Lewis Acidic Behavior of $B(C_6Cl_5)_3$

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Supplementary Information

General Considerations. Commercially available chemicals were purchased and used as provided (Commercial sources: Aldrich for $Me_3SiF_2S(NMe_2)_3$ (TASF), *n*Bu_4NF, *n*Bu_4NCN, *n*Bu_4NN_3, BCl_3 in *n*-heptane, DMAP; *n*Bu_4NBr, *n*Bu_4NI, Ph_4PCl; Alpha Aesar for *n*-butyllithium (2.6 M in hexanes)). $B(C_6Cl_5)_3$ was prepared by reaction of pentachlorophenyl lithium with BCl_3 as reported by O'Hare (A. E. Ashley; T. J. Herrington; G. G. Wildgoose; H. Zaher; A. L. Thompson; N. H. Rees; T. Krämer; D. O'Hare, *J. Am. Chem. Soc.*, 2011, **133**, 14727-14740). Diethyl ether and THF were dried over Na/K and freshly distilled prior to use. Dichloromethane and pentane were dried over alumina using a pressure driven solvent purification system. Air-sensitive compounds were handled under N_2 atmosphere using standard Schlenk and glovebox techniques. UV-vis spectra were recorded on an Ocean Optics USB4000 spectrometer with an Ocean Optics ISS light source. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for ^1H, 376.03 MHz for ^{19}F, 128.19 MHz for ^{11}B, 100.45 MHz

for ^{13}C) spectrometers at ambient temperature. Chemical shifts δ are given in ppm and are referenced against external $BF_3 \cdot Et_2O$ (^{11}B and ^{19}F) or $SiMe_4$ (^{1}H and ^{13}C).

Crystallography. The crystallographic measurements were performed using a Bruker APEX-II CCD area detector diffractometer (Mo-K_α radiation, λ = 0.71069 Å) for $[S(NMe_2)_3][FB(C_6Cl_5)_3]$ and DMAP-$B(C_6Cl_5)_3$. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of $[S(NMe_2)_3][FB(C_6Cl_5)_3]$. TASF (11 mg, 0.040 mmol) was added to a solution of $B(C_6Cl_5)_3$ (30 mg, 0.040 mmol) in THF (5 mL) at room temperature. The mixture was stirred for ten minutes. The solvent was removed under vacuum to yield a solid which was washed with diethyl ether to afford $[S(NMe_2)_3][FB(C_6Cl_5)_3]$ as a pale product (35 mg, yield 84%). Single crystals were obtained by slow diffusion of pentane into a THF solution of $[S(NMe_2)_3][FB(C_6Cl_5)_3]$ at -25ºC. ^{1}H NMR (399.59MHz, $CDCl_3$): δ 2.96 (N-CH_3). ^{13}C NMR (100.45 MHz, $CDCl_3$): δ 38.65 (N-CH_3), 129.03, (s, ortho-C_6Cl_5), 130.23, 130.66, 136.89, 137.49 (C_{ipso} not detected). ^{11}B NMR (128.19 MHz, $CDCl_3$): 6.8 (broad signal). ^{19}F NMR (376.03 MHz, $CDCl_3$) -168 (broad). Anal. Calcd for $C_{24}H_{18}BFCl_{15}S$-1/2THF: C 31.93; H 2.27. Found: C 31.99; H 2.38. (The sample used for EA was obtained by recrystallization from THF. As shown

by X-ray diffraction, these crystals contain one THF molecule per molecule of the fluoroborate. The EA results indicate partial loss of the interstitial THF).

Synthesis of DMAP-B(C_6Cl_5)$_3$. DMAP (5 mg, 0.041 mmol) was added to a solution of B(C_6Cl_5)$_3$ (30 mg, 0.040 mmol) in THF (5 mL) at room temperature. The mixture was stirred for ten minutes. The solvent was removed under vacuum to yield a solid which was washed with diethyl ether to afford B(C_6Cl_5)$_3$-DMAP as a pale product (28 mg, yield 79%). Single crystals were obtained by slow diffusion of pentane into a THF solution of DMAP-B(C_6Cl_5)$_3$ at -25ºC. ^{1}H NMR (399.59 MHz, THF-d_8): δ 3.17 (s, 6H, N-CH_3), 6.85 (d, 2H, *meta*-CH, J = 7.6 Hz), 7.87 (broad signal, 2H, *ortho*-CH). ^{13}C NMR (100.45 MHz, THF-d_8): δ 39.61 (N-CH_3), 107.57 (s, *meta*-NC_5H_4), 129.77, 130.45, 131.53 (s, *ortho*-NC_5H_4), 137.97, 139.14, 157.90 (s, *para*-NC_5H_4). ^{11}B NMR (128.19 MHz, THF-d_8): 2.0 (s). Anal. Calcd. for $C_{25}H_{10}BCl_{15}N_2$-1/3THF: C 34.95; H 1.41. Found: C 34.18; H 1.63. (The sample used for EA was obtained by recrystallization from THF. As shown by X-ray diffraction, these crystals contain 3 THF molecule per molecule of DMAP-B(C_6Cl_5)$_3$. The EA results indicate partial loss of the interstitial THF).

