, 22.2 Hz), 65.0, 7.8 (d, *J* = 5.1 Hz), 4.9 (d, *J* = 10.1 Hz) ppm; ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ = −1.5 (s), −4.1 (s), −5.8 to −16.1 (m) ppm; ^{11}B NMR: δ = −1.5 (d, *J* = 133.1 Hz), −4.1 (d, *J* = 139.5 Hz), −5.8 to −16.8 (m) ppm; ^{31}P{^{1}H} (162 MHz, CDCl$_3$): δ = −3.7 ppm; ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$): δ = −98.1 ppm; FT-IR (ranked intensity, cm^{-1}): 2562 (6), 1591 (8), 1499 (9), 1402 (13), 1250 (4), 1163 (10), 1118 (7), 1070 (11), 911 (12), 829 (2), 727 (5), 691 (15), 516 (1), 459 (14), 438 (3). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5767.

[Et$_3$NSiEt$_3$][HB*o*Cb$_3$]

NEt$_3$: 0.10 mmol, 13.9 μL; B*o*Cb$_3$: 0.10 mmol, 44.0 mg; HSiEt$_3$: 0.105 mmol, 16.7 μL. The solids were washed with *n*-pentane (4 × 2 mL) to afford the product as white powder. Yield: 81%, 53.2 mg; d.p: 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.61 (s, 3H), 3.23 (q, J = 8 Hz, 6H), 2.74–1.73 (m, 30H), 1.45 (t, J = 8 Hz, 9H), 1.27–1.18 (m, 15H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 65.0, 51.3, 9.7, 7.7, 5.4 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = −1.4 (s), −4.1 (s), −5.8 to −16.3 (m) ppm; ^{11}B NMR: δ = −1. 5 (d, J = 137.0 Hz), −4.1 (d, J = 138.2 Hz), −5.8 to −16.5 (m) ppm; FT-IR (ranked intensity, cm^{-1}): 3183 (11), 3136 (8), 2556 (1), 1458 (9), 1393 (6), 1262 (13), 1115 (4), 1070 (5), 1029 (2), 889 (12), 798 (7), 725 (3), 653 (14), 514 (10), 455 (15). HRMS (−ESI): calculated for $[C_6B_{31}H_{34}]^-$ $[M]^-$ 441.5758; found 441.5766; (+ESI): calculated for $[C_{12}H_{30}NSi]^+$ $[M]^+$ 216.2142; found 216.2136.

Conflicts of interest

There are no conflicts to declare.

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