Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Borole-Based Half-Sandwich Complexes of Germanium and Tin

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Experimental Details

General Information

All manipulations requiring handling under inert conditions were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox with an Ar atmosphere. Benzene was obtained from an MBraun SPS and stored over molecular sieves, toluene and ether were distilled from sodium. Dichloromethane was distilled from CaH_2. Hexane and pentane were distilled from Na/K alloy. THF was distilled from potassium. Dichloromethane-*d₂* was distilled from CaH_2, THF-*d₈* was dried over $LiAlD_4$ and vacuum transferred, benzene-*d₆* was distilled from potassium, toluene-*d₈* was distilled from potassium and solvents were degassed and stored in a glove box. All solvents were routinely degassed three times using freeze-pump-thaw cycles.

Elemental analysis was performed by the Analytisches Labor, Institut für Anorganische Chemie, Universität Göttingen

Mass spectrometry

Mass spectra were recorded by the Zentrale Analytik within the Faculty of Chemistry, Göttingen applying a Liquid Injection Field Desorption Ionisation-technique (LIFDI) on a JEOL accuTOF instrument with an inert-sample application setup under argon atmosphere. The injection capillary was washed several times with dry, distilled and inertly injected toluene before the samples were injected. Samples usually had a concentration of 1 – 2 mmol/L in toluene and were prepared in a glovebox. When appropriate, isotopic patterns have been simulated using the web service provided by www.cheminfo.org.

NMR spectroscopy

NMR spectra were recorded with either a Bruker Avance III 400 NMR spectrometer equipped with a 5 mm BBFO ATM probe head and operating at 400.13 MHz (^1H), 100.61 MHz (^{13}C), 128.38 MHz (^{11}B) and 376.45 MHz (^{19}F) along with a variable temperature set-up or a Bruker Avance Neo 400 NMR spectrometer with a CryoProbeProdigy BB ATM probe head operating at 400.25 MHz (^1H) and 100.65 MHz (^{13}C) or a Bruker AVIII HD 500 NMR spectrometer with a CryoProbeProdigy ATM probe head and operating at 500.25 MHz (^1H), 125.80 MHz (^{13}C), 160.50 MHz (^{11}B), 186.19 MHz (^{119}Sn), and 99.37 MHz (^{29}Si) or a Bruker Avance II 300 NMR operating at 300.13 MHz (^1H) and 116.64 MHz (^7Li). Chemical shifts are reported in δ values in ppm relative to external Me_4Si and, if not otherwise stated, referenced using the chemical shift of the solvent ^2H lock resonance frequency and Ξ = 19.867187% for ^{29}Si, Ξ = 38.863797 % for ^7Li, Ξ = 32.083974% for ^{11}B, and Ξ = 37.290632% for ^{119}Sn.[1] ^1H and ^{13}C spectra have been referenced on specific values for the respective solvent signal. The proton and carbon signals were assigned where possible via a detailed analysis of ^1H, ^{13}C, ^1H-^1H COSY, ^1H-^1H NOESY, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC NMR spectra.

Young-type teflon-valve borosilicate NMR tubes have been used throughout the study.

Starting materials and reagents

1,3,4-(2',5'-*t*$Bu_2(C_6H_3)$)-2,4-($SiMe_3$)-Borole **A** was prepared as recently reported.[2] *tert*-Butyllithium solutions (1.6 M in pentane) were obtained from Sigma Aldrich und used within two month from purchase.

Cp*GeCl was prepared as previously described in the literature.[3]

$3,5\text{-}Me_2(C_6H_3)\text{-}CC\text{-}SiMe_3$ (Xyl-CC-TMS) was prepared along modified literature procedures.[2, 4] A 1000 mL Schlenk-flask was charged with a mixture of palladium(II)acetate (0.62 g, 2.8 mmol, 0.5 mol%), copper(I)iodide (0.67 g, 3.5 mmol, 0.6 mol%) and triphenylphosphine (2.85 g, 10.9 mmol, 2 mol%). Bromo-3,5-dimethylbenzene (100 g, 540.34 mmol. 1 eq.) and triethyl amine (500 mL) were added and the resulting suspension was degassed one time using the *freeze-pump-thaw*-method. After the addition of trimethylsilyl acetylene (85 mL, 594.37 mL, 1.1 eq.) the suspension was stirred overnight at 80-90 °C. A greyish solid precipitated and was filtered off and washed with hexane until the hexane washes remained colorless. The solvents were removed in *vacuo* giving a dark brown liquid which was subsequently purified via vacuum distillation (1.0 · 10-3 mbar, 74 °C head temperature, 120 °C oil bath). (3,5-Dimethylphenyl)trimethylsilyl acetylene was obtained as a yellow liquid (101.86 g, 503.34 mmol, 93 %). NMR-spectroscopic features are found identical to those reported previously.[4]

^1H (300.13 MHz, 298 K, $CDCl_3$, $CHCl_3$ at 7.26 ppm): 7.10 (s, 2H, *o-H*), 6.95 (s, 1H, *p-H*), 2.27 (s, 6H, *m-C*H3), 0.24 (s, 9H, TMS).

1,4-Diiodo-1,4-TMS$_2$-2,3-Xyl$_2$-buta-1,3-diene was prepared along modified literature procedures.[2] Under inert conditions, a 1000 mL two-necked Schlenk-flask was charged with freshly grinded Cp_2ZrCl_2 (24.60 g, 84.15 mmol, 0.57 eq.). THF (500 mL, SPS grade) was added. The resulting solution was then cooled to –78 °C. *n*-Butyllithium (66 mL, 2.5 M in hexane, 1.1 eq.) was added dropwise over a period of 25 min to the cold solution. The dropping funnel was rinsed with THF (10 mL, SPS grade) and the resulting yellow suspension was continuosly stirred for 1.5 h at –78 °C. (3,5-Dimethylphenyl)trimethylsilyl acetylene (30 g, 148 mmol, 1 eq.) was added dropwise and the reaction was subsequently allowed to warm to ambient temperature overnight. The resulting orange suspension was cooled to 0 °C and copper(I)chloride (8.26 g, 83.5 mmol, 0.56 eq.) was added. A solution of iodine (39.74 g, 156.6 mmol, 1.05 eq.) in THF (60 mL, SPS grade) was added over a period of 45 min via dropping funnel. The flask was wrapped with aluminium foil and the dark suspension was stirred for three days at room temperature. A solution of sodium dithionite (ca. 5 g in 150 mL H_2O) and diethyl ether (100 mL) were added. The phases were separated and the aqueous phase was extracted with diethylether (2 x 100 mL). The combined organic phases were dried over $MgSO_4$ and filtered. After the removal of the solvents in vacuo, the viscous suspension was diluted in hexane and then filtered through celite. The celite pad was rinsed with hexane until the solvent running through turned colorless. The orange filtrate was concentrated to brownish oil which slowly started to crystallize. The oil was stored at –30 °C overnight. The dark green supernatant was removed and slightly greenish crystals were recrystallized from acetone (50 mL, p. a. grade). The supernatant was removed and the crystals were then washed with portions of cold (–25°C) acetone. After drying under reduced pressure, the 1,4-Diiodo-1,4-TMS$_2$-2,3-Xyl$_2$-buta-1,3-diene was obtained as colorless crystals (27.83 g, 42.26 mmol, 57 %). **Note:** The aluminium foil was used to protect the reaction from light. We observed that if the nearly colorless product was stored under daylight it increasingly darkens. The product has an unpleasant odor.

^{1}H (300.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.90 (s, 2H, *p-H*), 6.76 (s, 4H, *o-H*), 2.22 (s, 12H, *m*-C*H*$_3$), –0.04 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 163.4 (Xy-*C*), 139.3 (*m*-C$_{ar}$ or *ipso-C$_{ar}$*), 137.0 (*m-C$_{ar}$* oder *ipso-C$_{ar}$*), 129.8 (*p-C$_{ar}$*), 127.4 (*o-C$_{ar}$*), 112.0 (*C*-I), 21.4 (*m-C*H$_3$), 1.1 (TMS).

Elemental Analysis: ($C_{26}H_{36}I_2Si_2$) calcd C 47.42, H 5.51, I 38.54, Si 8.53, observed C 47.45, H 5.51.

HR-ESI-MS: calcd exact mass: 658.0445 m/z, observed m/z: 676.0783 $[M+NH_4]^+$, 681.0337 $[M+Na]^+$, calcd for $[C_{26}H_{37}I_2Si_2]^+$: 659.0523 m/z, observed m/z: 659.0518.

1,4-Dilithio-1,4-TMS$_2$-2,3-Xyl$_2$-buta-1,3-diene was prepared along modified literature procedure.[2] In a Schlenk-flask, 1,4-Diiodo-1,4-TMS$_2$-2,3-Xyl$_2$-buta-1,3-diene (5.05 g, 7.67 mmol, 1 eq.) was dissolved in diethyl ether (35 mL, SPS grade) and the solution is cooled to –78 °C. A solution of *tert*-Butyllithium (19.5 mL, 1.6 M in pentane, 31.2 mmol, 4.06 eq (2.03 eq per iodine-atom)) was slowly added via syringe and the resulting red suspension was allowed to warm to ambient temperature overnight. The solvents were thoroughly removed in vacuo and the solid residue was suspended in hexane (20 mL). The suspension was filtered through a filter canula through a pad of glass fiber (Whatman GF/A). The residual solid extracted twice with further amounts of hexane until the filtrate was only of pale orange colour. The dark red filtrate was concentrated under reduced pressure until dryness and transferred into a glovebox. The solid was again suspended in hexane (10 mL, distilled) and then filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B) to remove remaining traces of LiI. The solvent was removed in vacuo to yield 1,4-Dilithio-1,4-TMS$_2$-2,3-Xyl$_2$-buta-1,3-diene as an orange crystalline solid (3.003 g, 7.174 mmol, 94 %).

^{1}H (300.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.74 (s, 4H, *o-H*), 6.49 (s, 2H, *p-H*), 2.12(s, 12H, *m*-C*H*$_3$), 0.06 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 197.2 (*C*-Li), 170.8 (Xy-*C*), 149.7 (*m-C$_{ar}$* or *ipso-C$_{ar}$*), 136.1 (*m-C$_{ar}$* or *ipso-C$_{ar}$*), 126.7 (two signals superimposed, *p-C$_{ar}$* and *o-C$_{ar}$*), 21.3 (*m-C*H$_3$), 0.8 (TMS).

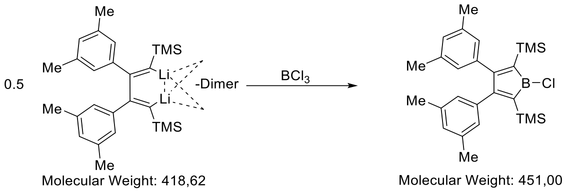
^{7}Li{^{1}H} (116.64 MHz, 298 K, C_6D_6): 2.13.

Elemental Analysis: ($C_{26}H_{36}Li_2Si_2$) calcd C 74.60, H 8.67, Li 3.32, Si 13.42, observed C 73.67, H 8.90.

LIFDI-MS: calcd exact mass: 418.3 m/z, observed m/z: 407.7 (protonated butadiene).

Synthesis and Analytical Data

Compound 1



A 500 mL Schlenk-flask was charged with dilithio butadiene (3.212 g, 7.67 mmol, 1 eq.) and hexane (250 mL, SPS grade) and the dark red solution was cooled to 0 °C. A stock solution of boron trichloride (7.7 mL, 1 M in hexane, 1 eq.) was further diluted with additional hexane (90 mL) and subsequently added dropwise over a period of 25 min to the vigorously stirred red solution which then quickly turns into an orange suspension. After the addition was completed, the dark red suspension was stirred over night at room temperature. The solvent was removed under reduced pressure and thoroughly dried under vacuum and the flask containing an orange brown solid was transferred into a glovebox. The residue was again suspended in hexane (15 mL, distilled) and filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B). Few drops of diethyl ether were added to the dark red filtrate which was then stored at –35 °C over night upon which a thick sponge of fine crystal needles of the Et_2O-adduct to chloroborole **1** form. The sponge of fine crystals was isolated by filtration and washed with small portions of cold (–35°C) pentane. The mother liquors were then again cooled to –35 °C with another drop of diethyl ether for a further crop of crystals. This process was repeated until no worthwhile amount of crystalline material could be isolated. The combined crystalline yields were then dissolved hexane and solvents/volatiles were subsequently removed to eliminate coordinating ether by co-evaporation. In case ether was not entirely removed, the residue was again dissolved in hexane and the co-evaporation repeated. The chloroborole **1** is finally obtained as a deep red crystalline material (1.605 g, 3.56 mmol, 46 %).

Note: (1) In our hands chloroborole **1** did not crystallize reliably or in satisfactory yields from crude reaction mixtures and only the detour of isolating the ether adduct for an initial purification yields satisfactory access. Sometimes addition of Et_2O for crystallization purposes lead to an instant precipitation of crystalline material. **(2)** In our attempts to increase the yield we noted a distinct dependency on concentrations of the solutions with more dilute solutions leading to higher yields. However, further extensive further dilution from the conditions described above did not result in improvements.

Analytical Data for Compound 1

NMR:

^{1}H (300.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.56 (m, 2H, *p*-H), 6.55 (m, 4H, *o*-H), 1.96 (m, 12H, *m*-CH_3), 0.15 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 181.3 (C_β), 139.3 (*ipso*-C_{ar}), 136.6 (*m*-C_{ar}), 135.4 (C_α), 129.5 (*p*-C_{ar}), 126.1 (*o*-C_{ar}), 21.1 (*m*-CH_3), 1.0 (TMS).

^{29}Si-INEPT (79.49 MHz, 298 K, C_6D_6): –8.9.

^{11}B (128.37 MHz, 298 K, C_6D_6): 69.6 ($\omega_{1/2}$ = 910 Hz).

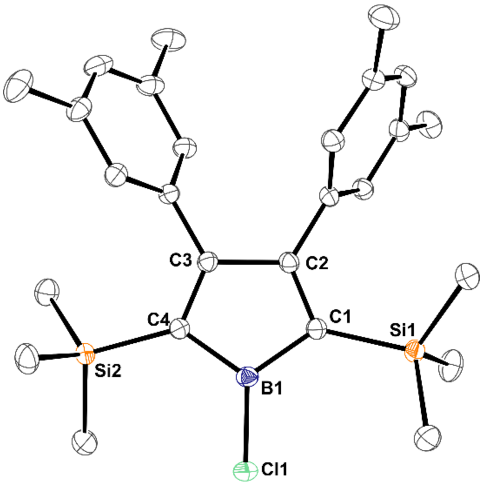
Elemental Analysis: ($C_{26}H_{36}BClSi_2$) calcd C 69.24, H 8.05, B 2.40, Cl 7.86, Si 12.45, observed C 68.89, H 8.31.

LIFDI-MS: calcd exact mass: 450.2 m/z, observed m/z: 451.2 according to isotope pattern in agreement with hydrolysis product after chloride loss $[M-Cl+2(H_2O)]^+$, around m/z 882.3 further dimeric hydrolysis aggregates]$^+$.

UV-*vis*: λ_{max} at 454 nm (hexane)

Crystal structure of Compound 1

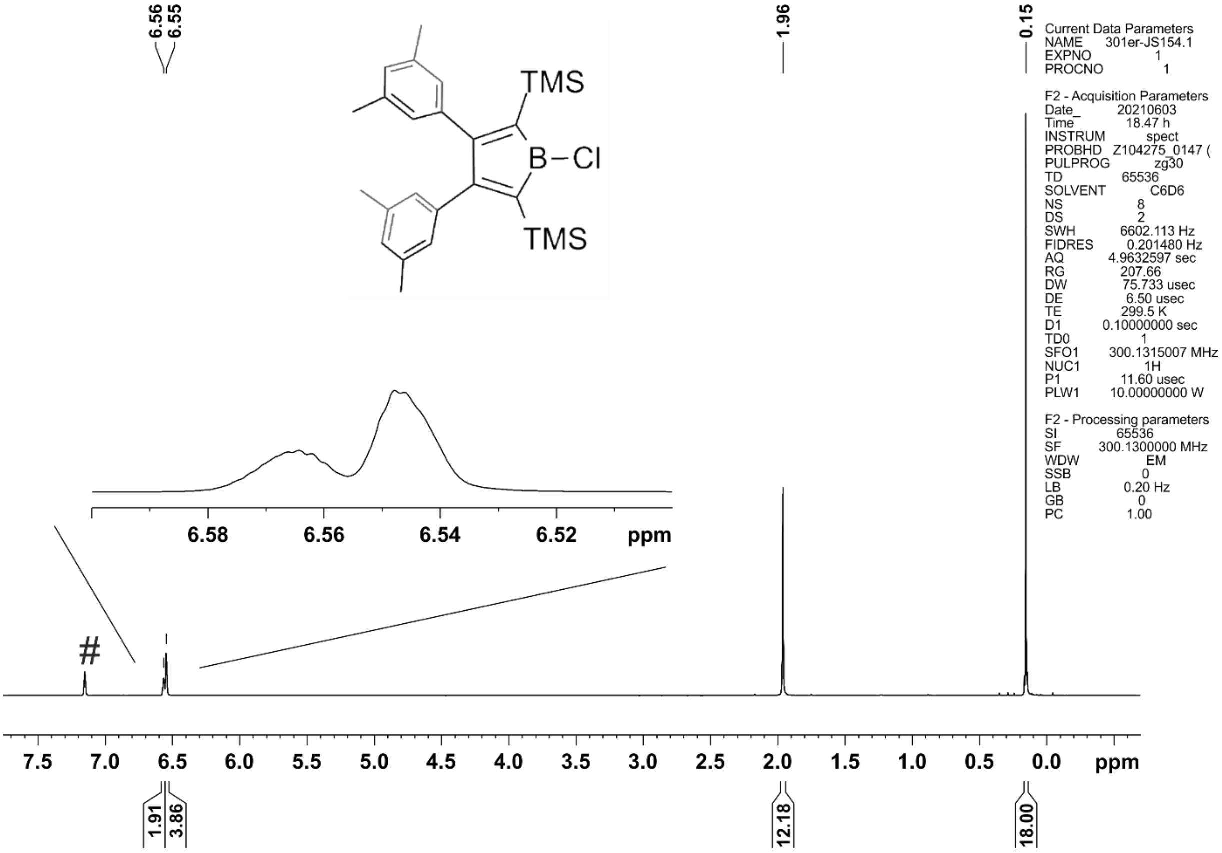
1 crystallised from solutions in hexane in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



ORTEP plot of the molecular structure of **1**. Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond length in Å: B1-C1 1.576(1), C1-C2 1.360(2), C2-C3 1.536(1), C3-C4 1.363(2), C4-B1 1.577(2), B1–Cl1 1.757(1). The structure was deposited with the CCSD.

Spectra Plots for Compound 1

1H-NMR-spectrum of chloroborole 1 in C6D6
referenced to C6D5H at 7.15 ppm



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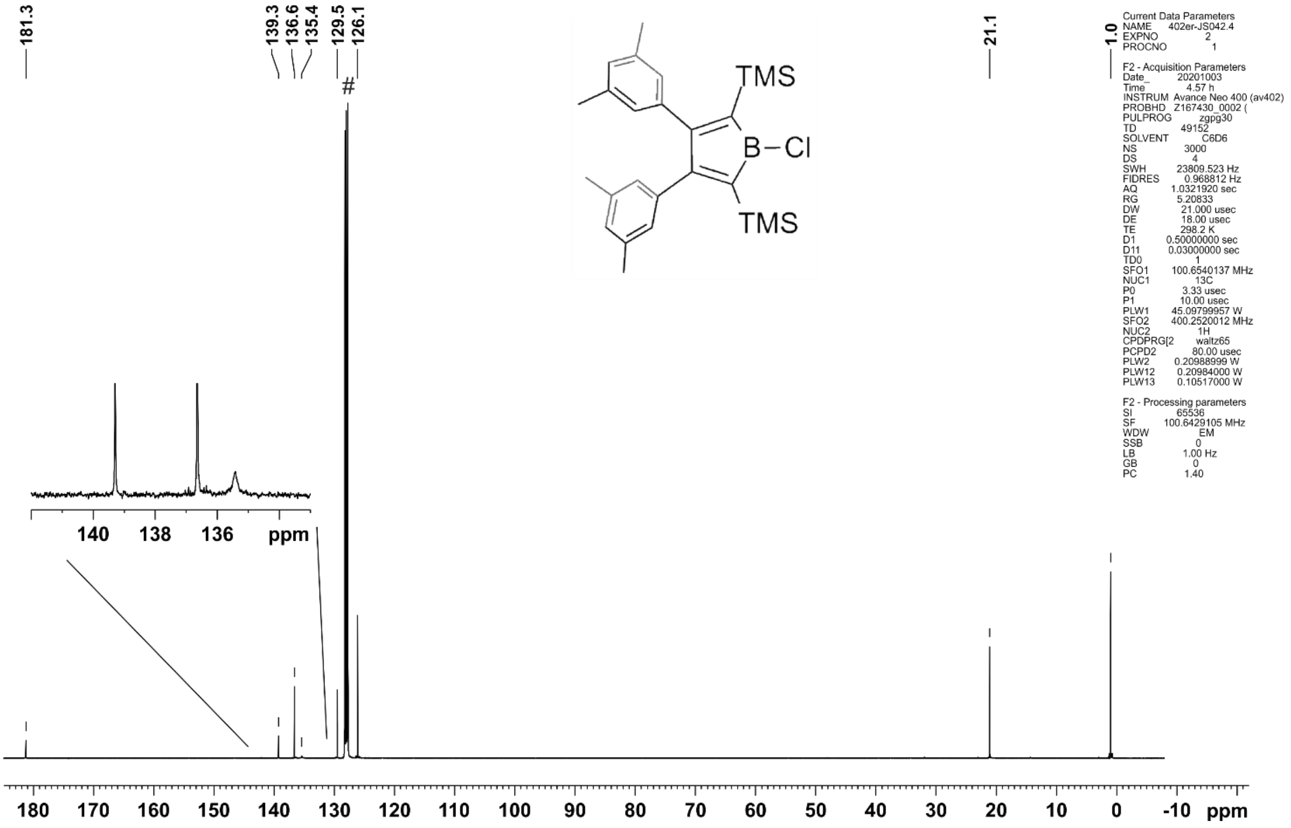
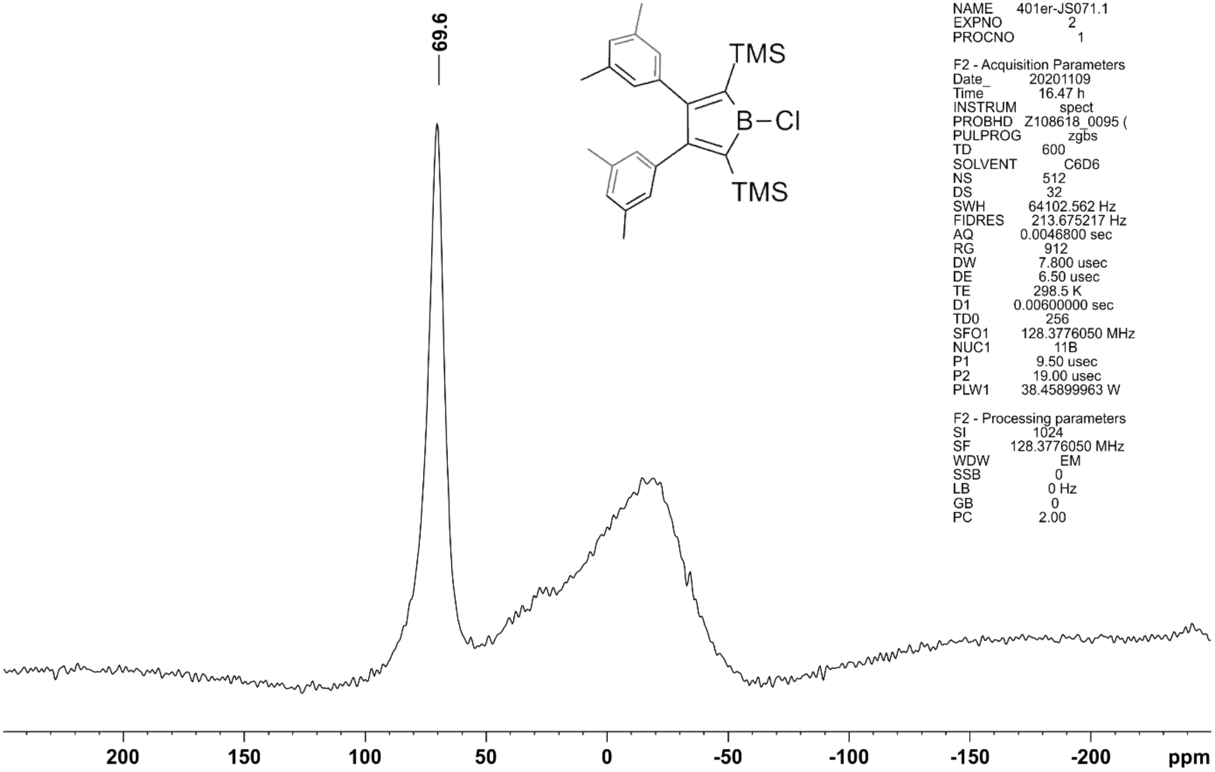


11B(background suppressed)-NMR spectrum of chloroborole **1** in C6D6



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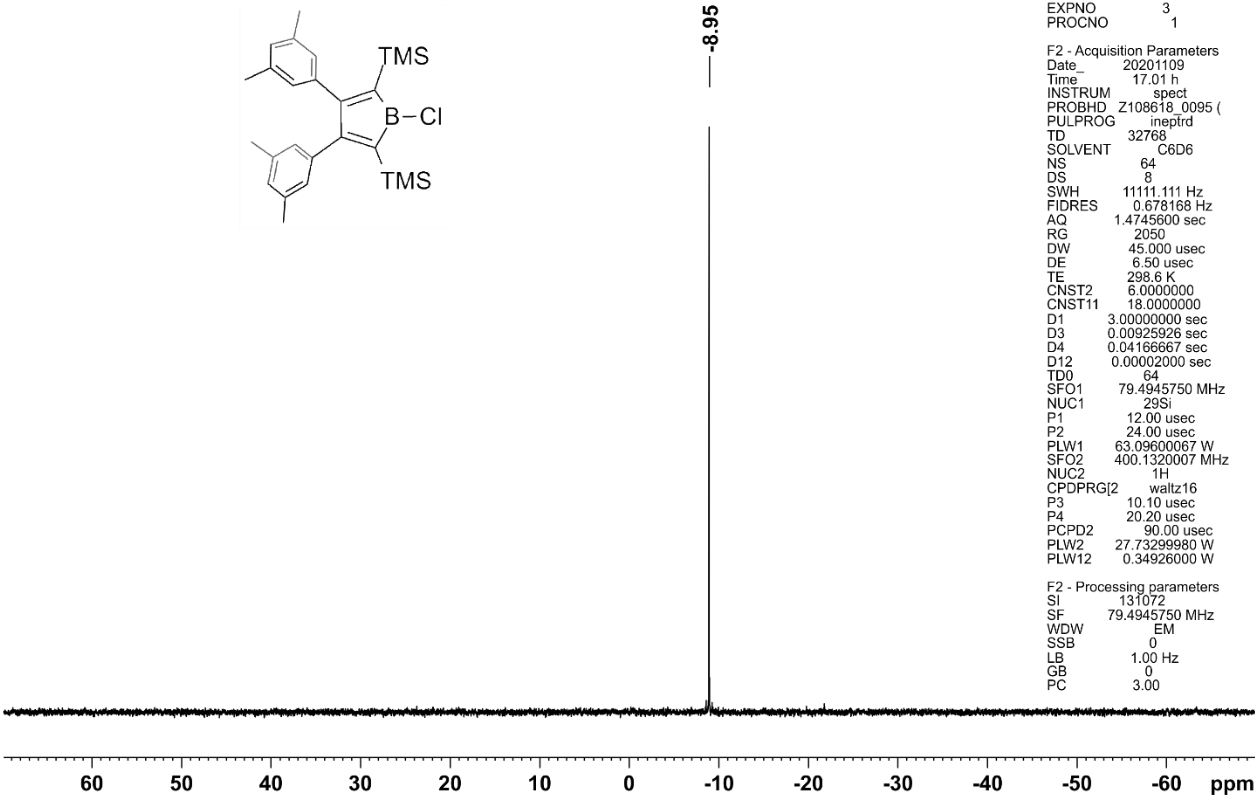

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CPDPRG[2        waltz16
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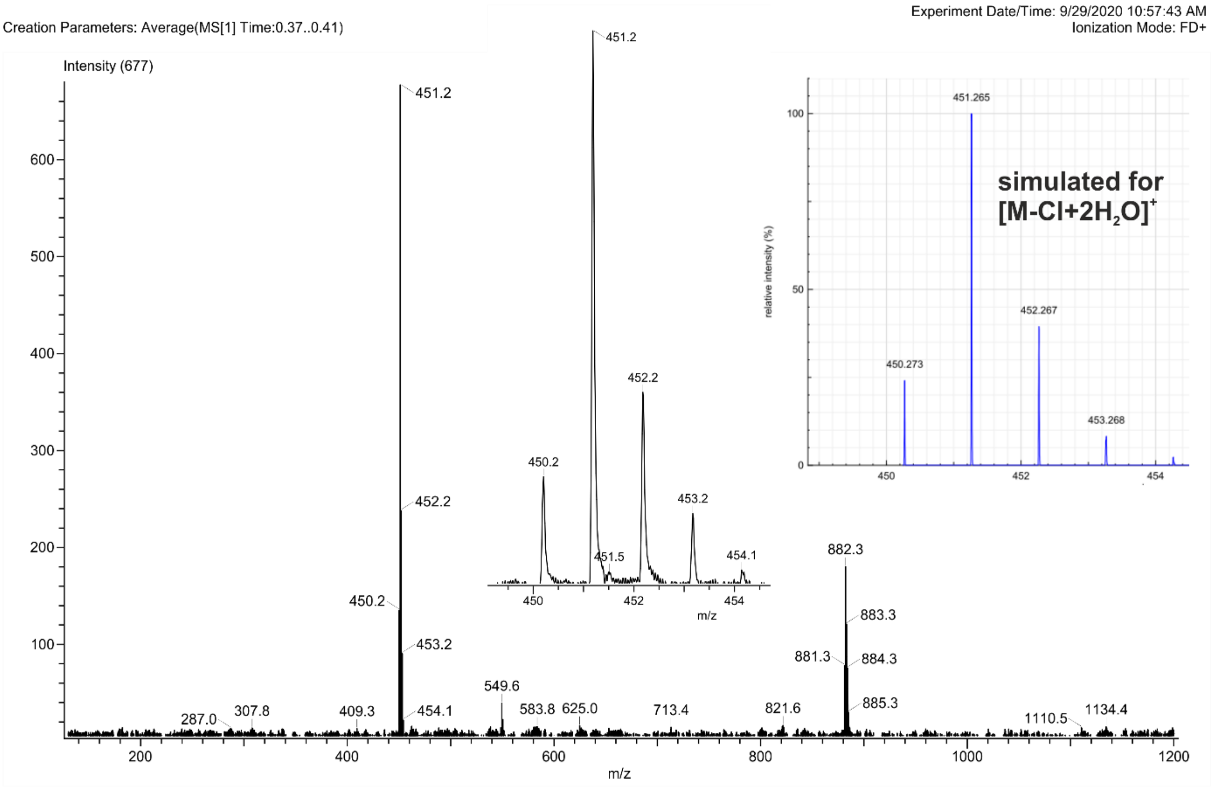
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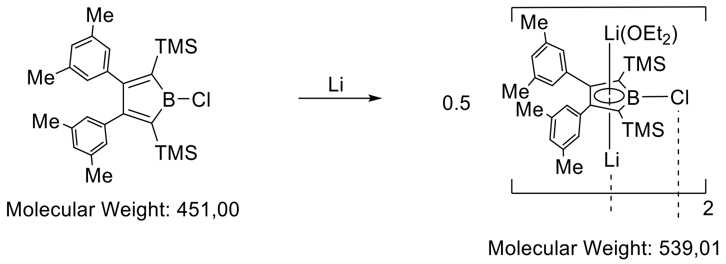
Compound 2



In a glove box, lithium chips were freshly rolled out and some of the resulting flakes of thin Li-foil (12.1 mg, 1.76 mmol, 2.1 equiv.) were added into a red solution of chloroborole **1** (396.8 mg, 0.880 mmol, 1 equiv.) in diethyl ether (10 mL, distilled) and the mixture was then stirred over night at ambient temperature. The ether was removed from the brown suspension under reduced pressure and the brown residue was suspended in toluene (2 mL, distilled). The suspension was subsequently filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B), and the filter was rinsed with additional toluene (1 mL). The toluene was removed in vacuo and the brown residue was then washed with small amounts of pentane until the residue turns into a slightly yellowish powder, which was subsequently dried under reduced pressure to give the ether solvate of lithium borolediide (213.5 mg, 0.396 mmol, 45 %). Crystals can be obtained from toluene.

Note: When thoroughly dried the dimeric adduct with one molecule of ether per borolediide is reliably obtained. When drying to short, the products contain between 1 and 2 equiv. of ether per borole, which affects on the NMR chemical shifts.

Analytical Data for Compound 2

NMR:

^{1}H (400.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.59 (s, 6H, *o-H* and *p-H*, superimposed), 3.10 (q, $^3J_{H,H}$ = 7.1 Hz, 8H, OCH_2CH_3), 2.10 (s, 12H, *m*-CH_3), 0.91 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, OCH_2CH_3), 0.38 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 143.4 (*ipso*-C_{ar}), 135.8 (*m*-C_{ar}), 130.0 (*o*-C_{ar} or *p*-C_{ar}), ca. 128.0 (C_β, superimposed by solvent signal), 126.3 (*o*-C_{ar} or *p*-C_{ar}), 99.4 (C_α), 66.3 (OCH_2CH_3), 21.4 (*m*-CH_3), 14.7 (OCH_2CH_3), 4.3 (TMS).

^{7}Li{^{1}H} (116.64 MHz, 298 K, C_6D_6): –6.9.

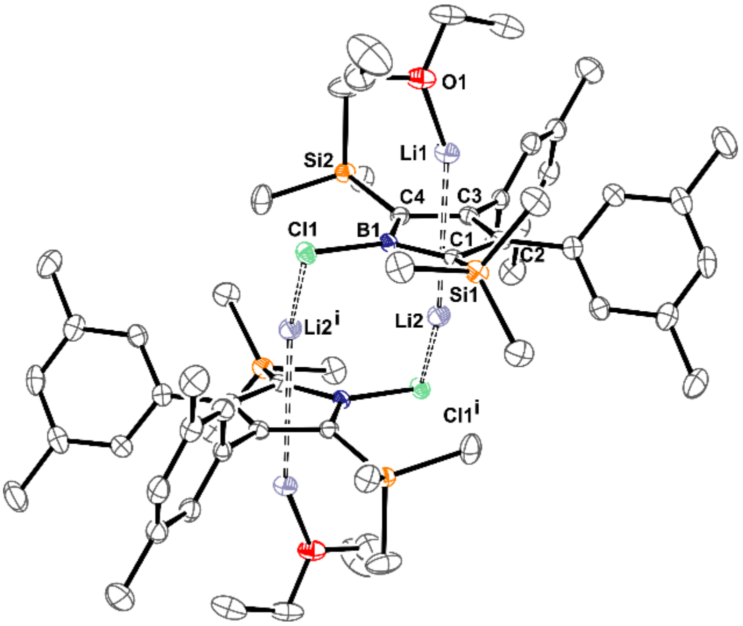
^{11}B (128.37 MHz, 298 K, C_6D_6): 31.6 ($\omega_{1/2}$ = 438 Hz).

