Electronic Supporting Information for

Stable lead(II) boroxides

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Contents

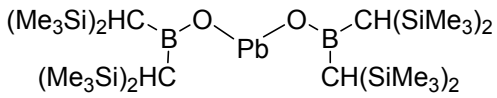
S1- Experimental section

General procedures:

All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O_2 < 1 ppm, H_2O < 5 ppm) for catalyst loading. $[Pb[N(SiMe_3)_2]_2]$[1] was prepared following literature protocol. Solvents (THF, Et_2O, pentane, and toluene) were purified and dried (water contents below 8 ppm) over columns of alumina (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw vacuum cycles.

NMR spectra were recorded on Bruker AM-400 spectrometer. All ^1H and $^{13}C\{^1H\}$ chemical shifts (reported in ppm) were determined using residual signals of the deuterated solvents and were calibrated vs $SiMe_4$. Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, HMBC, HSQC) NMR experiments. ^{207}Pb NMR spectra were referenced against a solution of $[Pb[N(SiMe_3)_2]_2]$ in benzene-d_6 ($\delta^{207}Pb$ = +4916 ppm at 298 K). ^{29}Si NMR spectra were referenced against $SiMe_4$. Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyzer instrument at the London Metropolitan University and were the average of two independent measurements. Melting points were measured in sealed glass capillaries loaded with ca. 3-5 mg of the complex.

Synthesis of $[Pb(OB\{CH(SiMe_3)_2\}_2)_2]$ (1)



A solution of $[Pb(N(SiMe_3)_2)_2]$ (76 mg, 0.145 mmol) in Et_2O (7 mL) was added dropwise at room temperature to a solution of $\{(Me_3Si)_2CH\}_2BOH$ (100 mg, 0.289 mmol) in Et_2O (7 mL) under stirring. The reaction mixture was stirred for a further 2 h at room temperature. The volatiles were then removed under vacuum to give **1** 0.125 g, (96%) as a colourless solid. X-ray quality single crystals of the title compound were obtained readily as enormous pale yellow hexagonal blocks upon recrystallisation from a concentrated pentane solution stored overnight at –40 °C.

^1H NMR (C_6D_6, 400.13 MHz, 298 K): δ = 0.58 (s, 4H, C*H*), 0.28 (s, 72H, CH_3) ppm.

$^{13}C\{^1H\}$ NMR (C_6D_6, 100.62 MHz, 298 K): δ = 26.14 (s, *C*H), 3.74 (s, *C*H_3) ppm.

$^{11}B\{^1H\}$ NMR (C_6D_6, 128.4 MHz, 298 K): δ = 53.53 ppm.

^{29}Si NMR (C_6D_6, 79.49 MHz, 298 K): δ = –3.26 ppm.

^{207}Pb NMR (C_6D_6, 83.714 MHz, 298 K): δ = +1805 ppm.

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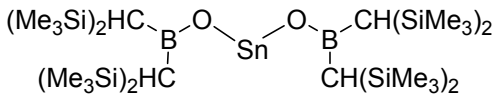
[1] T. Heidemann, S. Mathur, *Eur. J. Inorg. Chem.*, 2014, 506.

Satisfactory, reproducible elemental analysis for $C_{28}H_{76}B_2O_2PbSi_8$ (898.41 g·mol^{-1}; calcd: C, 37.43%; H, 8.53%) could not be obtained despite repeated attempts performed on crystalline material, presumably reflecting the high air- and moisture-sensitivity of this complex.

Melting temperature could not be determined for this complex, which seemed to decompose in the range 110-130 °C upon gradual change of colour from pale yellow to orange and, finally, dark red. Upon cooling, the compound solidified to an unidentified dark red product, which then melted at 123 °C; no further change of colour was detected.

Synthesis of [Sn(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (2)



A solution of [Sn(N(SiMe$_3$)$_2$)$_2$] (79 mg, 0.180 mmol) in pentane (7 mL) was added dropwise at room temperature to a solution of {(Me$_3$Si)$_2$CH}$_2$BOH (125 mg, 0.361 mmol) in pentane (7 mL). The reaction mixture was then stirred for 2 h at room temperature. The volatiles were vacuumed off to yield **2** as a colourless solid (0.12 g, 82%). The title compound crystallised from a concentrated pentane solution stored at –26 °C to afford X-ray quality single crystals.

^{1}H NMR (C$_6$D$_6$, 400.13 MHz, 298 K): δ = 0.55 (s, 4H, C*H*), 0.29 (s, 72H, C*H*$_3$) ppm.

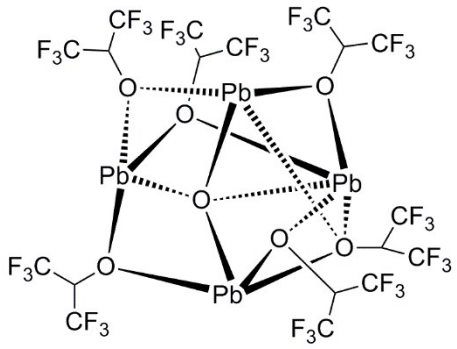
^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.62 MHz, 298 K): δ = 25.52 (s, *C*H), 3.84 (s, $^1J_{Si\text{-}C}$ = 50.6 Hz, $^5J_{Sn\text{-}C}$ = 15.3 Hz, *C*H$_3$) ppm.

^{11}B{^{1}H} NMR (C$_6$D$_6$, 128.4 MHz, 298 K): δ = 53.23 ppm.

^{29}Si NMR (C$_6$D$_6$, 79.49 MHz, 298 K): δ = –3.07 (s, $^1J_{Si\text{-}C}$ = 50.9 Hz) ppm.

^{119}Sn NMR (C$_6$D$_6$, 149.17 MHz, 298 K): δ = –186 ppm.

Satisfactory, reproducible elemental analysis for $C_{28}H_{76}B_2O_2Si_8Sn$ (809.91 g·mol^{-1}; calcd: C, 41.52%; H, 8.46%) could not be obtained despite repeated attempts performed on crystalline material, presumably reflecting the high air- and moisture-sensitivity of this complex.



Synthesis of [Pb$_4$(μ^4-O)(μ^2-OCH(CF$_3$)$_2$)$_5$(μ^3-OCH(CF$_3$)$_2$)] (3)

A mixture of (CF$_3$)$_2$CHOH (0.26 g, 1.892 mmol) and pentane (5 mL) was added at room temperature to a solution of [Pb(N(SiMe$_3$)$_2$)$_2$] (0.40 g, 0.947 mmol) in pentane (10 mL). The reaction mixture was then stirred for 30 min at room temperature. The volatiles were vacuumed off to isolate **3** as a colourless sticky solid (0.38 g, 87%). The title compound crystallised from a

concentrated pentane solution stored at –10 °C to afford X-ray quality single crystals.

^{1}H NMR (C_6D_6, 400.13 MHz, 298 K): δ = 4.82 (hp, $^{3}J_{H\text{-}F}$ = 6.0 Hz, 6H, C*H*$(CF_3)_2$) ppm.

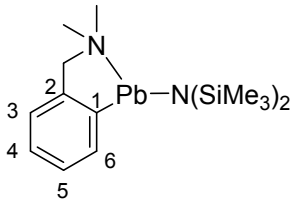
^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 298 K): δ = 124.40 (q, $^{1}J_{C\text{-}F}$ = 284 Hz, *C*F_3), 70.71 (hp, $^{2}J_{C\text{-}F}$ = 31.2 Hz, *C*$(CF_3)_2$) ppm.

^{19}F NMR (C_6D_6, 376.47 MHz, 298 K): δ = –75.48 (s, 36F, C*F*$_3$) ppm

^{207}Pb NMR (C_6D_6, 83.714 MHz, 298 K): δ = +693 ppm.