UV-vis titration experiments in CH_2Cl_2. To determine the binding constant of B(C_6Cl_5)$_3$ with various Lewis bases (denoted as X), a CH_2Cl_2 solution of B(C_6Cl_5)$_3$ (3 ml, c = 4.84 × 10^{-5} M for X = F^-, c = 5.80 × 10^{-5} M for X = N_3^-, c = 6.80 × 10^{-5} M for X = CN^-, c = 3.48 × 10^{-5} M for X = Cl^-, c = 6.84 × 10^{-5} M for X = DMAP) inside a UV-cuvette was titrated with incremental amounts of the Lewis base dissolved in CH_2Cl_2

(nBu$_4$NF for X = F$^-$ (4.7 mM), nBu$_4$NN$_3$ for X = N$_3^-$ (30 mM), nBu$_4$NCN for X = CN$^-$ (8.5 mM), Ph$_4$PCl for X = Cl$^-$ (89 mM), or DMAP (26 mM)). All experiments were carried out with dry solvent in an open atmosphere. The absorbance of B(C$_6$Cl$_5$)$_3$ was monitored at λ = 331 nm. The binding constants were calculated by fitting the experimental data to a 1:1 binding isotherm. No changes was observed when 5 equivalents of Br$^-$ or I$^-$ where added to a CH$_2$Cl$_2$ solution of B(C$_6$Cl$_5$)$_3$ (3 ml, c = 4.56 × 10^{-5} M for X = Br$^-$, and c = 4.53 × 10^{-5} M for X = I$^-$) indicating the absence of any significant interaction.

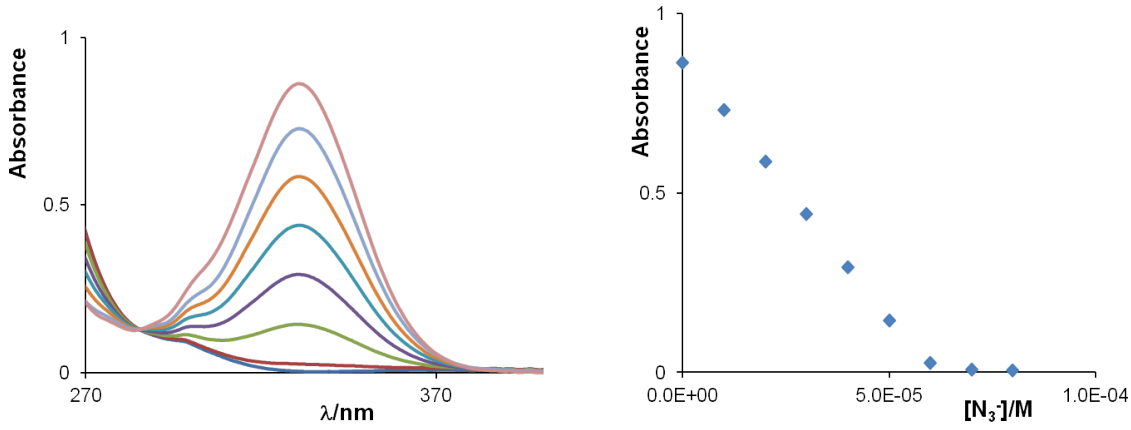


Figure S1. Absorbance changes upon addition of TBAN$_3$ in CH$_2$Cl$_2$ to a CH$_2$Cl$_2$ solution of B(C$_6$Cl$_5$)$_3$ (left) and binding isotherm monitored at λ = 331 nm (right).

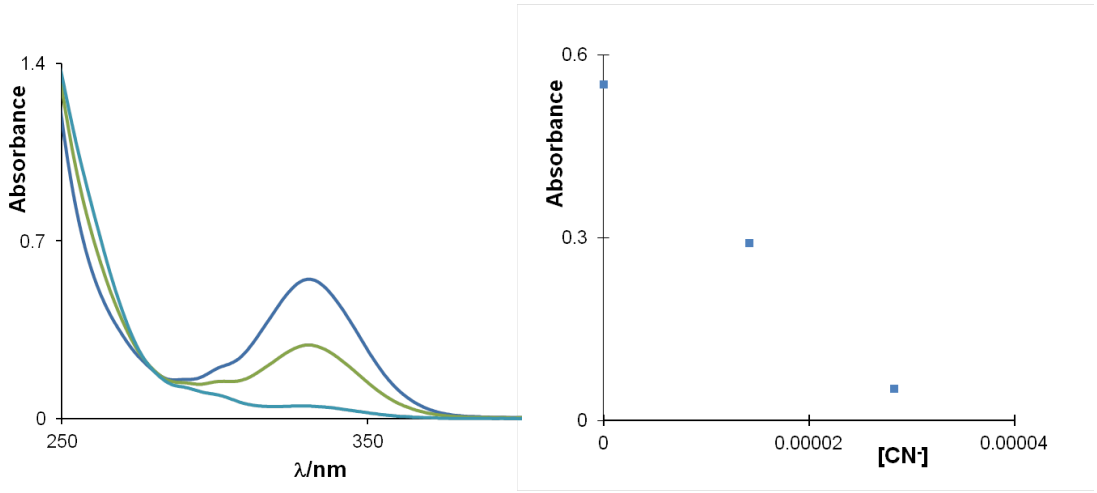


Figure S2. Absorbance changes upon addition of TBACN in CH_2Cl_2 to a CH_2Cl_2 solution of $B(C_6Cl_5)_3$ (left) and binding isotherm monitored at $\lambda = 331$ nm (right). When 0.91 equiv. CN^- was added, the quenching of absorbance is ca. 90.4%, indicating the CN^- binding is quantitative.