^{29}Si-INEPT (79.49 MHz, 298 K, C_6D_6): (79.49 MHz, 298 K, C_6D_6): –12.16.

Elemental Analysis: ($C_{30}H_{46}BClLi_2OSi_2$) calcd C 66.85, H 8.60, B 2.01, Cl 6.58, Li 2.58, O 2.97, Si 10.42, observed C 66.87, H 8.99.

Crystal structure of Compound 2

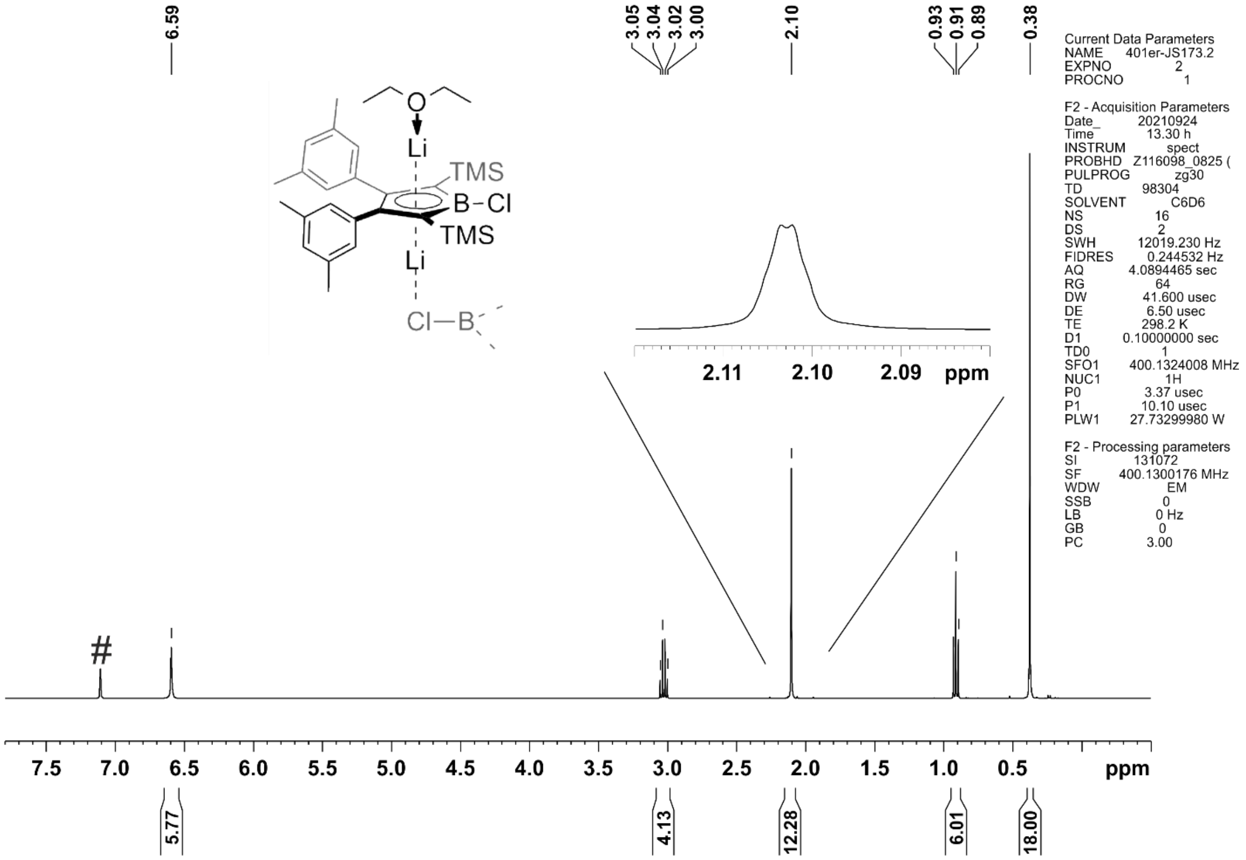
2 crystallised from solutions in toluene in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



ORTEP of the solid state molecular structure of the dimeric aggregate [Li$_2$(OEt$_2$)][**2**]. ADP drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths in Å: B1–Cl1 1.868(2), Li2-Cl1’ 2.373(3), Li1–Ct 1.825, Li2–Ct 1.854 and Table 1 of the manuscript. The structure was deposited with the CCSD.

Spectra Plots for Compound 2

1H-NMR-spectrum of compound **2** in C6D6
referenced to C6D5H at 7.15 ppm



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AQ           4.0894465 sec
RG                  64
DW              41.600 usec
DE                6.50 usec
TE               298.2 K
D1          0.10000000 sec
TD0                  1
SFO1       400.1324008 MHz
NUC1                1H
P0                3.37 usec
P1               10.10 usec
PLW1       27.73299980 W

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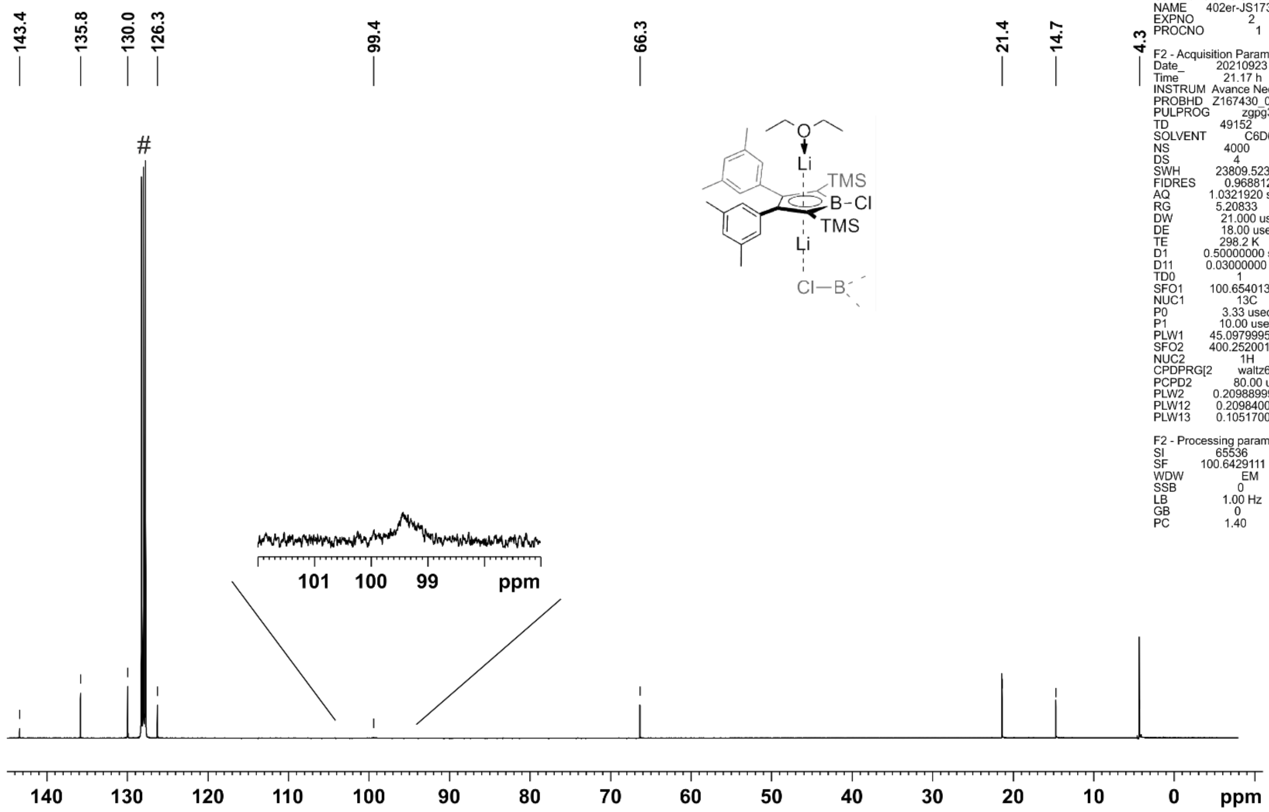
13C{1H}-NMR-spectrum of compound **2** in C6D6
referenced to C6D6 at 128.0 ppm



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RG           5.20833
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DE            18.00 usec
TE            298.2 K
D1        0.50000000 sec
D11       0.03000000 sec
TD0               1
SFO1     100.6540137 MHz
NUC1             13C
P0             3.33 usec
P1            10.00 usec
PLW1     45.09799957 W
SFO2     400.2520012 MHz
NUC2              1H
CPDPRG[2      waltz65
PCPD2         80.00 usec
PLW2      0.20988999 W
PLW12     0.20984000 W
PLW13     0.10517000 W

F2 - Processing parameters
SI             65536
SF       100.6429111 MHz
WDW               EM
SSB                0
LB           1.00 Hz
GB                 0
PC              1.40
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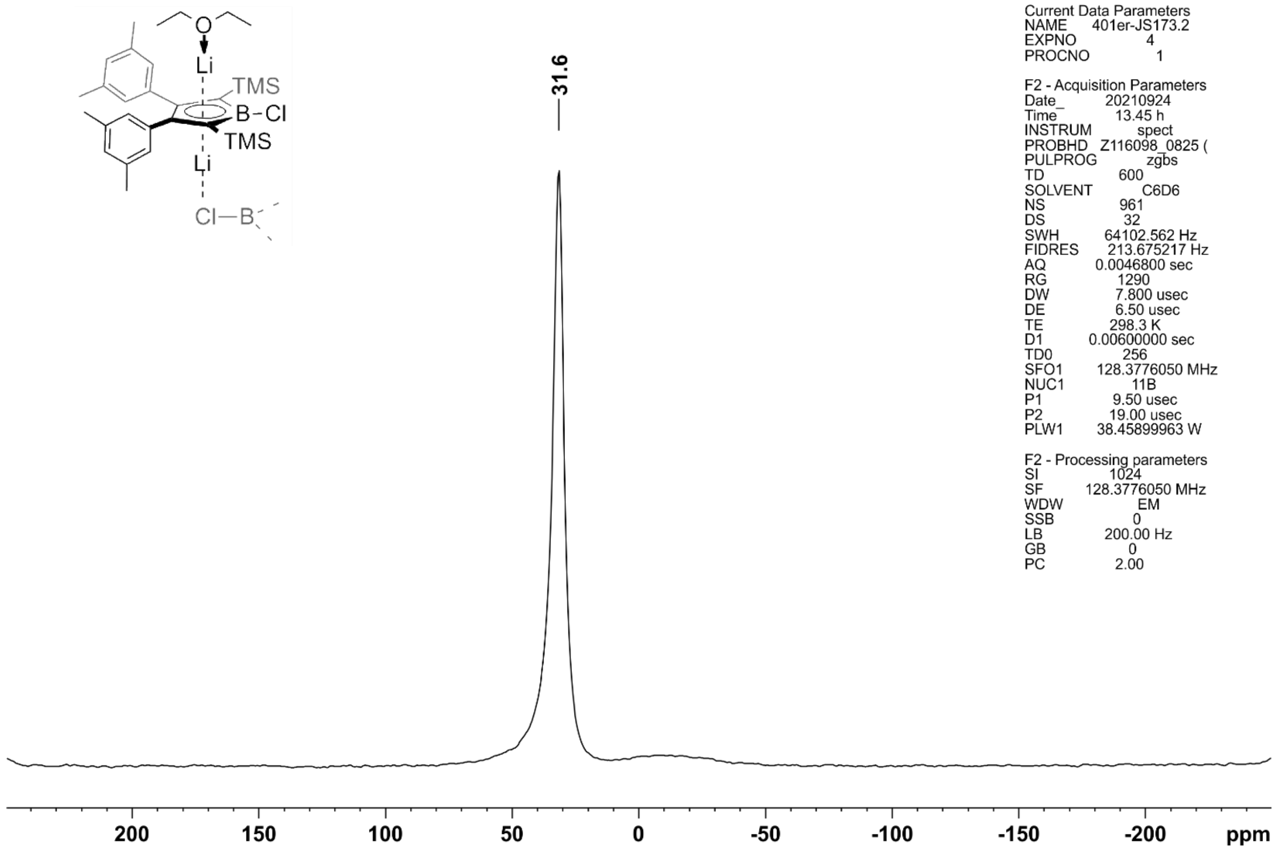
11B-NMR spectrum (background suppressed) of compound **2** in C6D6



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Current Data Parameters
NAME     401er-JS173.2
EXPNO            4
PROCNO           1

F2 - Acquisition Parameters
Date_        20210924
Time          13.45 h
INSTRUM         spect
PROBHD   Z116098_0825 (
PULPROG          zgbs
TD              600
SOLVENT          C6D6
NS              961
DS               32
SWH       64102.562 Hz
FIDRES   213.675217 Hz
AQ        0.0046800 sec
RG             1290
DW            7.800 usec
DE             6.50 usec
TE            298.3 K
D1       0.00600000 sec
TD0             256
SFO1    128.3776050 MHz
NUC1            11B
P1             9.50 usec
P2            19.00 usec
PLW1    38.45899963 W

F2 - Processing parameters
SI             1024
SF      128.3776050 MHz
WDW              EM
SSB               0
LB           200.00 Hz
GB                0
PC             2.00
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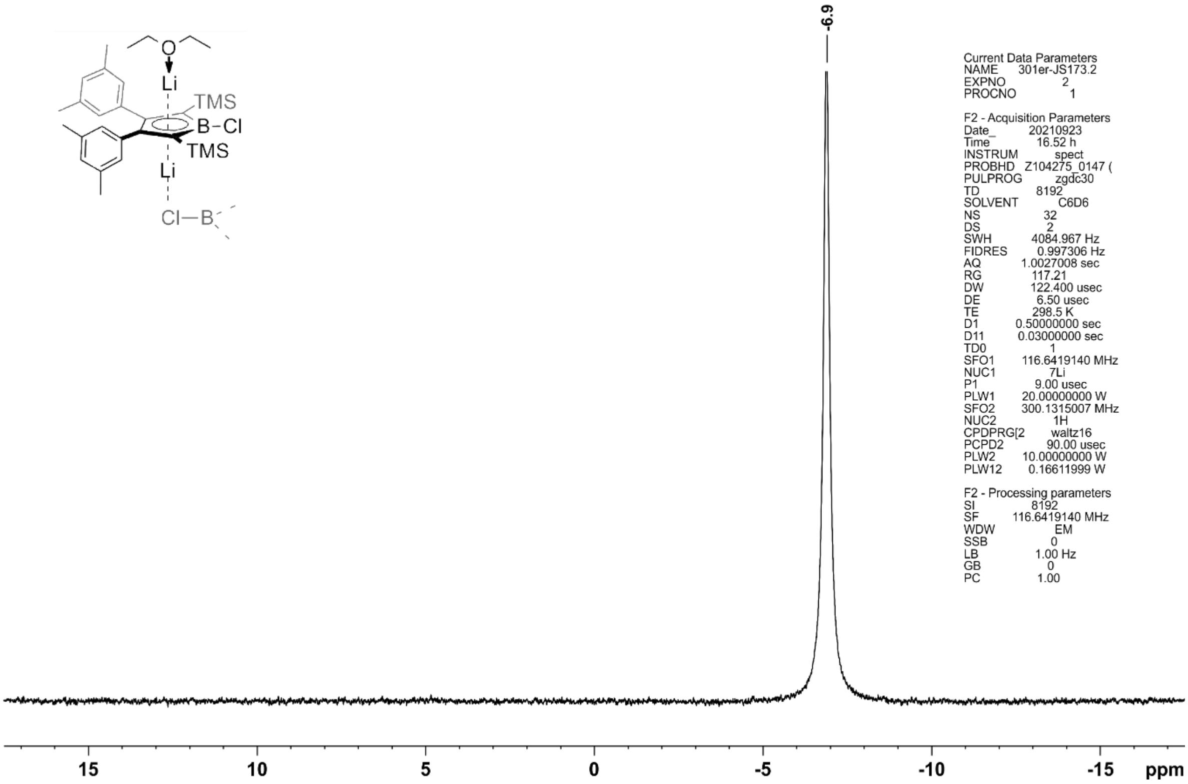
7Li-NMR-spectrum of compound **2** in C6D6



Current Data Parameters

NAME	301er-JS173.2
EXPNO	2
PROCNO	1

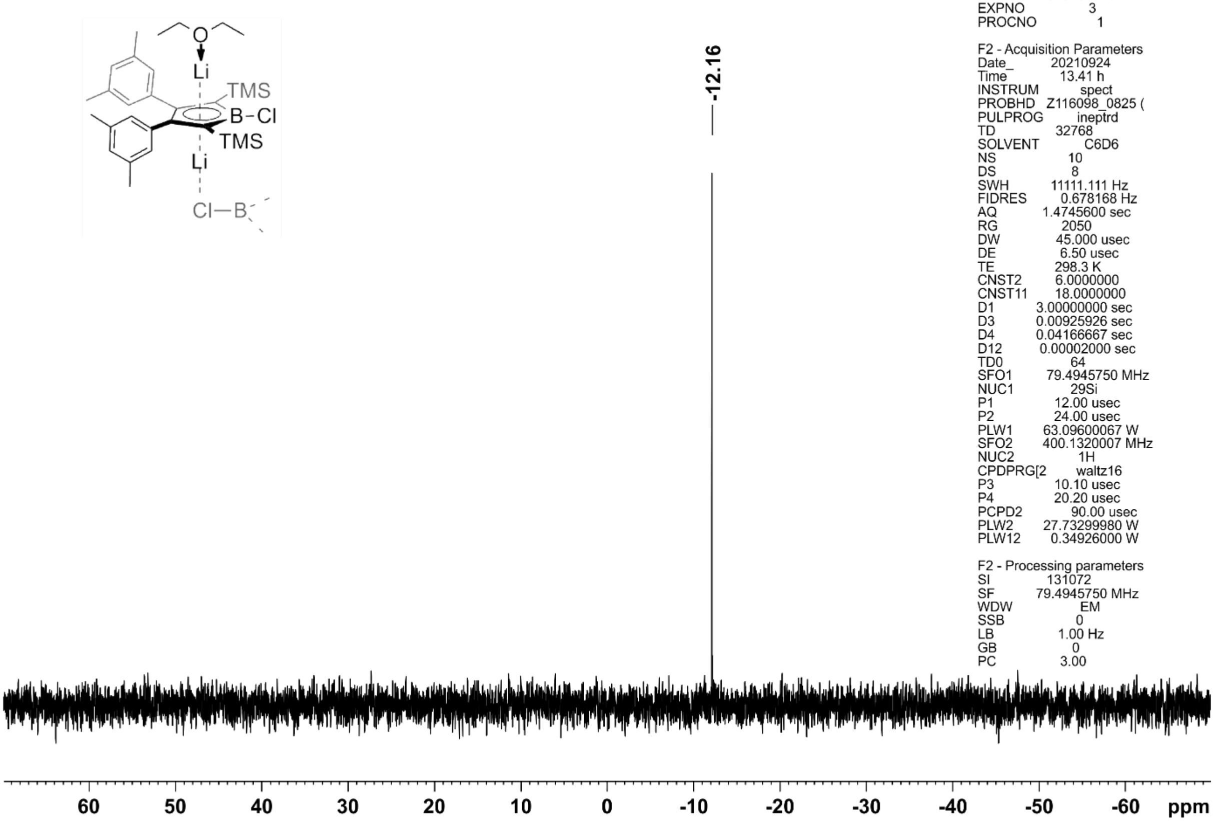
F2 - Acquisition Parameters

Date_	20210923
Time	16.52 h
INSTRUM	spect
PROBHD	Z104275_0147 (
PULPROG	zgdc30
TD	8192
SOLVENT	C6D6
NS	32
DS	2
SWH	4084.967 Hz
FIDRES	0.997306 Hz
AQ	1.0027008 sec
RG	117.21
DW	122.400 usec
DE	6.50 usec
TE	298.5 K
D1	0.50000000 sec
D11	0.03000000 sec
TD0	1
SFO1	116.6419140 MHz
NUC1	7Li
P1	9.00 usec
PLW1	20.00000000 W
SFO2	300.1315007 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	90.00 usec
PLW2	10.00000000 W
PLW12	0.16611999 W

F2 - Processing parameters

SI	8192
SF	116.6419140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

29Si-INEPT-NMR spectrum of compound **2** in C6D6



Current Data Parameters

NAME	401er-JS173.2
EXPNO	3
PROCNO	1

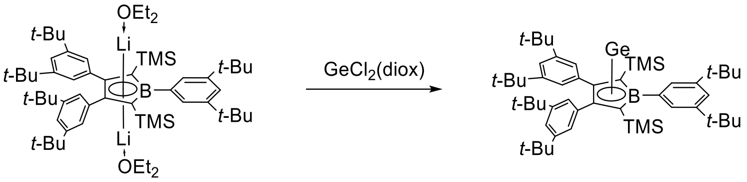
F2 - Acquisition Parameters

Date_	20210924
Time	13.41 h
INSTRUM	spect
PROBHD	Z116098_0825 (
PULPROG	ineptrd
TD	32768
SOLVENT	C6D6
NS	10
DS	8
SWH	11111.111 Hz
FIDRES	0.678168 Hz
AQ	1.4745600 sec
RG	2050
DW	45.000 usec
DE	6.50 usec
TE	298.3 K
CNST2	6.0000000
CNST11	18.0000000
D1	3.00000000 sec
D3	0.00925926 sec
D4	0.04166667 sec
D12	0.00002000 sec
TD0	64
SFO1	79.4945750 MHz
NUC1	29Si
P1	12.00 usec
P2	24.00 usec
PLW1	63.09600067 W
SFO2	400.1320007 MHz
NUC2	1H
CPDPRG[2	waltz16
P3	10.10 usec
P4	20.20 usec
PCPD2	90.00 usec
PLW2	27.73299980 W
PLW12	0.34926000 W

F2 - Processing parameters

SI	131072
SF	79.4945750 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	3.00

Compound 3a



[Li(OEt$_2$)]$_2$[A-Ph*]

Molecular Weight: 934,7753

3a

Molecular Weight: 846,5182

In a glovebox, compound **[Li(OEt$_2$)]$_2$[A-Ph*]** (50.3 mg, 0.054 mmol, 1 eq) was dissolved in dry and degassed diethyl ether (1 mL). This solution was added to a suspension of GeCl$_2$·1,4-dioxane (12.5 mg, 0.054 mmol, 1 eq) in dry and degassed diethyl ether (1.5 mL). The suspension was stirred for ten minutes at ambient temperature and the solvent of the reaction mixture was afterwards removed under reduced pressure. The resulting solid was extracted with dry and degassed hexane (1 x 1 mL, 2 x 0.5 mL) and the solvent of the colourless extract was once again removed under reduced pressure. Compound **3a** (43.8 mg, 0.052 mmol, 96 %) was obtained as a colourless solid in a purity of approximately 95 % according to NMR analysis.

Note: Further purification by means of quantitative crystallization remained unsuccessful due to the high solubility of compound **3a**. Crystals suitable for x-ray crystallography were grown from a saturated hexane solution by slow evaporation of the solvent at ambient temperature.

Analytical Data for Compound 3a

NMR:

^{1}H (400.13 MHz, 298 K, C$_6$D$_6$, CD$_5$H at 7.15 ppm): 7.68 (d, $^4J_{HH}$ = 1.9 Hz, 2H, *o-H$_{ar1}$*), 7.48 (t, $^4J_{HH}$ = 1.9 Hz, 1H, *p-H$_{ar1}$*), 7.21 (t, $^4J_{HH}$ = 1.8 Hz, 2H, *p-H$_{ar3,4}$*), 7.12 (d, $^4J_{HH}$ = 1.8 Hz, 4H, *o-H$_{ar3,4}$*), 1.43 (s, 36H, Ar$_1$-C(*Me*)$_3$), 1.15 (s, 36H, Ar$_{3,4}$-C(*Me*)$_3$), –0.02 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, C$_6$D$_6$, solvent signal at 128.0 ppm): 150.1 (*m-C$_{ar3,4}$*), 148.8 (*m-C$_{Ar1}$*), 142.5 (*ipso-C$_{ar1}$*), 141.8 (borole-*C$_{3,4}$*), 136. 3 (*ipso-C$_{ar3,4}$*), 129.6 (*o-C$_{ar1}$*), 126.8 (br, *o-C$_{ar3,4}$*), 120.7 (*p-C$_{ar3,4}$*), 119.6 (*p-C$_{ar1}$*), 113.2 (borole-*C$_{2,5}$*), 34.9 (Ar$_1$-*C*(CH$_3$)$_3$), 34.7 (Ar$_{3,4}$-*C*(CH$_3$)$_3$),31.9 (Ar$_1$-(C(*C*H$_3$)$_3$), 31.5 (Ar$_{3.4}$-(C(*C*H$_3$)$_3$), 2.3 (Si(*C*H$_3$)$_3$).

^{11}B (128.38 MHz, 298 K, C$_6$D$_6$): 30.2.

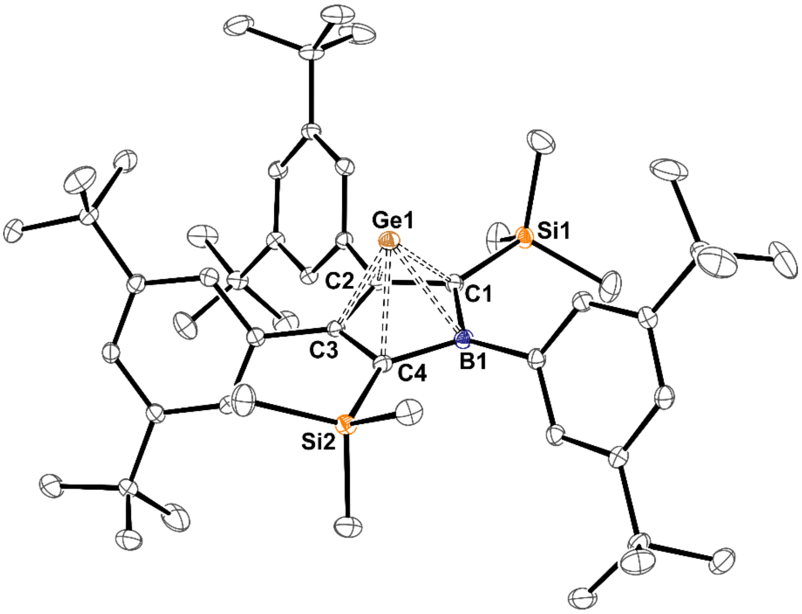
^{29}Si (99.37 MHz, 298 K, C$_6$D$_6$): (79.49 MHz, 298 K, C$_6$D$_6$): –7.4.

Elemental Analysis: $C_{52}H_{81}BSi_2Ge$ calcd C 73.84, H 9.65; observed C 74.49, H 10.25.

LIFDI-MS: calcd exact mass: 846.5 m/z; observed m/z: 846.3 [M]$^+$.

Crystal structure of Compound 3a

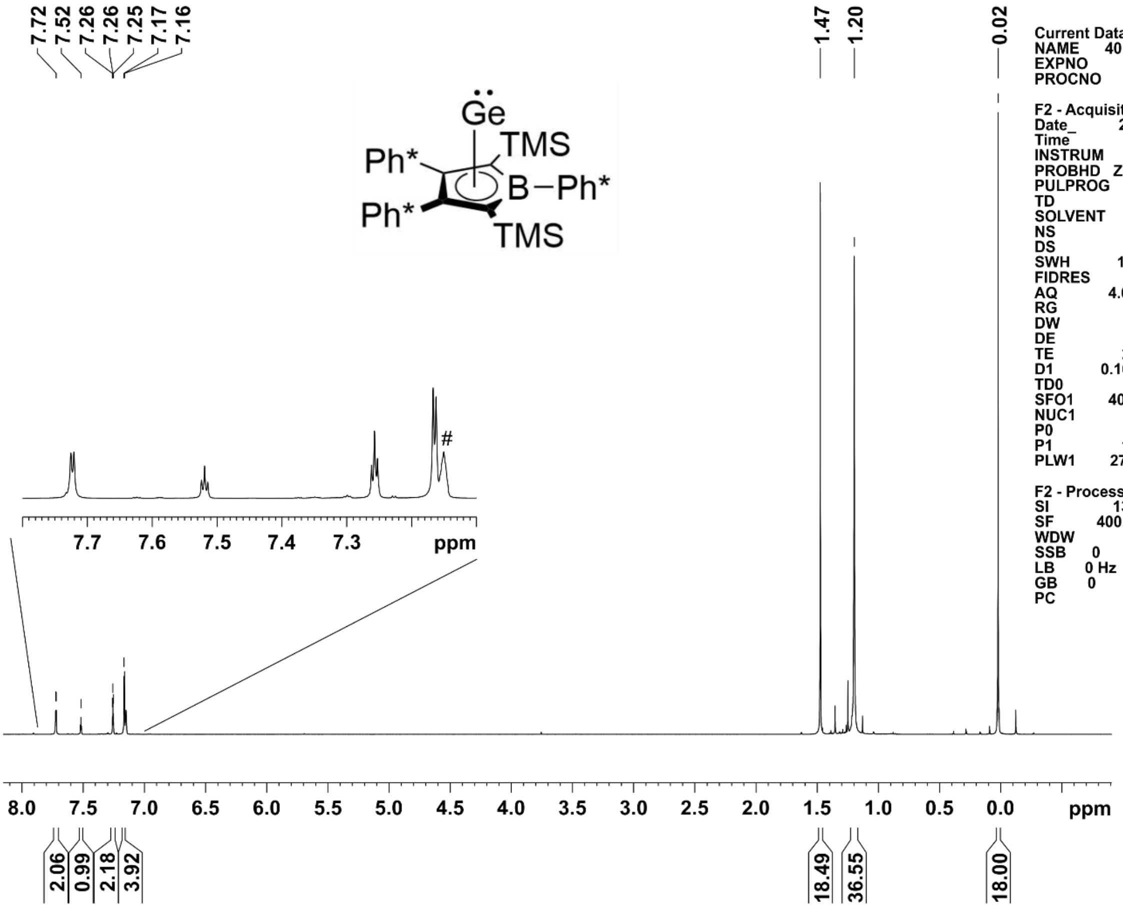
A few crystals of **3a** suitable for X-ray diffraction were isolated from evaporation of hexane solutions. For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



ORTEP plot of the molecular structure of **3a.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms and a lattice hexane molecule have been omitted for the sake of clarity. Selected bond length: B1–C1 1.560(2), C1–C2 1.460(2), C2–C3 1.439(1), C3–C4 1.460(2), C4–B1 1.559(2), B1–Ge1 2.272(1), C1–Ge1 2.211(1), C2–Ge1 2.193(1), C3–Ge1 2.205(1), C4–Ge1 2.206(1).

