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Supporting Information

Reactivity of a dihydroboron species: Synthesis of a hydroborenium complex and an expedient entry to stable thioxo- and selenoxo-boranes **

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Contents

(1) General Procedure

(2) Heteronuclear NMR Spectra of Compound 2

(3) Heteronuclear NMR Spectra of Compound 3

(4) Heteronuclear NMR Spectra of Compound 4

(5) X-ray Crystallography for Compounds 2, 3 and 4

(6) Table for Crystallographic data and refinement parameters for compounds 2, 3 and 4.

(7) Details of Computational Calculation of Compound 2

(1) General procedures

All syntheses were carried out under an inert atmosphere of dinitrogen in oven dried glassware using standard Schlenk techniques, and other manipulations were accomplished in an Ar filled glove box. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from commercial sources used without further purification. LBH_2 (**1**) was prepared as reported in the literature.[20] ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Bruker Avance DPX 400 MHz spectrometer. High resolution mass spectrometry was performed with Waters SYNAPT G2S.

(2) Heteronuclear NMR spectra of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^+BHCl_3^-$ (2)

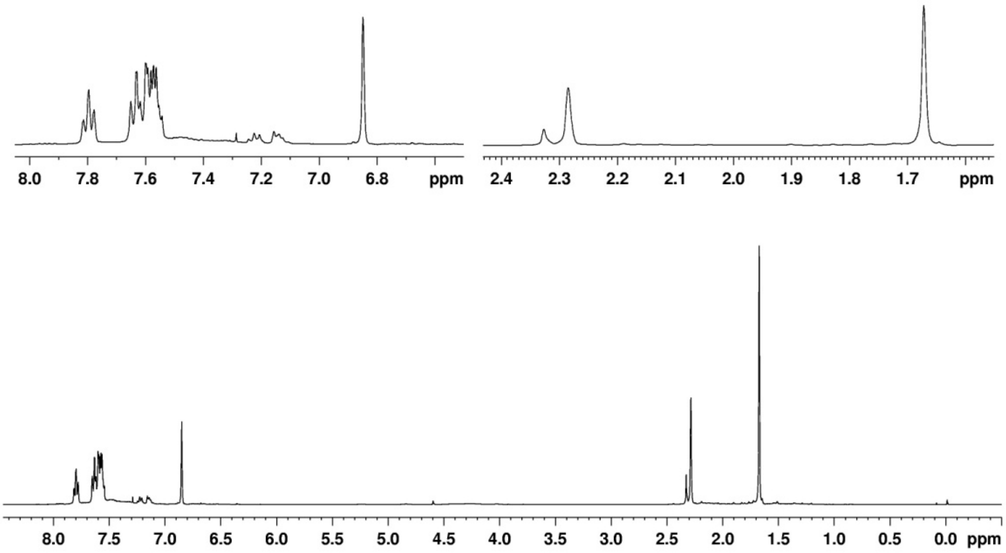

Figure S1. ^1H NMR spectrum (400 MHz, $CDCl_3$) of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^+BHCl_3^-$ (**2**).

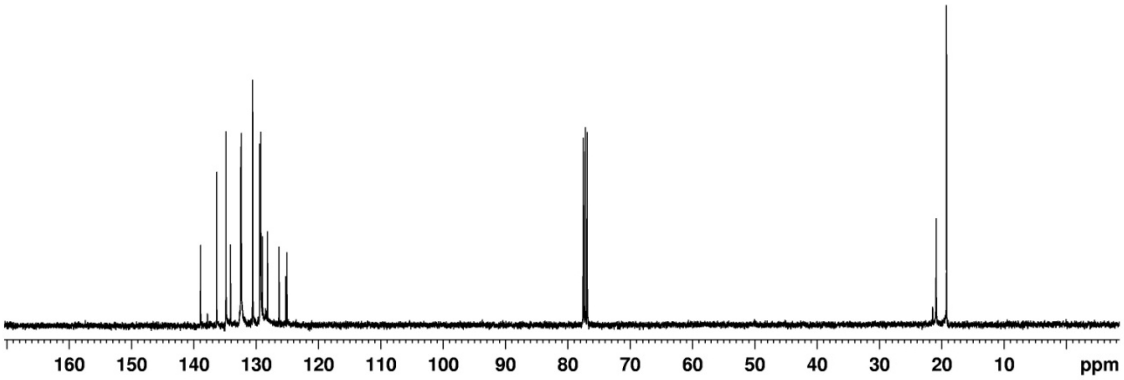

Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^+BHCl_3^-$ (**2**).

