Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

for

Lewis Base Complexes of Sila[2]aluminocenophanes

1. Experimental Details

All manipulations were carried out under an inert gas atmosphere (argon 5.0), using either Schlenk line techniques of a glovebox. 1,2-dichlorotetramethyldisilane was purchased from ABCR and used as received. Dicyclopentadiene was purchased from ABCR, and cracked and distilled prior to use. Lithium aluminum hydride solution (1.0 M in diethyl ether), aluminum trichloride, aluminum tribromide and *n*-butyl-*sec*-butylmagnesium solution (0.7 M in hexane) were purchased from Sigma Aldrich and used as received. All other starting materials (NHC, NHC=S, $HAlX_2 \cdot (THF)_2$) were synthesized following literature established procedures.[1-2]

NMR-spectra were recorded on a Bruker Avance III 300 and a Bruker Avance 400. ^{1}H and ^{13}C NMR spectra were referenced using the solvent signals (δ ^{1}H (C_6HD_5) = 7.20; δ ^{13}C (C_6D_6) = 128.0), ^{27}Al and ^{29}Si NMR spectra were referenced using external standards (δ ^{27}Al ($AlCl_3$ in D_2O) = 0) (δ ^{29}Si ($SiMe_4$) = 0). Single crystal X-ray diffraction analysis were carried out at low temperatures on a Bruker AXS X8 Apex CCD diffractometer operating with graphite monochromated Mo Kα radiation. Structure solution and refinement were performed using SHELX.[3] Crystal structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and are available free of charge from the Cambridge Structural Database (see CCDC numbers).

Synthesis of Cp_2Mg

Magnesocene was prepared by treating 20 g (303 mmol) freshly cracked and distilled cyclopentadiene with a solution of *n*-butyl-*sec*-butylmagnesium (0.7 M in hexane, 216 mL, 151.3 mmol) at 0°C. The colorless solid was collected by filtration, washed with small portions of cold hexane and dried in vacuum.

Yield: 10.1 g / 43%

^{1}H NMR (300 MHz, C_6D_6): δ = 6.05 (s, 10 H);

$^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ = 107.8.

Synthesis of *ansa*-$Me_4Si_2(C_5H_5)_2$

Method A:

Magnesocene (10 g, 64.7 mmol) was suspended in 350 mL of hexane. 1,2-dichloro-1,1,2,2-tetramethyldisilane (purity: 90%, 13.5 g, 64.7 mmol) was slowly added. The mixture was stirred at room temperature for 2 h. After filtration, all volatiles were removed under reduced pressure and the residue was distilled in vacuum (0.03 mbar, 67-95°C) to give the product as a colorless to light yellow oil.

Yield: 10.6 g / 66%

Method B:

Freshly cracked and distilled cyclopentadiene (19.4 g, 293 mmol) was added slowly to a solution of *n*-butyllithium (2.5 M solution in hexane, 279.5 mmol, 111.8 ml) in 350 ml hexane at -70°C. The mixture warmed to room temperature and stirred for 2 h. Subsequently, 1,2-dichloro-1,1,2,2-tetramethyldisilane (25 g, 119.8 mmol) was added slowly at room temperature and the resulting mixture was stirred overnight. After filtration, all volatiles were removed under vacuum and the residue was distilled in vacuum (0.03 mbar, 67-95°C) to give the product as a colorless to light yellow oil.

Yield: 22.0 g / 67%

Purity of the ligand was checked and confirmed by GC-MS and ^{29}Si NMR spectroscopy. The compound is obtained as a mixture of six isomers, as indicated by nine signals in the ^{29}Si NMR spectrum (3 symmetrically and 3 unsemmatrically substituted isomers). It is only marginally stable at room temperature and should therefore be stored at low temperature or used directly for follow-up synthesis.

$^{29}Si\{^{1}H\}$ NMR (60 MHz, C_6D_6): δ = -15.1,-16.1,-16.3,-27.2,-27.5,-28.1,-28.3, -28.5, -28.7.