Elem. Anal. Calcd. for $C_{18}H_6F_{36}O_7Pb_4$ (1846.98 g·mol^{-1}): calcd, C, 11.71%; H, 0.33%; Found: C, 11.80%; H, 0.34%.

Synthesis of [{N^C}PbN(SiMe$_3$)$_2$] (4)



A solution of [Pb(N(SiMe$_3$)$_2$)$_2$] (0.40 g, 0.758 mmol) in Et$_2$O (10 mL) was added dropwise at room temperature to a solution of [{N^C}$_2$Pb] (0.36 g, 0.758 mmol) in Et$_2$O (10 mL). The reaction mixture was stirred overnight. The solution was filtered, concentrated to ca. 7 mL and stored in the freezer (–40 °C) to give the title compound as X-ray quality off-white crystals (0.65 g, 85%).

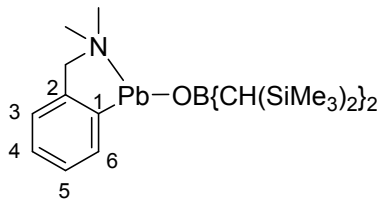
^{1}H NMR (C_6D_6, 400.13 MHz, 298 K): δ = 8.05 (dd, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{2}J_{H\text{-}H}$ = 0.8 Hz, 1H, Ar*H*-H6), 7.47 (td, $^{3}J_{HH}$ = 7.2 Hz, $^{2}J_{H\text{-}H}$ = 1.1 Hz, Ar*H*-H5), 7.41 (d, 1H, $^{3}J_{H\text{-}H}$, 7.5 Hz, Ar*H*-H3), 7.14 (td, $^{3}J_{H\text{-}H}$ 7.5 Hz, $^{2}J_{H\text{-}H}$ = 1.3 Hz 1H, Ar*H*-H4), 3.70 (s, 2H, ArC*H*$_2$), 1.94 (s, 6H, NC*H*$_3$), 0.28 (s, 18H, $^{2}J_{Si\text{-}H}$ = 6.3 Hz, $^{1}J_{C\text{-}H}$ = 117.0 Hz, SiC*H*$_3$) ppm.

^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 298 K): δ = 249.62 (s, *C*$_6$H$_4$-C1), 152.40 (s, *C*$_6$H$_4$-C2), 138.50 (s, *C*$_6$H$_4$-C6), 129.32 (*C*$_6$H$_4$-C5), 128.86 (*C*$_6$H$_4$-C3), 126.65 (*C*$_6$H$_4$-C4), 73.29 (s, $^{3}J_{207PbC}$ = 29.0 Hz, *C*H$_2$), 45.88 (s, N*C*H$_3$), 7.26 (s, $^{1}J_{29SiC}$ = 54.3 Hz, Si*C*H$_3$) ppm.

^{207}Pb NMR (C_6D_6, 83.71 MHz, 298 K): δ = +2595 ppm.

Satisfactory, reproducible elemental analysis for $C_{15}H_{30}N_2PbSi_2$ (501.78 g·mol^{-1}; calcd: C, 35.90%; H, 6.03%; N, 5.58%) could not be obtained despite repeated attempts performed on crystalline material, presumably reflecting the high air- and moisture-sensitivity of this complex.

Synthesis of [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (5)



A solution of {(Me$_3$Si)$_2$CH}$_2$BOH (100 mg 0.289 mmol) in Et$_2$O (15 mL) was added dropwise to a solution of **4** (145 mg, 0.289 mmol) in Et$_2$O (10 mL), after what the resulting reaction mixture was stirred for 3 h at room temperature. All the volatiles were removed in vacuo, and pentane (10 mL) was added to the resulting solid. The insoluble fraction was eliminated by filtration, and the solution was then concentrated and stored in the freezer to yield **5** (82 mg, 41%) as colourless crystals suitable for X-ray diffraction crystallography.

^{1}H NMR (C$_6$D$_6$, 400.13 MHz, 298 K): δ = 8.18 (d, $^3J_{HH}$ = 6.9 Hz, 1H, Ar*H*-H6), 7.52 (m, 2H, Ar*H*-H5 and Ar*H*-H3), 7.18 (td, $^3J_{HH}$ = 7.5 Hz, $^2J_{HH}$ = 1.3 Hz, 1H, Ar*H*-H4), 4.08 (br, 2H, ArCH_2), 2.03 (br, 6H, NCH_3), 0.44 (s, 2H, BC*H*), 0.28 (s, 36H, SiCH_3) ppm.

^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ = 219.03 (s, C_6H_4-C1), 153.24 (s, C_6H_4-C2), 137.85 (s, C_6H_4-C6), 129.34 (s, C_6H_4-C5), 128.54 (s, C_6H_4-C3), 127.05 (s, C_6H_4-C4), 71.66 (s, ArCH_2), 44.54 (s, NCH_3), 25.44 (s, *C*H), 3.59 (s, $^1J_{29Si\text{-}13C}$ = 50.3 Hz, *C*H$_3$) ppm.

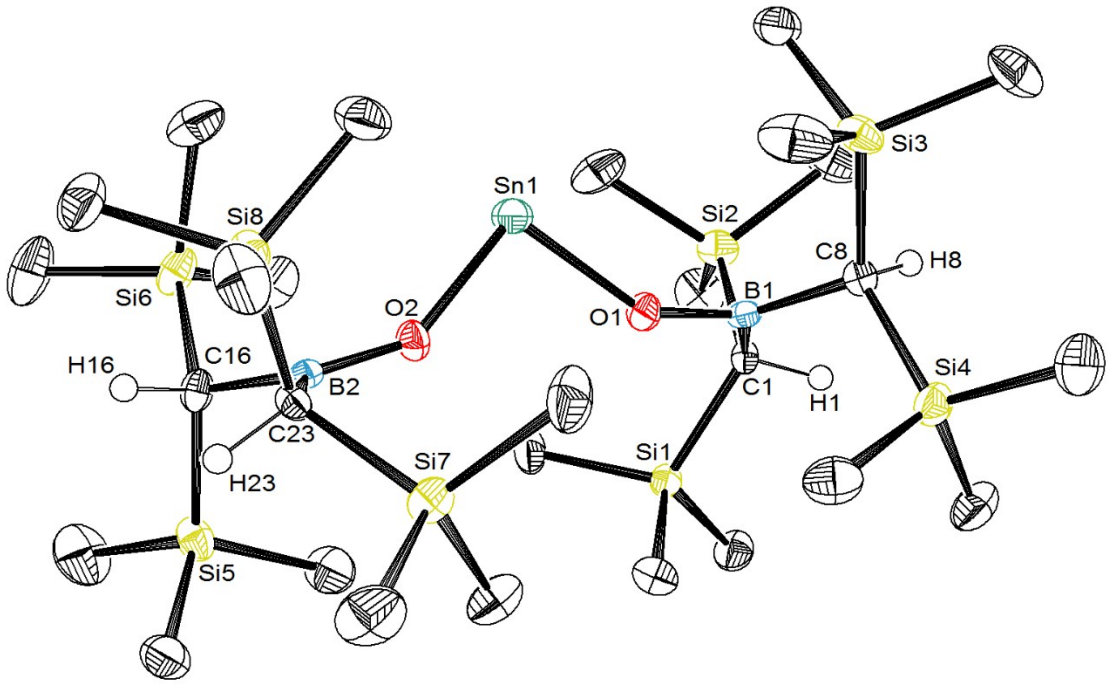
^{11}B{^{1}H} NMR (C$_6$D$_6$, 128.4 MHz, 298 K): δ = 48.15 ppm.

^{207}Pb NMR (C$_6$D$_6$, 83.92 MHz, 298 K): δ = +3095 ppm.