Spectra Plots for Compound 3a

1H-NMR-spectrum of **3a** in C6D6
referenced to C6D5H at 7.15 ppm



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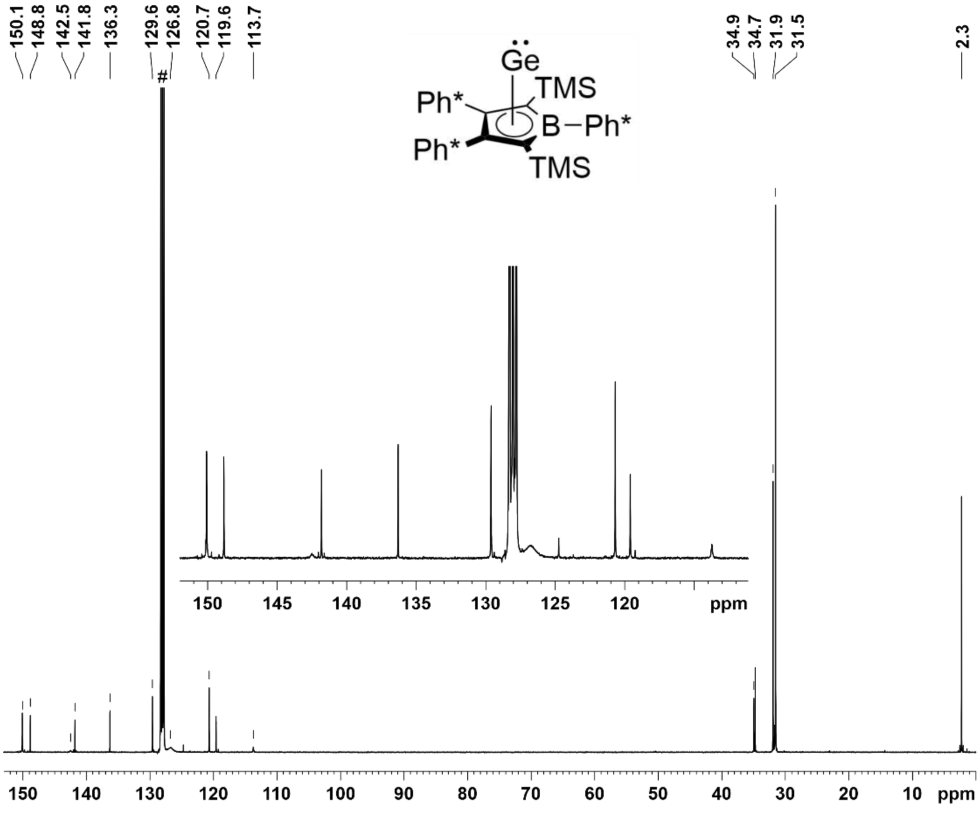
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20200608
Time             19.27 h
INSTRUM          spect
PROBHD   Z108618_0095 (
PULPROG          zg30
TD              98304
SOLVENT          C6D6
NS                 16
DS                  2
SWH         12019.230 Hz
FIDRES       0.244532 Hz
AQ          4.0894465 sec
RG               71.8
DW             41.600 usec
DE              6.50 usec
TE             298.3 K
D1        0.10000000 sec
TD0                 1
SFO1      400.1324008 MHz
NUC1               1H
P0               3.37 usec
P1              10.10 usec
PLW1      27.73299980 W

F2 - Processing parameters
SI              131072
SF        400.1300006 MHz
WDW                EM
SSB    0
LB     0 Hz
GB     0
PC               3.00
```

13C{1H}-NMR-spectrum of **3a** in C6D6
referenced to C6D6 at 128.0 ppm



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Current Data Parameters
NAME      402er-TH399.A
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_          20200609
Time              1.04 h
INSTRUM  Avance Neo 400 (av402)
PROBHD   Z167430_0002 (
PULPROG          zgpg30
TD              49152
SOLVENT          C6D6
NS               4096
DS                  4
SWH         23809.523 Hz
FIDRES       0.968812 Hz
AQ          1.0321920 sec
RG            5.20833
DW             21.000 usec
DE             18.00 usec
TE             298.2 K
D1        0.50000000 sec
D11       0.03000000 sec
TD0                 1
SFO1      100.6540137 MHz
NUC1               13C
P0               3.33 usec
P1              10.00 usec
PLW1      45.09799957 W
SFO2      400.2520012 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2           80.00 usec
PLW2       0.20988999 W
PLW12      0.20984000 W
PLW13      0.10517000 W

F2 - Processing parameters
SI              65536
SF        100.6429074 MHz
WDW                EM
SSB    0
LB              1.00 Hz
GB     0
PC              1.40
```
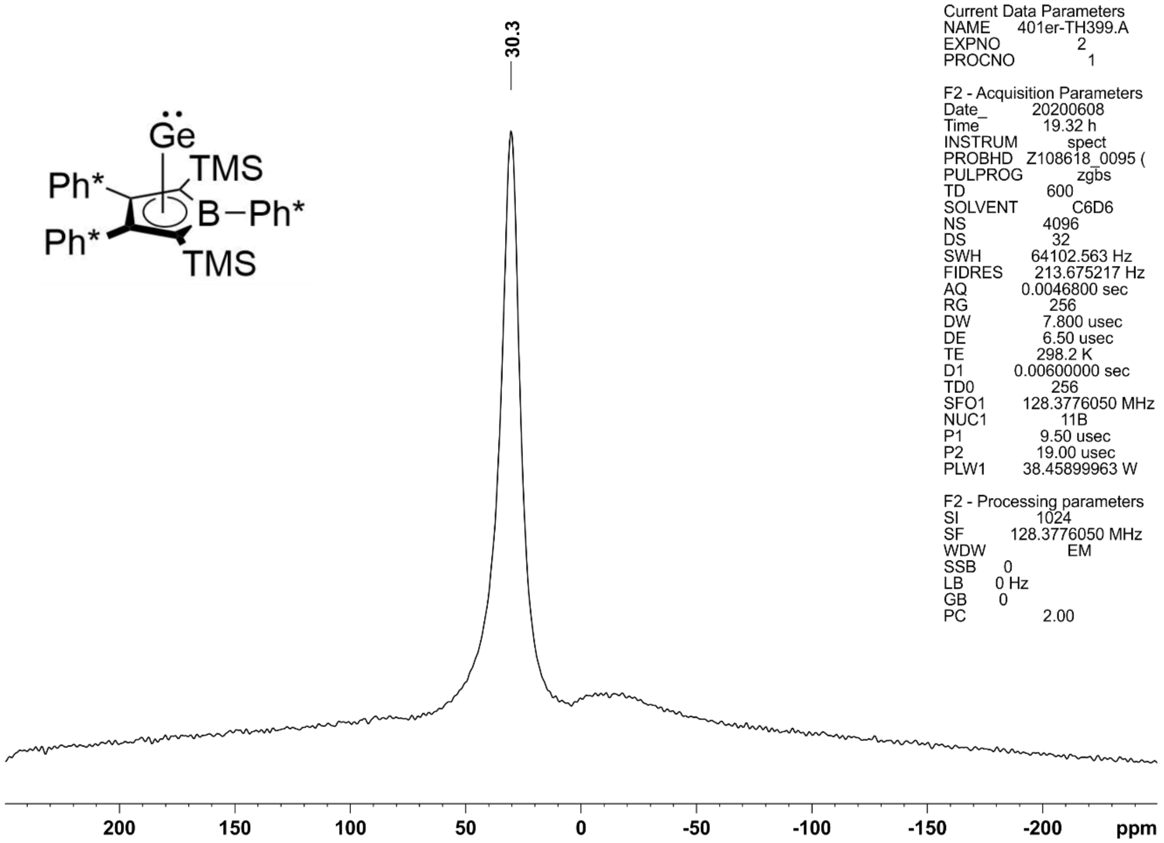
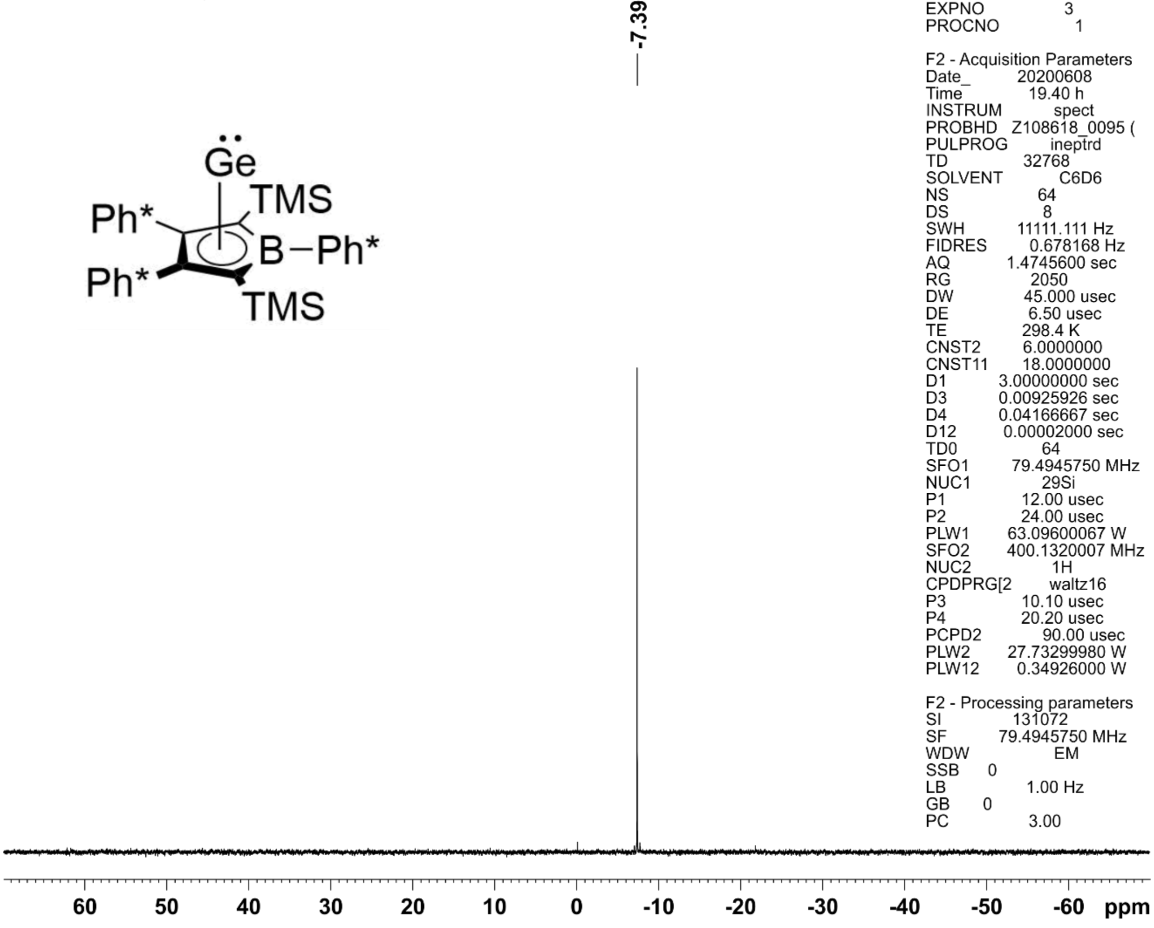

11B-NMR spectrum (background suppressed) of **3a** in C6D6



```
Current Data Parameters
NAME      401er-TH399.A
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_          20200608
Time              19.32 h
INSTRUM           spect
PROBHD   Z108618_0095 (
PULPROG            zgbs
TD                  600
SOLVENT            C6D6
NS                 4096
DS                   32
SWH          64102.563 Hz
FIDRES      213.675217 Hz
AQ          0.0046800 sec
RG                  256
DW              7.800 usec
DE              6.50 usec
TE              298.2 K
D1         0.00600000 sec
TD0                 256
SFO1      128.3776050 MHz
NUC1                11B
P1              9.50 usec
P2             19.00 usec
PLW1      38.45899963 W

F2 - Processing parameters
SI                 1024
SF        128.3776050 MHz
WDW                  EM
SSB    0
LB     0 Hz
GB     0
PC                 2.00
```

29Si-INEPT-NMR spectrum of **3a** in C6D6



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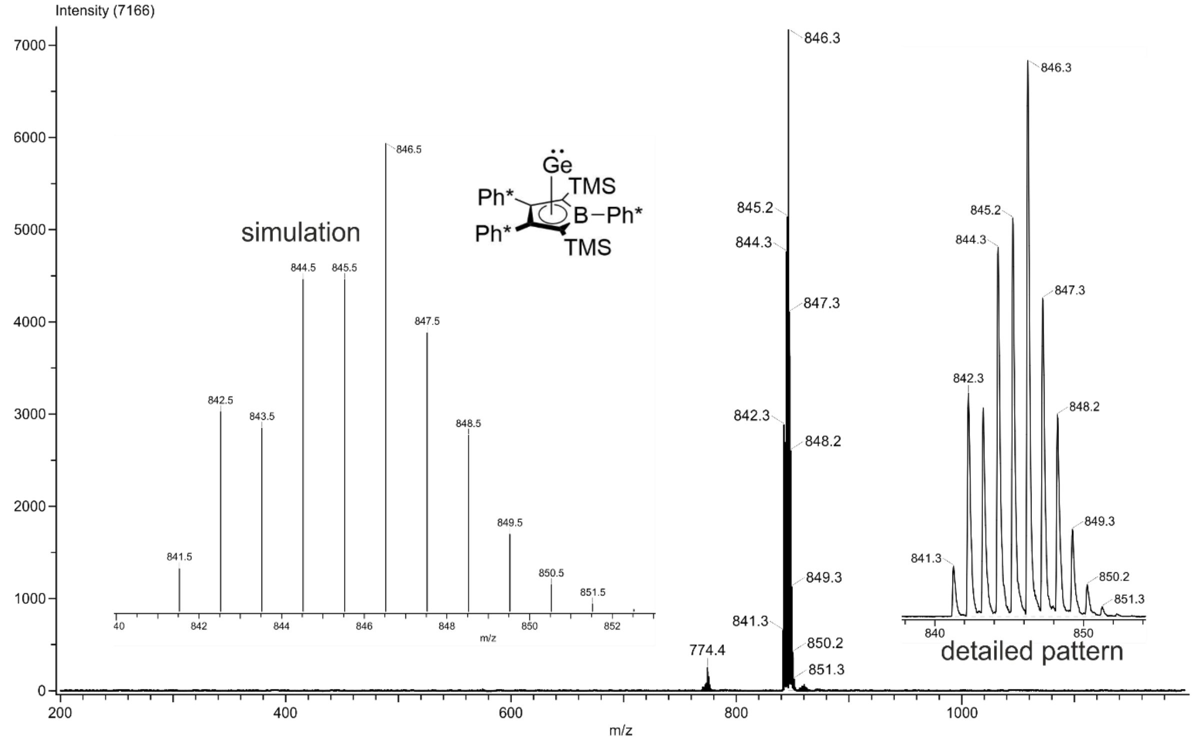
Current Data Parameters
NAME      401er-TH399.A
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_          20200608
Time              19.40 h
INSTRUM           spect
PROBHD   Z108618_0095 (
PULPROG          ineptrd
TD                32768
SOLVENT            C6D6
NS                   64
DS                    8
SWH          11111.111 Hz
FIDRES        0.678168 Hz
AQ          1.4745600 sec
RG                 2050
DW             45.000 usec
DE              6.50 usec
TE              298.4 K
CNST2         6.0000000
CNST11       18.0000000
D1         3.00000000 sec
D3         0.00925926 sec
D4         0.04166667 sec
D12        0.00002000 sec
TD0                  64
SFO1       79.4945750 MHz
NUC1               29Si
P1             12.00 usec
P2             24.00 usec
PLW1      63.09600067 W
SFO2      400.1320007 MHz
NUC2                 1H
CPDPRG[2        waltz16
P3             10.10 usec
P4             20.20 usec
PCPD2          90.00 usec
PLW2      27.73299980 W
PLW12      0.34926000 W

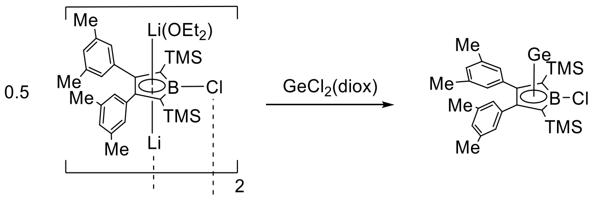
F2 - Processing parameters
SI               131072
SF         79.4945750 MHz
WDW                  EM
SSB    0
LB              1.00 Hz
GB     0
PC                 3.00
```

Experiment Date/Time: 7/1/2020 10:21:27 AM
Ionization Mode: FD+

LIFDI-MS of compound **3a**



Compound 3b



$2[Li_2(OEt)_2]$

Molecular Weight: 539,01

3b

Molecular Weight: 523,63

In a glovebox, a solution of $GeCl_2$-dioxane (168.7 mg, 0.729 mmol, 1 equiv.) in diethyl ether (6 mL) was added to a solution of borolediide **2** (431.0 mg, 0.800 mmol, 1.1 equiv.) in diethyl ether (3 mL) at ambient temperature. The resulting beige suspension was stirred at ambient temperature overnight. The ether was removed in vacuo to give a beige solid. The solid was subsequently suspended two times in hexane (10 mL, 5 mL) and volatiles are thoroughly removed in vacuo to co-evaporate 1,4-dioxane. The solid was again suspended in hexane (10 mL) and filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B), and the filter cake was washed with toluene (5 mL). The filtrate was carefully concentrated under reduced pressure until incipient crystallization to give slightly yellowish crystals which were isolated and washed with small portions of pentane to give the product **3b** (298.3 mg, 0.570 mmol, 79 %) after drying.

Analytical Data for Compound 3b

NMR:

^{1}H (400.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.81 (m, 4H, *o-H*), 6.47 (m, 2H, *p-H*) 1.93 (s, 12H, *m*-CH_3), 0.19 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 138.8 (C_β), 136.9 (*m*-C_{ar}), 135.5 (*ipso*-C_{ar}), 130.1 (*o*-C_{ar}), 129.5 (*p*-C_{ar}), 106.6 (C_α), 21.0 (*m*-CH_3), 1.8 (TMS).

^{11}B (128.37 MHz, 298 K, C_6D_6): 29.2 ($\omega_{1/2}$ = 580 Hz).

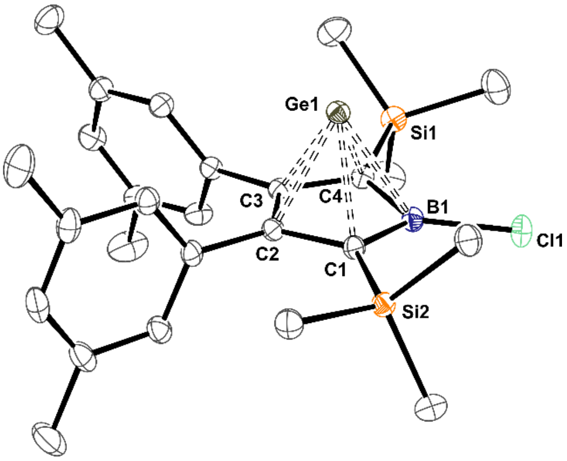
^{29}Si-INEPT (79.49 MHz, 298 K, C_6D_6): –7.03.

Elemental Analysis: ($C_{26}H_{36}BClSi_2Sn$) calcd C 59.64, H 6.93, B 2.06, Cl 6.77, Ge 13.87, Si 10.73, observed C 59.60, H 6,89.

LIFDI-MS: calcd exact mass: 524.1 m/z, observed m/z: 524.6.

Crystal structure of Compound 3b

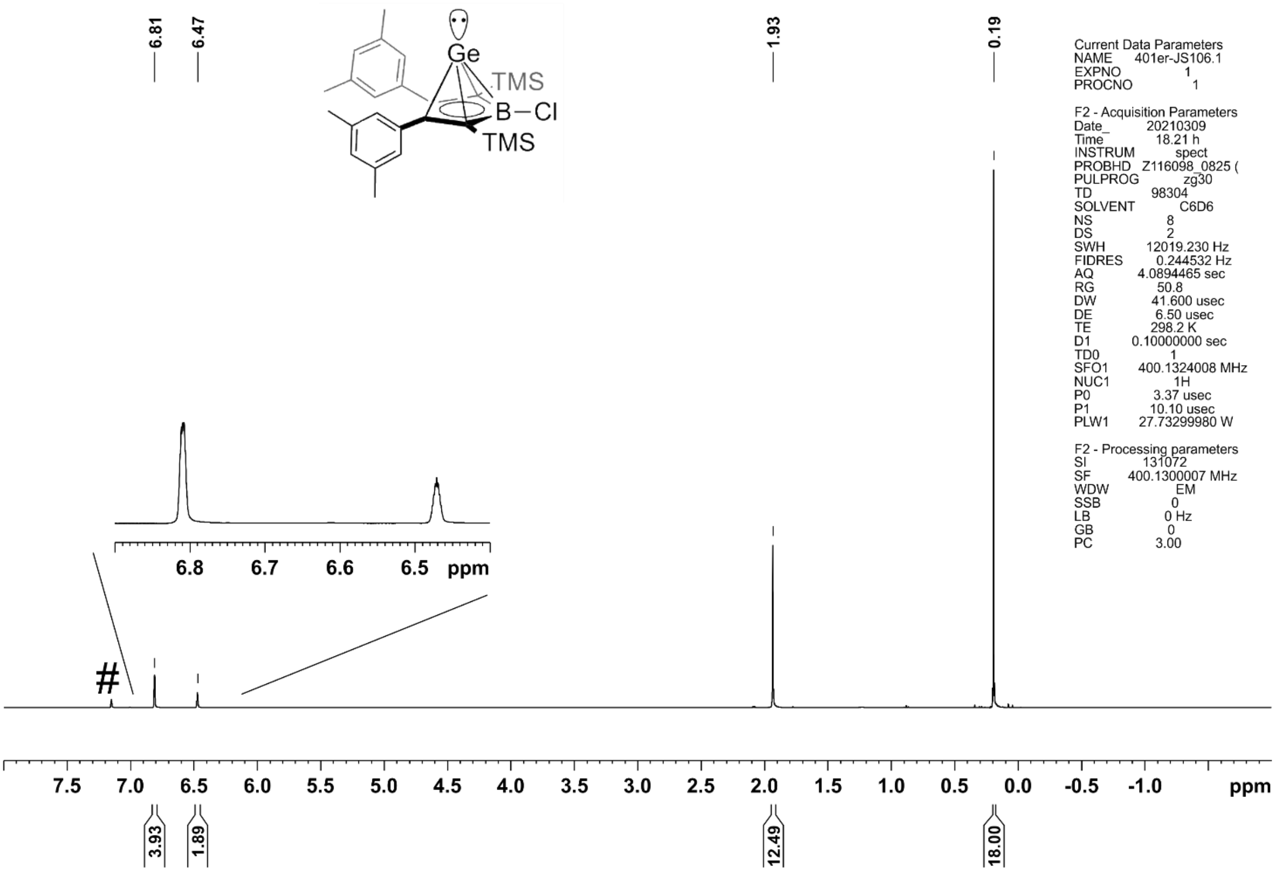
3b crystallised from hexane solutions in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



ORTEP plot of the molecular structure of **3b.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms have been omitted for the sake of clarity. The germanium vertex atom was modelled to occupy a minor fraction (ca. 2-3%) on the opposite side of the borole moiety and only the major contribution is shown. Selected bond length: B1–Cl1 1.801(1), B1–C1 1.534(2), C1–C2 1.457(2), C2–C3 1.434(2), C3–C4 1.464(2), C4–B1 1.535(2), B1–Ge1 2.297(1), C1–Ge1 2.224(1), C2–Ge1 2.204(1), C3–Ge1 2.211(1), C4–Ge1 2.225(1).

Spectra Plots for Compound 3b

1H-NMR-spectrum of compound **3b** in C6D6
referenced to C6D5H at 7.15 ppm



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Current Data Parameters
NAME      401er-JS106.1
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20210309
Time           18.21 h
INSTRUM          spect
PROBHD   Z116098_0825 (
PULPROG           zg30
TD               98304
SOLVENT           C6D6
NS                   8
DS                   2
SWH        12019.230 Hz
FIDRES      0.244532 Hz
AQ        4.0894465 sec
RG                50.8
DW          41.600 usec
DE            6.50 usec
TE             298.2 K
D1       0.10000000 sec
TD0                  1
SFO1    400.1324008 MHz
NUC1                1H
P0            3.37 usec
P1           10.10 usec
PLW1     27.73299980 W

F2 - Processing parameters
SI              131072
SF      400.1300007 MHz
WDW                 EM
SSB                  0
LB                0 Hz
GB                   0
PC                3.00
```
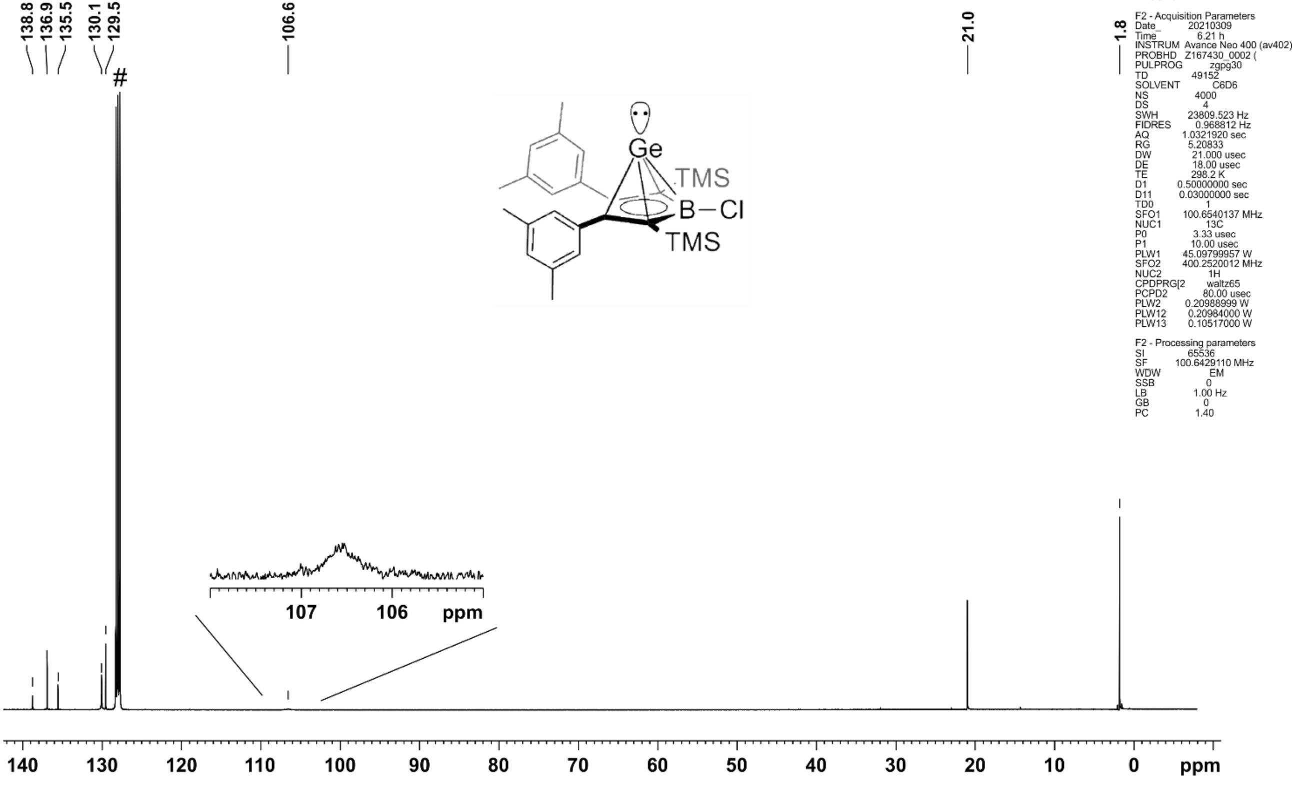
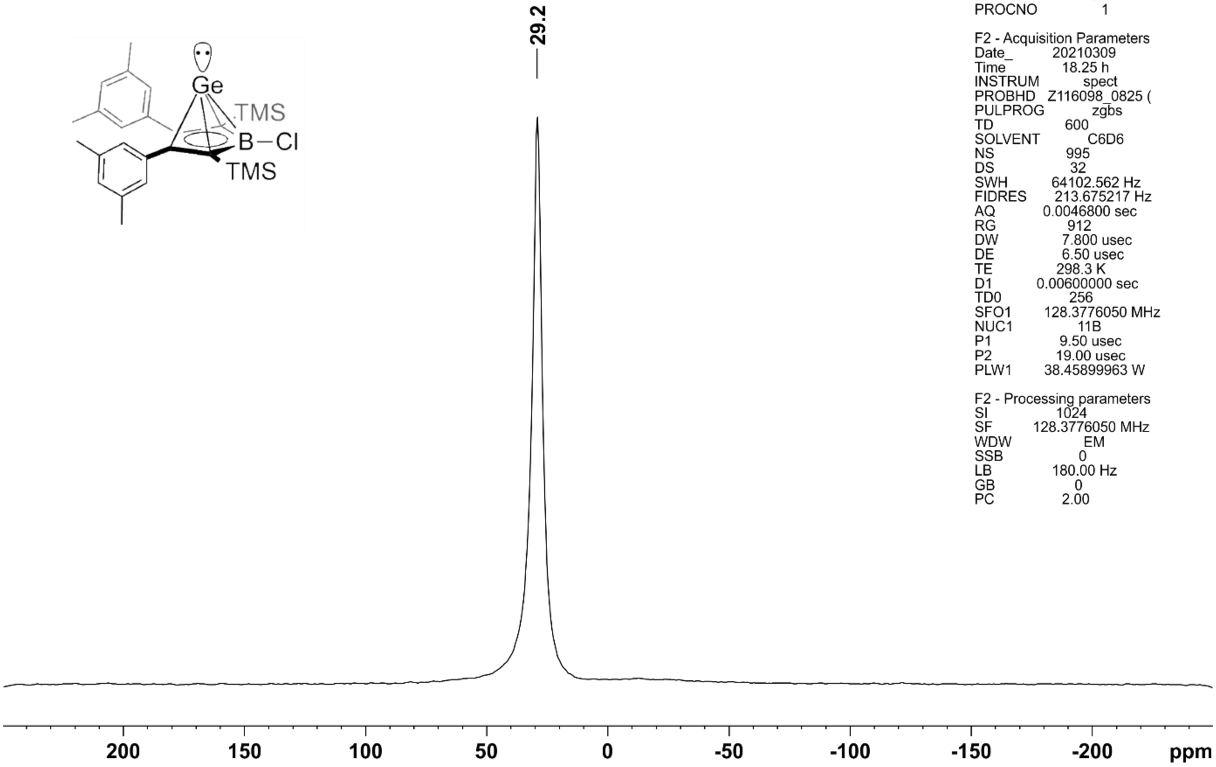

13C{1H}-NMR-spectrum of compound **3b** in C6D6
referenced to C6D6 at 128.0 ppm



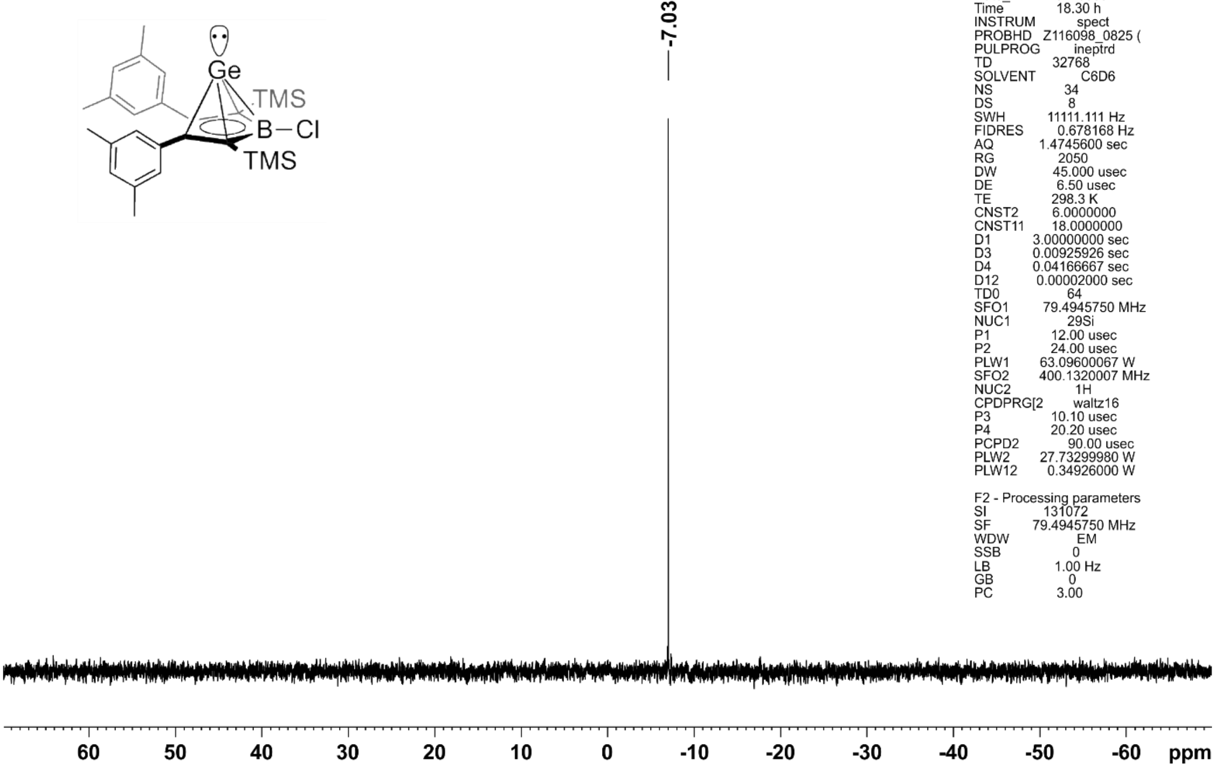
```
Current Data Parameters
NAME      402er-JS106.1
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20210309
Time            6.21 h
INSTRUM  Avance Neo 400 (av402)
PROBHD   Z167430_0002 (
PULPROG         zgpg30
TD               49152
SOLVENT           C6D6
NS                4000
DS                   4
SWH        23809.523 Hz
FIDRES      0.968812 Hz
AQ        1.0321920 sec
RG             5.20833
DW          21.000 usec
DE           18.00 usec
TE             298.2 K
D1       0.50000000 sec
D11      0.03000000 sec
TD0                  1
SFO1    100.6540137 MHz
NUC1               13C
P0            3.33 usec
P1           10.00 usec
PLW1     45.09799957 W
SFO2    400.2520012 MHz
NUC2                1H
CPDPRG[2       waltz65
PCPD2        80.00 usec
PLW2      0.20988999 W
PLW12     0.20984000 W
PLW13     0.10517000 W

F2 - Processing parameters
SI               65536
SF      100.6429110 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                1.40
```

11B-NMR spectrum (background suppressed) of compound **3b** in C6D6



```
Current Data Parameters
NAME     401er-JS106.1
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20210309
Time            18.25 h
INSTRUM          spect
PROBHD   Z116098_0825 (
PULPROG           zgbs
TD                 600
SOLVENT           C6D6
NS                 995
DS                  32
SWH        64102.562 Hz
FIDRES     213.675217 Hz
AQ       0.0046800 sec
RG                 912
DW           7.800 usec
DE           6.50 usec
TE             298.3 K
D1      0.00600000 sec
TD0                256
SFO1   128.3776050 MHz
NUC1               11B
P1           9.50 usec
P2          19.00 usec
PLW1    38.45899963 W

F2 - Processing parameters
SI                1024
SF     128.3776050 MHz
WDW                 EM
SSB                  0
LB           180.00 Hz
GB                   0
PC                2.00
```

29Si-INEPT-NMR spectrum of compound **3b** in C6D6



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Current Data Parameters
NAME     401er-JS106.1
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_         20210309
Time            18.30 h
INSTRUM          spect
PROBHD   Z116098_0825 (
PULPROG        ineptrd
TD               32768
SOLVENT           C6D6
NS                  34
DS                   8
SWH        11111.111 Hz
FIDRES      0.678168 Hz
AQ       1.4745600 sec
RG                2050
DW          45.000 usec
DE           6.50 usec
TE             298.3 K
CNST2        6.0000000
CNST11      18.0000000
D1      3.00000000 sec
D3      0.00925926 sec
D4      0.04166667 sec
D12     0.00002000 sec
TD0                 64
SFO1    79.4945750 MHz
NUC1              29Si
P1          12.00 usec
P2          24.00 usec
PLW1    63.09600067 W
SFO2   400.1320007 MHz
NUC2                1H
CPDPRG[2       waltz16
P3          10.10 usec
P4          20.20 usec
PCPD2       90.00 usec
PLW2    27.73299980 W
PLW12    0.34926000 W

F2 - Processing parameters
SI              131072
SF      79.4945750 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                3.00
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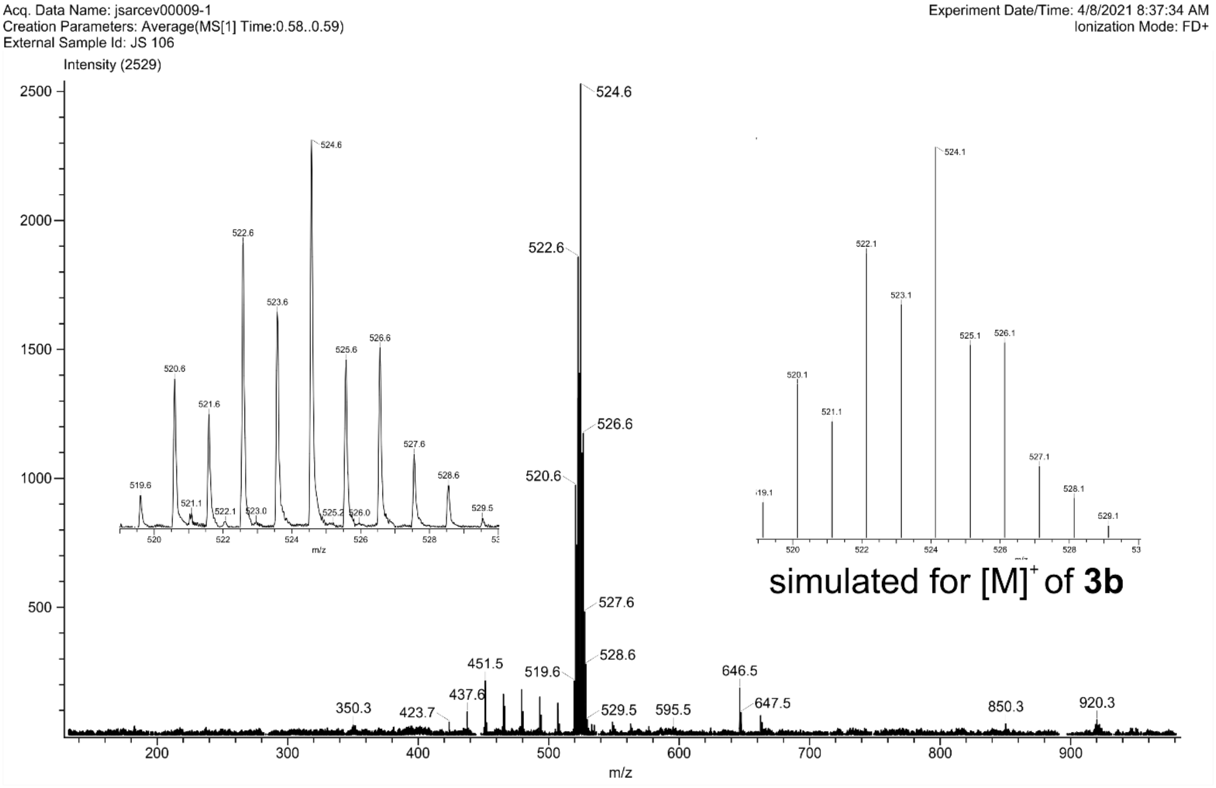
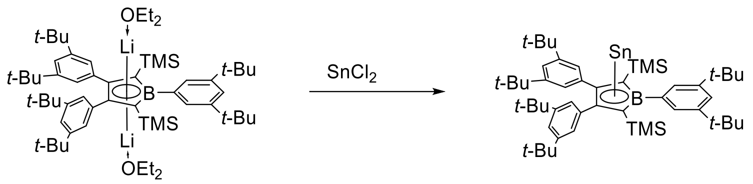


simulated for $[M]^+$ of **3b**

Compound 4a



[Li(OEt$_2$)]$_2$[A-Ph*]

Molecular Weight: 934,7753

4a

Molecular Weight: 892,4992

In a glovebox, compound **[Li(OEt$_2$)]$_2$[A-Ph*]** (47.3 mg, 0.051 mmol, 1 eq) was dissolved in dry and degassed diethyl ether (1.5 mL). The pale yellow solution was added to a suspension of $SnCl_2$ (9.6 mg, 0.051 mmol, 1 eq) in dry and degassed diethyl ether (0.5 mL). After completed addition a colourless precipitate had formed and a yellow solution was obtained. The reaction was stirred for 45 min at ambient temperature. Subsequently the reaction mixture was filtered through a syringe equipped with a thin plug of glass fiber (Whatman GF/B) and the solvent of the yellow filtrate was removed under reduced pressure. The obtained yellow solid was dissolved in dry and degassed hexane (0.2 mL) and this solution was stored openly in a glovebox. After most of the solvent evaporated, crystals of compound **4a** started to form. The mother liquor was carefully decanted off with a syringe and the crystals were washed with a small amount of cold hexane (–40 °C, few drops). The isolated crystals were dried under reduced pressure to yield compound **4a** (24.3 mg, 0.027 mmol, 54 %) as a yellow powder.