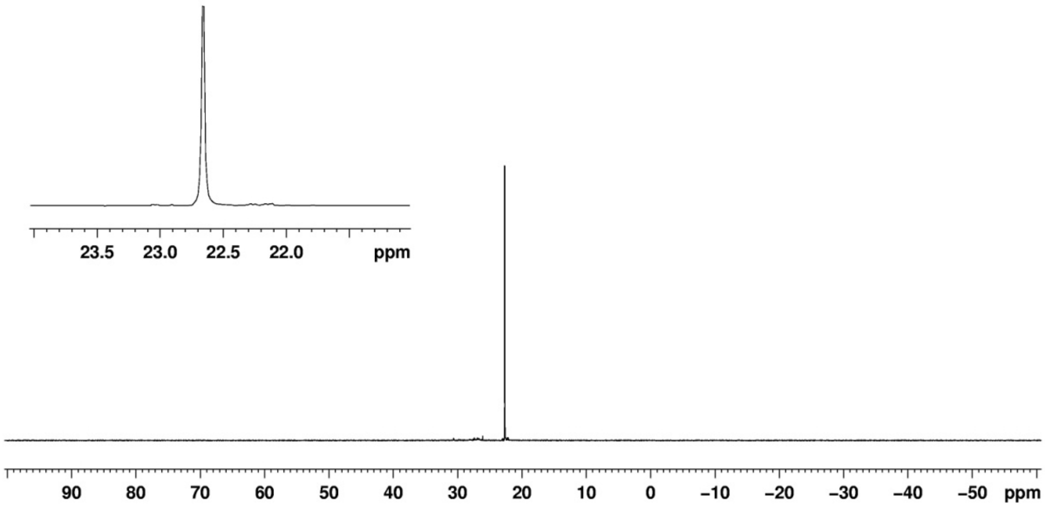

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^{+}BHCl_3^{-}$ (**2**).