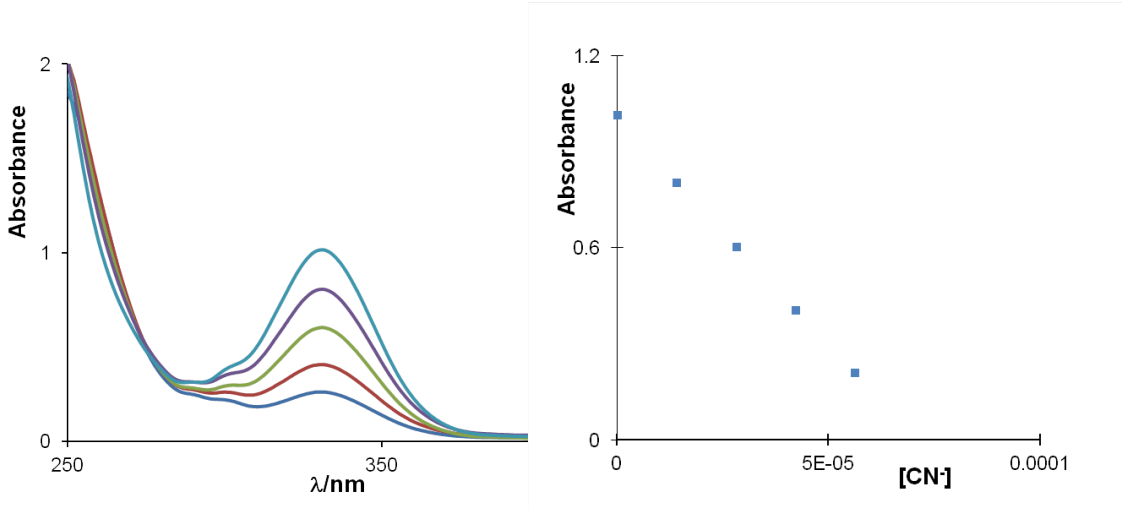


Figure S3. Absorbance changes upon addition of TBACN in CH_2Cl_2 to a CH_2Cl_2 solution of $B(C_6Cl_5)_3$ (left) and binding isotherm monitored at $\lambda = 331$ nm (right). The binding process is slow such that the titration could not be completed.

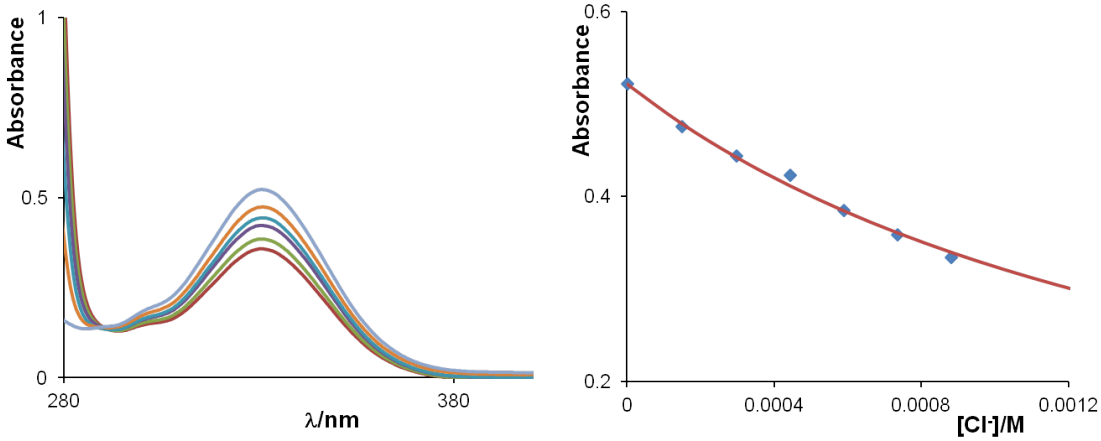


Figure S3. Absorbance changes upon addition of PPh_4PCl in CH_2Cl_2 to a CH_2Cl_2 solution of $B(C_6Cl_5)_3$ (left) and binding isotherm monitored at $\lambda = 331$ nm. The data could be satisfactorily modeled with $K = 600$ (±50) M^{-1} ($\varepsilon = 15000$ for $B(C_6Cl_5)_3$, $\varepsilon = 0$ for $[ClB(C_6Cl_5)_3]^-$) (right).