Analytical Data for Compound 4a

NMR:

^{1}H (500.25 MHz, 298 K, C_6D_6, CD_5H at 7.15 ppm): 7.70 (d, $^4J_{HH}$ = 1.9 Hz, 2H, *o-H$_{ar1}$*), 7.50 (t, $^4J_{HH}$ = 1.9 Hz, 1H, *p-H$_{ar1}$*), 7.24 (t, $^4J_{HH}$ = 1.8 Hz, 2H, *p-H$_{ar3,4}$*), 7.16 (br d, 4H, *o-H$_{ar3,4}$*), 1.48 (s, 18H, Ar$_1$-C(*Me*)$_3$), 1.20 (s, 36H, Ar$_{3,4}$-C(*Me*)$_3$), 0.04 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, C_6D_6, solvent signal at 128.0 ppm): 149.9 (*m-C$_{ar3,4}$*), 148.6 (*m-C$_{Ar1}$*), 145.7 (borole-*C$_{3,4}$*), 143.1 (*ipso-C$_{ar1}$*), 137.2 (*ipso-C$_{ar3,4}$*), 130.5 (*o-C$_{ar1}$*), ca. 128.0 (*o-C$_{ar3,4}$*, completely overlapped by the solvent signal, assigned via HSQC), 120.4 (*p-C$_{ar3,4}$*), 119.3 (*p-C$_{ar1}$*), 114.3 (borole-*C$_{2,5}$*), 34.9 (Ar$_1$-*C*(CH$_3$)$_3$), 34.7 (Ar$_{3,4}$-*C*(CH$_3$)$_3$), 31.9 (Ar$_1$-(C(*C*H$_3$)$_3$), 31.6 (Ar$_{3.4}$-(C(*C*H$_3$)$_3$), 3.1 (Si(*C*H$_3$)$_3$).

^{11}B (160.50 MHz, 298 K, C_6D_6): 32.2.

^{29}Si-INEPT (99.38 MHz, 298 K, C_6D_6): –8.5.

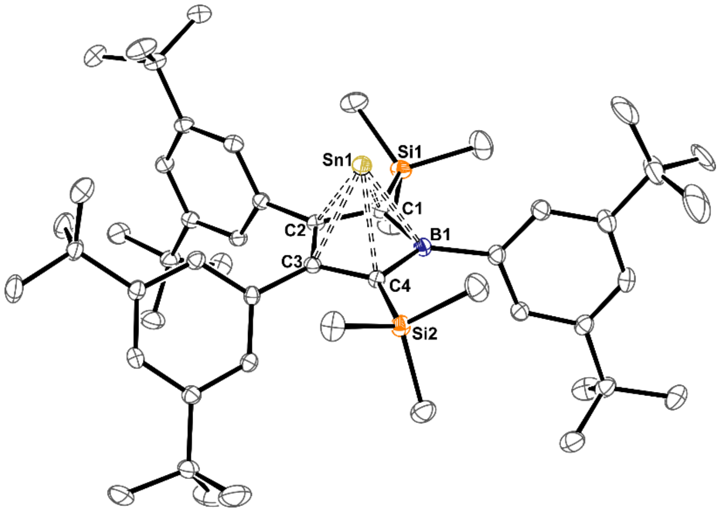
^{119}Sn{^{1}H} (186.19 MHz, 298 K, C_6D_6): –1896.94 (^{10}B isotopologue), –1897.19 (^{11}B isotopologue).

Elemental Analysis: $C_{60}H_{101}BLi_2O_2Si_2$ calcd C 77.05, H 10.88; observed C 76.70, H 11.06.

LIFDI-MS: calcd exact mass: 892.5 m/z; observed m/z: 892.3 [M]$^+$.

Crystal structure of Compound 4a

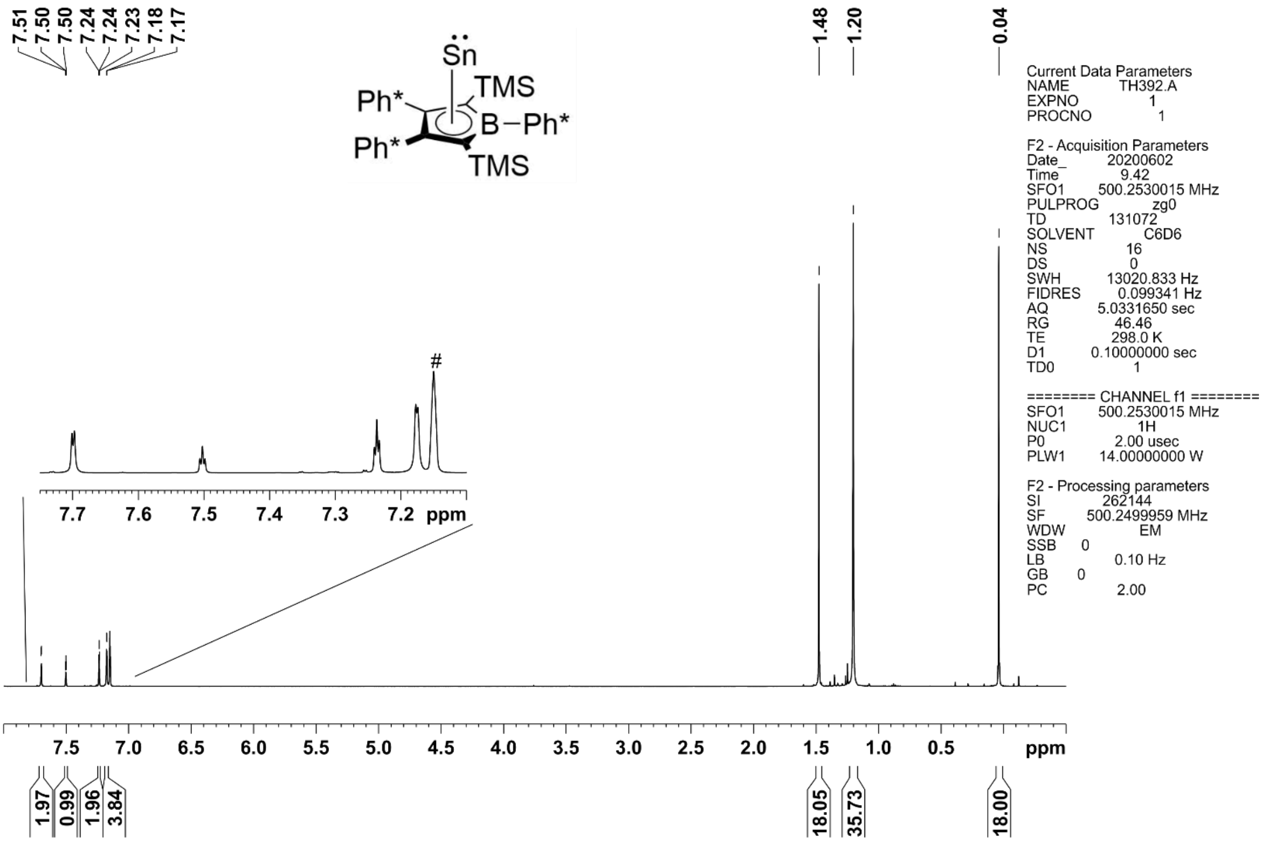
4a crystallised from pentane solutions through concentration by evaporation at ambient temperature. For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



ORTEP plot of the molecular structure of **4a.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms, disordered *t*Bu-groups and a second molecule in the asymmetric unit have been omitted for the sake of clarity. Selected bond length: B1–C1 1.555(2), C1–C2 1.459(2), C2–C3 1.437(2), C3–C4 1.459(2), C4–B1 1.561(2), B1–Sn1 2.462(2), C1–Sn1 2.398(2), C2–Sn1 2.386(2), C3–Sn1 2.422(2), C4–Sn1 2.392(2).

Spectra Plots for Compound 4a

1H-NMR-spectrum of **4a** in C6D6
referenced to C6D5H at 7.15 ppm



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PROCNO              1

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TD               131072
SOLVENT            C6D6
NS                   16
DS                    0
SWH        13020.833 Hz
FIDRES      0.099341 Hz
AQ        5.0331650 sec
RG                46.46
TE              298.0 K
D1       0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1      500.2530015 MHz
NUC1                 1H
P0               2.00 usec
PLW1      14.00000000 W

F2 - Processing parameters
SI               262144
SF        500.2499959 MHz
WDW                  EM
SSB    0
LB                0.10 Hz
GB     0
PC                 2.00
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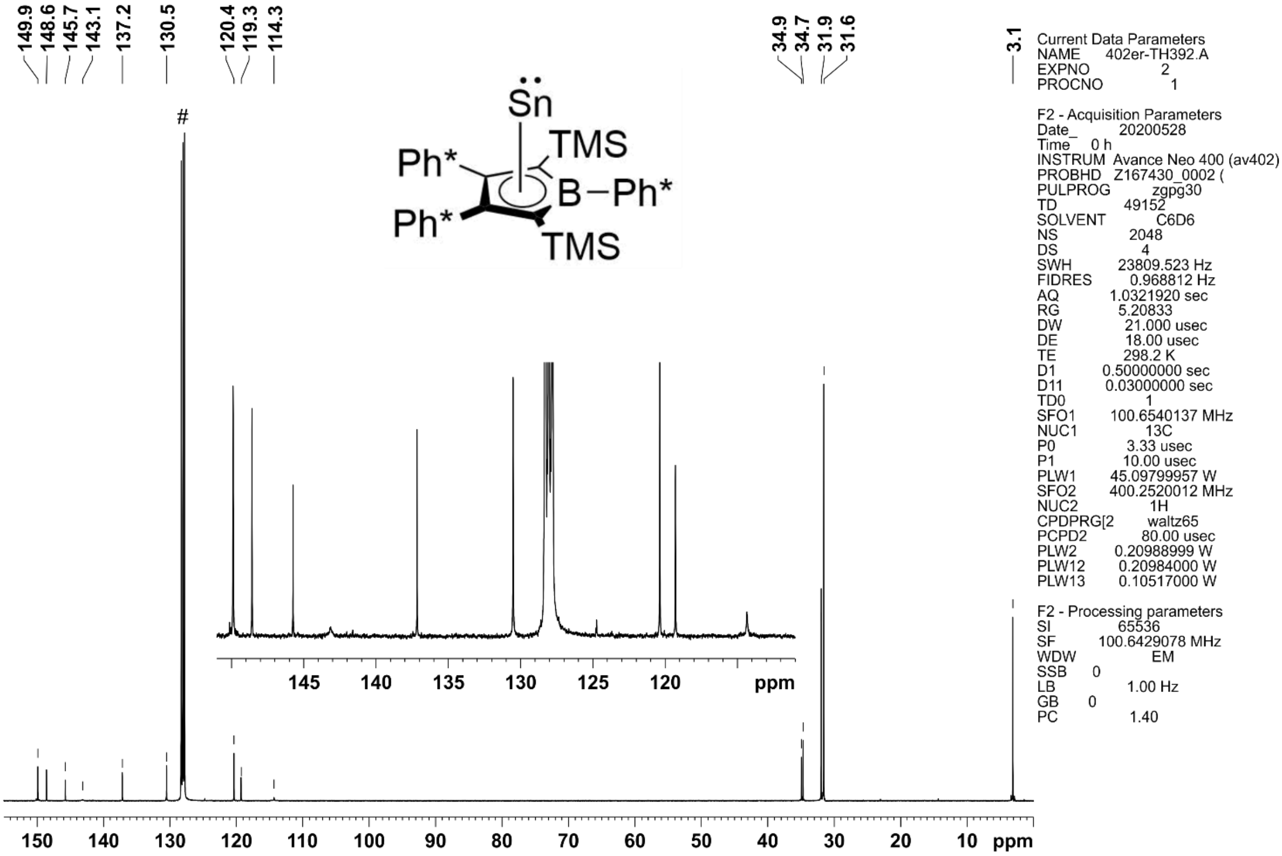
13C{1H}-NMR-spectrum of **4a** in C6D6
referenced to C6D6 at 128.0 ppm



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Current Data Parameters
NAME     402er-TH392.A
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
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Time      0 h
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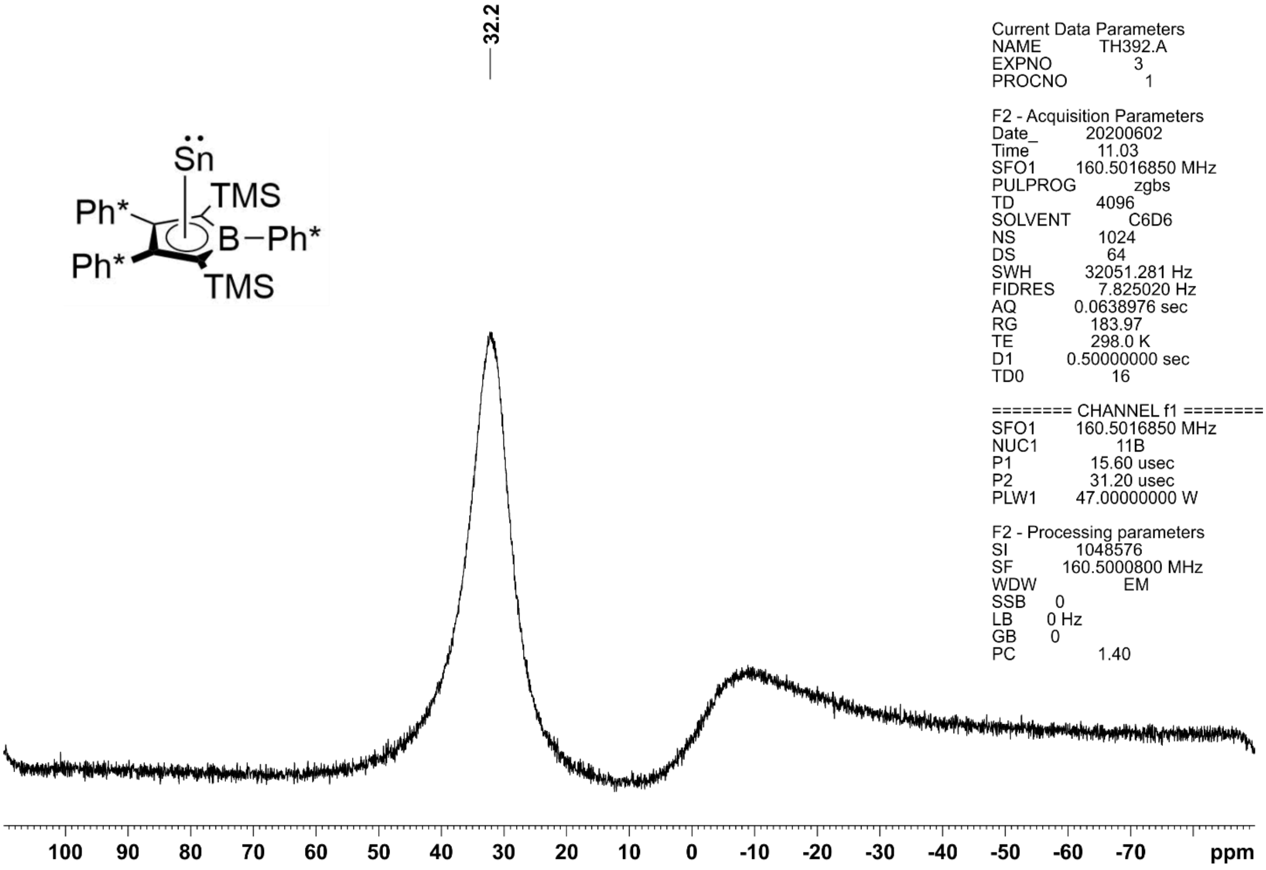
PROBHD   Z167430_0002 (
PULPROG          zgpg30
TD                49152
SOLVENT            C6D6
NS                 2048
DS                    4
SWH        23809.523 Hz
FIDRES      0.968812 Hz
AQ        1.0321920 sec
RG              5.20833
DW               21.000 usec
DE                18.00 usec
TE              298.2 K
D1       0.50000000 sec
D11      0.03000000 sec
TD0                   1
SFO1      100.6540137 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1      45.09799957 W
SFO2      400.2520012 MHz
NUC2                 1H
CPDPRG[2         waltz65
PCPD2             80.00 usec
PLW2       0.20988999 W
PLW12      0.20984000 W
PLW13      0.10517000 W

F2 - Processing parameters
SI                65536
SF        100.6429078 MHz
WDW                  EM
SSB    0
LB                1.00 Hz
GB     0
PC                 1.40
```

11B-NMR spectrum (background suppressed) of **4a** in C6D6



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EXPNO               3
PROCNO              1

F2 - Acquisition Parameters
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Time            11.03
SFO1     160.5016850 MHz
PULPROG          zgbs
TD               4096
SOLVENT          C6D6
NS               1024
DS                 64
SWH        32051.281 Hz
FIDRES      7.825020 Hz
AQ         0.0638976 sec
RG             183.97
TE              298.0 K
D1        0.50000000 sec
TD0                16

======== CHANNEL f1 ========
SFO1     160.5016850 MHz
NUC1              11B
P1              15.60 usec
P2              31.20 usec
PLW1      47.00000000 W

F2 - Processing parameters
SI            1048576
SF       160.5000800 MHz
WDW                EM
SSB     0
LB      0 Hz
GB      0
PC               1.40
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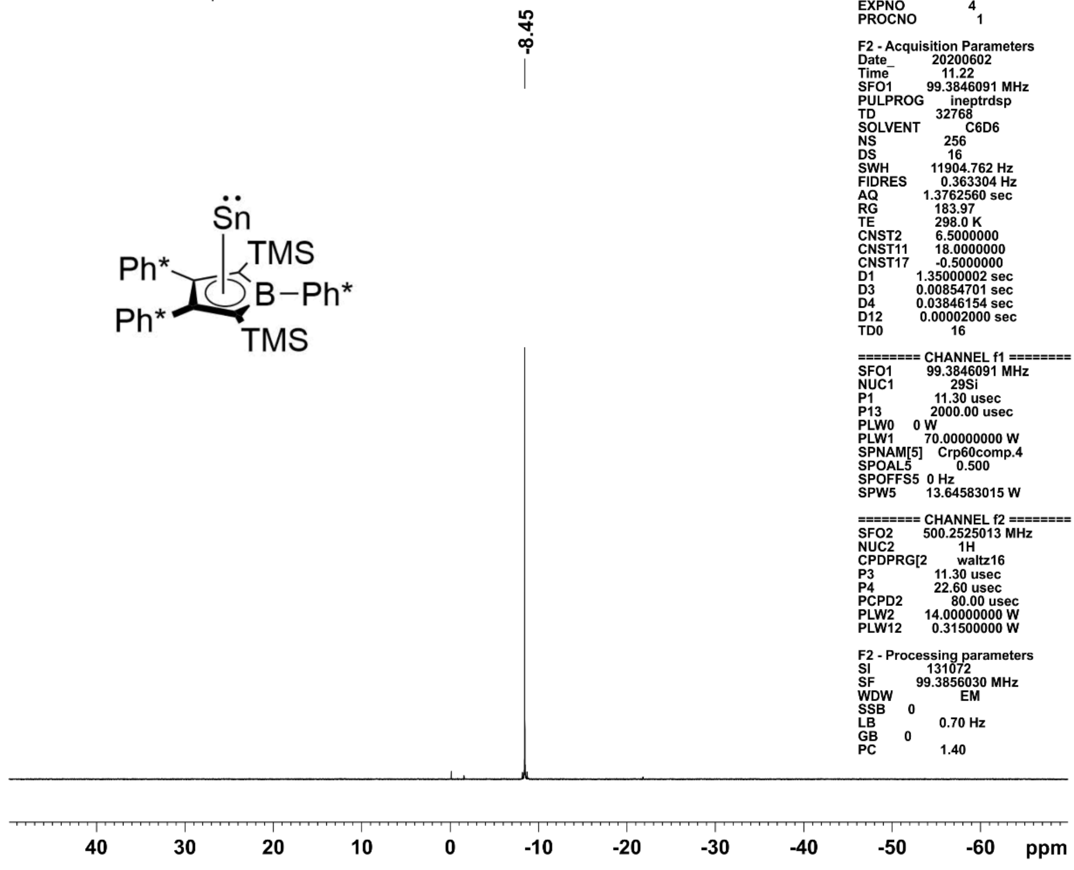
29Si-INEPT-NMR spectrum of **4a** in C6D6



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EXPNO              4
PROCNO             1

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TD             32768
SOLVENT         C6D6
NS               256
DS                16
SWH       11904.762 Hz
FIDRES     0.363304 Hz
AQ        1.3762560 sec
RG            183.97
TE             298.0 K
CNST2      6.5000000
CNST11    18.0000000
CNST17    -0.5000000
D1       1.35000002 sec
D3       0.00854701 sec
D4       0.03846154 sec
D12      0.00002000 sec
TD0               16

======== CHANNEL f1 ========
SFO1     99.3846091 MHz
NUC1            29Si
P1             11.30 usec
P13          2000.00 usec
PLW0    0 W
PLW1     70.00000000 W
SPNAM[5]   Crp60comp.4
SPOAL5          0.500
SPOFFS5  0 Hz
SPW5     13.64583015 W

======== CHANNEL f2 ========
SFO2    500.2525013 MHz
NUC2              1H
CPDPRG[2      waltz16
P3             11.30 usec
P4             22.60 usec
PCPD2          80.00 usec
PLW2     14.00000000 W
PLW12     0.31500000 W

F2 - Processing parameters
SI            131072
SF       99.3856030 MHz
WDW               EM
SSB     0
LB              0.70 Hz
GB      0
PC              1.40
```
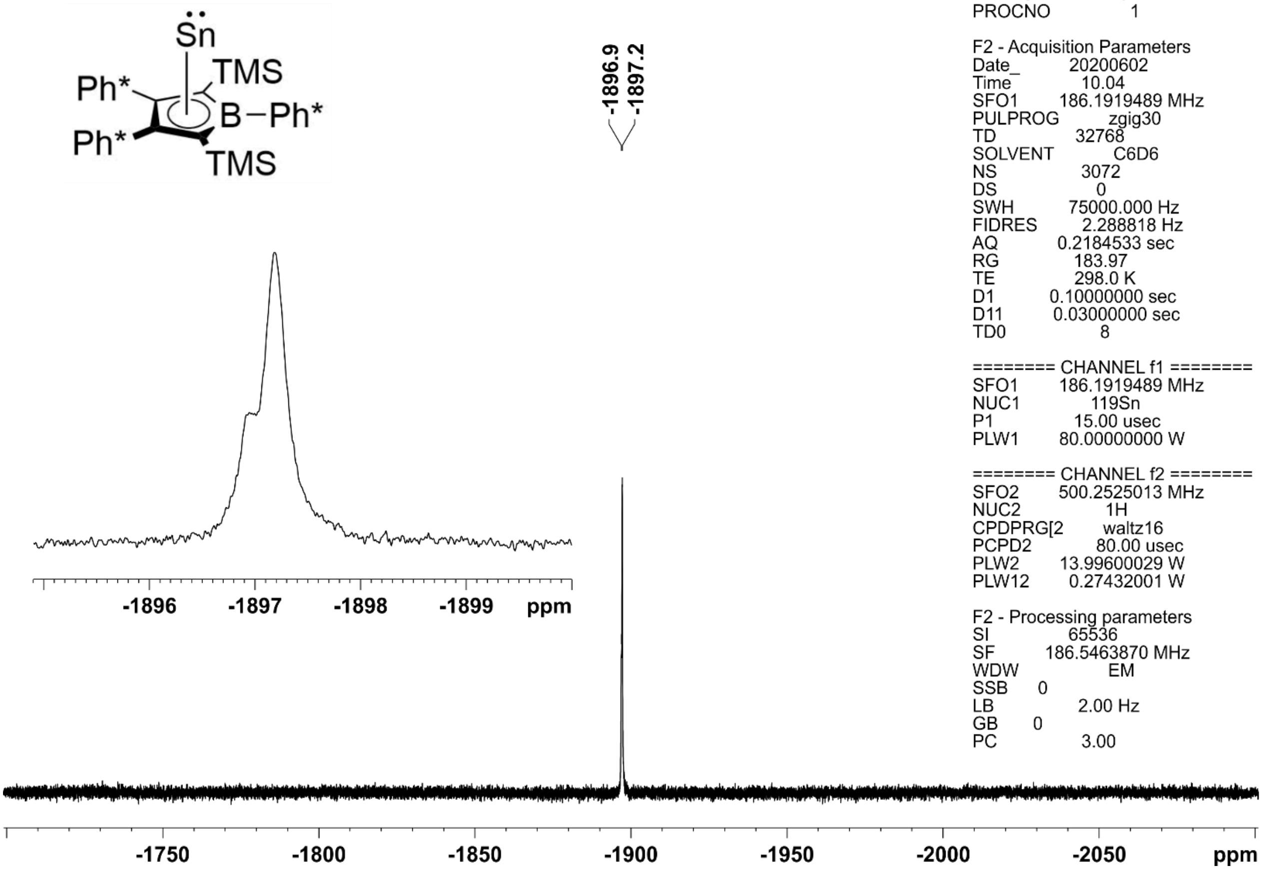

119Sn{1H}-NMR-spectrum of **4a** in C6D6



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EXPNO               5
PROCNO              1

F2 - Acquisition Parameters
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PULPROG        zgig30
TD              32768
SOLVENT          C6D6
NS               3072
DS                  0
SWH         75000.000 Hz
FIDRES       2.288818 Hz
AQ          0.2184533 sec
RG             183.97
TE              298.0 K
D1         0.10000000 sec
D11        0.03000000 sec
TD0                 8

======== CHANNEL f1 ========
SFO1      186.1919489 MHz
NUC1            119Sn
P1              15.00 usec
PLW1      80.00000000 W

======== CHANNEL f2 ========
SFO2      500.2525013 MHz
NUC2               1H
CPDPRG[2      waltz16
PCPD2           80.00 usec
PLW2      13.99600029 W
PLW12      0.27432001 W

F2 - Processing parameters
SI              65536
SF        186.5463870 MHz
WDW                EM
SSB      0
LB               2.00 Hz
GB       0
PC               3.00
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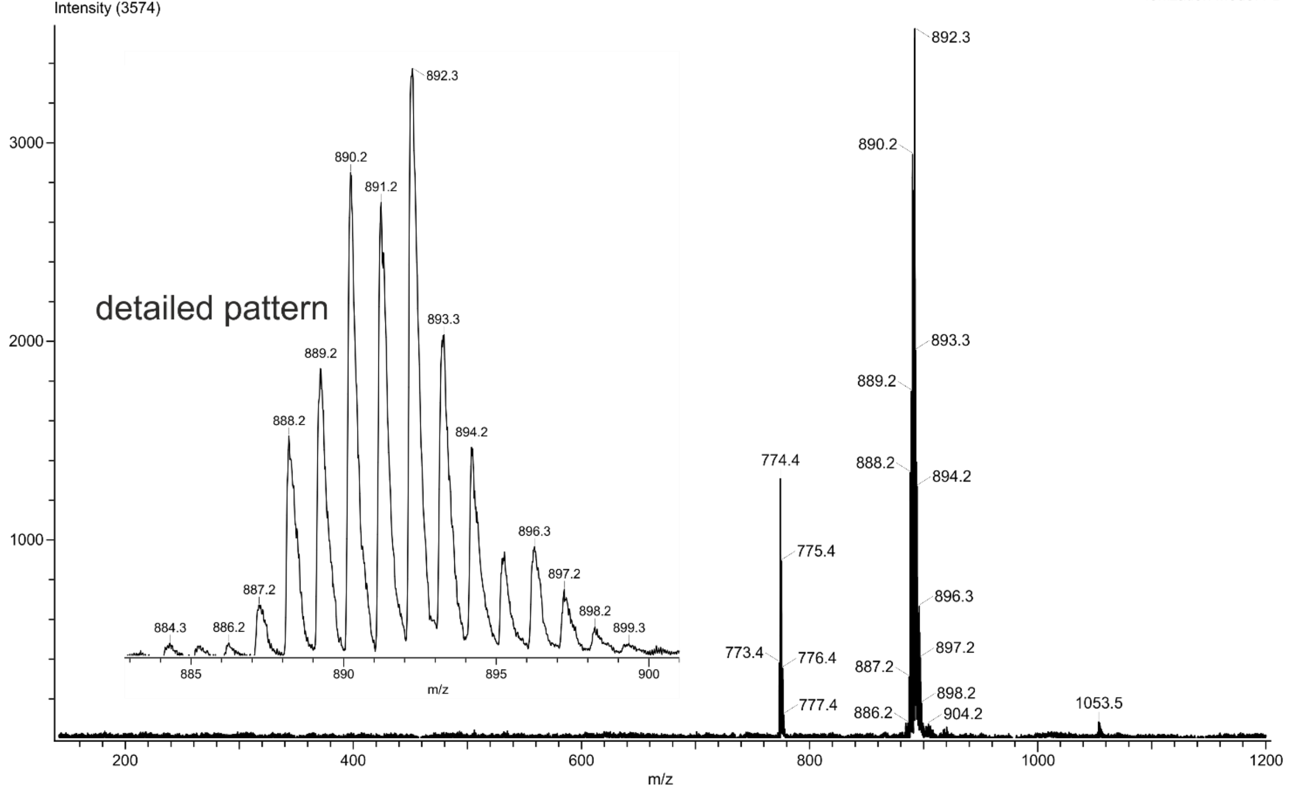
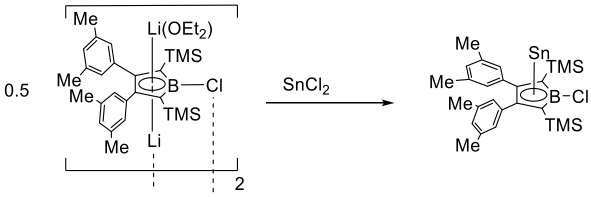
LIFDI-MS of compound **4a**

Experiment Date/Time: 7/1/2020 9:57:10 AM
Ionization Mode: FD+



Compound 4b



2[Li$_2$(OEt)$_2$]

Molecular Weight: 539,01

4b

Molecular Weight: 569,71

In a glovebox, a mixture of tin(II)chloride (63.9 mg, 0.338 mmol, 1 eq.) and borolediide **2** (206.7 mg, 0.3835 mmol, 1.1 eq.) was suspended in diethyl ether (7 mL, distilled). The pale-yellow suspension was stirred for 3 h at room temperature. The ether was removed in vacuo, giving a pale-yellow powder which was then suspended in toluene (2 mL, distilled). The suspension was filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B), and the filter cake was washed with toluene (2 mL). The pale-orange filtrate was concentrated to dryness to give an orange, crystalline solid. The solid was then washed with pentane (4 × 1 mL) to give the product **4b** in form of a pale orange solid (132.6 mg, 0.2335 mmol, 69 %).

Note: Crystals of **4b** are pale yellow/colourless. In an attempt to remove the colored impurity from the initial crop, the product was recrystallized from toluene (1 mL, –35°C). This removed the orange contamination to give a yellow solid but reduced the overall yield to 37 %. The NMR-spectra did not change.

Analytical Data for Compound 3b

NMR:

^{1}H (500.25 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 6.82 (m, 4H, *o-H*), 6.47 (s, 2H, *p-H*) 1.95 (s, 12H, *m*-C*H*$_3$), 0.21 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 142.4 (C_β), 136.7 (*m*-C_{ar} and *ipso*-C_{ar}), 131.2 (*o*-C_{ar}), 129.1 (*p*-C_{ar}), 106.8 (C_α), 21.0 (*m*-*C*H$_3$), 2.5 (TMS).

^{11}B (160.50 MHz, 298 K, C_6D_6): 30.3 ($\omega_{1/2}$ = 431 Hz).

^{29}Si-INEPT (99.39 MHz, 298 K, C_6D_6): –8.1.

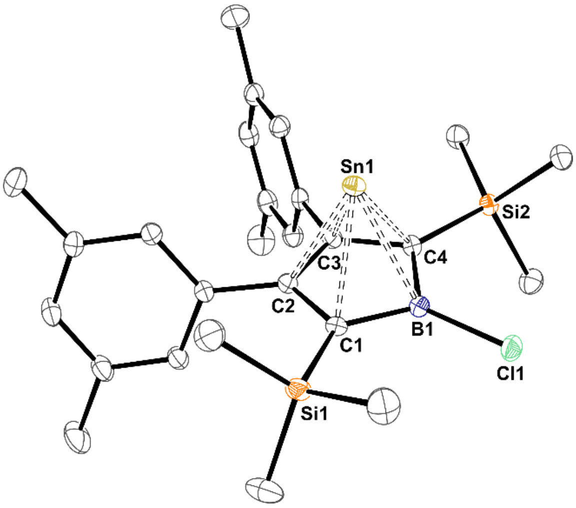
^{119}Sn (186.19 MHz, 298 K, C_6D_6): –1952.4 (^{119}Sn-^{10}B isotopolog), –1952.6 (^{119}Sn-^{11}B isotopolog).