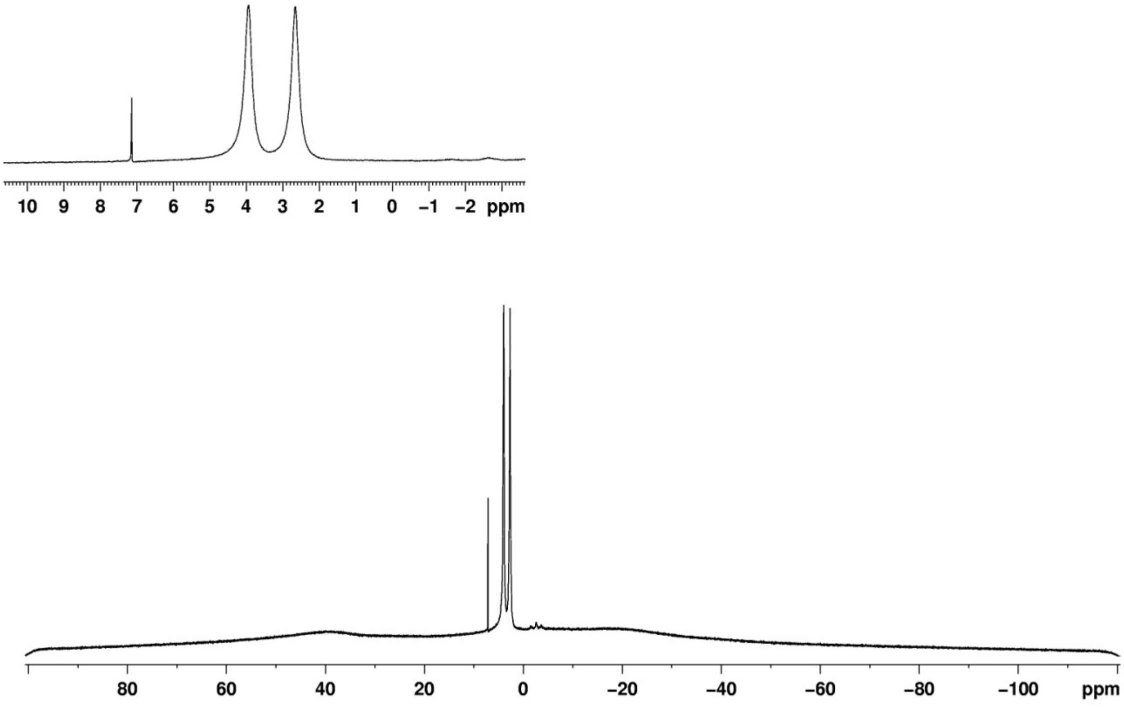

Figure S4. ^{11}B NMR spectrum (162 MHz, $CDCl_3$) of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^{+}BHCl_3^{-}$ (**2**).

(3) Heteronuclear NMR Spectra of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BS] (3)

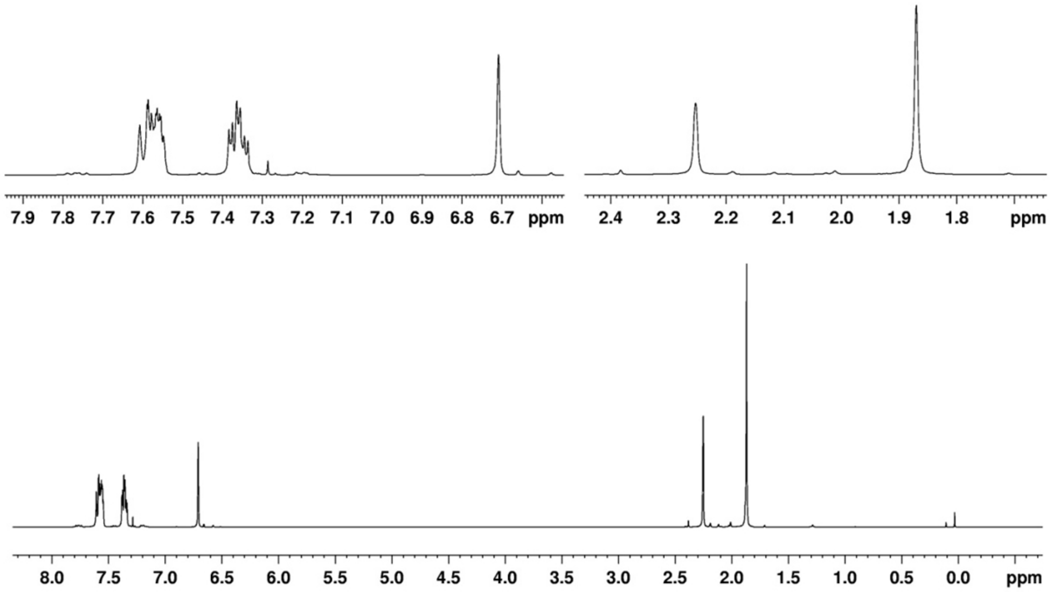

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BS] (**3**).