UV-vis titration experiments in THF. To determine the binding constant of $B(C_6Cl_5)_3$ with DMAP and pyridine, a THF solution of $B(C_6Cl_5)_3$ (3 ml, $c = 5.40 \times 10^{-5}$ M for DMAP and 7.00×10^{-5} M for pyridine) was placed inside a UV-cuvette and titrated with incremental amounts of the Lewis base dissolved in THF (9.9 mM for

DMAP, and 12.36 M for pyridine). The absorbance of $B(C_6Cl_5)_3$ was monitored at λ = 331 nm. The binding constants were calculated by fitting the experimental data to a 1:1 binding isotherm.

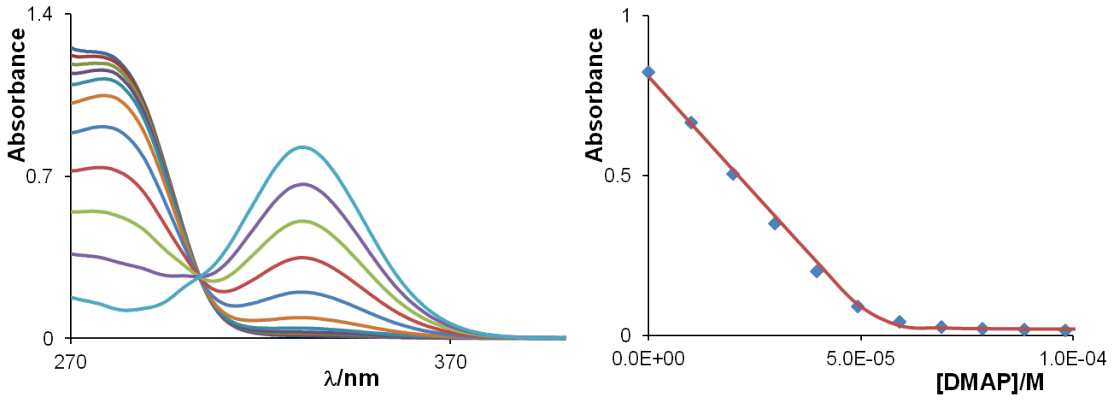


Figure S4. Absorbance changes upon addition of DMAP in THF to a THF solution of $B(C_6Cl_5)_3$ (left) and binding isotherm monitored at λ = 331 nm. The data could be satisfactorily modeled with K = 1.0 (±0.1) × 10^7 M^{-1} (ε = 15000 for $B(C_6Cl_5)_3$, ε = 0 for DMAP-$B(C_6Cl_5)_3$) (right).

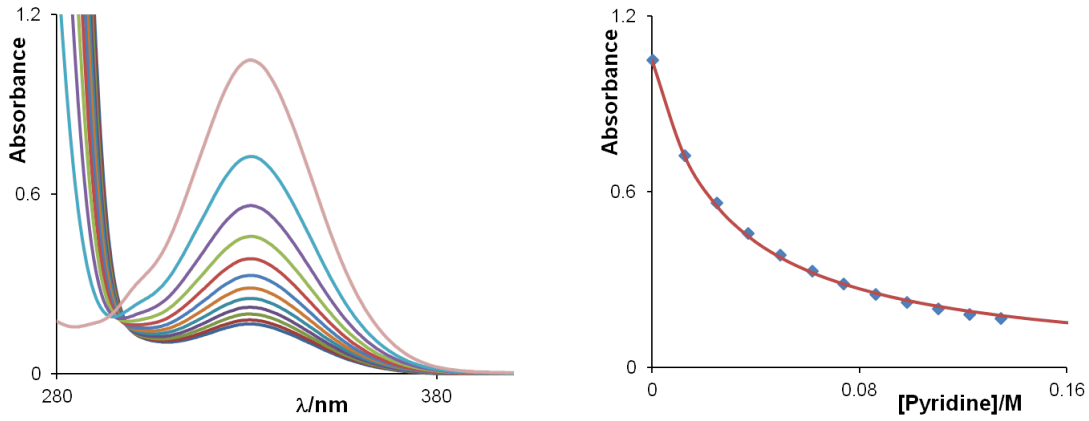


Figure S5. Absorbance changes upon addition of pyridine to a THF solution of $B(C_6Cl_5)_3$ (left) and binding isotherm monitored at $\lambda = 331$ nm. The data could be satisfactorily modeled with $K = 36$ (±4) M^{-1} ($\varepsilon = 15000$ for $B(C_6Cl_5)_3$, $\varepsilon = 0$ for pyridine-$B(C_6Cl_5)_3$) (right).

Computational details. DFT calculations (full geometry optimization) were carried out with the Gaussian 03 program using the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang-Parr correlation functional. Geometry optimization was carried out with the following mixed basis set: 6-31+g(d') for the boron, carbon, hydrogen and fluorine atoms, 6-31+g(d) for the chlorine atoms. Frequency calculations, which were carried out on the optimized structure of the compounds, confirmed the absence of any imaginary frequencies. To calculate the fluoride ion affinity (FIA) of the boranes, the optimized geometries of the boranes (BPh_3, $B(C_6F_5)_3$, $B(C_6Cl_5)_3$) and fluoroborates ($[FBPh_3]^-$, $[FB(C_6F_5)_3]^-$, $[FB(C_6Cl_5)_3]^-$ were