Elemental Analysis: ($C_{26}H_{36}BClSi_2Sn$) calcd C 54.81, H 6.37, B 1.90, Cl 6.22, Si 9.86, Sn 20.84, observed C 54.78, H 6.16.

LIFDI-MS: calcd exact mass: 570.1 m/z, observed m/z: 570.3.

Crystal structure of Compound 4b

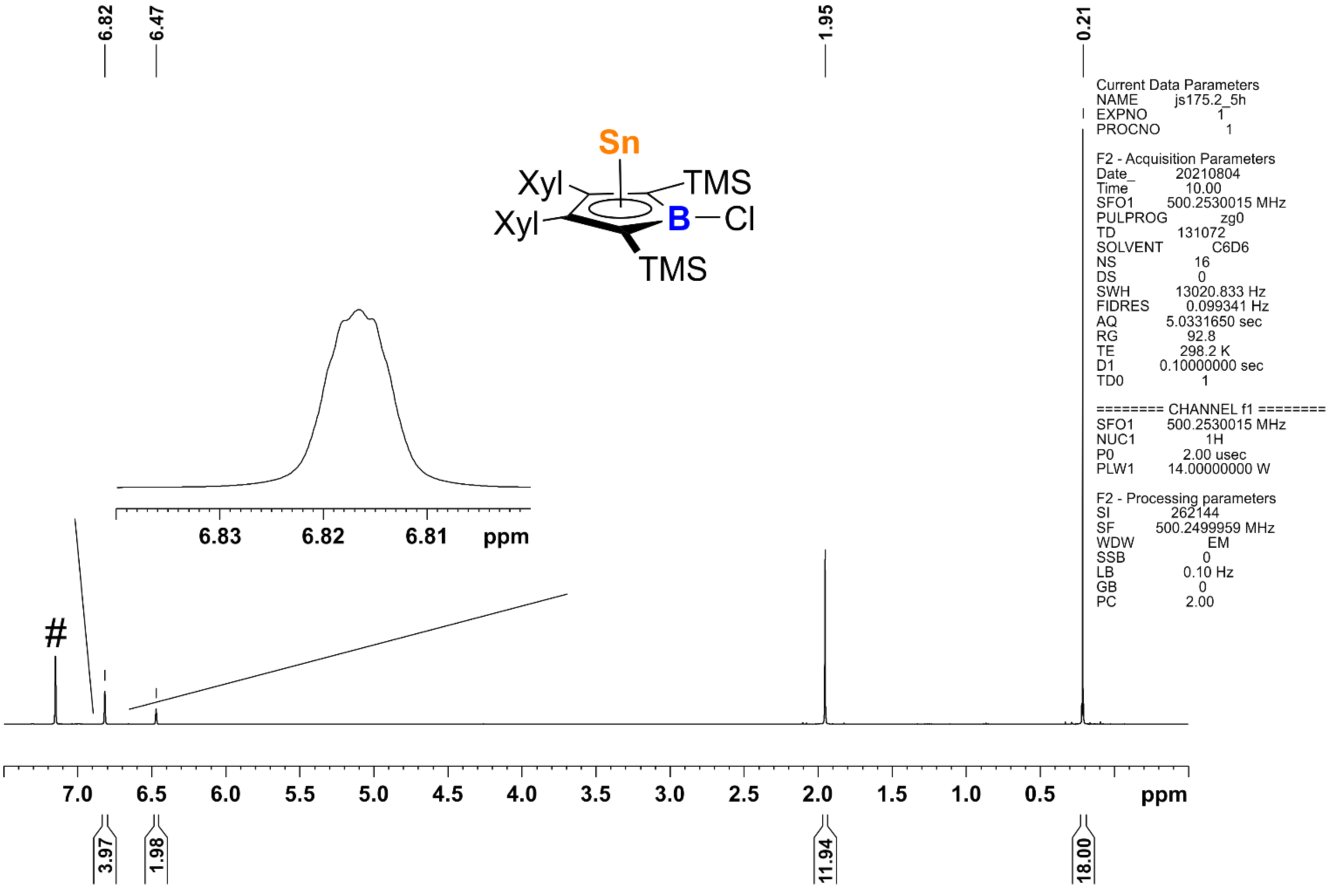
4b crystallised from hexane or toluene solutions in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.



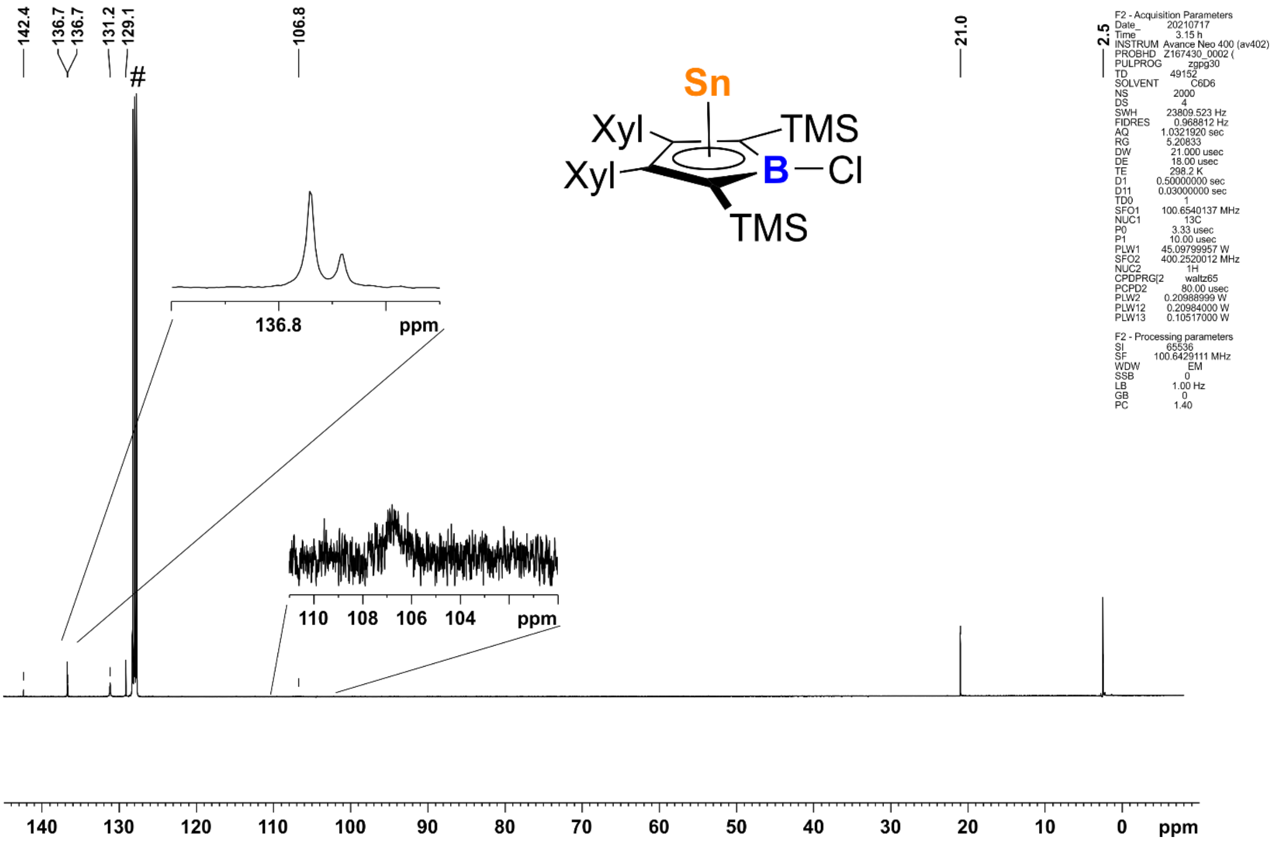
ORTEP plot of the molecular structure of **4b.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms have been omitted for the sake of clarity. Selected bond length: B1–Cl1 1.809(1), B1–C1 1.538(2), C1–C2 1.461(1), C2–C3 1.438(2), C3–C4 1.457(1), C4–B1 1.541(2), B1–Sn1 2.487(1), C1–Sn1 2.426(1), C2–Sn1 2.407(1), C3–Sn1 2.404(1), C4–Sn1 2.418(1).

Spectra Plots for Compound 4b

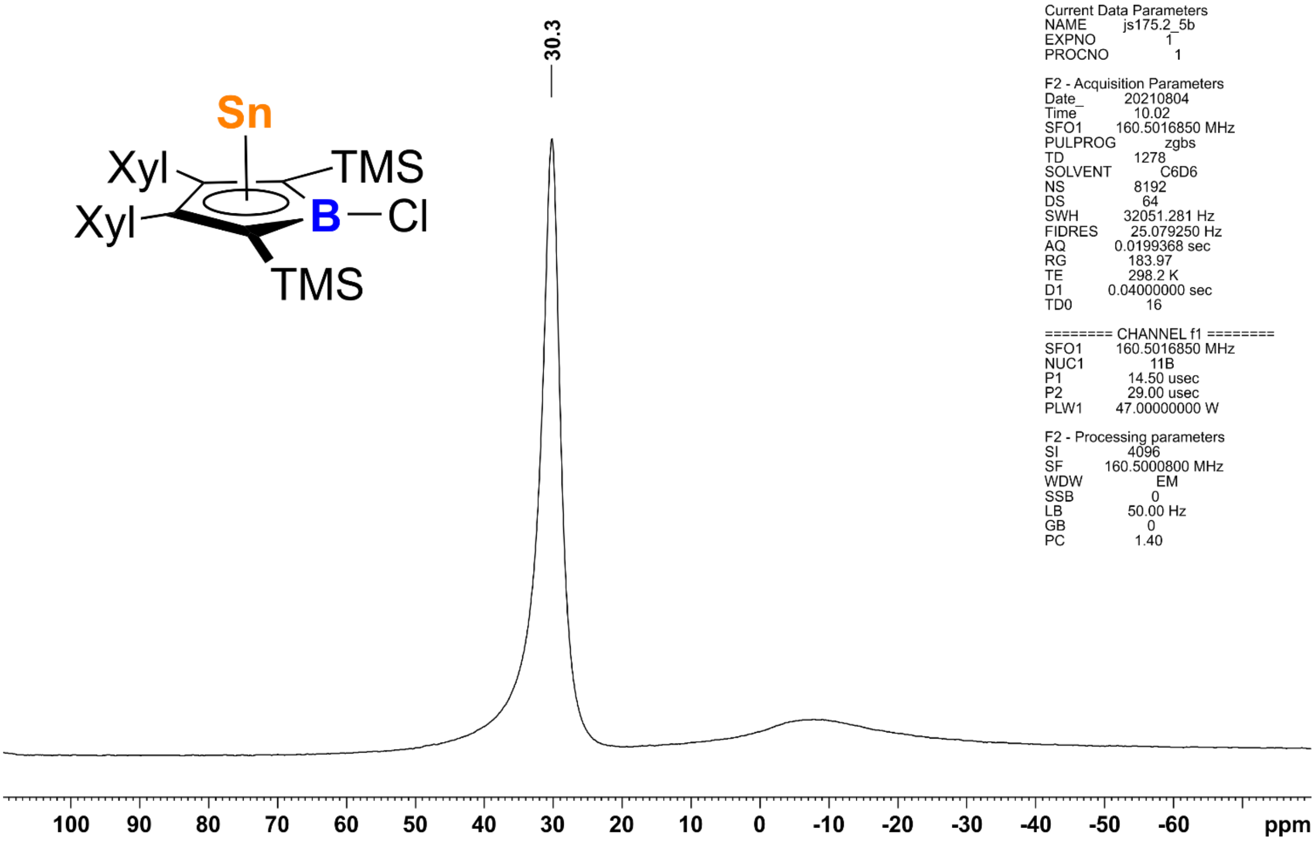
1H-NMR-spectrum of compound **4b** in C6D6
referenced to C6D5H at 7.15 ppm



13C{1H}-NMR-spectrum of compound **4b** in C6D6
referenced to C6D6 at 128.0 ppm



11B-NMR spectrum (background suppressed) of compound **4b** in C6D6



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PROCNO             1

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PULPROG         zgbs
TD             1278
SOLVENT         C6D6
NS             8192
DS               64
SWH        32051.281 Hz
FIDRES     25.079250 Hz
AQ         0.0199368 sec
RG            183.97
TE             298.2 K
D1        0.04000000 sec
TD0               16

======== CHANNEL f1 ========
SFO1       160.5016850 MHz
NUC1             11B
P1             14.50 usec
P2             29.00 usec
PLW1       47.00000000 W

F2 - Processing parameters
SI              4096
SF         160.5000800 MHz
WDW               EM
SSB                0
LB             50.00 Hz
GB                 0
PC              1.40
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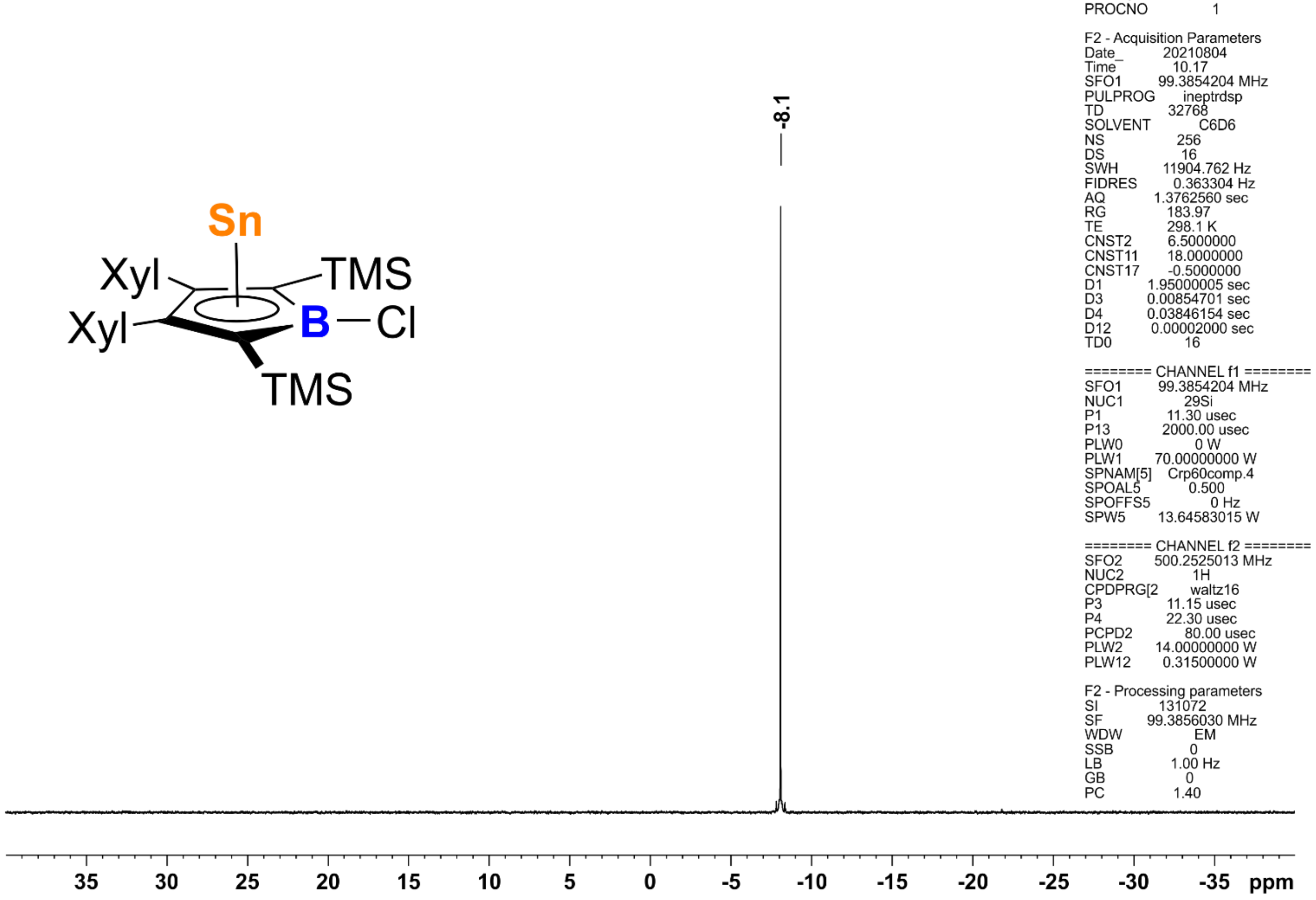
29Si-INEPT-NMR spectrum of compound X in C6D6



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Current Data Parameters
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EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
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Time           10.17
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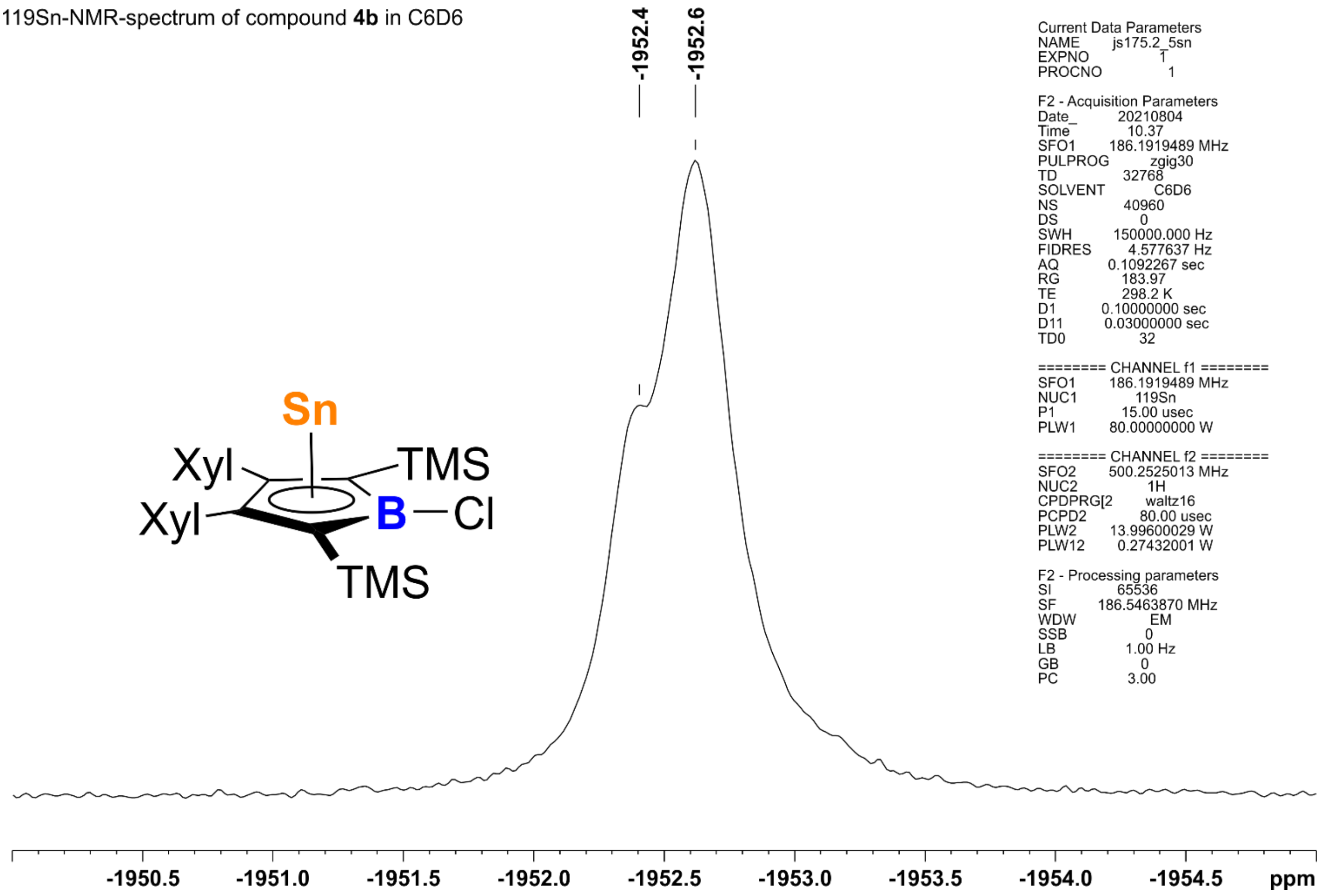
PULPROG     ineptrdsp
TD             32768
SOLVENT         C6D6
NS               256
DS                16
SWH        11904.762 Hz
FIDRES      0.363304 Hz
AQ         1.3762560 sec
RG            183.97
TE             298.1 K
CNST2      6.5000000
CNST11    18.0000000
CNST17    -0.5000000
D1        1.95000005 sec
D3        0.00854701 sec
D4        0.03846154 sec
D12       0.00002000 sec
TD0               16

======== CHANNEL f1 ========
SFO1       99.3854204 MHz
NUC1             29Si
P1             11.30 usec
P13          2000.00 usec
PLW0               0 W
PLW1       70.00000000 W
SPNAM[5]   Crp60comp.4
SPOAL5          0.500
SPOFFS5            0 Hz
SPW5       13.64583015 W

======== CHANNEL f2 ========
SFO2       500.2525013 MHz
NUC2              1H
CPDPRG[2      waltz16
P3             11.15 usec
P4             22.30 usec
PCPD2          80.00 usec
PLW2       14.00000000 W
PLW12       0.31500000 W

F2 - Processing parameters
SI            131072
SF         99.3856030 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

119Sn-NMR-spectrum of compound **4b** in C6D6



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EXPNO                 1
PROCNO                1

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PULPROG         zgig30
TD               32768
SOLVENT           C6D6
NS               40960
DS                   0
SWH         150000.000 Hz
FIDRES        4.577637 Hz
AQ           0.1092267 sec
RG              183.97
TE               298.2 K
D1          0.10000000 sec
D11         0.03000000 sec
TD0                 32

======== CHANNEL f1 ========
SFO1      186.1919489 MHz
NUC1             119Sn
P1               15.00 usec
PLW1       80.00000000 W

======== CHANNEL f2 ========
SFO2      500.2525013 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       13.99600029 W
PLW12       0.27432001 W