Satisfactory, reproducible elemental analysis for $C_{23}H_{50}BNOPbSi_4$ (687.00 g·mol^{-1}; calcd: C, 40.21%; H, 7.34%; N, 2.04%) could not be obtained despite repeated attempts performed on crystalline material, presumably reflecting the high air- and moisture-sensitivity of this complex.

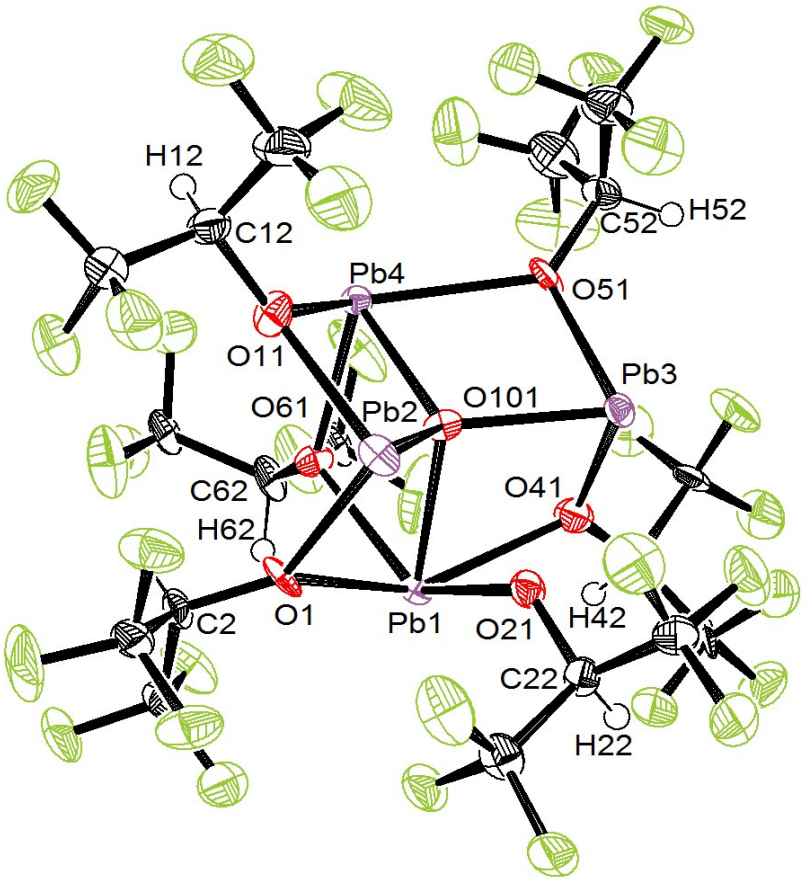
The melting temperature of **5** was determined by analyses of a sample sealed in a glass capillary. It melts at 141 °C; the same melting temperature was determined from the same sample three consecutive times, upon iterative melting-cooling processes, showing that the complex preserved its integrity.

S2- X-ray structure (ORTEP) of complex [Sn(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (2)



ORTEP representation of the solid state structure of [Sn(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**2**). Ellipsoids drawn at the 50% probability level. All methyl H atoms omitted for clarity. Selected bond lengths (Å): Sn1-O2 = 1.9724(18), Sn1-O1 = 1.9812(17), O1-B1 = 1.367(3), O2-B2 = 1.362(3), B1-C8 = 1.589(4), B1-C1 = 1.593(4), B2-C23 = 1.588(4), B2-C16 = 1.596(4). Selected angles (°): O2-Sn1-O1 = 97.92(7), B1-O1-Sn1 = 146.71(17), B2-O2-Sn1 = 148.32(17).

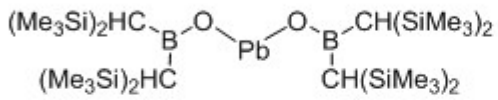
S3- XRD structure (ORTEP) of $[Pb_4(\mu^4\text{-}O)(\mu^2\text{-}OCH(CF_3)_2)_5(\mu^3\text{-}OCH(CF_3)_2)]$ (3)



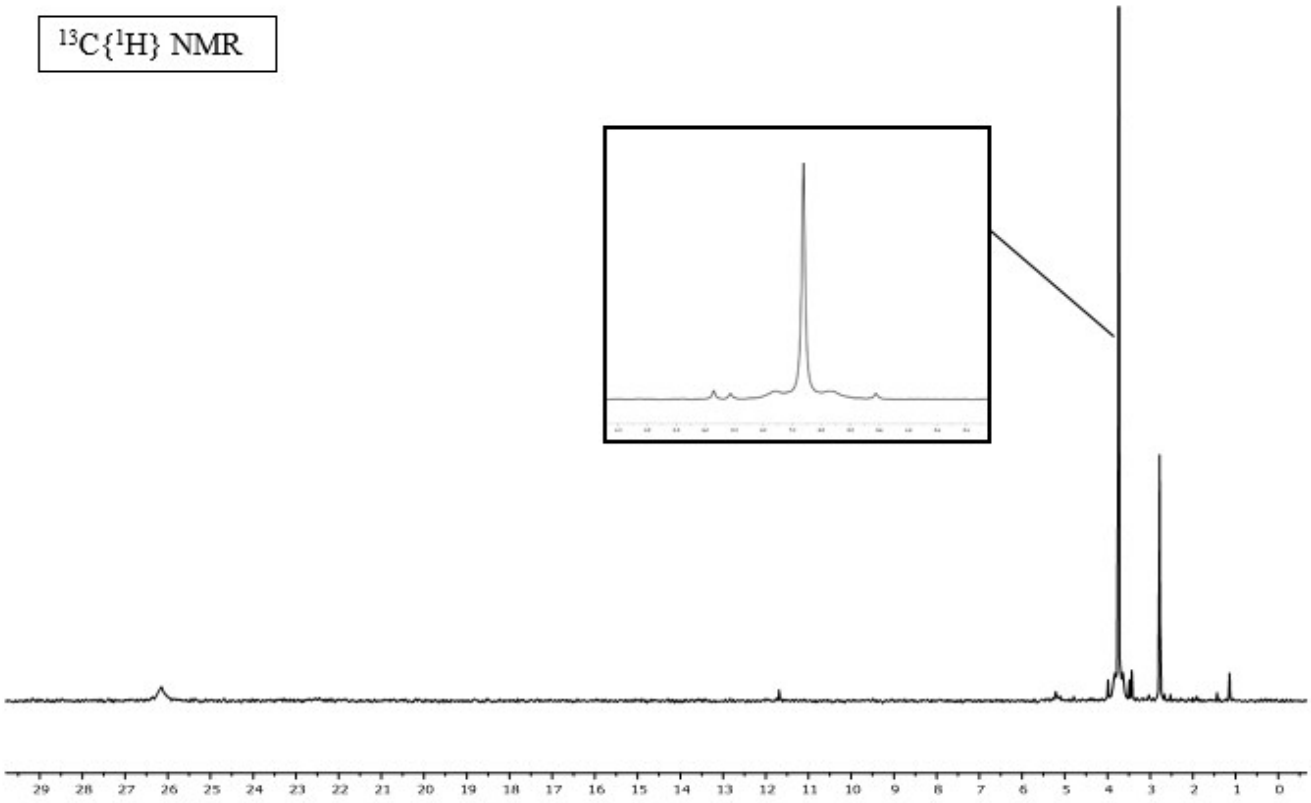
ORTEP representation of the solid state structure of $[Pb_4(\mu^4\text{-}O)(\mu^2\text{-}OCH(CF_3)_2)_5(\mu^3\text{-}OCH(CF_3)_2)]$ (**3**). Ellipsoids drawn at the 50% probability level. Selected bond lengths (Å): Pb1-O101 = 2.325(8), Pb1-O61 = 2.413(9), Pb1-O41 = 2.455(9), Pb1-O1 = 2.468(9), Pb1-O21 = 2.508(9), O1-Pb2 = 2.265(8), O11-Pb4 = 2.384(9), O11-Pb2 = 2.403(10), Pb2-O101 = 2.272(7)Pb2-O21 = 2.611(9), O41-Pb3 = 2.272(10), Pb3-O101 = 2.235(9), Pb3-O51 = 2.295(9), O51-Pb4 = 2.483(9), Pb4-O101 = 2.233(8), Pb4-O61 = 2.351(9).