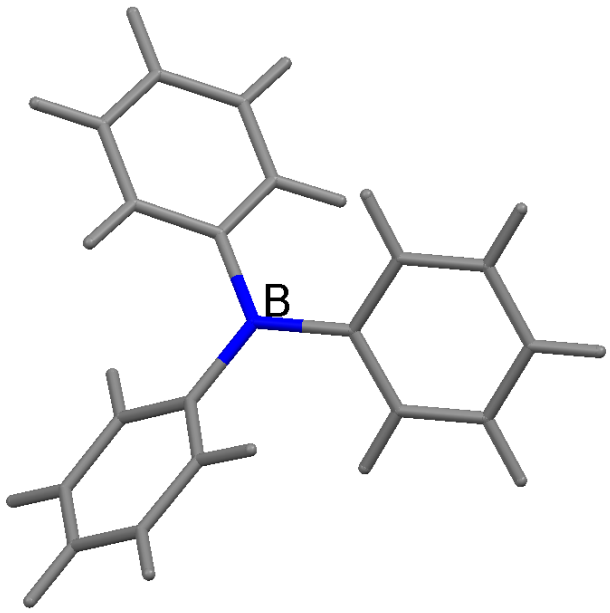
subjected to a single-point energy calculation using the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang–Parr correlation functional and the 6 -311+g(2d,p) basis set for all atoms. The fluoride ion affinities were calculated as shown in eq 1 (FIA = -Δ*H*). The reaction enthalpies Δ*H* were derived from the energy of each molecule (from the single-point calculation) corrected to enthalpy by the "thermal correction to enthalpy term" obtained in the frequency calculations (Table S1).

$$\text{borane} + F^- \xrightarrow{\Delta H} \text{fluoroborate} \qquad \text{eq. 1}$$

Table S1. Computed energies in Hartree

	SCF Energies	Correction to enthalpy term	Enthalpy
BPh_3	-720.0230278	0.292782	-719.7302458
$[FBPh_3]^-$	-820.0187719	0.294027	-819.7247449
$B(C_6F_5)_3$	-2208.989185	0.183468	-2208.805717
$[FB(C_6F_5)_3]^-$	-2309.035134	0.185668	-2308.849466
$B(C_6Cl_5)_3$	-7614.29414	0.164988	-7614.129152
$[FB(C_6Cl_5)_3]^-$	-7714.32235	0.167566	-7714.154784
F-	-99.8886932	0.00236	-99.8863332

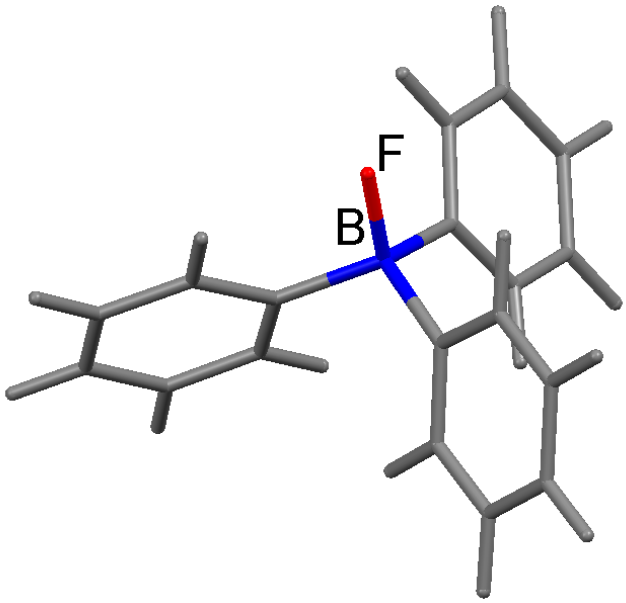
Optimized geometry of BPh_3:



Cartesian coordinates for the optimized geometry of BPh_3:

Atom	x	y	z
B	0.020109	-0.066527	-0.106619
C	-0.004555	-0.075390	1.463911
C	1.113483	-0.499027	2.218727
C	1.101445	-0.492966	3.615885
C	-0.049771	-0.091863	4.302927
C	-1.178572	0.317413	3.584217
C	-1.146290	0.339688	2.187520
C	0.825275	-1.167682	-0.885524
C	0.936405	-2.488894	-0.394008
C	1.638196	-3.475423	-1.091482
C	2.281448	-3.157853	-2.293004
C	2.203686	-1.854943	-2.797632
C	1.472482	-0.882953	-2.110082
C	-0.760547	1.043318	-0.898034
C	-1.367516	0.773400	-2.146259
C	-2.074965	1.754069	-2.846284
C	-2.167974	3.051300	-2.329799
C	-1.564550	3.354226	-1.104111
C	-0.887205	2.358826	-0.395050
H	-0.067041	-0.098131	5.391689
H	1.985040	-0.808200	4.168697
H	2.013411	-0.823742	1.699399
H	-2.029359	0.670688	1.643783
H	-2.079348	0.626387	4.112294
H	0.449874	-2.749800	0.544188
H	1.690440	-4.488449	-0.695530
H	2.840113	-3.920973	-2.832735
H	2.705876	-1.599733	-3.729502
H	1.413449	0.123307	-2.521109
H	-1.295955	-0.228092	-2.566902
H	-0.431977	2.608231	0.561784
H	-1.629106	4.362671	-0.698390
H	-2.707658	3.821331	-2.878936
H	-2.546545	1.510047	-3.796952