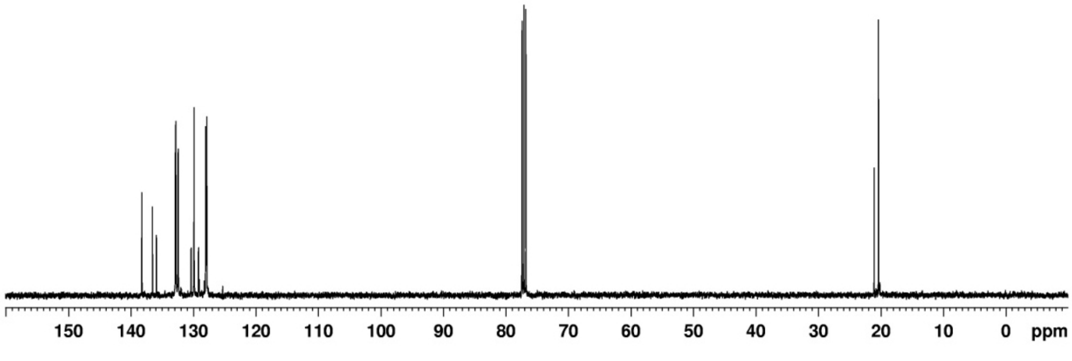

Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BS] (**3**).

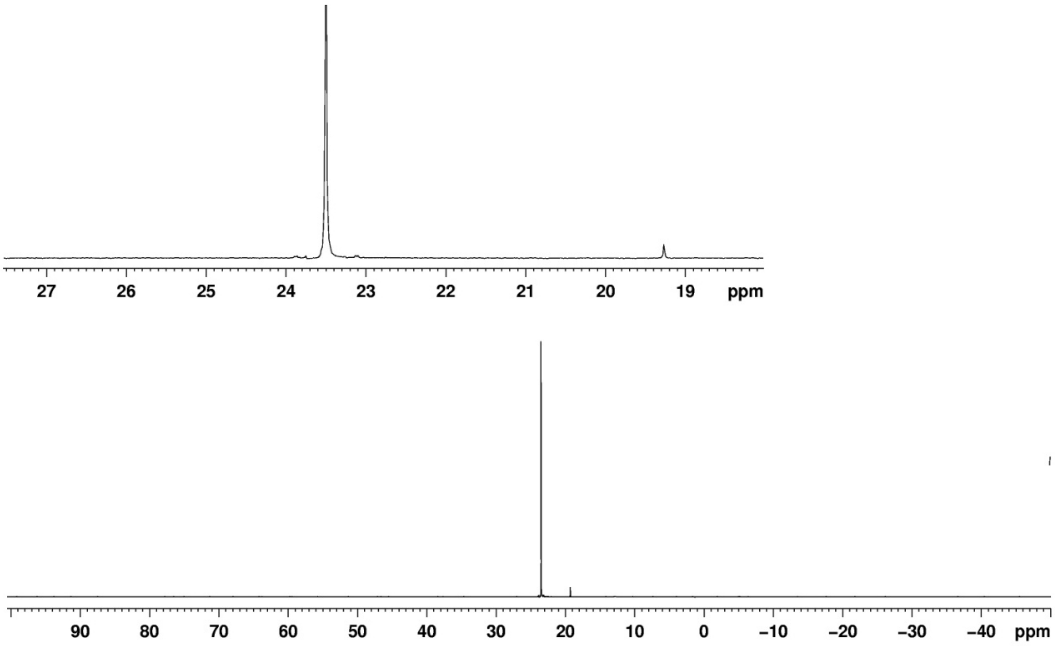

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BS] (**3**).

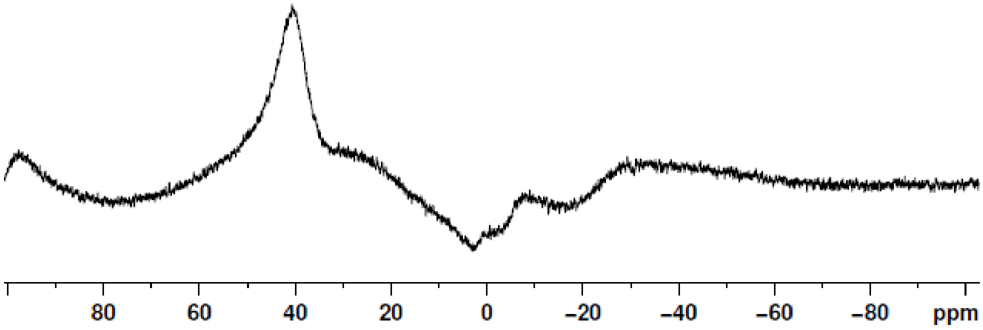

Figure S8. ^{11}B NMR spectrum (162 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BS] (**3**).