S4- ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (298 K, C_6D_6) for $[Pb(OB\{CH(SiMe_3)_2\}_2)_2]$ (1)

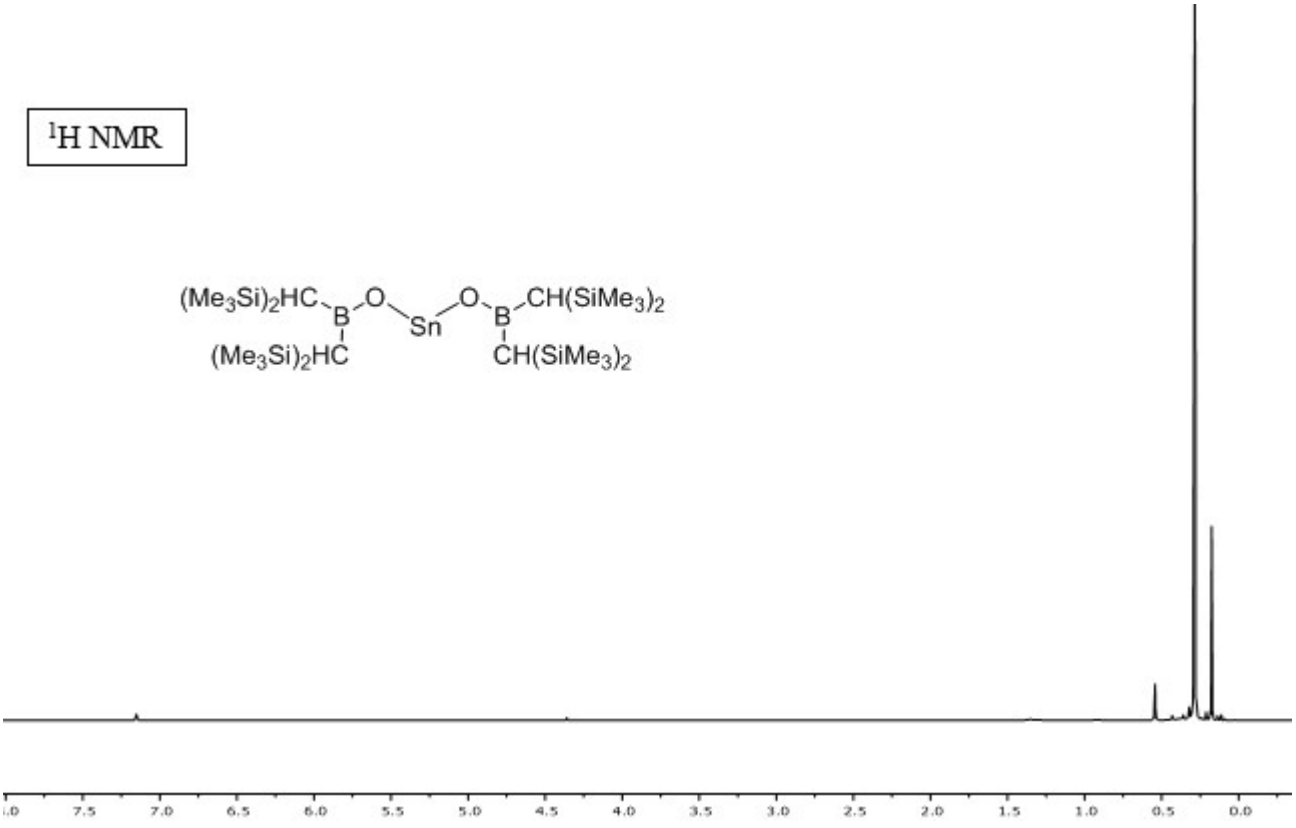
^{1}H NMR

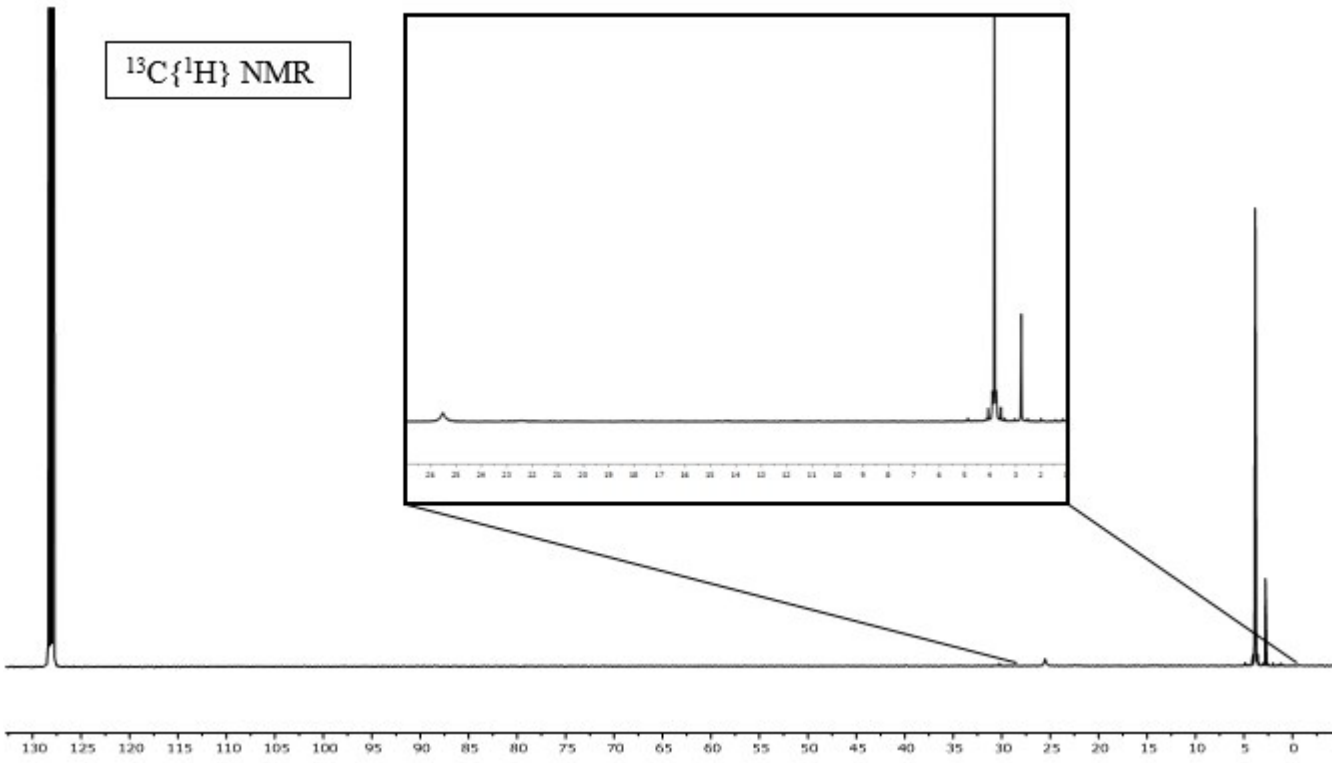