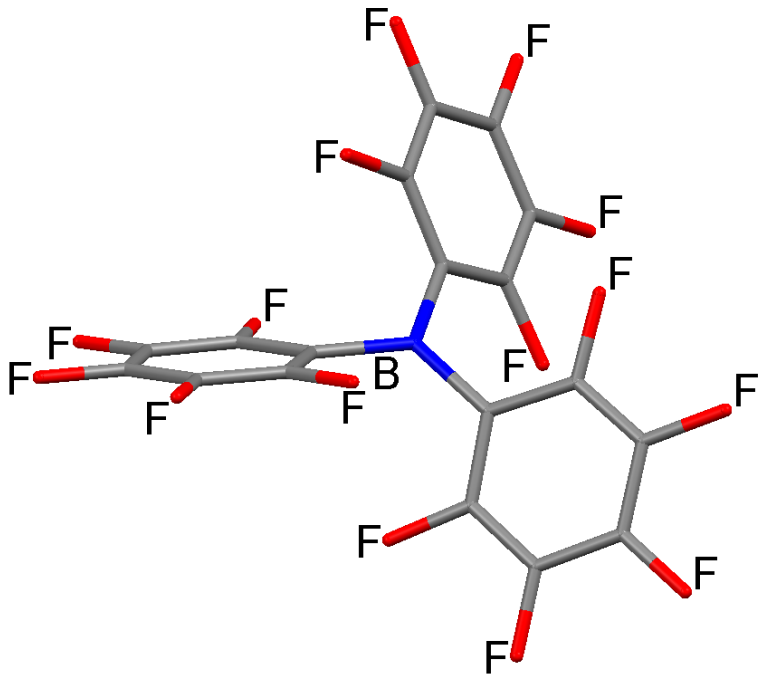
Optimized geometry of $[FBPh_3]^-$:



Cartesian coordinates for the optimized geometry of $[FBPh_3]^-$:

Atom	x	y	z
C	0.071865	-0.000652	-0.044097
C	0.037544	-0.111791	1.361989
C	1.201734	-0.139388	2.138923
C	2.459747	-0.053674	1.528545
C	2.527723	0.051902	0.134962
C	1.352137	0.072376	-0.628312
C	-1.838457	1.611874	-1.110729
C	-0.973004	2.698995	-1.345490
C	-1.445187	4.000932	-1.562175
C	-2.819485	4.263250	-1.541484
C	-3.705526	3.205549	-1.299185
C	-3.217188	1.910325	-1.090450
C	-1.204441	-0.733406	-2.328047
C	-0.747129	-0.139371	-3.521335
C	-0.615122	-0.860657	-4.716043
C	-0.950428	-2.218500	-4.758551
C	-1.418923	-2.835535	-3.591411
C	-1.539239	-2.101715	-2.405404
F	-2.363982	-0.630948	-0.097475
B	-1.333214	0.062054	-0.895201
H	-3.918341	1.099204	-0.897774
H	-4.780696	3.392356	-1.272574
H	-3.193684	5.274501	-1.704968
H	-0.737625	4.813030	-1.738595
H	1.129074	-0.229087	3.224407
H	0.104387	2.529249	-1.343252
H	-0.933139	-0.185413	1.850901
H	3.370425	-0.075048	2.128193
H	3.498333	0.109066	-0.360904
H	-0.501545	0.923250	-3.524516
H	-1.910926	-2.594179	-1.507573
H	1.436948	0.130209	-1.714148
H	-0.258051	-0.358653	-5.616999
H	-0.854071	-2.784871	-5.685532
H	-1.691881	-3.892352	-3.607079

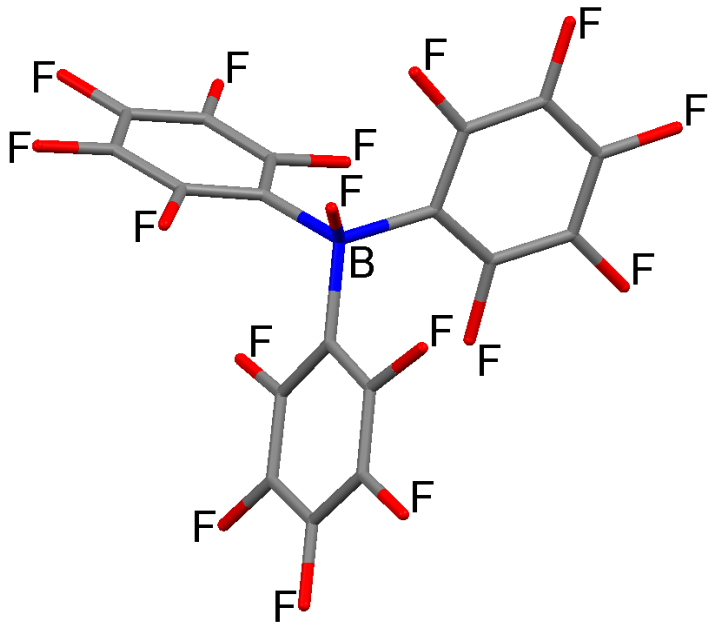
Optimized geometry of $B(C_6F_5)_3$:



Cartesian coordinates for the optimized geometry of $B(C_6F_5)_3$

Atom	x	y	z
B	-0.001586	0.000810	0.000152
C	1.364014	-0.775119	0.006908
C	2.456295	-0.362501	0.786188
C	3.668708	-1.043795	0.815134
C	3.832125	-2.177506	0.019085
C	2.780509	-2.620869	-0.782910
C	1.574452	-1.927975	-0.765890
C	-0.011679	1.571244	-0.003452
C	0.891374	2.324605	-0.770254
C	0.890508	3.715423	-0.795270
C	-0.027579	4.410225	-0.007890
C	-0.938182	3.707563	0.781227
C	-0.923595	2.316763	0.760532
C	-1.355665	-0.794803	-0.003473
C	-2.456645	-0.397239	-0.778596
C	-3.658331	-1.097371	-0.806076
C	-3.801880	-2.235661	-0.012793
C	-2.741463	-2.664451	0.785497
C	-1.546440	-1.952709	0.767195
F	1.755993	4.389237	-1.558953
F	-0.034906	5.741462	-0.009789
F	-1.811582	4.373991	1.542350
F	-1.816892	1.687000	1.545284
F	1.790987	1.702187	-1.553701
F	2.346750	0.720104	1.577845
F	4.673489	-0.625094	1.590666
F	4.989630	-2.835152	0.024793
F	2.940860	-3.701648	-1.552683
F	0.594316	-2.391416	-1.562964
F	-0.557630	-2.402758	1.561066
F	-2.883131	-3.749366	1.553074
F	-4.671677	-0.692344	-1.577657
F	-2.366857	0.688821	-1.567801
F	-4.948869	-2.911418	-0.017372

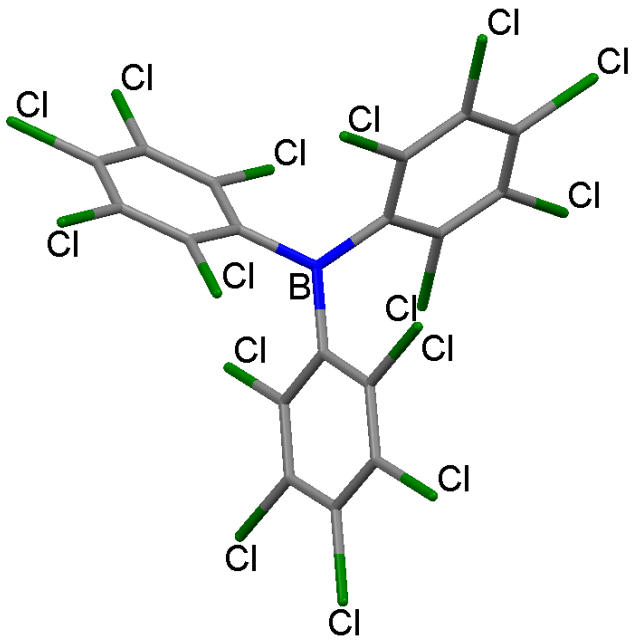
Optimized geometry of $[FB(C_6F_5)_3]^-$:



Cartesian coordinates for the optimized geometry of $[FB(C_6F_5)_3]^-$:

Atom	x	y	z
C	-0.092677	1.590778	0.305523
C	-0.974802	2.457573	0.961876
C	-1.079540	3.818155	0.677058
C	-0.284545	4.373715	-0.320066
C	0.593833	3.552979	-1.016712
C	0.665969	2.196801	-0.696872
C	-1.330123	-0.876271	0.308146
C	-2.223033	-0.529676	-0.706716
C	-3.362306	-1.267967	-1.028415
C	-3.646512	-2.429187	-0.320446
C	-2.778732	-2.833186	0.688832
C	-1.651234	-2.064886	0.974866
C	1.425157	-0.715917	0.302434
C	1.565900	-1.674632	-0.701962
C	2.774548	-2.291308	-1.026867
C	3.927363	-1.943532	-0.333757
C	3.848613	-0.978069	0.664494
C	2.619714	-0.387390	0.954596
F	0.004698	0.000980	2.217359
B	0.001985	-0.000263	0.782605
F	-1.949472	4.603236	1.346137
F	-0.369774	5.686558	-0.609917
F	-1.815716	1.992177	1.910329
F	2.642041	0.573628	1.902769
F	4.966535	-0.618930	1.329385
F	1.363087	4.077205	-1.993619
F	-2.012551	0.571129	-1.470866
F	0.502249	-2.057519	-1.451678
F	2.839574	-3.217911	-2.005709
F	5.105184	-2.527061	-0.628724
F	-4.189466	-0.871612	-2.018222
F	-3.035448	-3.970309	1.368474
F	-0.838009	-2.555161	1.934868
F	-4.742478	-3.156605	-0.611286
F	1.530855	1.471075	-1.448813