Synthesis of sila[2]magnesocenophane 1

A solution of *ansa*-$Me_4Si_2(C_5H_5)_2$ (16.3 g, 66.0 mmol) in 500 ml hexane was treated with a solution of *n*-butyl-*sec*-butylmagnesium (0.7 M in hexane, 66.0 mmol, 94.2 ml). After stirring for 90 min at room temperature, the mixture was stored at -25°C overnight. A colorless precipitate formed and was isolated, washed with small portions of cold hexane and dried in vacuum.

Yield: 9.5 g / 54%

^{1}H NMR (300 MHz, C_6D_6): δ = 6.10 (s, 8H), 0.51 (s, 12H);

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 117.8, 114.6, 109.6, -3.6;

$^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6): δ = -24.2

Crystals of **1**·DME, suitable for single crystal X-ray diffraction, were obtained by addition of ~3 eq of dimethoxyethane to a solution of sila[2]magnesocenophane, **1**, in toluene, and subsequent storing of the solution at -25°C overnight.

^{1}H NMR (300 MHz, C_6D_6): δ = 6.38 – 6.34 (m, 4H), 6.30 – 6.26 (m, 4H), 2.61 (s, 6H), 2.32 (s, 4H), 0.70 (s, 12H);

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 111.6, 111.0, 109.6, 68.3, 58.9, -1.8;

$^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6): δ = -27.2.

Elemental analysis for $C_{18}H_{30}MgO_2Si_2$: found: C: 56.2%, H: 7.46%; calc.: C: 60.24%, H: 8.43% (elemental analysis repeatedly and reproducibly yielded low carbon content, presumably due to the formation of silicon carbide).

Synthesis of sila[2]aluminocenophane·(THF) complexes 2a-b

Method A:

Dihaloalane bis(tetrahydrofuran) (0.91 g, 3.72 mmol $HAlCl_2{\cdot}(THF)_2$ / 1.23 g, 3.72 mmol $HAlBr_2{\cdot}(THF)_2$) and sila[2]-magnesocenophane, **1**, (1.0 g, 3.72 mmol) were charged into a flask. 40 mL of toluene were added and the mixture was stirred overnight at room temperature. After filtration, all volatiles were removed in vacuum and hexane was added. After filtration, the hexane solution was concentrated and stored at -20°C overnight, resulting in the crystallization of complexes **2a**-**b**. The products were obtained as colorless to light yellow crystalline solids.

Yield: **2a**: 747 mg, 1.97 mmol/ 53%; **2b**: 267 mg, 0.63 mmol / 17%

Method B:

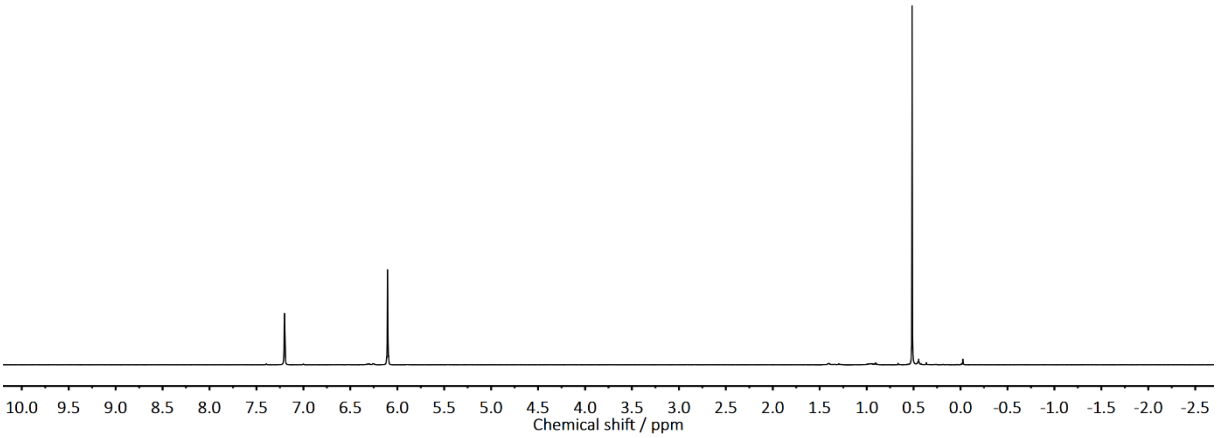
Aluminum trihalide (50 mg, 0.37 mmol $AlCl_3$ / 99 mg, 0.37 mmol $AlBr_3$) and sila[2]magnesocenophane, **1**, (100 g, 0.37 mmol) were charged into a flask. 5 mL of THF were added and the mixture was stirred at room temperature overnight. Workup was identical to that described in method A.