$^{13}C\{^{1}H\}$ NMR

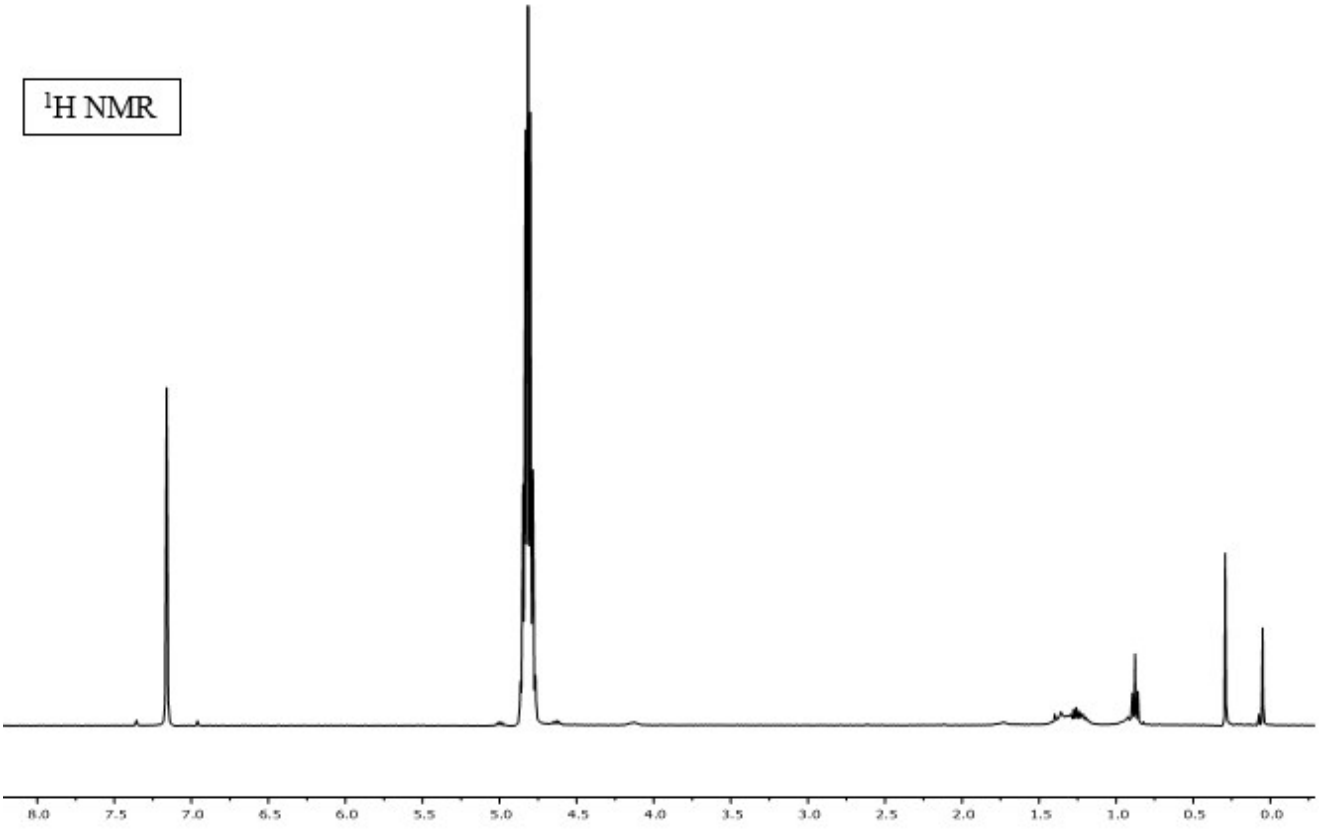


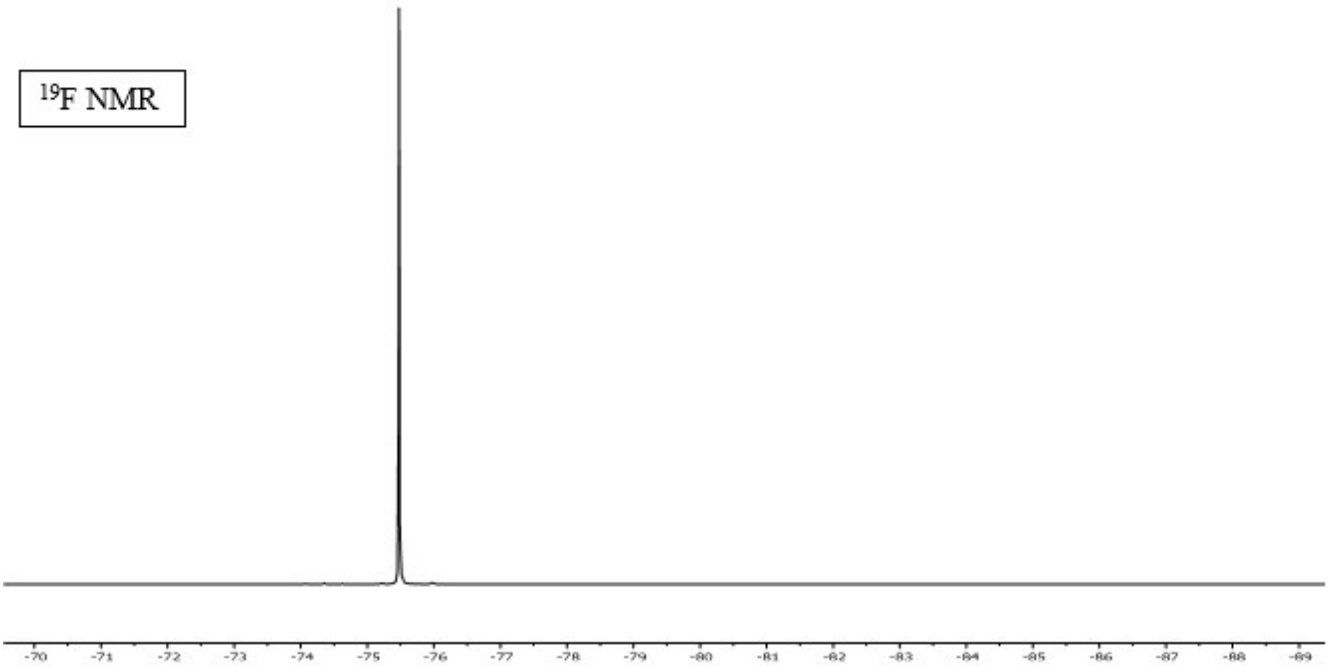
S5- ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (298 K, C_6D_6) for $[Sn(OB\{CH(SiMe_3)_2\}_2)_2]$ (2)