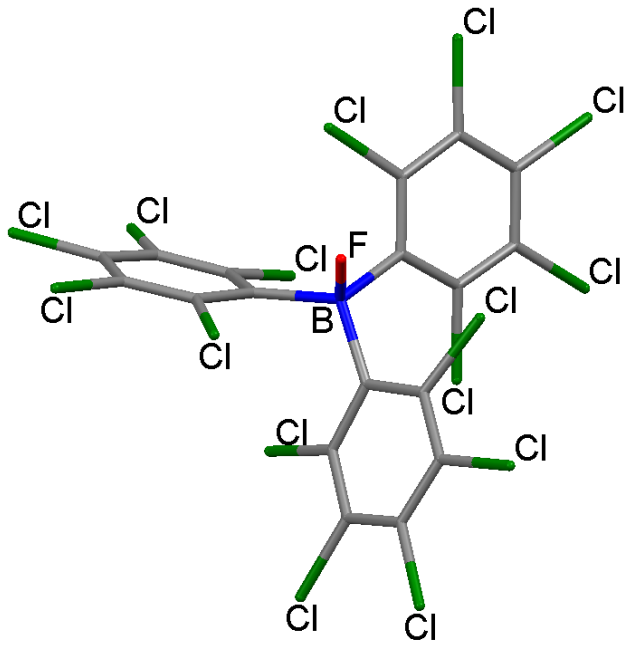
Optimized geometry of $B(C_6Cl_5)_3$:



Cartesian coordinates for the optimized geometry of $B(C_6Cl_5)_3$:

Atom	x	y	z
B	-0.005494	0.000110	0.000849
C	0.752245	1.402597	-0.001976
C	0.481298	2.393487	0.962130
C	1.145882	3.630371	0.979075
C	2.114142	3.906296	-0.002444
C	2.408026	2.943619	-0.984134
C	1.730773	1.713739	-0.966880
C	-1.598583	-0.047119	0.000364
C	-2.360644	0.645301	-0.961618
C	-3.764284	0.611100	-0.978543
C	-4.447741	-0.132918	-0.000623
C	-3.721480	-0.834432	0.977814
C	-2.318345	-0.783845	0.961957
C	0.834062	-1.355074	0.003138
C	0.621889	-2.360241	-0.960977
C	1.358646	-3.555492	-0.978709
C	2.342141	-3.773808	0.002115
C	2.578571	-2.795797	0.984136
C	1.829588	-1.608227	0.967561
Cl	-0.667342	2.055675	2.236065
Cl	0.787846	4.813077	2.198274
Cl	2.942842	5.428716	-0.002733
Cl	3.595211	3.284618	-2.203909
Cl	2.069319	0.566710	-2.241869
Cl	-1.541316	1.521654	-2.232987
Cl	-4.657712	1.471440	-2.193063
Cl	-6.180199	-0.184826	-0.001089
Cl	-4.562318	-1.747121	2.191657
Cl	-1.448380	-1.608269	2.234389
Cl	-0.545730	-2.091348	-2.234042
Cl	1.070402	-4.757170	-2.197870
Cl	3.259814	-5.244209	0.001322
Cl	3.783889	-3.066556	2.203716
Cl	2.099993	-0.443985	2.243265

Optimized geometry of $[FB(C_6Cl_5)_3]^-$:



Cartesian coordinates for the optimized geometry of $[FB(C_6Cl_5)_3]^-$:

Atom	x	y	z
C	-0.142978	1.630480	0.165314
C	-1.023957	2.444302	0.915565
C	-1.039792	3.848366	0.828144
C	-0.172159	4.499546	-0.059653
C	0.658885	3.730690	-0.884457
C	0.643100	2.328171	-0.773149
C	-1.341684	-0.942050	0.163602
C	-2.336808	-0.611021	-0.777418
C	-3.561609	-1.294796	-0.886575
C	-3.816072	-2.394785	-0.057472
C	-2.819890	-2.821037	0.831880
C	-1.609617	-2.108923	0.917168
C	1.486432	-0.694145	0.168471
C	1.699875	-1.723385	-0.770008
C	2.906775	-2.438483	-0.878493
C	3.986249	-2.103587	-0.051023
C	3.853968	-1.027065	0.836990
C	2.629750	-0.339074	0.922264
Cl	-2.232383	1.718411	1.962796
Cl	-2.127471	4.803894	1.807422
Cl	-0.145815	6.242488	-0.155110
Cl	1.698442	4.535076	-2.036680
Cl	1.611213	1.447921	-1.945444
Cl	-2.051813	0.660956	-1.955507
Cl	-4.775848	-0.796638	-2.040945
Cl	-5.341865	-3.238000	-0.149787
Cl	-3.108434	-4.236407	1.816001
Cl	-0.377971	-2.793697	1.965179
Cl	0.456782	-2.120498	-1.946193
Cl	3.086078	-3.741060	-2.030231
Cl	5.482762	-2.997741	-0.143439
Cl	5.223216	-0.563098	1.819384
Cl	2.602427	1.068755	1.971657
F	-0.003369	-0.002495	2.003133
B	0.000226	-0.002065	0.565258