(4) Heteronuclear NMR Spectra of [{N(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}BSe] (4)

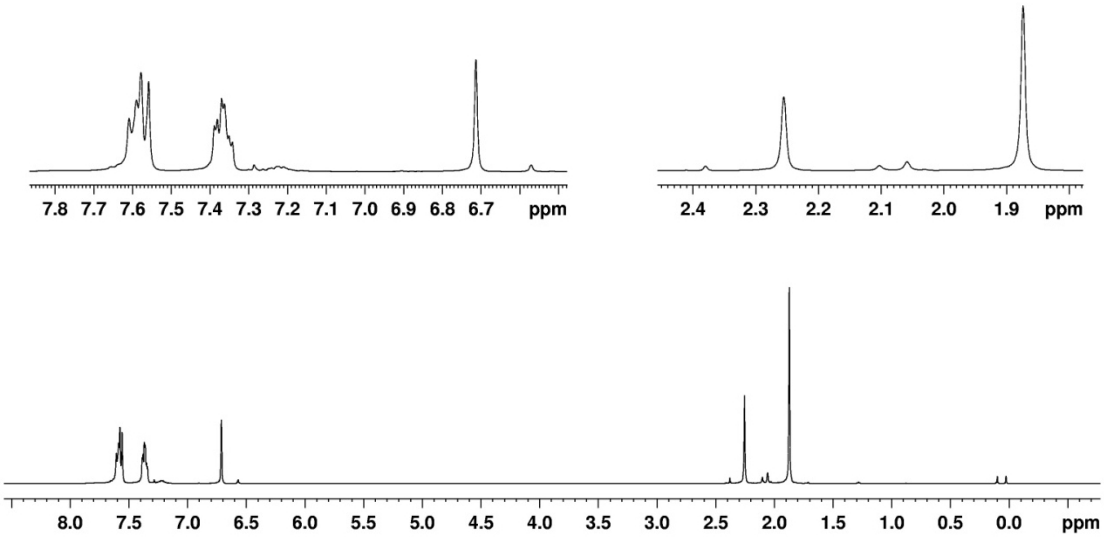

Figure S9. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of [{N(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}BSe] (**4**).

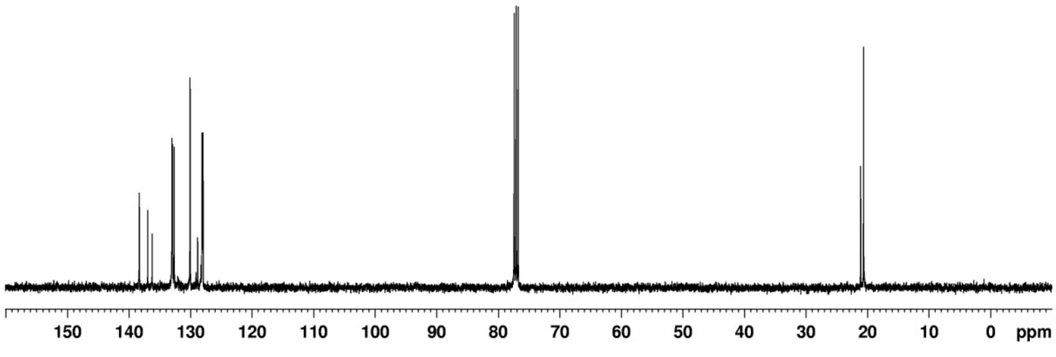

Figure S10. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of [{N(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}BSe] (**4**).