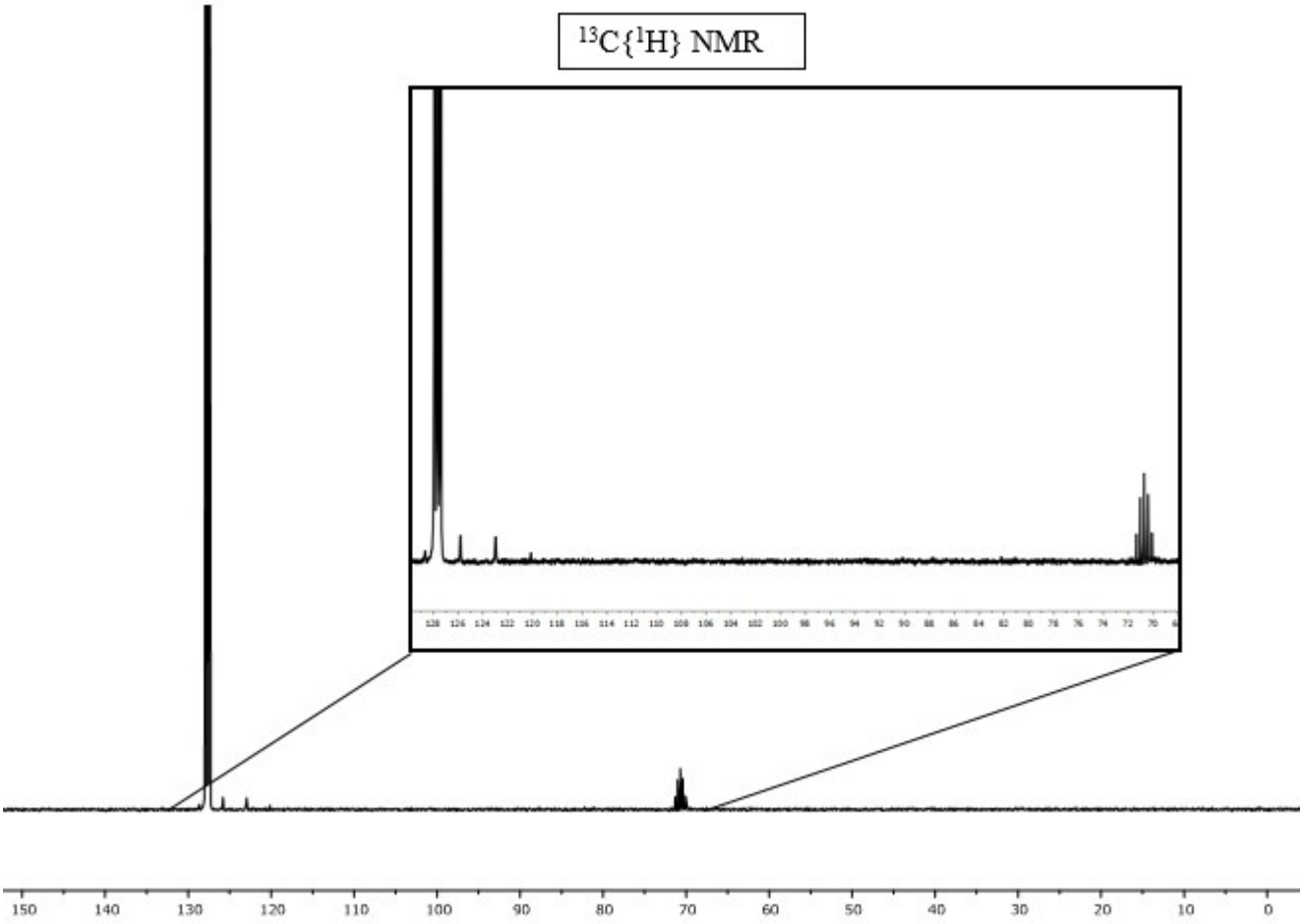




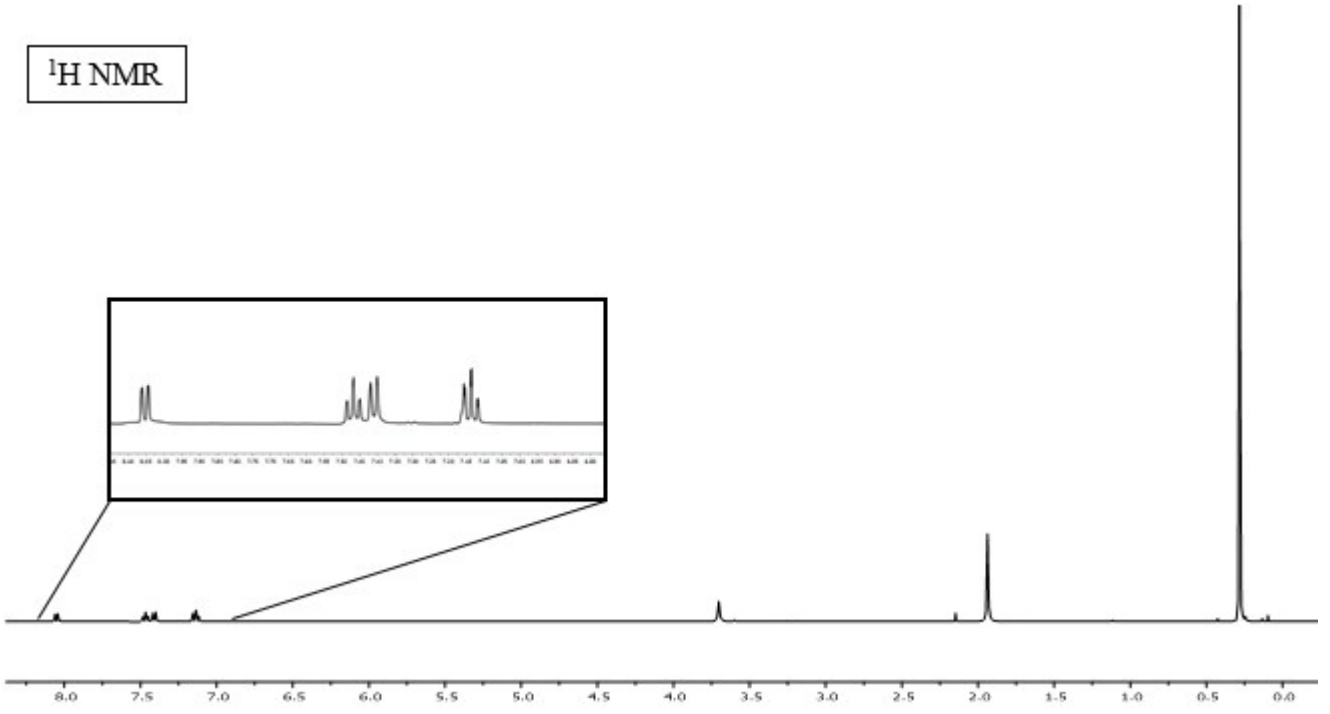
S6- ^{1}H (top), ^{19}F (middle) and $^{13}C\{^{1}H\}$ (bottom) NMR data (298 K, C_6D_6) for complex $[Pb_4(\mu^4\text{-}O)(\mu^2\text{-}OCH(CF_3)_2)_5(\mu^3\text{-}OCH(CF_3)_2)]$ (3)