F2 - Processing parameters
SI               65536
SF        186.5463870 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                3.00
```
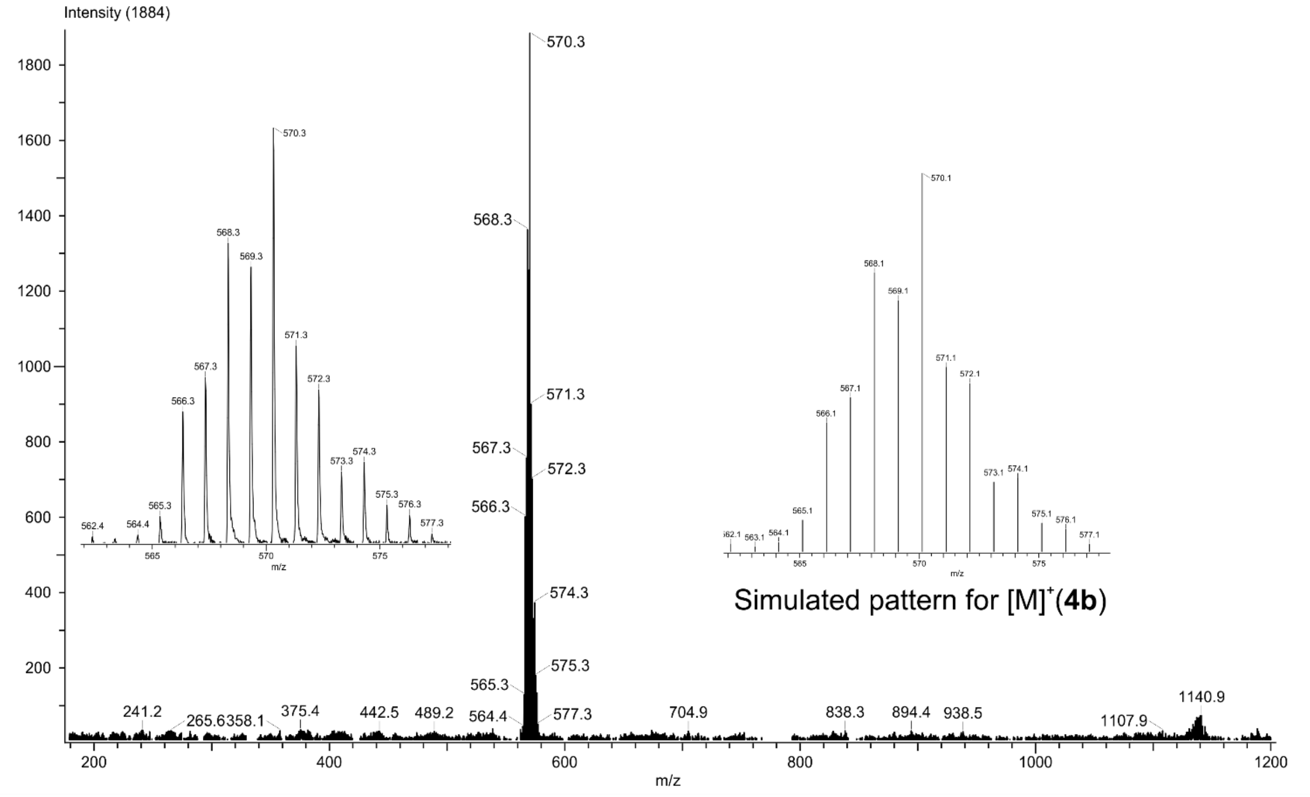
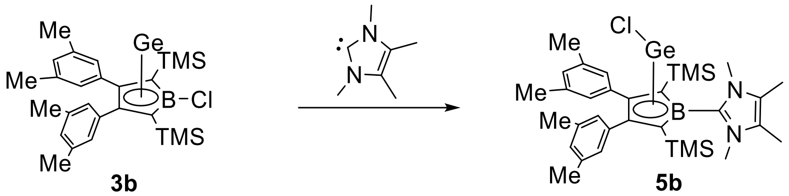

Acq. Data Name: jsarcev00015-1
Creation Parameters: Average(MS[1] Time:0.46..0.47)
External Sample Id: JS 175

Experiment Date/Time: 8/11/2021 10:42:40 AM
Ionization Mode: FD+



Simulated pattern for $[M]^+$(**4b**)

Compound 5b



3b

Molecular Weight: 523,63

5b

Molecular Weight: 647,82

In a glovebox, a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (10.8 mg, 0.0877 mmol, 1 eq.) in toluene (1 mL, distilled) was added dropwise via syringe to a stirred solution of germanium compound **3b** (46.1 mg, 0.0885 mmol, 1 eq.) in toluene (2 mL, distilled). The resulting suspension was stirred at room temperature over night. Toluene (2 mL) was added to the yellow suspension, which was subsequently filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B). The filter was then washed with toluene (1 mL) and the combined filtrate was concentrated to a volume of about 2 mL and stored at –35°C for crystallization for several days. The colorless to slightly yellowish crystals were then washed with cold (–35°C) toluene (0.5 mL) to obtain the product **5b** (41.2 mg, 0.0636 mmol, 72 %) after drying in vacuo as colorless crystalline material which contained ca. 0.5 equiv. of lattice toluene.

Analytical Data for Compound 5b

NMR:

^{1}H (400.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.34 (s, 4H, *o-H*), 6.60 (m, 2H, *p-H*), 3.84 (s, 3H, N-C*H*$_3$), 3.16 (s, 3H, N-C*H*$_3$), 2.10 (s, 12H, *m*-C*H*$_3$), 1.27 (s, 3H, C_{NHC}-C*H*$_3$), 1.21 (s, 3H, C_{NHC}-C*H*$_3$), 0.00 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, C_6D_6 solvent signal at 128.0 ppm): 158.9 (N-*C*-N, only via HMBC), 146.6 (C_β), 140.2 (*ipso*-C_{ar}), 136.4 (*m*-C_{ar}), 130.7 (*o*-C_{ar}), 128.5 (*p*-C_{ar}), 125.6 (C_{NHC}=C_{NHC}), 125.0 (C_{NHC}=C_{NHC}), 123.6 (C_α), 35.9 (N-*C*H$_3$), 33.9 (N-*C*H$_3$), 21.2 (*m*-*C*H$_3$), 8.0 (C_{NHC}-*C*H$_3$), 7.7 (C_{NHC}-*C*H$_3$), 1.8 (TMS).

^{11}B (128.38 MHz, 298 K, C_6D_6): 15.7 ($\omega_{1/2}$ = 340 Hz).

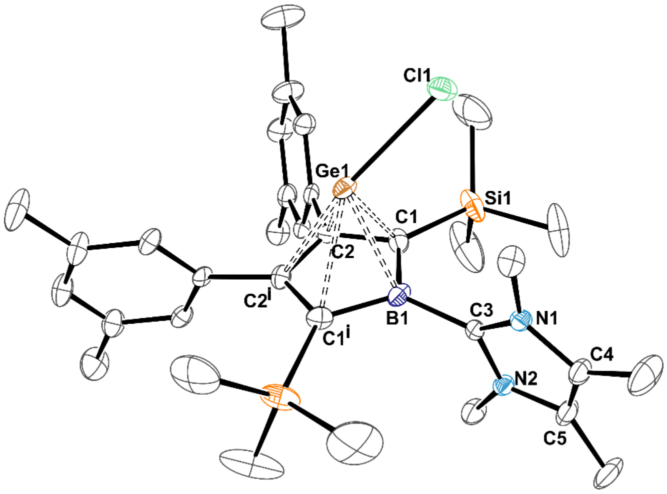
^{29}Si-INEPT (79.49 MHz, 298 K, C_6D_6): –9.2.

Elemental Analysis: $C_{33}H_{48}BClN_2Si_2Ge$) × 0.5 (toluene) calcd C 63.18, H 7.55, N 4.04, B 1.56, Cl 5.11, Si 8.09, Ge 10.47; observed C 63.38, H 7.14, N 4.06.

LIFDI-MS: calcd exact mass: 648.2 m/z, observed m/z: 613.4 ([M-Cl]$^+$ $C_{33}H_{48}BN_2Si_2Ge^+$).

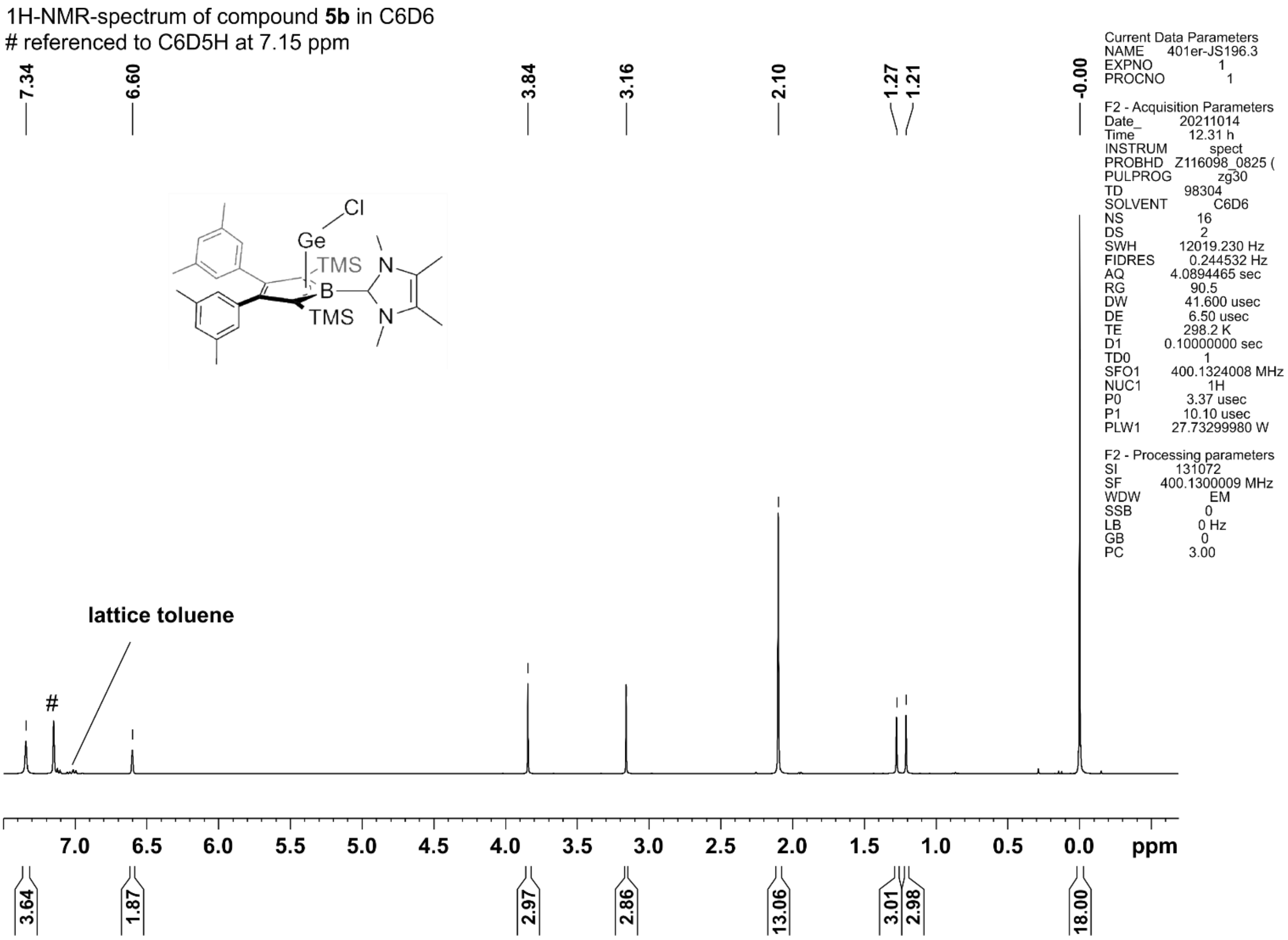
Crystal structure of Compound 5b

4b crystallised from toluene solutions in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.

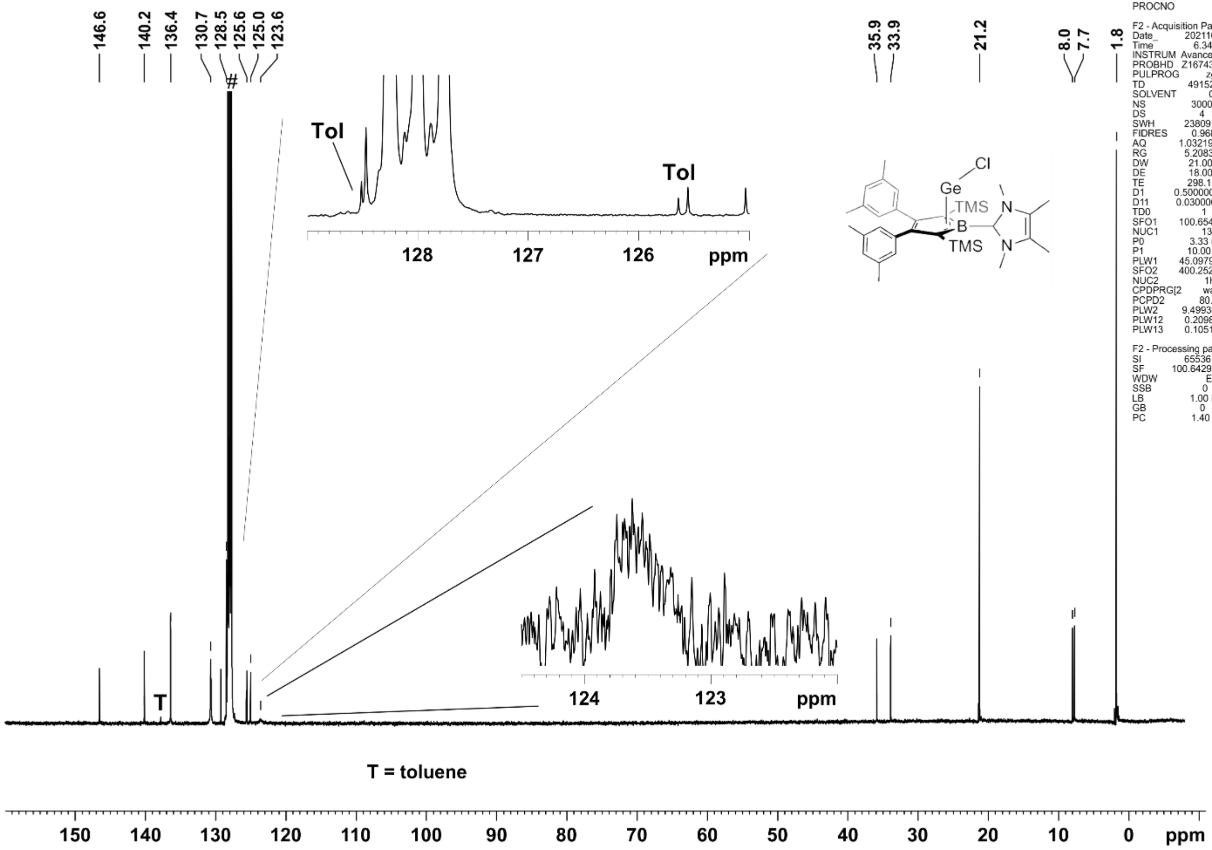


ORTEP plot of the molecular structure of **5b.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms, disorders of the Xylyl-group and a lattice toluene molecule have been omitted for the sake of clarity. Selected bond length: B1–C3 1.592(5), B1–C1 1.535(4), C1–C2 1.437(3), C2–C2' 1.428(3), B1–Ge1 2.291(3), C1–Ge1 2.266(3), C2–Ge1 2.369(2), C2'–Ge1 2.482(2), C1'–Ge1 2.465(3), Ge1–Cl1 2.543(2).

Spectra Plots for Compound 5b



13C{1H}-NMR-spectrum of compound **5b** in C6D6
referenced to C6D6 at 128.0 ppm



T = toluene

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PROCNO             1

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D11       0.03000000 sec
TD0                1
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NUC1             13C
P0              3.33 usec
P1             10.00 usec
PLW1     45.09799957 W
SFO2     400.2520012 MHz
NUC2              1H
CPDPRG[2     waltz65
PCPD2          80.00 usec
PLW2      9.49930000 W
PLW12     0.20983779 W
PLW13     0.10517070 W

F2 - Processing parameters
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GB                 0
PC              1.40
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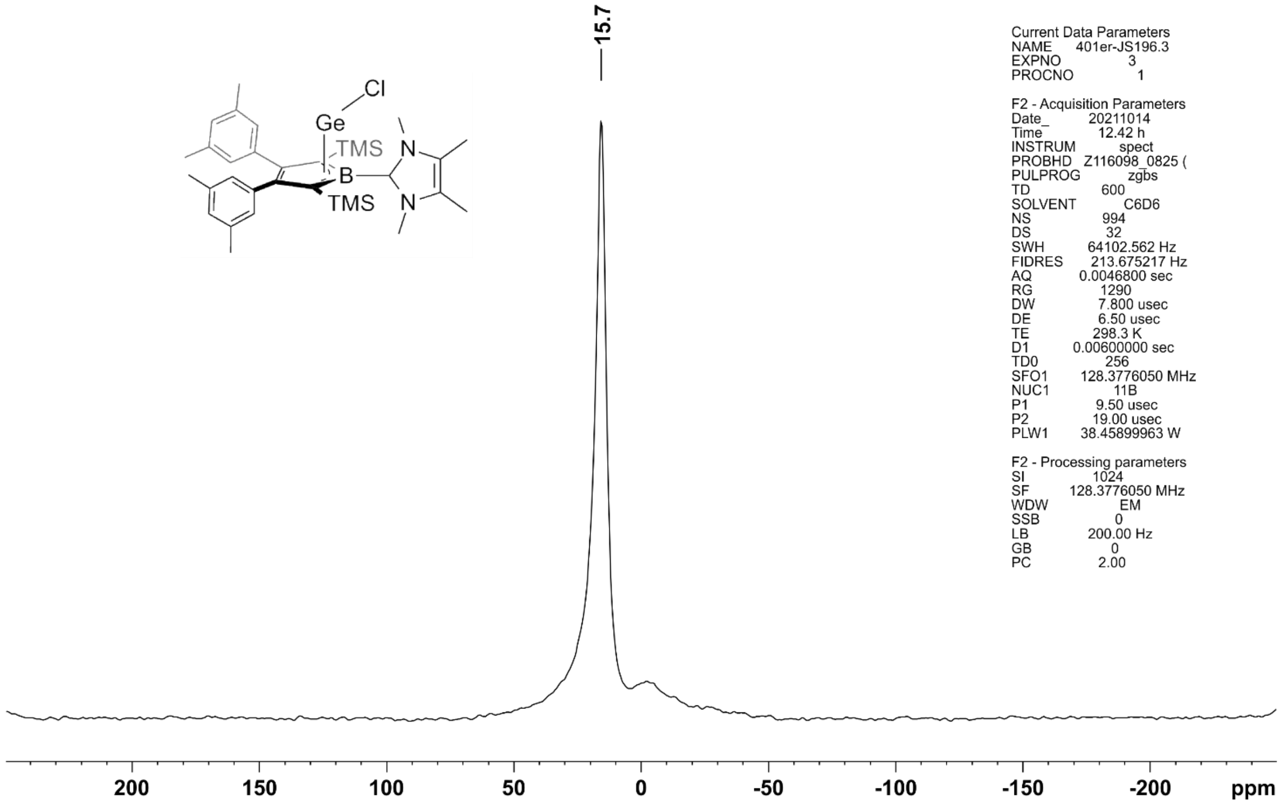
11B-NMR spectrum (background suppressed) of compound **5b** in C6D6



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PROCNO             1

F2 - Acquisition Parameters
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TD               600
SOLVENT          C6D6
NS               994
DS                32
SWH        64102.562 Hz
FIDRES    213.675217 Hz
AQ         0.0046800 sec
RG              1290
DW             7.800 usec
DE              6.50 usec
TE             298.3 K
D1        0.00600000 sec
TD0              256
SFO1     128.3776050 MHz
NUC1             11B
P1              9.50 usec
P2             19.00 usec
PLW1     38.45899963 W

F2 - Processing parameters
SI              1024
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WDW               EM
SSB                0
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GB                 0
PC              2.00
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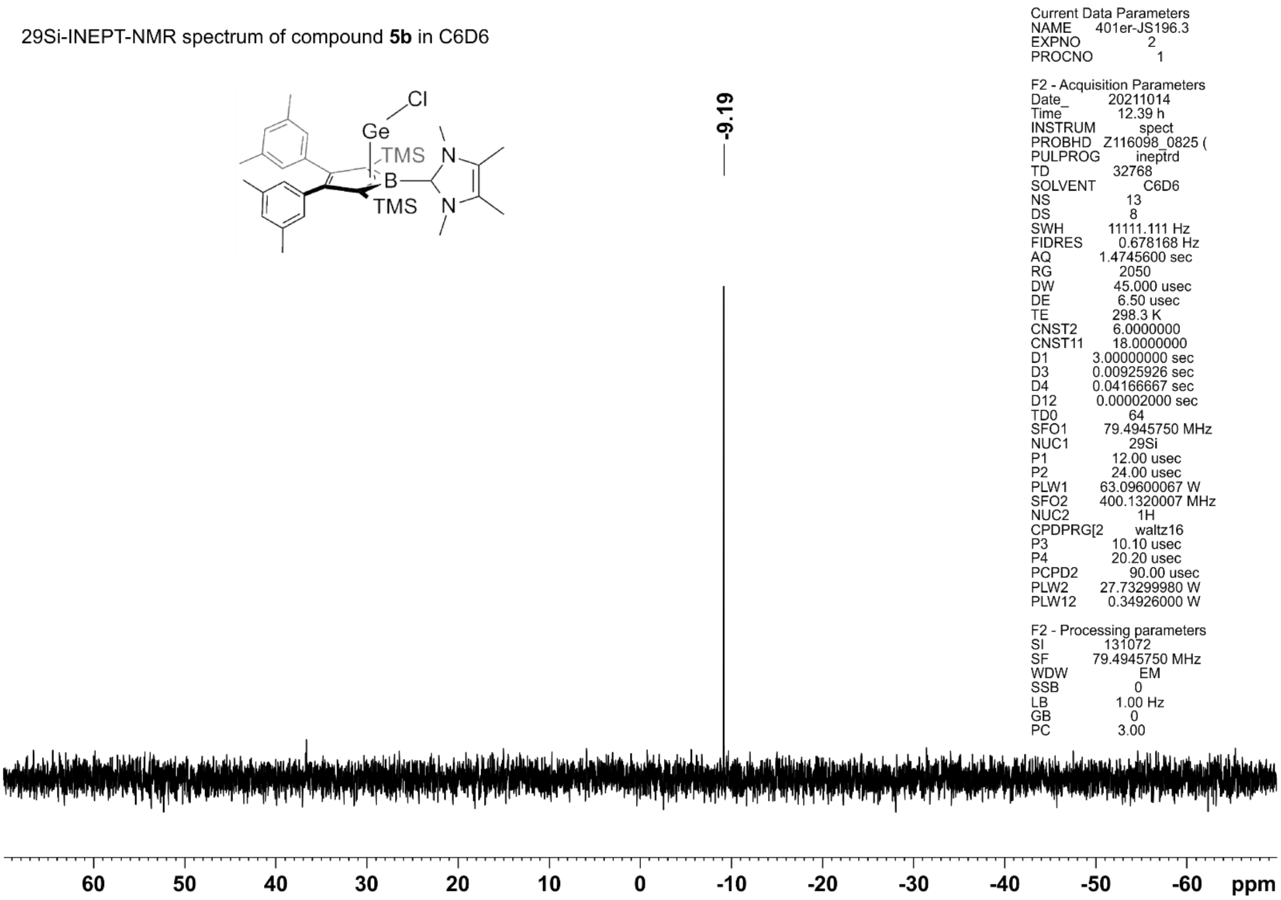
29Si-INEPT-NMR spectrum of compound **5b** in C6D6



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PROCNO 1

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SOLVENT C6D6
NS 13
DS 8
SWH 11111.111 Hz
FIDRES 0.678168 Hz
AQ 1.4745600 sec
RG 2050
DW 45.000 usec
DE 6.50 usec
TE 298.3 K
CNST2 6.0000000
CNST11 18.0000000
D1 3.00000000 sec
D3 0.00925926 sec
D4 0.04166667 sec
D12 0.00002000 sec
TD0 64
SFO1 79.4945750 MHz
NUC1 29Si
P1 12.00 usec
P2 24.00 usec
PLW1 63.09600067 W
SFO2 400.1320007 MHz
NUC2 1H
CPDPRG[2 waltz16
P3 10.10 usec
P4 20.20 usec
PCPD2 90.00 usec
PLW2 27.73299980 W
PLW12 0.34926000 W

F2 - Processing parameters
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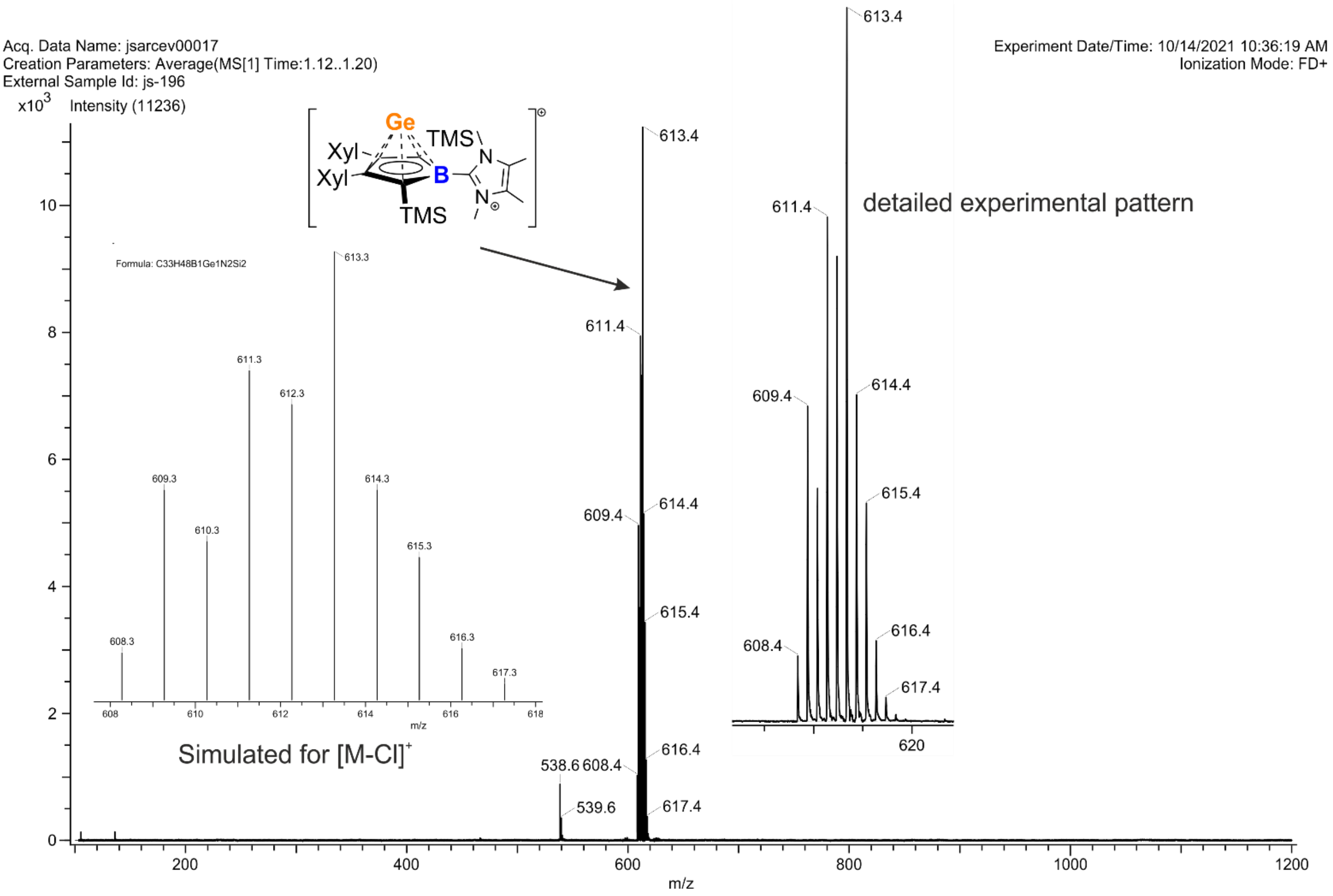
SSB 0
LB 1.00 Hz
GB 0
PC 3.00



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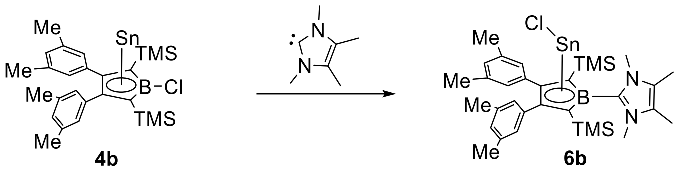
Creation Parameters: Average(MS[1] Time:1.12..1.20)
External Sample Id: js-196

Experiment Date/Time: 10/14/2021 10:36:19 AM
Ionization Mode: FD+

Compound 6b



4b **6b**

Molecular Weight: 569,71 Molecular Weight: 693,9

In a glovebox, a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (12.6 mg, 0.101 mmol, 1 eq.) in toluene (1 mL, distilled) was added dropwise via syringe to a stirred solution of **4b** (57.2 mg, 0.100 mmol, 1 eq.) in toluene (2 mL, distilled). The resulting yellow suspension was stirred at room temperature for 1 h and the solvent was subsequently removed in vacuo. The resulting yellow solid was washed three times with 1 mL of a 1:1 pentane/toluene mixture. After drying, the solid was suspended in toluene (5 mL, 3 mL) and filtered through a syringe filter equipped with a thin plug of glass fiber (Whatman GF/B). The yellow filtrate was then stored at –35 °C for crystallization. The resulting crystals were removed and washed with hexane to give the desired product **6b** (23.6 mg, 0.0340 mmol, 34 %). The supernatant from the crystallization was concentrated to dryness and washed with cold toluene (0.5 mL, 0.3 mL) which also led to the spectroscopically pure product **6b** (19.0 mg, 0.0274 mmol, 27 %).

Note: Solubility in toluene was only very limited and was greatly increased in more polar solvents.

Analytical Data for Compound 6b

NMR:

^{1}H (500.25 MHz, 298 K, CD$_2$Cl$_2$, CDHCl$_2$ at 5.32 ppm): 6.88 (s, 4H, *o-H*), 6.76 (m, 2H, *p-H*), 4.15 (s, 3H, N-C*H*$_3$), 3.59 (s, 3H, N-C*H*$_3$), 2.28 (two s, partially superimposed, 6H, C$_{\mathrm{NHC}}$-C*H*$_3$) 2.20 (m, 12H, *m*-C*H*$_3$), –0.37 (s, 18H, TMS).

^{1}H (400.13 MHz, 298 K, toluene-*d*$_8$, C$_6$D$_5$-CD$_2$H at 2.11 ppm): 7.23 (s, 4H, *o-H*), 6.60 (m, 2H, *p-H*), 3.87 (s, 3H, N-C*H*$_3$), 3.19 (s, 3H, N-C*H*$_3$), 2.14 (m, 12H, *m*-C*H*$_3$), 1.41 (m, 3H, C$_{\mathrm{NHC}}$-C*H*$_3$), 1.33 (m, 3H, C$_{\mathrm{NHC}}$-C*H*$_3$), –0.04 (s, 18H, TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, CD$_2$Cl$_2$ solvent signal at 54.24 ppm): ca. 159 (N-*C*-N, only via HMBC), 148.7 (C_β), 140.5 (*ipso-C$_{ar}$*), 136.9 (*m-C$_{ar}$*), 131.9 (*o-C$_{ar}$*), 128.3 (*p-C$_{ar}$*), 126.7 (*C$_{NHC}$=C$_{NHC}$*), 126.5 (*C$_{NHC}$=C$_{NHC}$*), 121.3 (C_α), 36.8 (N-*C*H$_3$), 35.4 (N-*C*H$_3$), 21.7 (*m*-*C*H$_3$), 9.7 (C$_{\mathrm{NHC}}$-*C*H$_3$), 9.5 (C$_{\mathrm{NHC}}$-*C*H$_3$), 1.9 (TMS).

^{13}C{^{1}H} (100.64 MHz, 298 K, toluene-*d*$_8$ solvent signal at 21.37 ppm): ca. 161 (N-*C*-N, only via HMBC), 149.6 (C_β), 141.8 (*ipso-C$_{ar}$*), 137.2 (*m-C$_{ar}$*), 132.4 (*o-C$_{ar}$*), ca. 129 (*p-C$_{ar}$*, superimposed by solvent signal), 125.5 (*C$_{NHC}$=C$_{NHC}$*), ca. 123 (C_α, only via HMBC), 36.9 (N-*C*H$_3$), 35.2 (N-*C*H$_3$), 22.2 (*m*-*C*H$_3$), 9.0 (C$_{\mathrm{NHC}}$-*C*H$_3$), 8.7 (C$_{\mathrm{NHC}}$-*C*H$_3$), 3.1 (TMS).

^{11}B (160.50 MHz, 298 K, CD$_2$Cl$_2$): 16.6 ($\omega_{1/2}$ = 180 Hz).

^{11}B (128.38 MHz, 298 K, toluene-*d*$_8$): 16.2 ($\omega_{1/2}$ = 350 Hz).

^{29}Si (99.39 MHz, 298 K, CD$_2$Cl$_2$): –9.8.

^{29}Si (79.49 MHz, 298 K, toluene-*d*$_8$): –9.9.

^{119}Sn (186.19 MHz, 298 K, CD$_2$Cl$_2$): –1542.4.

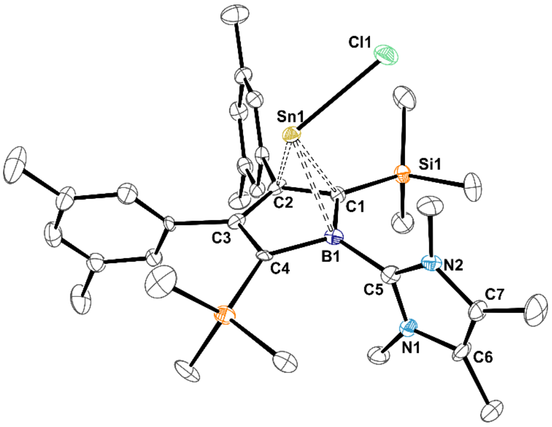
^{119}Sn (186.19 MHz, 298 K, toluene-*d*$_8$): –1333.6

Elemental Analysis: ($C_{33}H_{48}BClN_2Si_2Sn$)×0.5(toluene) calcd C 59.25, H 7.08, N 3.79, B 1.46, Cl 4.79, Si 7.59, Sn 16.04; observed C 59.30, H 6.79, N 3.72.

LIFDI-MS: calcd exact mass: 694.2 m/z, observed m/z: 659.3 ($[M-Cl]^+$, $C_{33}H_{48}BN_2Si_2Sn^+$).

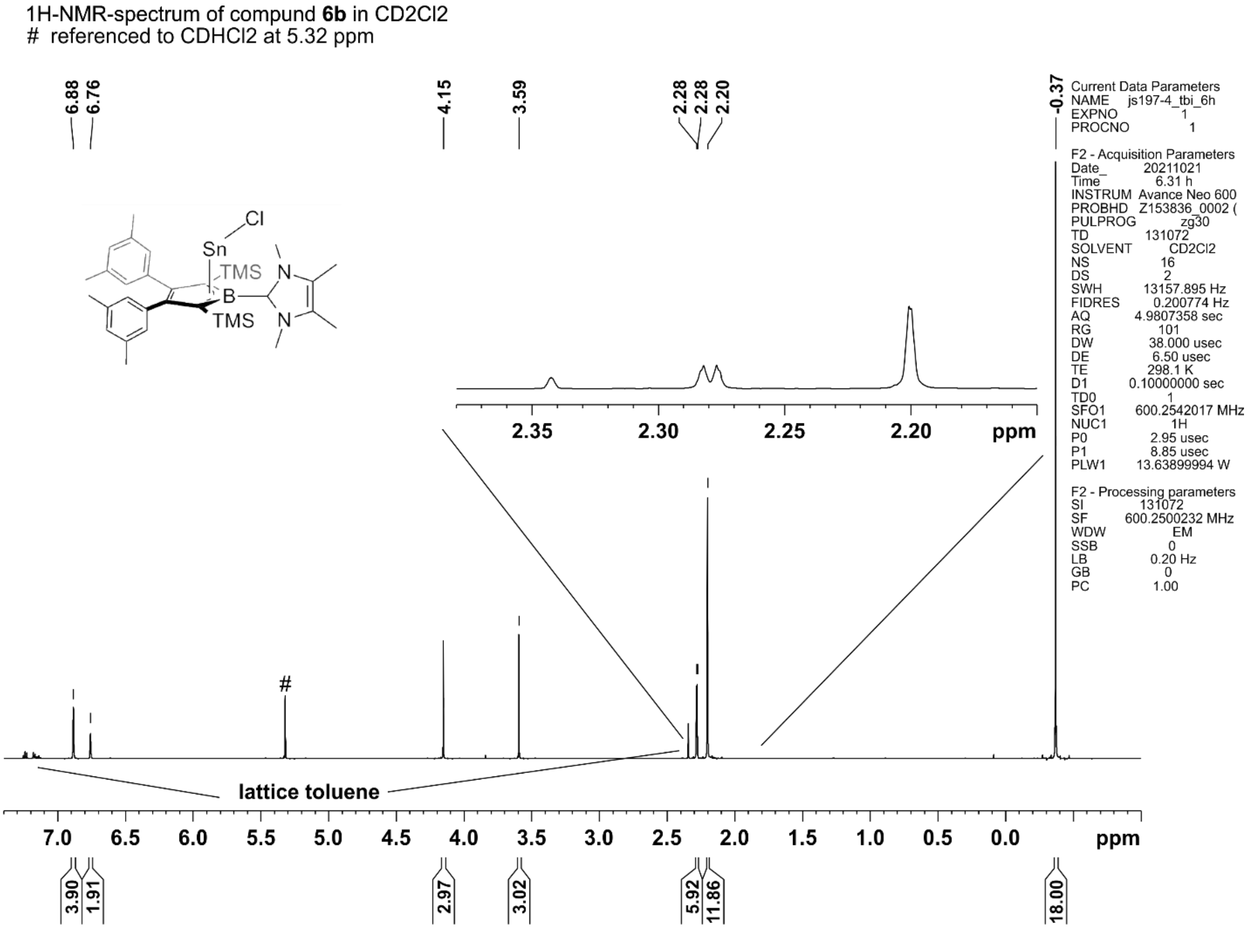
Crystal structure of Compound 6b

6b crystallised from toluene solutions in a freezer (–35°C). For further details on the diffraction measurement and refinement please see the respective section and the respective CIF-file.

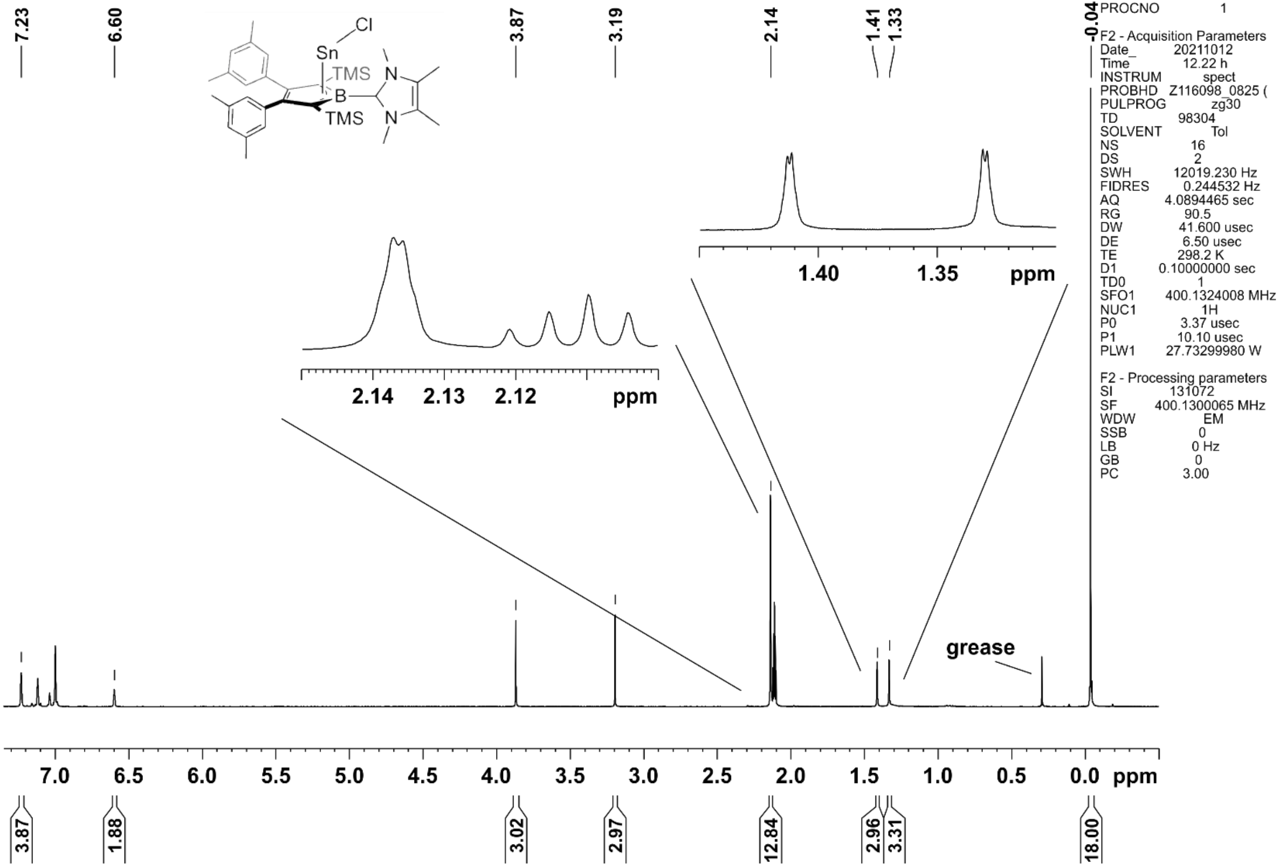


ORTEP plot of the molecular structure of **6b.** Atomic displacement parameters are drawn at 50% probability level. Hydrogen atoms, a lattice toluene and a second independent molecule within the asymmetric unit have been omitted for the sake of clarity. Selected bond length: B1–C5 1.59(2), B1–C1 1.56(1), C1–C2 1.47(1), C2–C3 1.41(1), C3–C4 1.44(1), C4–B1 1.58(1), B1–Sn1 2.45(1), C1–Sn1 2.407(8), C2–Sn1 2.493(8), C3–Sn1 2.684(8), C4–Sn1 2.715(8), Sn1–Cl1 2.649(1).

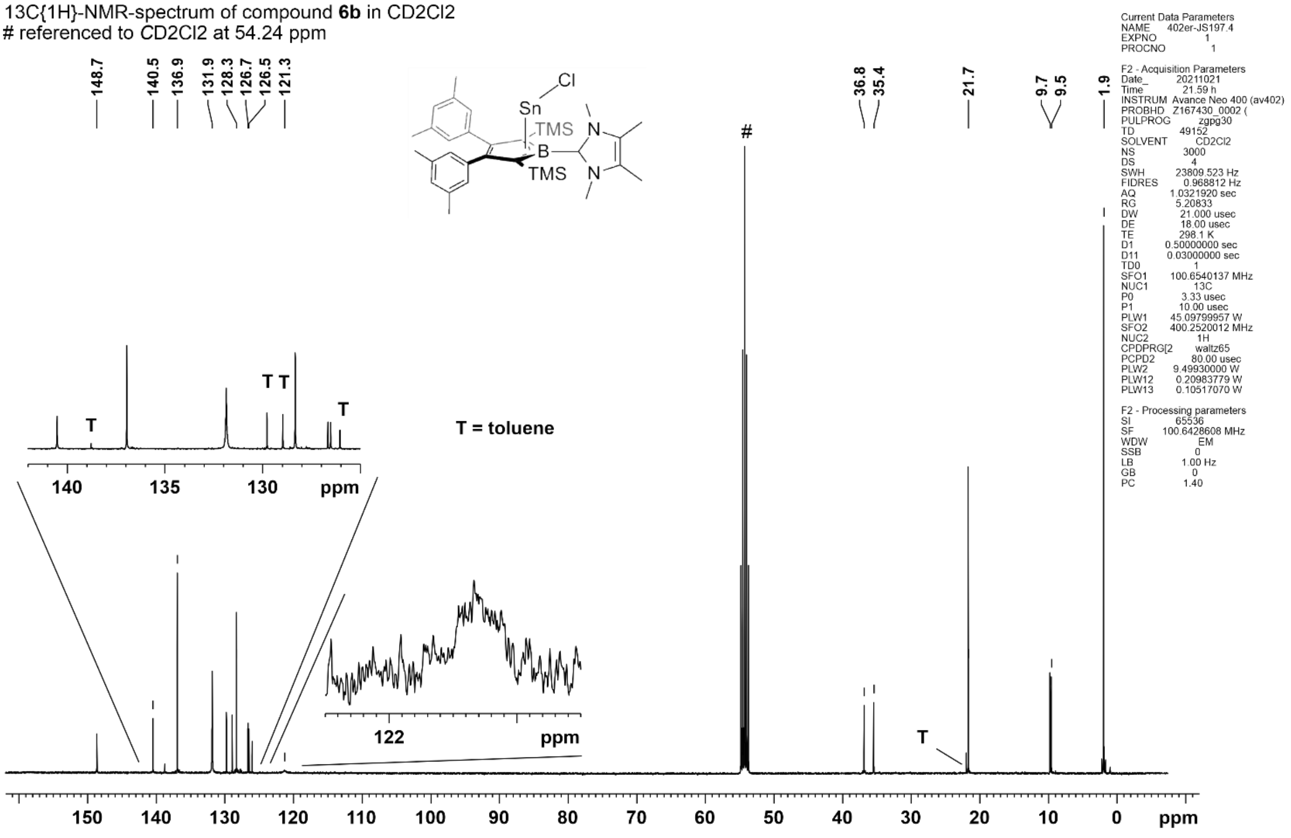
Spectra Plots for Compound 6b



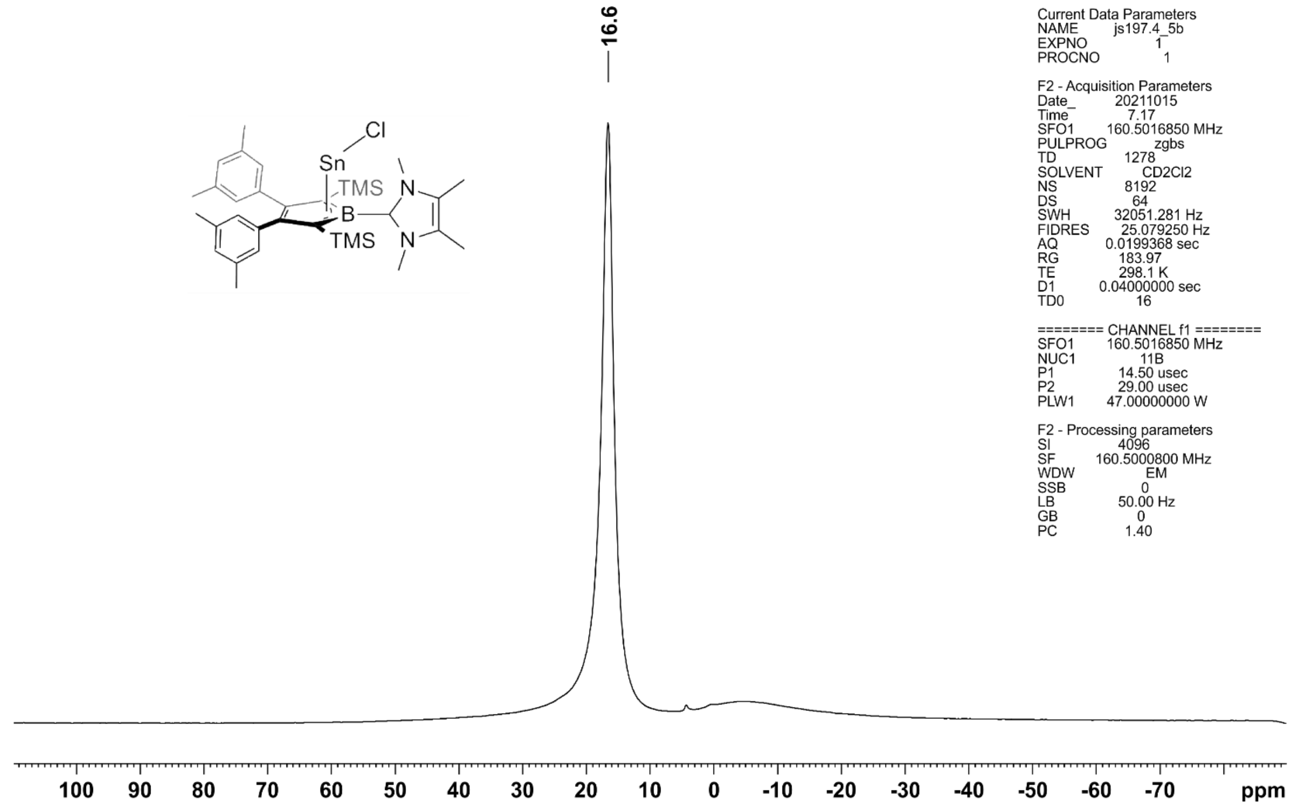
1H-NMR-spectrum of compound **6b** in toluene-d8
referenced to C6D5CD2*H* at 2.11 ppm



13C{1H}-NMR-spectrum of compound **6b** in CD2Cl2
referenced to *C*D2Cl2 at 54.24 ppm



11B-NMR spectrum (background suppressed) of compound **6b** in CD2Cl2



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RG             183.97
TE              298.1 K
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TD0                16

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F2 - Processing parameters
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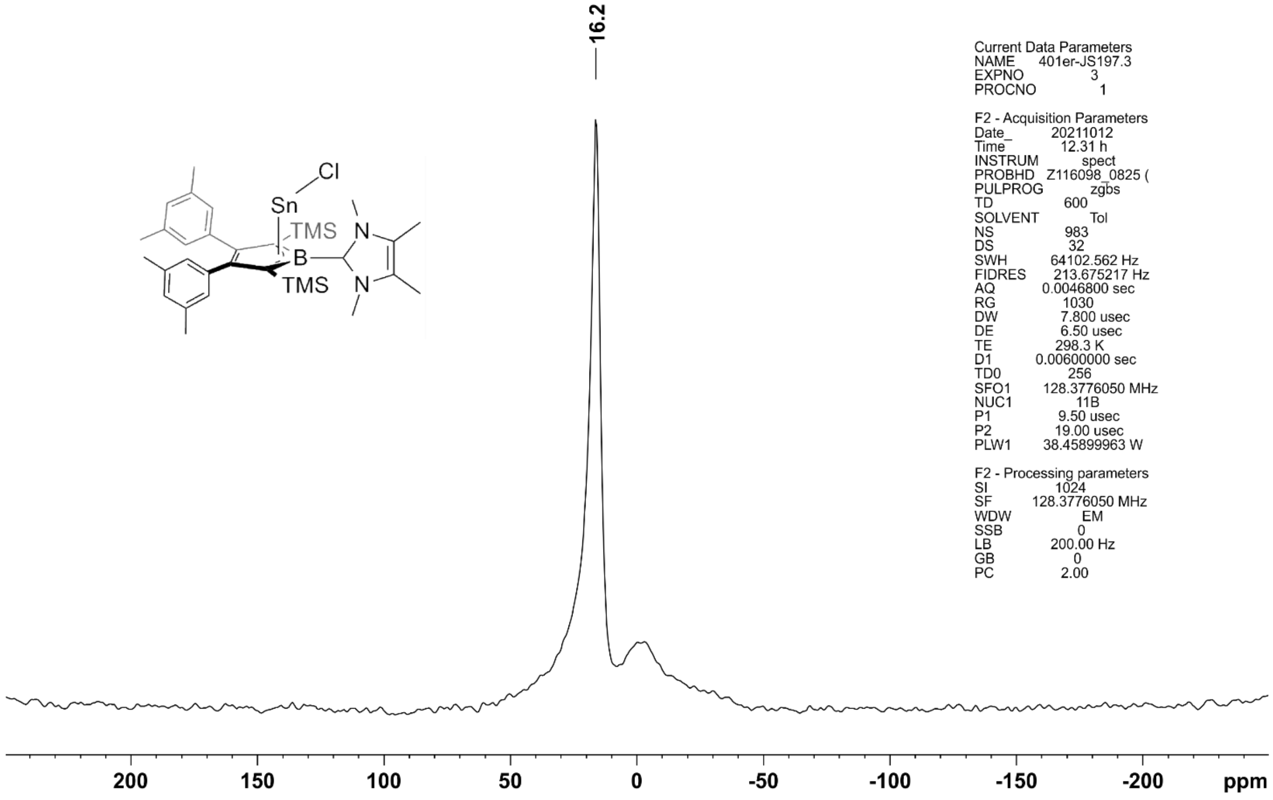
11B-NMR spectrum (background suppressed) of compound **6b** in toluene-d8



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FIDRES     213.675217 Hz
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RG               1030
DW              7.800 usec
DE               6.50 usec
TE              298.3 K
D1         0.00600000 sec
TD0               256
SFO1     128.3776050 MHz
NUC1              11B
P1               9.50 usec
P2              19.00 usec
PLW1      38.45899963 W

F2 - Processing parameters
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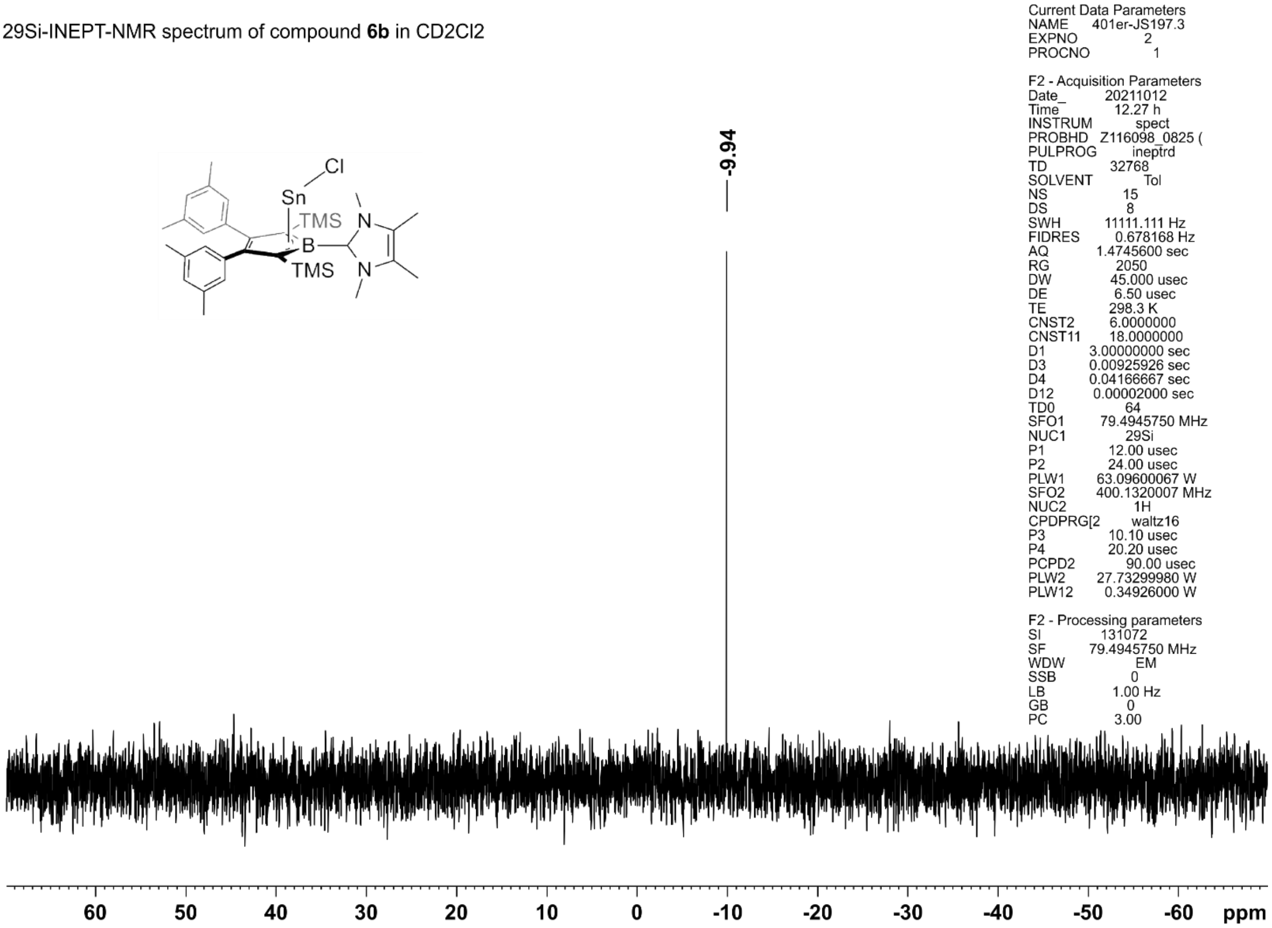
29Si-INEPT-NMR spectrum of compound **6b** in CD2Cl2



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TD               32768
SOLVENT            Tol
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TE              298.3 K
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D4       0.04166667 sec
D12      0.00002000 sec
TD0                 64
SFO1     79.4945750 MHz
NUC1              29Si
P1            12.00 usec
P2            24.00 usec
PLW1      63.09600067 W
SFO2    400.1320007 MHz
NUC2                1H
CPDPRG[2       waltz16
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PLW12      0.34926000 W

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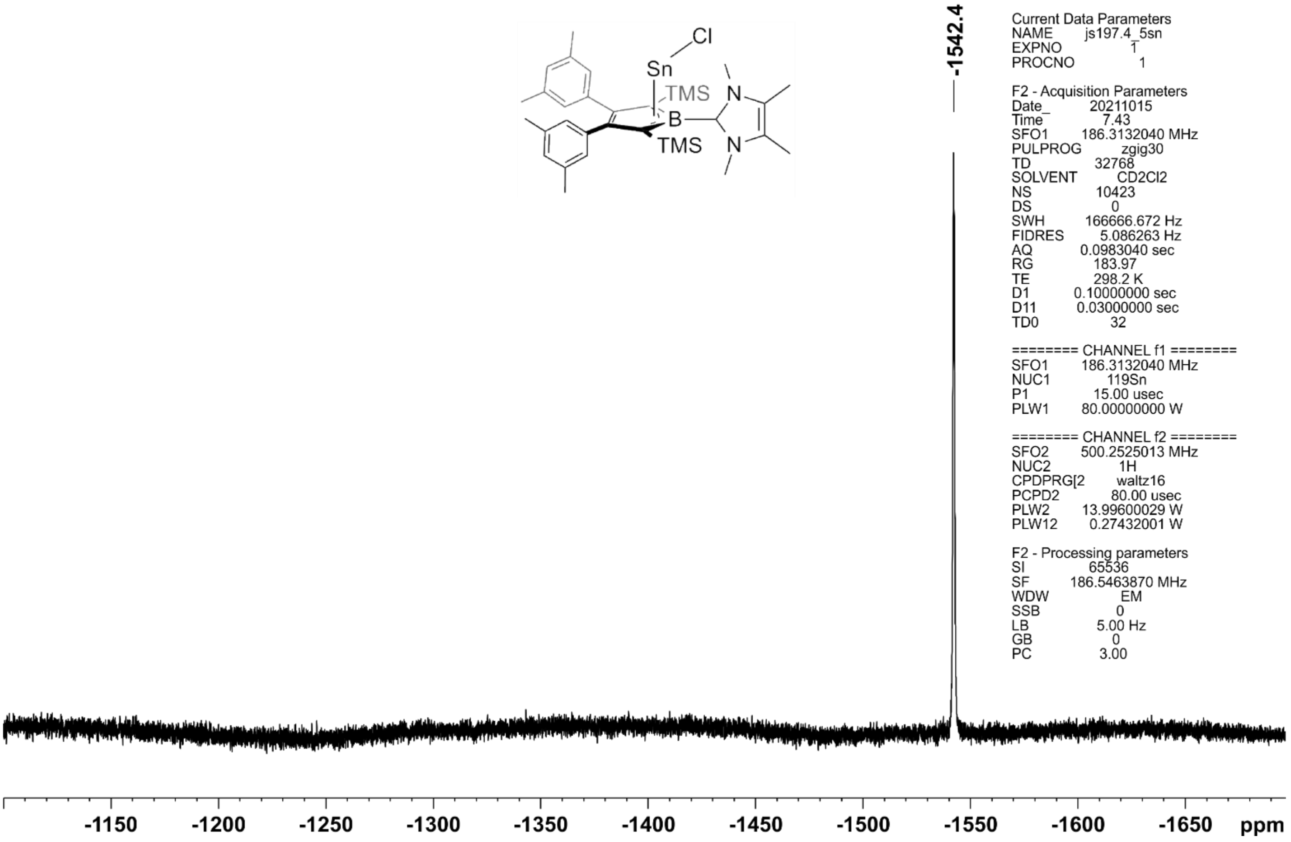
119Sn-NMR spectrum of compound **6b** in CD2Cl2



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NS               10423
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AQ         0.0983040 sec
RG              183.97
TE              298.2 K
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D11       0.03000000 sec
TD0                 32

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NUC1             119Sn
P1            15.00 usec
PLW1      80.00000000 W

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NUC2                1H
CPDPRG[2       waltz16
PCPD2         80.00 usec
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PLW12      0.27432001 W

F2 - Processing parameters
SI               65536
SF      186.5463870 MHz
WDW                 EM
SSB                  0
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GB                   0
PC                3.00
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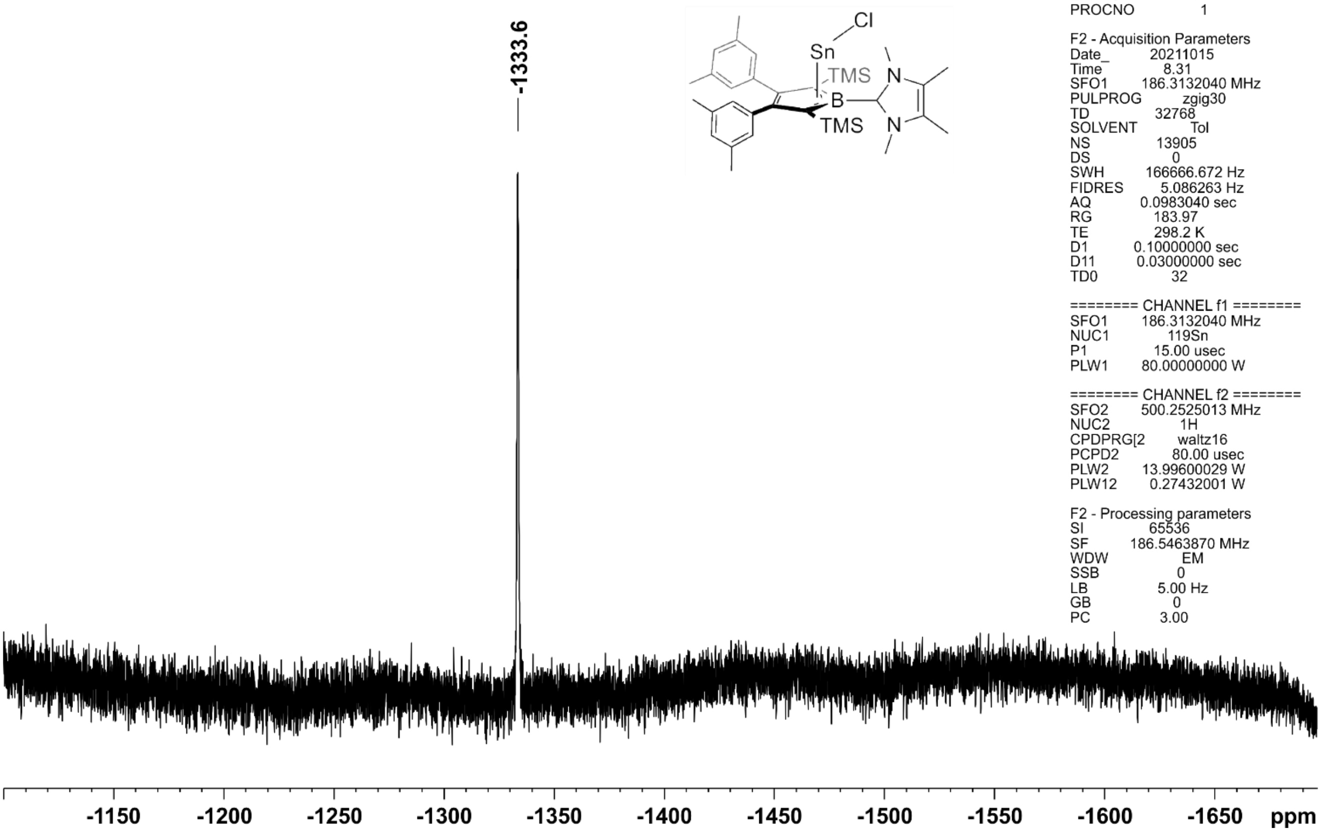
119Sn-NMR spectrum of compound **6b** in toluene-d8



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DS                  0
SWH        166666.672 Hz
FIDRES       5.086263 Hz
AQ          0.0983040 sec
RG             183.97
TE              298.2 K
D1        0.10000000 sec
D11       0.03000000 sec
TD0                32

======== CHANNEL f1 ========
SFO1      186.3132040 MHz
NUC1            119Sn
P1              15.00 usec
PLW1      80.00000000 W

======== CHANNEL f2 ========
SFO2      500.2525013 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      13.99600029 W
PLW12      0.27432001 W

F2 - Processing parameters
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WDW                EM
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LB               5.00 Hz
GB                  0
PC               3.00
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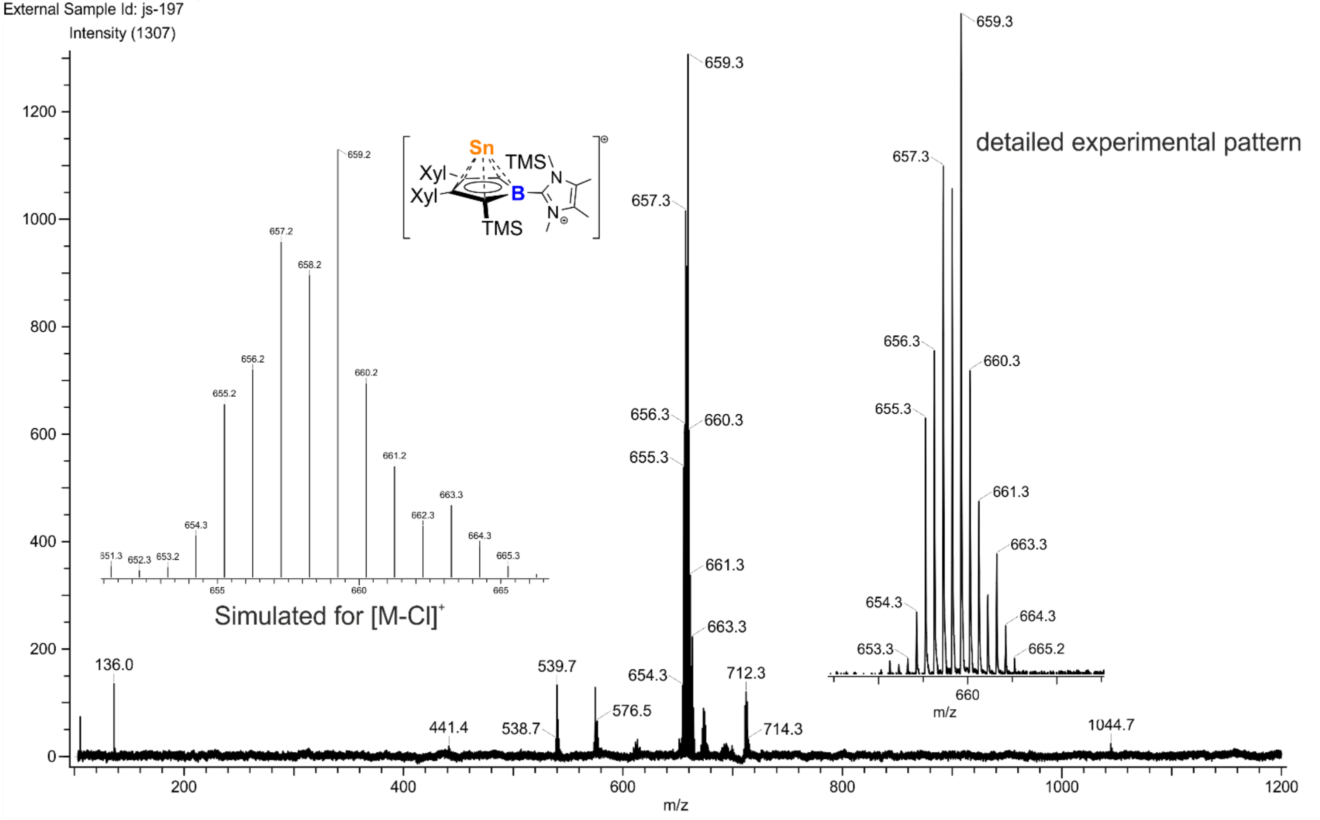


Crystallographic Details

General Data Acquisition and Processing

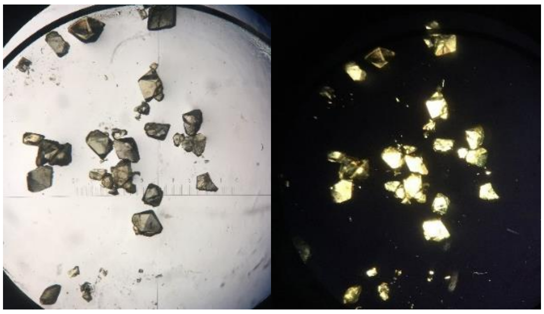
X-ray data for **1, 2, 3a, 3b, 4a, 4b, 5b** and **6b** were collected on Bruker APEX II CCD diffractometers with Mo Kα radiation. If not otherwise stated the data were obtained from crystals cooled to –173 °C via a cryo-stream. The data were integrated using SAINT implemented in Bruker's APEX3 programme suite.[5] SADABS was used for multi-scan absorption correction.[6] Two domains in twinned crystal of **2** were identified in the reciprocal lattice, sorted, integrated and absorption corrected as a two domain twin using TWINABS.[7] Structure solution was performed with SHELXT[8] and refined on F^2 using SHELXL[9] within the graphical user interphase of ShelXle.[10] In some cases DSR has been applied to treat disordered solvent molecules.[11] Hydrogen atoms were usually placed with a riding model. Further details on the individual data sets are tabulated in the analytical section of each compound.