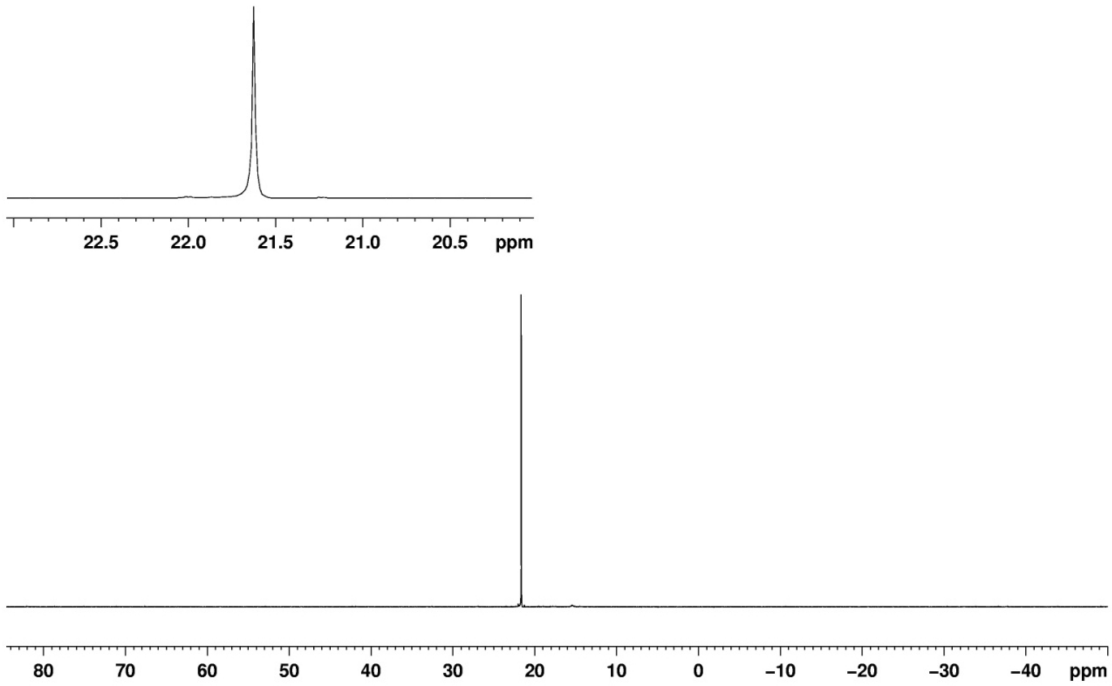

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BSe] (**4**).

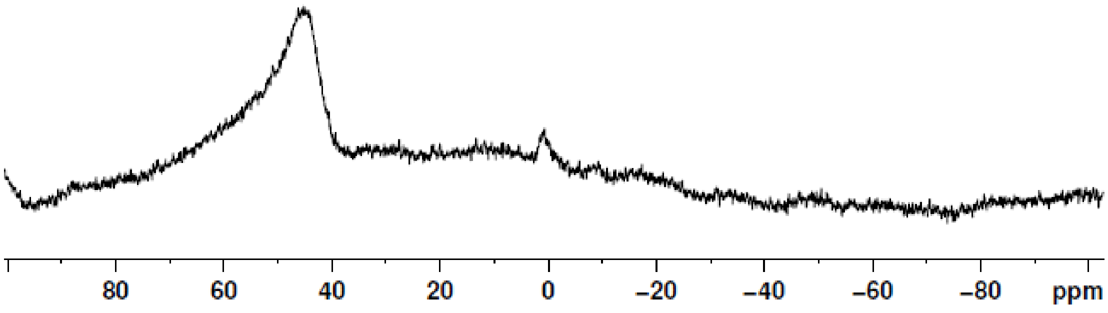

Figure S12. ^{11}B NMR spectrum (162 MHz, $CDCl_3$) of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}BSe] (**4**).