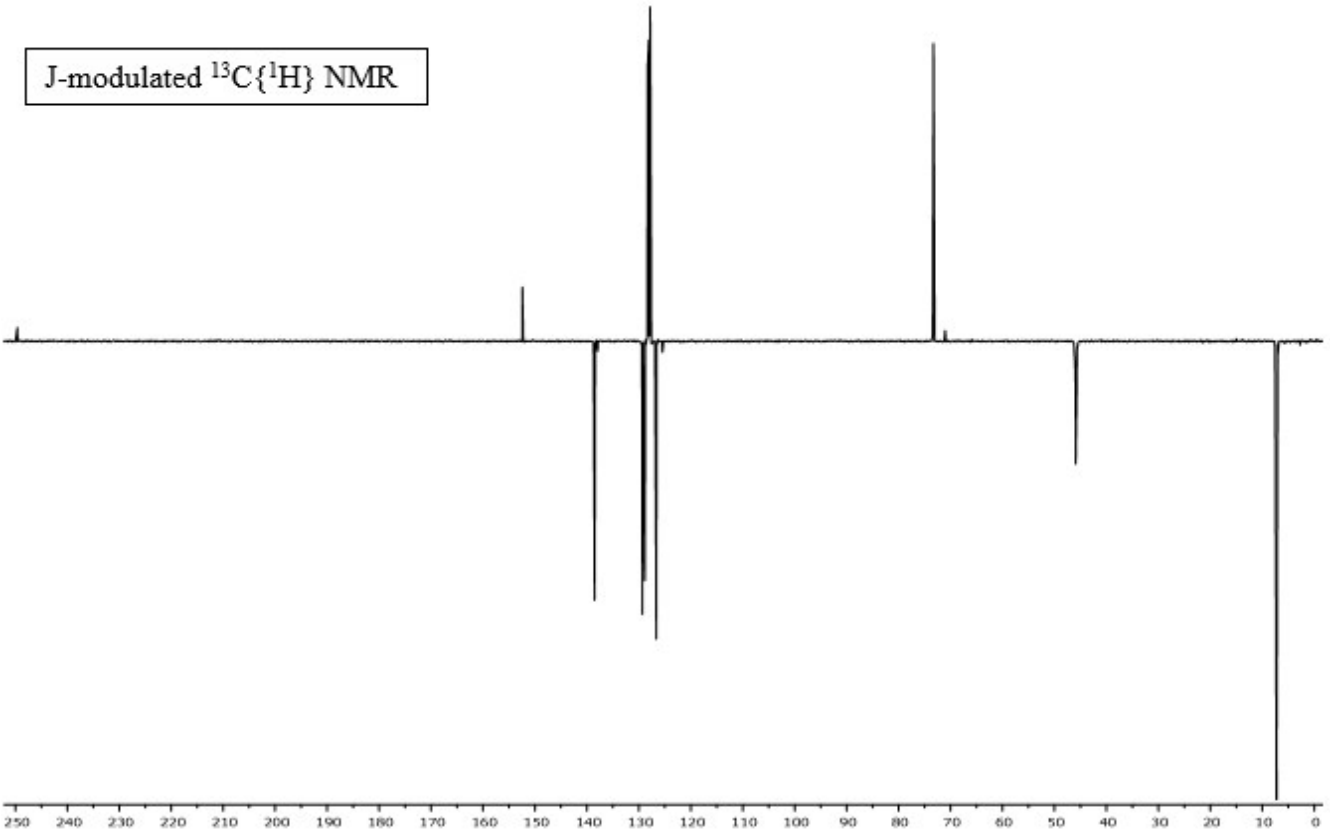




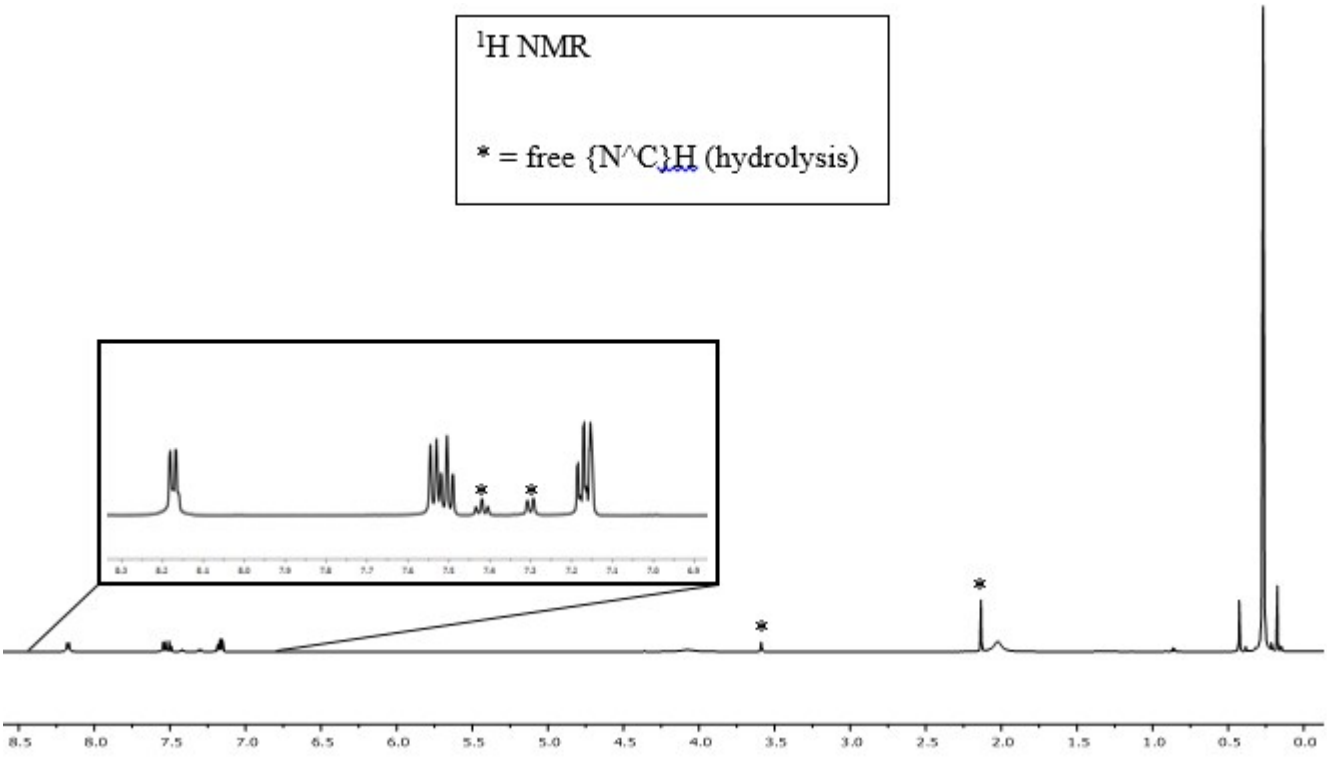

$^{13}C\{^{1}H\}$ NMR
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

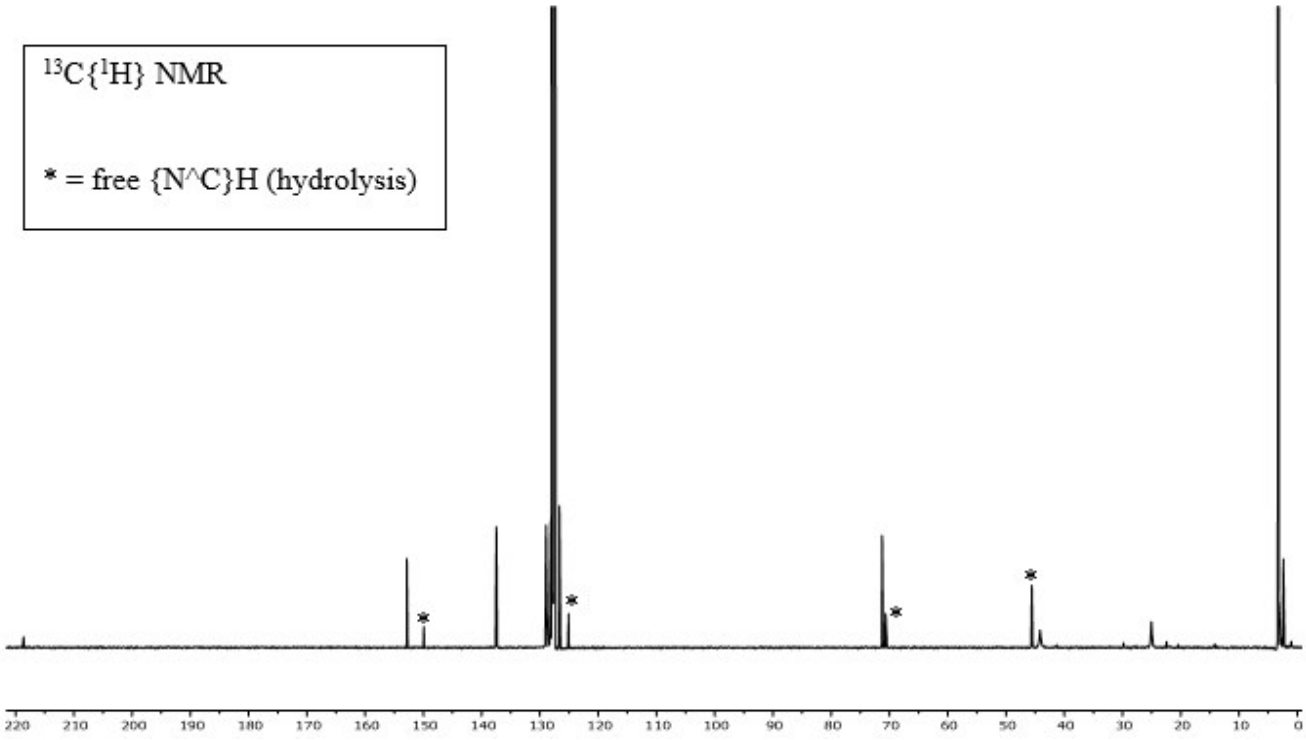
S7- ^{1}H and $^{13}C\{^{1}H\}$ NMR data (298 K, C_6D_6) for [{N^C}PbN(SiMe$_3$)$_2$] (4)