Crystallographic and Refinement Details 1

Bright orange crystals from a homogenous crop were picked from per-fluorinated oil and did only very slowly decompose.

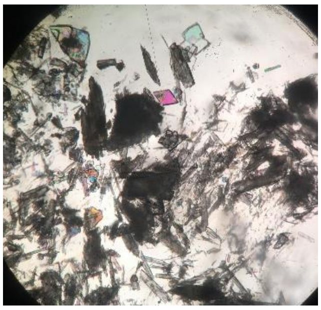
Crystallographic and Refinement Details 2

Colourless crystals were found to be twinned. Two domains were identified from the reciprocal lattice and the data were integrated as a 2-component twin. Absorption correction was performed using TWINABS. Hydrogen atoms of a methyl group were found disordered and modelled accordingly.



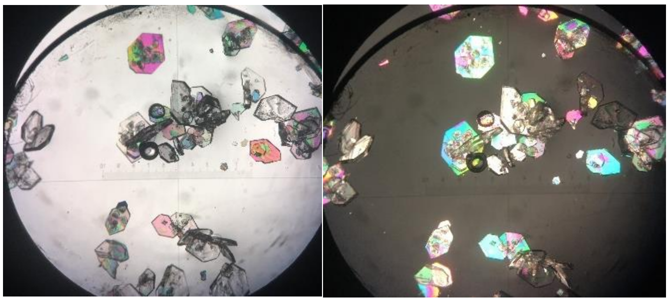
Crystallographic and Refinement Details 3a

Colourless crystals were picked from per-fluorinated oil and crystal quality only deteriorated very slowly when exposed to ambient atmosphere.



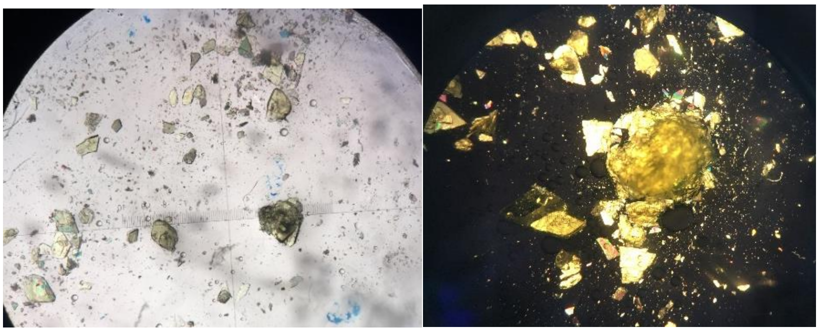
Crystallographic and Refinement Details 3b

Colourless crystals were picked from per-fluorinated oil and crystal quality only deteriorated very slowly when exposed to ambient atmosphere. Small amounts of residual electron density were found on the other side of the borole and was modelled as a minor (2-3%) occupational disorder of the Ge-apex position und modelled using SADI, SIMU and RIGU restraints.



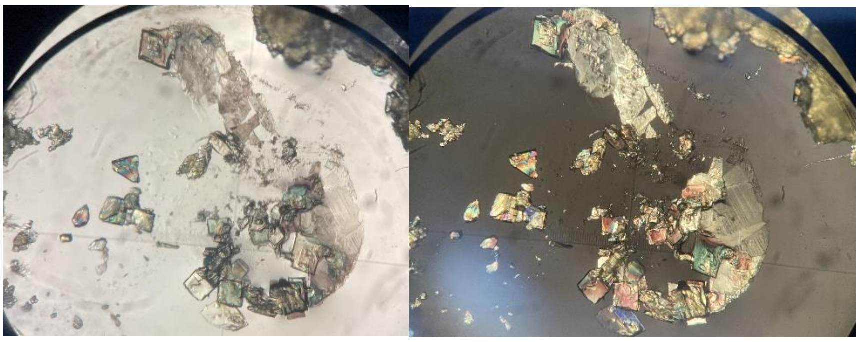
Crystallographic and Refinement Details 4a

Colourless to pale yellow crystals were picked from per-fluorinated oil and crystal quality only deteriorated very slowly when exposed to ambient atmosphere. Crystals revealed notable physical deterioration and loss in crystallinity when shock-cooled to 100K in a N_2 cryostream. The data acquisition was thus performed at 110 K. Several inner reflections (1 0 0, 0 0 1, 1 0 1, 0 1 0, 1 1 0, 0 1 1, 1 1 1) seemed to be affected by the beam stop and have been omitted in the final refinement.



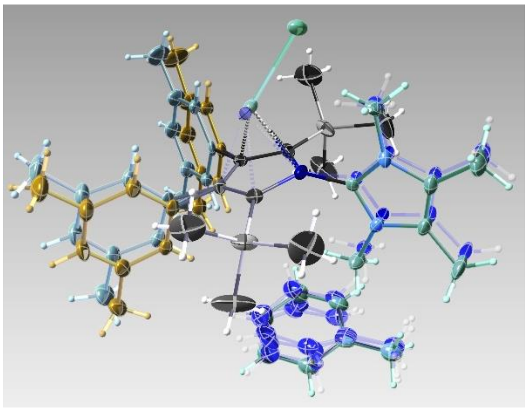
Crystallographic and Refinement Details 4b

Brittle, colourless crystals were picked from per-fluorinated oil. When removed from the mother liquor crystals immediately deteriorated and turned opaque. Successful picking, mounting and data acquisition was performed on a relatively large block. Reflection 6 1 2 was omitted in the final refinement.



Crystallographic and Refinement Details 5b

Colourless crystals were picked from per-fluorinated oil. The main molecules is located on a special position and the GeCl unit and the NHC are disordered and refined in part -1. The entire tertiary Xylyl-group is found slightly disordered and modelled accordingly over two positions using SADI SIMU and RIGU restraints. A disordered lattice toluene molecule occupying a special position was refined in Part -1.



Depiction of the refinement modelling of disordered moieties. (Light Blue: Part 1; Orange: Part 2, Bluegreen: Part -1). Blue coloured moieties represent symmetry generated positions.

Crystallographic and Refinement Details 6b

Colourless crystals were picked from per-fluorinated oil. The compound crystallised as a non-merohedral twin with the twin law 0 -1 0 -1 0 0 0 0 -1. The fractional contribution of the minor component refines to 0.48.[12]

Tabulated Crystallographic Details 1, 2, 3a, 3b, 4a, 4b, 5b and 6b

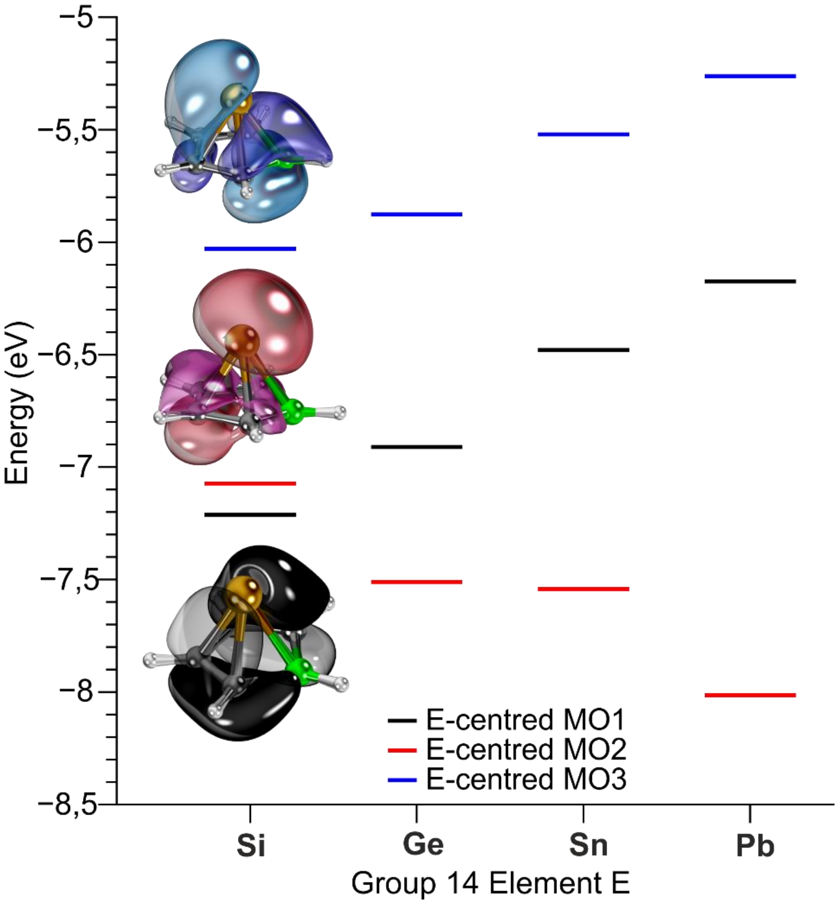
	1	**2**	**3a**	**3b**	**4a**	**4b**	**5b**	**6b**
CCDC number	2119904	2119903	2119907	2119906	2119905	2119910	2119908	2119909
empirical formula	$C_{26}H_{36}BClSi_2$	$C_{60}H_{92}B_2Cl_2Li_4O_2Si_4$	$C_{55}H_{88}BGeSi_2$	$C_{52}H_{72}B_2Cl_2Ge_2Si_4$	$C_{52}H_{81}BSi_2Sn$	$C_{26}H_{36}BClSi_2Sn$	$C_{73}H_{104}B_2Cl_2Ge_2N_4Si_4$	$C_{73}H_{104}B_2Cl_2N_4Si_4Sn_2$
formula weight	450.99	1077.97	888.83	1047.15	891.84	569.68	1387.66	1479.86
T / K	100(2)	100(2)	100(2)	100(2)	110(2)	100(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic	tetragonal	orthorhombic
space group (number)	$P\overline{1}$ (2)	$P2_1/n$ (14)	$P2_1/n$ (14)	$Pbca$ (61)	$P\overline{1}$ (2)	$Pbca$ (61)	$P\overline{4}2_1m$ (113)	$Iba2$ (45)
a / Å	9.2086(10)	14.109(2)	13.6558(16)	19.048(2)	15.8126(13)	18.8007(8)	18.172(3)	25.802(3)
b / Å	11.0462(12)	14.636(2)	15.5207(18)	11.2539(12)	16.2239(14)	11.4507(5)	18.172(3)	25.796(3)
c / Å	14.4968(16)	15.670(2)	26.337(3)	25.727(3)	22.9218(19)	25.8667(11)	11.769(3)	23.532(2)
α	111.740(2)	90	90	90	87.921(2)	90	90	90
β / °	94.288(2)	90.751(3)	99.937(2)	90	74.394(2)	90	90	90
γ	96.866(2)	90	90	90	68.826(2)	90	90	90
V / Å^3	1348.5(3)	3235.5(8)	5498.3(11)	5514.9(10)	5269.1(8)	5568.6(4)	3886.4(17)	15662(3)
Z	2	2	4	4	4	8	2	8
ρ / Mg m^{-3}	1.111	1.106	1.074	1.261	1.124	1.359	1.186	1.255
μ / mm^{-1}	0.241	0.212	0.632	1.306	0.561	1.111	0.944	0.808
F(000)	484	1160	1932	2192	1904	2336	1468	6160
crystal size / mm^3	0.646×0.495×0.444	0.467×0.413×0.329	0.356×0.136×0.095	0.315×0.198×0.185	0.451×0.323×0.158	0.239×0.232×0.152	0.418×0.112×0.080	0.168×0.090×0.052
Crystal colour	orange	colourless	colourless	colourless	colourless	colourless	colourless	colourless
Crystal shape	block	block	block	block	block	block	block	block
Radiation	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)
2θ range / °	3.05 to 59.89 (0.71 Å)	3.81 to 52.15 (0.81 Å)	3.06 to 59.16 (0.72 Å)	3.17 to 60.36 (0.71 Å)	3.70 to 59.42 (0.72 Å)	3.15 to 61.02 (0.70 Å)	3.17 to 55.00 (0.77 Å)	2.23 to 53.52 (0.79 Å)
index ranges	-12 ≤ h ≤ 12 -15 ≤ k ≤ 15 -20 ≤ l ≤ 20	≤ h ≤ ≤ k ≤ ≤ l ≤	-18 ≤ h ≤ 18 -21 ≤ k ≤ 21 -36 ≤ l ≤ 36	-26 ≤ h ≤ 26 -15 ≤ k ≤ 15 -36 ≤ l ≤ 36	-21 ≤ h ≤ 22 -22 ≤ k ≤ 22 -31 ≤ l ≤ 31	-26 ≤ h ≤ 26 -16 ≤ k ≤ 16 -36 ≤ l ≤ 36	-23 ≤ h ≤ 23 -23 ≤ k ≤ 23 -15 ≤ l ≤ 15	-32 ≤ h ≤ 32 -32 ≤ k ≤ 32 -29 ≤ l ≤ 29
Refl. collected	54731	6409	163225	119874	115246	207042	103383	111471
indep. reflections/ R_{int}	7795 R_{int} = 0.0246 R_{sigma} = 0.0152	6409 R_{int} = 0.0439 R_{sigma} = 0.0275	15429 R_{int} = 0.0512 R_{sigma} = 0.0261	8142 R_{int} = 0.0542 R_{sigma} = 0.0214	29875 R_{int} = 0.0354 R_{sigma} = 0.0331	8515 R_{int} = 0.0487 R_{sigma} = 0.0124	4667 R_{int} = 0.0492 R_{sigma} = 0.0209	16679 R_{int} = 0.0454 R_{sigma} = 0.0302
completeness to θ$_{max}$	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %
Data/Restr./Params.	7795/0/281	6409/0/347	15429/0/557	8142/3/300	29875/588/1181	8515/0/290	4667/631/380	16679/166/818
GooF on F^2	1.033	1.043	1.036	1.020	1.016	1.095	1.079	1.039
final R indices [I>2σ(I)]	R_1 = 0.0315 wR_2 = 0.0877	R_1 = 0.0413 wR_2 = 0.0977	R_1 = 0.0314 wR_2 = 0.0774	R_1 = 0.0282 wR_2 = 0.0716	R_1 = 0.0322 wR_2 = 0.0775	R_1 = 0.0182 wR_2 = 0.0488	R_1 = 0.0264 wR_2 = 0.0611	R_1 = 0.0216 wR_2 = 0.0494
R indices (all data)	R_1 = 0.0357 wR_2 = 0.0909	R_1 = 0.0566 wR_2 = 0.1045	R_1 = 0.0416 wR_2 = 0.0823	R_1 = 0.0365 wR_2 = 0.0756	R_1 = 0.0441 wR_2 = 0.0845	R_1 = 0.0204 wR_2 = 0.0503	R_1 = 0.0289 wR_2 = 0.0622	R_1 = 0.0231 wR_2 = 0.0503
largest peak/hole [eÅ^{-3}]	0.44/-0.26	0.41/-0.29	0.43/-0.30	0.52/-0.55	1.07/-0.65	0.48/-0.28	0.26/-0.18	0.44/-0.48
absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
miscellaneous		2-component twin					Flack X param. 0.010(3)	Flack X param. -0.022(5)

Computational Details

Structure Optimisation, Frequency Calculation and Electronic Structure Analyses

Computational examination was performed using ORCA (version 4.2.1.).[13] All structures were optimised starting from (modified) experimental X-Ray structures (where available) on RI-BP86-D3BJ[14] def2SVP/J model chemistry[15] in the gas phase followed by a frequency calculation on the same level of theory and thermochemical corrections were taken from these frequency calculations. For numerical accuracy, grid6 and finalgrid7 were applied. No imaginary frequencies were observed confirming true minima. All structures were then reoptimized using BP86-D3BJ-def2TZVP/J model chemistry and all considered SCF energies, property calculations as well as NBO analyses[16] are based on these gas phase structures. Graphical depictions were created using ChemCraft or IBOview.[17] For tin an ECP-28, and for Pb an ECP-46 as automatically assigned in ORCA was applied.[18]

The model complexes **[(HC)$_4$BH]E (E = Si, Ge, Sn, Pb)** were computationally assessed with the same level of theory as described above and the electronic structure probed by QTAIM and ELF analyses. The energies of the (occupied) Kohn-Sham frontier molecular orbitals of these species were probed and revealed a raise in energy of those MO's that represent formal the combination of the E-centred p_x and p_y-orbitals (that enable in-plane interactions) with the borole-diides π-system when descending the group from Si(II) to heavier group 14 congeners (depicted in BLUE and BLACK). This is likely associated with an increasing borole$_{\text{centroid}}$-E distance that leads to a mismatch overlap between the p-orbitals and the π-system. Conversely the MO bearing the (s)p_z contribution with an orbital lobe above the E-vertex position is continuously decreasing in energy which accounts for decreased nucleophilicity towards transition metal fragments such as the experimentally probed [W(CO)$_5$] (depicted in RED). Such fragments would then have to interact with the nucleophilic HOMO-lobe (depicted in blue) leading to an ever increasing angulation (i.e. deviation from linearity as observed in the Si(II)-complex) of the [M]-E-(Borole)$_{\text{centroid}}$. Similar observations were made for assessment of protonated structures.[19]



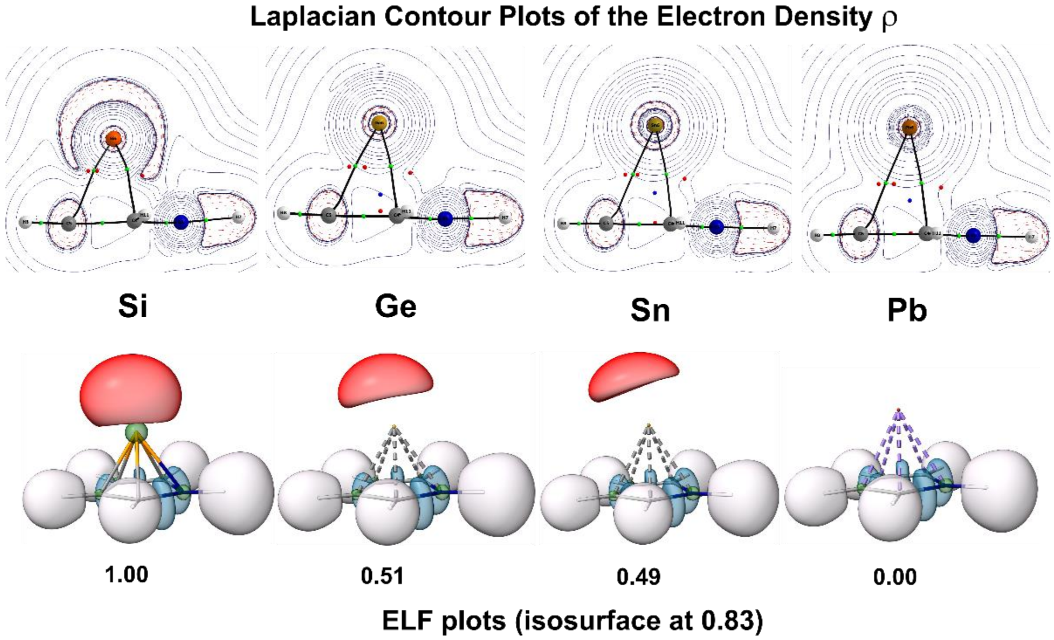
QTAIM and ELF (Electron Localization Function)

Topology analyses according to Bader's quantum theory of atoms in molecules (QTAIM)[20] and ELF analses on the model complexes **$[(HC)_4BH]E$ (E = Si, Ge, Sn, Pb)** were performed. The wavefunction files were created from single point calculations on structures obtained RI-PBE0-functional and def2-TZVPP/JK basis set on all elements except for Sn and Pb were all-electron "Sapporo-TZP-2012"(Sn) and "Sapporo-DKH3-TZP-2012"(Pb) basis sets without ECP and AutoAux were applied as implemented in ORCA 4.2.1.

The respective structures were obtained from optimisation in the gasphase (RI-BP86-D3BJ-def2TZVP/J). The QTAIM analyses were performed using the AIMAll programme suite.[21] The ELF analysis was performed using *multiwfn* software (version 3.6).[22]

The graphical representation was then created with UCSF ChimeraX.[23] Areas with negative Laplacian of the electron density (depicted in red) indicate areas of charge-concentration. In case of Si a clear valence shell charge concentration (VSCC) can be identified which is missing for the elements Ge to Pb.

The decreasing ELF blob sizes relative to the Si-lone pair of electron blob are given for Ge, Sn and Pb.



Computational assessment of ^{119}Sn NMR shifts

Computational prediction of ^{119}Sn NMR spectroscopic properties of **4a**,**4b**, **6b** and hypothetical cationic B-NHC bound borole [borole-Sn]$^+$ **E** was performed using GIAO method and RIJK-PBE0[24] functional and def2-TZVP basis set (C,H) and def2-TZVPP basis set (all hetero-atoms) on gas phase structures previously optimised using the RI-BP86-D3BJ-def2TZVP/J model chemistry. For Sn, an all-electron basis set "Sapporo-TZP-2012" without ECP and AutoAux was applied as implemented in ORCA 4.2.1. A set of reference Sn-compounds were used to assess the general viability of the computational model to reproduce ^{119}Sn-NMR chemical shifts. We have previously applied a similar set of reference compounds for computational investigations of ^{119}Sn NMR chemical shifts.[25] Our assessment reveals that the computational method is particularly well suited for the accurate prediction of high-field-shifted signals but significantly lacks performance for low-valent, low-field shifted signals. As the compounds under investigation all range in the high-field shifted region the computational predictions can be confidentially discussed.

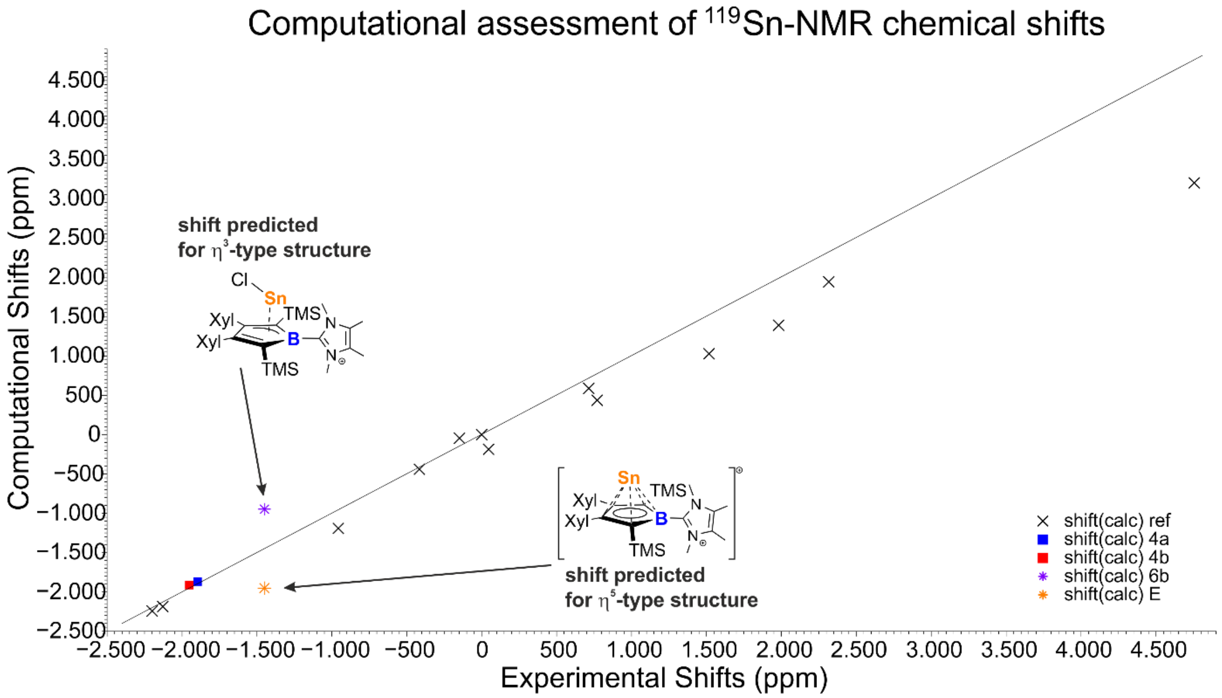
Calculated chemical shifts were obtained according to:

$$\delta_{calc} = \sigma_{ref} - \sigma_{calc}$$

$\sigma_{ref}(^{119}Sn)$ = 2608.9 ppm for Me_4Sn.

Compound	σ_{calc}	δ_{calc}	δ_{exp}
$SnMe_4$ (reference)	2608.9	0	0
$SnCl_4$	2653.8	–44.9	–149[26]
$SnCp^*_2$	4793.5	–2184.6	–2129[27]
$Sn(NTMS_2)_2$	2172.3	436.6	770[28]
$Sn(2,6\text{-}Mes_2(C_6H_3))_2$	1219.3	1389.6	1971[29]
$Sn(B[(N(Dipp)CH)]_2)_2$	–591.1	3200.0	4755[30]
(η^3-Allyl)-Sn(2,6-Trip$_2$(C_6H_3))	3800.9	–1192.0	–957[31]
$Sn[CH(TMS)_2]_2$	666.8	1942.1	2315[32]
(2,6-Trip$_2$(C_6H_3))SnPh	1580.0	1028.9	1517[33]
$[Trip_3Sn]^+$	2020.8	588.1	714[34]
Jones' cation $\{[R(R')N]Sn\}^+$	2794.6	–185.7	46[35]
$TripSnH_3$	3048.6	–439.3	–416[36]
4a	4477.1	–1868.2	–1897
4b	452.2	–1911.3	–1952
6b	3555.7	–946.8 (η^3)	–1438[a]
E	4.560.7	–1951.8 (η^5)	–1438[b]

a) Averaged between shifts in toluene und dichloromethane; b) arbitrarily assigned shift of **6b** for comparison; Mes = 2,4,6-$Me_3(C_6H_2)$; Trip = 2,4,6-*i*$Pr_3(C_6H_2)$;



XYZ-coordinates of optimised structures

All structures optimised at RI-BP86-D3BJ\def2TZVP\J level of theory (see above).

Molecular structure of borole-Si
E(SCF) = -469.870291549482 H

B	8.333475891	5.359923080	5.248405029
C	7.519131409	4.837047562	4.050520793
C	8.345295420	4.847508629	2.868868020
C	9.729002766	5.554702691	4.627083331
C	9.666805221	5.276669800	3.213651295
Si	9.176052423	3.529997958	4.296784767
H	8.011630956	5.426873867	6.398651571
H	10.500301687	5.305154349	2.513666204
H	8.053782020	4.510651038	1.875361792
H	6.504446313	4.440932927	4.010028740
H	10.680835346	5.797213170	5.099667974

Molecular structure of borole-Ge
E(SCF) = -2257.638347413681 H

B	8.335814994	5.351940235	5.249368744
C	7.514257181	4.837890641	4.048131790
C	8.344514592	4.844528702	2.869634389
C	9.733027189	5.558439645	4.627014281
C	9.668661433	5.274548140	3.215103402
Ge	9.207223878	3.410087307	4.326623225
H	8.006072556	5.445711470	6.396506203
H	10.494955655	5.330322031	2.507586148
H	8.046319403	4.535129401	1.868731605
H	6.489415492	4.468513376	4.000258146
H	10.680497080	5.829564124	5.093731584

Molecular structure of borole-Sn
E(SCF) = -394.808476624129 H

B	8.337644445	5.346698119	5.248876203
C	7.510044427	4.835232937	4.045437611
C	8.343531635	4.844511728	2.869561303
C	9.738660700	5.558985001	4.626887592
C	9.669394470	5.275093728	3.215475209
Sn	9.262767701	3.195900179	4.380355196
H	7.995777687	5.483023428	6.389516050
H	10.483043662	5.374742314	2.497338330
H	8.034681990	4.579628879	1.858558920
H	6.469452174	4.513425071	3.986619808
H	10.675760561	5.879433688	5.084063293

Molecular structure of borole-Pb
E(SCF) = -373.412876757961 H

B	8.338554489	5.344347884	5.248303919
C	7.507227189	4.838149191	4.043032102
C	8.342090164	4.846701100	2.870263165
C	9.740097560	5.563280672	4.625592451
C	9.668883839	5.277586551	3.216417645
Pb	9.289579925	3.094390346	4.404008054
H	7.991776496	5.497999848	6.386203291
H	10.477395635	5.392260703	2.494130355
H	8.030386538	4.597588217	1.855706139
H	6.461451825	4.533281716	3.980068956
H	10.673315793	5.901088845	5.078963439

Molecular structure of 4a
E(SCF) = -2849,83279149304 H

Si	5.663916000	4.195893380	4.038995020
C	7.490772439	4.628564751	4.004331035
B	8.305757859	5.354346122	5.118209688
Si	11.295926573	6.042530065	5.482293210
C	8.435242192	4.282393983	2.954280468
C	10.930079216	4.481807001	2.422312908