(5) X-ray Crystallography for Compounds 2, 3 and 4

Single crystal X-ray diffraction data for **3** was collected on a Bruker *AXS KAPPA APEX-II* CCD diffractometer (Monochromatic MoKα radiation) equipped with Oxford cryosystem 700 plus at 100 K. Data collection and unit cell refinement for the data sets were done using the Bruker APPEX-II suite, data reduction and integration were performed using SAINTV 7.685A (Bruker AXS, 2009) and absorption corrections and scaling were done using SADABSV2008/1 (Bruker AXS, 2009). Single crystal X-ray diffraction data of **2** and **4** were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with graphite monochromatic MoKα radiation (λ = 0.71073 Å) at 100.0(2) K using scans. During the data collection the detector distance was 50 mm (constant) and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[1] The crystal structures were solved by using either OLEX2[2] or WINGX package using SHELXS-97 and the structure were refined using SHELXL-97 2008.[3] All non hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and were refined using riding model except the hydrides (H(1) and H(2)) in complex **2** that were located from difference Fourier map and refined isotropically. A disordered THF molecule found in the asymmetric unit of **3** could not be treated using standard commands available in SHELXL. The squeeze method was used to remove the contribution of these disordered molecules from the original *hkl* file. The resulting squeezed *hkl* file was used for further refinement. Diamond version 2.1d was used to generate graphics for the X-ray structures.

[1] CrystalClear 2.0, Rigaku Corporation, Tokyo, Japan.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339-341.

[3] SHELXS-97, Program for Structure Solution: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.

(6) Table for Crystallographic data and refinement parameters for compounds 2, 3 and 4.

Table 1 Crystallographic data and refinement parameters for compounds **2, 3** and **4**.

Compound	**2**	**3**	**4**
Chemical formula	$C_{42}H_{44}N_3P_2B_2Cl_3$	$C_{42}H_{42}N_3P_2BS$	$C_{42}H_{42}N_3P_2BSe$
Molar mass	780.80	693.60	740.49
Crystal system	monoclinic	Orthorhombic	tetragonal
Space group	$P2_1/n$	$Pnc2$	$I4_1/a$
T[K]	100(2)	100(2)	100(2)
a [Å]	10.3449(2)	16.3423(2)	37.392(3)
b [Å]	24.2326(4)	15.9070(1)	37.392(3)
c [Å]	16.1667(3)	15.6840(1)	10.8529(2)
α[°]	90.00	90.00	90.00
β [°]	92.304(7)	90.00	90.00
γ[°]	90.00	90.00	90.00
V [Å^3]	4049.5(11)	4077.2(4)	15174(3)
Z	4	4	16
D(calcd.) [g·cm^{-3}]	1.28	1.13	1.297
μ(Mo-K_α) [mm^{-1}]	0.339	0.189	1.108
Index range	$-12 \leq h \leq 12$	$-19 \leq h \leq 19$	$-45 \leq h \leq 45$
	$-29 \leq k \leq 29$	$-19 \leq k \leq 19$	$-42 \leq k \leq 45$
	$-19 \leq l \leq 19$	$-18 \leq l \leq 18$	$-13 \leq l \leq 12$
Reflections collected	28454	63447	46219
Independent reflections	7400	7460	6935
Data/restraints/parameters	7400/0/489	7460/0/450	6935/0/448
$R1$, $wR2$ [$I>2\sigma(I)$][a]	0.0442, 0.1194	0.0341, 0.0884	0.0632, 0.1326
$R1$, $wR2$ (all data)[a]	0.0476, 0.1231	0.0378, 0.0901	0.0822, 0.1459
GOF	1.026	1.058	1.102

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

(7) Details of Computational Calculation of Compound 3

DFT calculation of compound **3** was carried out at B3LYP/cc-pVDZ level of theory with Gaussian 09 package.[4] Cartesian Co-ordinate of optimized geometry of compound 2 has been shown in Table 1. NBO charge analysis has been done at DFT optimized geometry.[5]

7.1. Supplementary Data of compound 3

Selected NBO Charges* of compound 3

B	0.68676e
S	-0.54710e
P	2.04187e & 2.04181e
N(Central)	-1.44155e
N(Bonded to B)	-1.10171e & -1.10187e