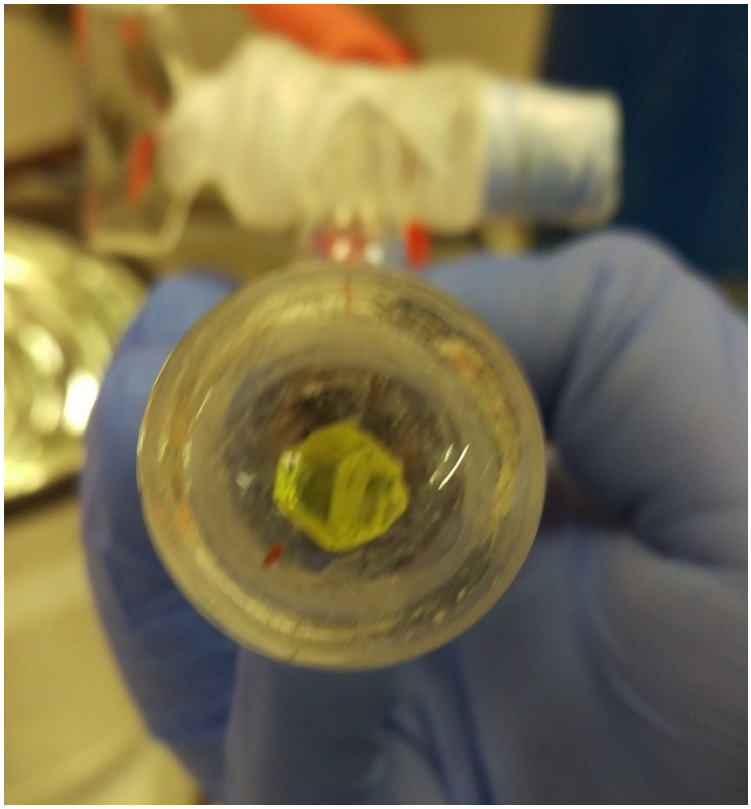
S8- ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (298 K, C_6D_6) for [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (5)





S9- Crystallographic data

Crystals of **1-5** suitable for X-ray diffraction analysis were obtained by recrystallisation of the purified products. Diffraction data were collected at 150 K using a D8 VENTURE Bruker AXS diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Relevant collection and refinement data are summarised in Tables 1 and 2 below. Crystal data and details of data collection and structure refinement for the three complexes (CCDC 1832389-1832393) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Pale yellow hexagonal blocks of crystalline [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**1**)

Table 1- Summary of crystallographic data for complexes **1**-**3**

	$[Pb(OB\{CH(SiMe_3)_2\}_2)_2]$ (**1**)	$[Sn(OB\{CH(SiMe_3)_2\}_2)_2]$ (**2**)	$[Pb_4(\mu^4\text{-}O)(\mu^2\text{-}OCH(CF_3)_2)_5(\mu^3\text{-}OCH(CF_3)_2)]$ (**3**)
Formula	C28 H76 B2 O2 Pb Si8	C28 H76 B2 O2 Si8 Sn	C18 H6 F36 O7 Pb4
CCDC	1832389	1832390	1832391
Mol. wt.	898.41	809.91	1846.99
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	$P2_1/c$
a (Å)	25.147(6)	25.1738(8)	18.8700(8)
b (Å)	18.137(4)	18.1907(6)	10.1801(4)
c (Å)	23.271(6)	24.6824(7)	19.4987(7)
α (°)	90	90	90
β (°)	118.845(8)	123.9170(10)	90.176(2)
γ (°)	90	90	90
V (Å^3)	9297(4)	9379.6(5)	3745.7(3)
Z	8	8	4
Density (g/cm^3)	1.284	1.147	3.275
Abs. coeff., (mm^{-1})	3.858	0.771	18.143
F(000)	3712	3456	3288
Crystal size, mm	0.580 × 0.490 × 0.350	0.600 × 0.520 × 0.330	0.250 ×0.190 × 0.080
θ range (°)	3.007 to 27.484	2.970 to 27.484	3.000 to 27.484
Limiting indices	–32 < h < 32 –23 < k < 33 –30 < l < 30	–32 < h < 32 –20 < k < 23 –32 < l < 32	–24 < h < 24 –12 < k < 13 –25 < l < 25
R(int)	0.0673	0.0617	0.0556
Reflections collected	30996	42335	23053
Refl. Unique [$I>2\sigma(I)$]	10368	10742	8505
Completeness to θ	0.974	0.999	0.989
Data/restraints/param.	10368 / 0 / 394	10742 / 0 / 394	8505 / 0 / 57
Goodness-of-fit	1.062	1.012	0.934
R_1 [$I>2\sigma(I)$] (all data)	0.0790 (0.1191)	0.0398 (0.0654)	0.0455 (0.0729)
wR_2 [$I>2\sigma(I)$] (all data)	0.1494 (0.1710)	0.0767 (0.0858)	0.1260 (0.1596)
Largest diff. (e·A^{-3})	4.689 and -4.867	2.423 and -1.925	3.570 and -4.045

Table 2- Summary of crystallographic data for complexes **4** and **5**

	[{N^C}PbN(SiMe$_3$)$_2$] (**4**)	[{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**5**)
Formula	C15 H30 N2 Pb Si2	C23 H50 B N O Pb Si4
CCDC	1832392	1832393
Mol. wt.	501.78	687.00
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a (Å)	8.9054(10)	9.1319(9)
b (Å)	10.6022(11)	18.6282(17)
c (Å)	12.4223(14)	18.929(2)
α (°)	103.574(4)	90
β (°)	110.985(4)	102.613(4)
γ (°)	103.843(4)	90
V (Å^3)	994.66(19)	3142.4(5)
Z	2	4
Density (g/cm^3)	1.675	1.452
Abs. coeff., (mm^{-1})	8.596	5.537
F(000)	488	1384
Crystal size, mm	0.560 × 0.450 × 0.340	0.530 × 0.320 × 0.220
θ range (°)	3.067 to 27.480	3.014 to 27.484
Limiting indices	–11 < h < 11 –13 < k < 9 –15 < l < 16	–11 < h < 11 –24 < k < 21 –24 < l < 24
R(int)	0.0475	0.0394
Reflections collected	12673	35346
Refl. Unique [$I>2\sigma(I)$]	4523	7187
Completeness to θ	0.990	0.998
Data/restraints/param.	4523 / 0 / 189	7187 / 0 / 294
Goodness-of-fit	1.159	1.122
R_1 [$I>2\sigma(I)$] (all data)	0.0240 (0.0264)	0.0234 (0.0285)
wR_2 [$I>2\sigma(I)$] (all data)	0.0624 (0.0632)	0.0565 (0.0581)
Largest diff. (e·A^{-3})	0.668 and -1.924	0.703 and -1.428