C	7.748147338	5.950660471	6.455304417
C	9.791597666	5.277831272	4.652933692
H	8.891989329	4.672733854	7.749152410
C	8.157141944	5.478258698	7.713490801
C	7.656114115	6.006051367	8.907666129
C	6.713223139	7.039719079	8.818315029
H	6.306243458	7.461206115	9.739391088
C	6.274479659	7.551592678	7.589747658
C	6.806977227	6.992502568	6.421165490
H	6.489837630	7.368406624	5.448503246
C	5.143242694	3.841836751	5.816288124
H	4.069723301	3.601800638	5.857273713
H	5.332994632	4.698965368	6.475311462
H	5.692990514	2.980024721	6.224517929
C	4.646562474	5.652628961	3.398007801
H	4.916364132	5.924861006	2.367858624
H	4.804089748	6.538584792	4.029370084
H	3.572135122	5.414796551	3.411197512
C	5.278845927	2.653999540	3.018154501
H	5.430399219	2.810609506	1.942720429
H	4.232669662	2.351071028	3.178439071
H	5.919079018	1.811495823	3.321792660
C	12.174400459	4.753743897	6.553008731
H	12.518600025	3.899224588	5.951240749
H	11.494629869	4.367925100	7.328019940
H	13.053498494	5.179884540	7.059783996
C	12.506096998	6.741395708	4.213054825
H	13.019477534	5.961454881	3.637255253
H	13.266967037	7.347560547	4.728533222
H	11.985845010	7.393666917	3.496380949
C	10.750043782	7.474054891	6.576828257
H	10.156776623	8.199706154	6.001556859
H	11.633402158	7.996534057	6.975040301
H	10.130872438	7.143478896	7.420171647
C	8.140135168	3.726533285	1.617807544
C	7.237226611	4.392825395	0.782085965
H	6.721038217	5.269448341	1.174705297
C	7.014490939	3.968786534	-0.534172077
C	6.003757300	4.723579009	-1.406816746
C	6.394190603	6.215312528	-1.475369582
H	7.390733958	6.337172034	-1.923594851
H	6.412767600	6.677392793	-0.479125990
H	5.670041089	6.770615112	-2.090194712
C	4.602843300	4.588340644	-0.772462867
H	3.855153544	5.128831908	-1.372485006
H	4.580961153	4.998489642	0.246342920
H	4.301679973	3.532423621	-0.714967823
C	5.945972702	4.175606430	-2.840552900
H	5.219282597	4.755670569	-3.427246622
H	5.627293460	3.123512750	-2.862951470
H	6.920962264	4.252448957	-3.343473500
C	7.732250400	2.858709483	-1.000893586
H	7.580817230	2.525810118	-2.024272621
C	8.647845768	2.170731789	-0.190838286
C	9.461635681	0.969542272	-0.687234583
C	9.101036446	-0.267690935	0.162497171
H	8.031162867	-0.504759871	0.072351684
H	9.320967549	-0.100701940	1.225933266
H	9.679281871	-1.142882857	-0.170570229
C	9.187594100	0.647398286	-2.163341452
H	9.440192993	1.495048257	-2.817019144
H	8.134397715	0.381504641	-2.334894970
H	9.802700374	-0.209144947	-2.474529244
C	10.965610538	1.278572752	-0.524703837
H	11.568934921	0.415528205	-0.845043086
H	11.224649945	1.511504858	0.516265994

H	11.257071103	2.147182064	-1.131101420
C	8.827878214	2.614451357	1.120606079
H	9.534565007	2.107025205	1.778152071
C	9.783037811	4.650426698	3.340245432
C	10.892306554	5.119906278	1.178859557
H	10.022142375	5.730393660	0.937536664
C	11.921716230	4.960079382	0.246694279
C	11.803983747	5.651064233	-1.117018108
C	11.754707335	7.178942842	-0.902313200
H	11.663556604	7.698446671	-1.868249975
H	12.668714291	7.532431509	-0.403798608
H	10.897586990	7.468353765	-0.279160350
C	10.500999877	5.189938714	-1.805079338
H	10.380243582	5.699838120	-2.772941780
H	9.616573689	5.404039760	-1.191240513
H	10.513310980	4.106089707	-1.985598468
C	12.985003533	5.323944046	-2.042233458
H	12.848287733	5.831033741	-3.008139496
H	13.059298962	4.244420857	-2.239249326
H	13.941513969	5.664217140	-1.619522718
C	13.013496714	4.155124137	0.600592297
H	13.818773530	4.015045226	-0.115651965
C	13.090339156	3.509079820	1.843322836
C	14.279137224	2.627288140	2.245556141
C	13.773009732	1.213018083	2.600844082
H	13.281051669	0.746323209	1.735500004
H	13.050361158	1.236299219	3.428008899
H	14.613812354	0.572250100	2.906265981
C	15.317742179	2.498944532	1.121492186
H	14.883189182	2.047550848	0.217740828
H	16.143482526	1.853922967	1.454470299
H	15.746049764	3.474266227	0.849093064
C	14.965104464	3.251964698	3.479487576
H	15.818475742	2.634820056	3.798916245
H	14.270945343	3.335627111	4.327014389
H	15.335479868	4.261392414	3.249984314
C	12.031225910	3.682236690	2.741016992
H	12.044128775	3.177713293	3.709186870
C	8.102922761	5.502211627	10.285889014
C	5.236024121	8.680933496	7.569984713
C	5.795585211	9.902894497	8.328899993
H	6.030008286	9.656920536	9.373615245
H	6.718424925	10.265751123	7.853929722
H	5.061257707	10.722889858	8.330248115
C	4.880017588	9.121151283	6.142007520
H	5.760875799	9.491752874	5.598366733
H	4.438358828	8.298270344	5.561548805
H	4.141659948	9.935196381	6.180053961
C	3.945070052	8.192309448	8.261246830
H	3.531016964	7.319157899	7.736632466
H	4.131244972	7.900628130	9.303949368
H	3.184815007	8.988371896	8.261707144
C	8.730713634	6.672289767	11.073118309
H	9.057076997	6.334203476	12.068529645
H	9.604827323	7.073927261	10.540535187
H	8.015645499	7.494552023	11.211981412
C	6.878069949	4.962762256	11.054234367
H	6.414140068	4.128367161	10.508744312
H	7.177140118	4.602053995	12.050300154
H	6.114043108	5.740254094	11.190946870
C	9.144989333	4.377688612	10.184039344
H	9.436425250	4.051571086	11.192944664
H	8.747377603	3.501871749	9.650852582
H	10.054862126	4.713377458	9.665363837
Sn	9.025753031	3.000304445	4.924802539
B	8.333475891	5.359923080	5.248405029

Molecular structure of 4b

E(SCF) = -2291,75234160886

Sn	8.196081632	3.314477141	7.729551414
C	8.156198892	4.931228935	9.541809995
Cl	8.745320074	7.138662740	7.601138395
B	9.031599431	5.570044338	8.438825422
Si	6.481238923	5.505738487	10.173140725
Si	11.621244131	4.895160998	6.977839208
C	8.904807446	3.766979542	10.001312669
C	5.470121775	6.124555493	8.707314786
H	5.251428970	5.304239322	8.006266663
H	6.003700746	6.907407002	8.152562299
H	4.507643990	6.535049217	9.048541511
C	10.207298854	4.596769300	8.176547455
C	10.087411032	3.561951559	9.193443791
C	6.732570226	6.925260108	11.388451982
H	7.315616365	7.729870460	10.917374946
H	7.270033366	6.600421924	12.290651833
H	5.766207149	7.345173101	11.706025027
C	5.502526111	4.107271885	10.978784336
H	5.454226930	3.228731735	10.317420219
H	4.469675107	4.439804558	11.165112859
H	5.935568755	3.777711873	11.931412539
C	10.891791617	5.176112615	5.262357456
H	11.668486433	5.474563229	4.542190095
H	10.127783854	5.965520435	5.290723578
H	10.419361029	4.256795943	4.883147691
C	12.503587821	6.450456245	7.571790371
H	13.322849147	6.727508251	6.891354378
H	12.931584310	6.295860522	8.573279212
H	11.801344986	7.293813456	7.629386930
C	12.872457233	3.489205546	6.878918579
H	12.425113934	2.562663974	6.493617935
H	13.318841103	3.260768218	7.856257316
H	13.682681544	3.782336504	6.192870584
C	11.086736785	2.513493088	9.505973124
C	11.217576274	1.344860213	8.746231352
H	10.559665806	1.192733200	7.886425946
C	12.168579019	0.373112878	9.068833314
C	12.985788437	0.585969147	10.188120928
H	13.726963924	-0.171041758	10.457969922
C	12.872021981	1.738438234	10.973654937
C	11.916696130	2.699108180	10.616944495
H	11.802842396	3.602828144	11.218982347
C	12.330606064	-0.858218709	8.215797705
H	11.388201858	-1.129941139	7.720758486
H	12.668944403	-1.718136273	8.810014545
H	13.079983817	-0.690163503	7.425688026
C	13.738135377	1.941951948	12.190005660
H	14.491385126	1.148652327	12.282408972
H	13.131530610	1.942025018	13.108592428
H	14.262663634	2.908002193	12.148877477
C	8.632066571	2.970003900	11.214150424
C	8.543371027	1.574194219	11.196197522
H	8.622186202	1.047545961	10.243220829
C	8.364481649	0.845956663	12.378165448
C	8.267316421	1.544358756	13.587568527
H	8.125233005	0.984215450	14.515646954
C	8.352076647	2.943173164	13.638476696
C	8.542275386	3.641697382	12.442985216
H	8.636612058	4.729043783	12.458243100
C	8.287414899	-0.658685721	12.337600443
H	7.453318904	-0.997979453	11.704967599
H	8.144066985	-1.079627992	13.341316505
H	9.209035579	-1.087739009	11.916158874
C	8.214596018	3.679895944	14.945967505
H	8.733357668	4.647598632	14.916249924
H	8.621671760	3.094893457	15.782207092
H	7.155453662	3.882012027	15.172762479

Molecular structure of 6b

E(SCF) = -2675,44563554094

Sn	17.947321499	12.953497178	14.817024398
B	20.064251446	12.833037358	16.314501199
Cl	16.338261759	11.149276548	15.585778353
Si	20.030030959	9.842819270	15.670404576
Si	20.618578979	15.832817523	16.167887856

C	20.586672359	14.075581165	15.542428351
C	20.779217748	13.649532657	14.199236533
C	20.420028142	12.264599643	14.027124669
C	19.996731641	11.671359010	15.287958479
N	19.133457491	12.626467890	18.820265662
N	21.276376443	12.716790157	18.571341416
C	20.104130279	12.713030786	17.874697051
C	21.046833985	12.636490115	19.942788037
C	19.684750248	12.584324344	20.101948198
C	22.592056672	12.721453833	17.948024508
H	23.203835449	13.532511855	18.362440039
H	22.451203259	12.884412662	16.873353718
H	23.095933051	11.760057073	18.116802653
C	22.150722553	12.612074424	20.938348758
H	21.743299719	12.542661624	21.953634365
H	22.767194421	13.522528349	20.885830771
H	22.818563323	11.750448526	20.785893667
C	18.861962612	12.497512526	21.337441663
H	19.512477798	12.507129725	22.219970390
H	18.269594276	11.570373484	21.370484557
H	18.165420883	13.344533731	21.425881172
C	17.703883873	12.634669852	18.540520465
H	17.170196989	12.209583631	19.396108941
H	17.483412493	12.024937786	17.656870743
H	17.355739907	13.662839127	18.370317777
C	21.845955659	9.326669667	15.531070570
H	21.983936914	8.261449058	15.771740384
H	22.480767996	9.915408847	16.210189451
H	22.208588593	9.494360172	14.505962140
C	19.447629707	9.546724315	17.444178481
H	19.494358766	8.470031230	17.668119792
H	18.401250034	9.862619247	17.563440376
H	20.063084146	10.066829413	18.191782517
C	19.012256958	8.708434584	14.563546102
H	19.006677692	7.693102573	14.990272415
H	19.430948761	8.649746319	13.550743230
H	17.971460026	9.054646642	14.497207324
C	19.598646689	15.928796443	17.763044940
H	19.524956679	16.971701010	18.106974798
H	20.044773020	15.343323878	18.580637727
H	18.576495052	15.558348585	17.595844383
C	22.357532390	16.435055840	16.624620584
H	22.301751696	17.404046377	17.144421335
H	22.989190827	16.569119228	15.736214493
H	22.865735343	15.726549117	17.295632846
C	19.859965189	17.035998540	14.929068905
H	19.817263300	18.055094274	15.343089634
H	18.834633013	16.727214361	14.676314796
H	20.436084543	17.066663833	13.994487174
C	21.222046647	14.504801923	13.079522879
C	22.424774885	15.222299206	13.180822002
H	23.025681392	15.112701218	14.085210246
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C	22.102368638	16.131751778	10.977335059
H	22.443722656	16.767188886	10.155513712
C	20.908554378	15.412952831	10.835245708
C	20.479219688	14.607279117	11.895485838
H	19.547548387	14.045135433	11.807028317
C	24.143791287	16.845355722	12.292402219
H	23.932084957	17.857172579	12.674371316
H	24.660351973	16.962126371	11.329410946
H	24.836413559	16.367084804	12.998681708
C	20.100002465	15.490441181	9.565245402
H	19.058116562	15.776488644	9.772668691
H	20.071261883	14.513760042	9.058180040
H	20.521715382	16.223714944	8.864995089
C	20.613150711	11.528849811	12.760109598
C	21.879431531	11.519938826	12.155583371
H	22.695124346	12.067896752	12.630868014
C	22.107975596	10.838331442	10.955150947
C	21.044574645	10.144152823	10.364947379
H	21.211120398	9.608186858	9.426565916
C	19.768032718	10.129780439	10.944199370
C	19.567926303	10.834858448	12.134487219
H	18.572687457	10.855971248	12.585455247
C	23.465737248	10.882553594	10.301475608
H	23.561696669	10.114301474	9.522487421
H	24.269110402	10.729064852	11.036414285
H	23.641455491	11.862447214	9.830090779
C	18.637069613	9.356526915	10.316440578
H	18.524725649	8.369799232	10.794053866
H	18.810434195	9.188215747	9.244872385
H	17.678987919	9.881564021	10.434803832

Molecular structure of [E]$^+$
E(SCF) = -2214.948785791217 H

Sn	18.447092340	13.252393247	14.715028928
B	20.259189037	12.800798725	16.337752004
Si	20.006914802	9.800170594	15.623351041
Si	20.537493795	15.876697787	16.168951619
C	20.576623718	14.095453361	15.545707181
C	20.770161147	13.676439268	14.166522098
C	20.534846956	12.250811410	14.025236183
C	20.203793284	11.649906777	15.307626257
N	19.181867029	12.495818098	18.765558100
N	21.308673969	12.850820127	18.687760512
C	20.209361668	12.703408856	17.903095303
C	20.980405336	12.744780706	20.038150631
C	19.626141379	12.523510635	20.088584255
C	22.664339527	13.029742758	18.182678188
H	23.112472476	13.930926957	18.618262798
H	22.613751990	13.137014586	17.094511743
H	23.280618519	12.158057806	18.438406989
C	21.993206413	12.858367591	21.119694799
H	21.515716554	12.739559977	22.098620539
H	22.493263301	13.838329299	21.107995321
H	22.770910579	12.085111616	21.031322765
C	18.711725694	12.333568122	21.244479117
H	19.269687420	12.419204656	22.183534490
H	18.235317108	11.341657787	21.229751537
H	17.912496441	13.089352557	21.260823355
C	17.793609734	12.281689415	18.389068200
H	17.408321523	11.377621950	18.875859832
H	17.745890999	12.148633061	17.304105655
H	17.177546706	13.142959428	18.679543974
C	21.280044026	8.827799096	14.641845359
H	21.264506293	7.772512263	14.953215414
H	22.294280731	9.214836319	14.816881186
H	21.088349423	8.869170556	13.562135814
C	20.316714475	9.492715751	17.461434499
H	20.336551165	8.409449789	17.652568463
H	19.535671671	9.921077560	18.104129870
H	21.285372219	9.900954815	17.784667855
C	18.258610452	9.218393873	15.221467253
H	18.123594751	8.165144149	15.509871554
H	18.042754496	9.296042092	14.147249897
H	17.503124536	9.807842480	15.763585042
C	19.541248047	15.885886498	17.775634464
H	19.388410102	16.921636002	18.113424824
H	20.046759080	15.348761268	18.591081745
H	18.546650722	15.436084152	17.636463679
C	22.258352382	16.546568841	16.550846876
H	22.170883153	17.466738506	17.148086422
H	22.808918450	16.798502894	15.635207905
H	22.867360707	15.835470604	17.126459359
C	19.680005274	16.994339498	14.922271525
H	19.658254091	18.031896927	15.287743642
H	18.636938943	16.684705249	14.753836524
H	20.193804869	16.985963967	13.951721031
C	21.220055722	14.539001748	13.056051553
C	22.409394400	15.261534559	13.209811601
H	22.972646770	15.166685479	14.139137618
C	22.901569220	16.073958697	12.179645499
C	22.179284435	16.138624019	10.983068502

H	22.553676838	16.765647157	10.169784524
C	20.991307620	15.414765446	10.794294488
C	20.524676380	14.616164530	11.841078313
H	19.606701363	14.039656193	11.709092859
C	24.164149040	16.873477539	12.368960969
H	23.934531021	17.884949881	12.739960309
H	24.711221471	16.990876994	11.424215834
H	24.834234162	16.399535471	13.098801181
C	20.237585140	15.504527056	9.493709937
H	19.824651741	16.513710101	9.344595504
H	19.404842916	14.790440630	9.463677467
H	20.897064785	15.296533887	8.638840237
C	20.724736220	11.520831294	12.753912869
C	21.984103110	11.533608839	12.147056010
H	22.791420906	12.111450300	12.600331234
C	22.220961790	10.816642640	10.965855703
C	21.165369299	10.093044892	10.401240111
H	21.338068460	9.537387667	9.476146687
C	19.886336962	10.073264720	10.979867751
C	19.682888197	10.796175692	12.157498011
H	18.689803874	10.810117888	12.612985108
C	23.587591035	10.824836629	10.333207069
H	23.559073412	10.426000266	9.311369600
H	24.292328134	10.208446612	10.912616005
H	24.000921114	11.842618715	10.295246089
C	18.766773711	9.292324339	10.343652129
H	18.976202041	8.212183693	10.368494015
H	18.635984100	9.570345408	9.287892519
H	17.813712549	9.462292205	10.861223174

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