Cartesian Co-ordinates of optimized structure of Compound 3

Table 2: Cartesian Co-ordinates (x, y, z) of compound **3**

B	16.342901	15.905259	12.955855
C	11.365572	14.566099	17.503610
H	10.396037	14.544464	18.006889
C	12.333919	15.497181	17.887745
H	12.127298	16.204597	18.694007
C	13.573500	15.526782	17.242637
H	14.339590	16.244749	17.537986
C	13.850462	14.623023	16.203905
C	14.365266	14.292940	13.006500
C	14.582524	13.002826	12.475727
C	13.511458	12.346654	11.852824

H	13.683644	11.346508	11.443805
C	12.251831	12.937153	11.704785
C	11.131273	12.208589	11.001477
H	11.292749	12.191337	9.909025
H	10.158371	12.690573	11.183228
H	11.059836	11.159467	11.332822
C	15.938929	12.342796	12.482587
H	16.711446	13.073054	12.199620
H	15.960662	11.522926	11.749767
H	16.202902	11.917021	13.461456
C	16.354422	13.137863	15.838035
C	15.755732	12.121163	16.595663
H	14.725304	12.220012	16.936404
C	16.481576	10.972199	16.930947
H	16.003791	10.186412	17.520384
C	17.808387	10.833218	16.520237
H	18.372985	9.935856	16.783604
C	18.414539	11.849556	15.771854
H	19.452646	11.748860	15.447626
C	17.693792	12.993933	15.433995
H	18.172078	13.777121	14.845187
C	11.639617	13.659083	16.474667
H	10.885700	12.930237	16.169665
C	12.875977	13.681128	15.825302
H	13.071785	12.972136	15.020568
C	12.087571	14.241970	12.178954
H	11.126756	14.745991	12.040476

C	13.123366	14.936333	12.816130
C	12.904520	16.366230	13.238857
H	12.972422	16.494441	14.331154
H	11.909449	16.714192	12.925527
H	13.660401	17.017025	12.770004
N	15.409451	14.997939	13.743775
N	16.335275	15.911997	16.144004
P	15.508333	14.722229	15.418369
S	16.345646	15.902920	11.218240
C	21.314443	17.221986	17.508884
H	22.283615	17.236318	18.013061
C	20.339104	16.297511	17.891231
H	20.540087	15.587563	18.696801
C	19.099938	16.277336	17.244968
H	18.328611	15.564436	17.538969
C	18.830263	17.183792	16.206634
C	18.316809	17.522075	13.007386
C	18.095567	18.811015	12.475193
C	19.165264	19.470830	11.854024
H	18.990024	20.470042	11.444034
C	20.427320	18.884902	11.708551
C	21.546661	19.617999	11.008172
H	21.382365	19.644392	9.916453
H	22.519566	19.133872	11.183580
H	21.619837	20.664267	11.347788
C	16.736407	19.465420	12.477538
H	15.967213	18.730863	12.195800

H	16.712646	20.282465	11.741240
H	16.469156	19.894059	13.454467
C	16.335698	18.684391	15.834038
C	16.945663	19.708606	16.572187
H	17.979136	19.610710	16.903488
C	16.227373	20.864272	16.900554
H	16.713979	21.655853	17.474834
C	14.896873	21.002676	16.502322
H	14.338200	21.905322	16.760131
C	14.279300	19.978743	15.773961
H	13.238032	20.078654	15.459950
C	14.992418	18.827536	15.443285
H	14.505243	18.038146	14.870280
C	21.047777	18.131786	16.480394
H	21.807107	18.855561	16.176689
C	19.812019	18.118809	15.829594
H	19.622443	18.829412	15.024728
C	20.595270	17.580549	12.182586
H	21.557905	17.079741	12.045177
C	19.560910	16.882591	12.818123
C	19.783485	15.452908	13.239492
H	19.712367	15.322599	14.331257
H	20.780717	15.108845	12.928739
H	19.031244	14.800579	12.766824
N	17.274001	16.814604	13.744315
P	17.172828	17.094231	15.418474

[4]. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[5]. NBO Version 3.1*,* E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.