2a:
^{1}H NMR (300 MHz, C_6D_6): δ = 7.08 (dt, *J* = 3.3 Hz, 1.3 Hz, 2H), 6.98 (td, *J* = 3.4 Hz, 0.7 Hz, 2H), 6.83 – 6.79 (m, 2H), 5.92 (d, *J* = 2.8 Hz, 2H), 3.26 (ddd, *J* = 6.8 Hz, 4.4 Hz, 2.7 Hz, 4H), 0.93 – 0.86 (m, 4H), 0.66 (s, 6H), 0.21 (s, 6H);
^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 133.6, 128.8, 127.3, 105.8, 96.7, 74.4, 24.5, -3.0, -3.2;
^{29}Si{^{1}H} NMR (60 MHz, C_6D_6) δ -23.4.
Elemental analysis for $C_{18}H_{28}AlClOSi_2$: found: C: 56.2%, H: 7.46%; calcd.: C: 57.0%, H: 7.45%.
2b:
^{1}H NMR (400 MHz, C_6D_6): δ = 7.18 – 7.03 (m, 2H), 7.06 – 6.91 (m, 2H), 6.81 (td, *J* = 3.1 Hz, 1.2 Hz, 2H), 5.93 (d, *J* = 2.5 Hz, 2H), 3.25 (s, 4H), 0.86 (s, 4H), 0.69 (s, 6H), 0.20 (s, 6H);
^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 134.1, 129.1, 127.6, 106.8, 74.6, 24.5, -2.5, -3.2;
^{29}Si{^{1}H} NMR (79 MHz, C_6D_6): δ = -23.3.
Elemental analysis for $C_{18}H_{28}AlBrOSi_2$: found: C: 50.96%, H: 6.86%; calcd.: C: 51.05%, H: 6.66%.

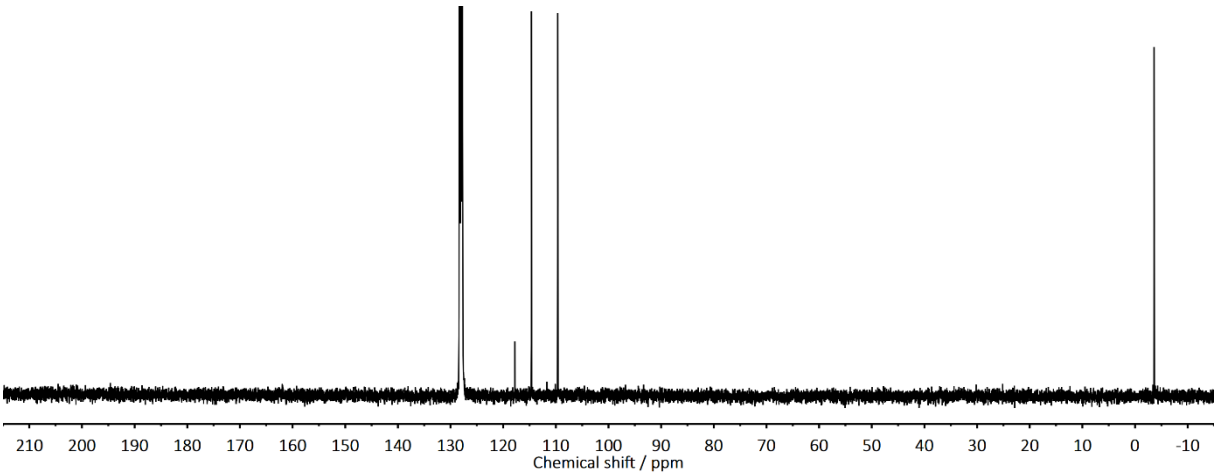
Synthesis of sila[2]-aluminocenophane·(NHC) complex 2c and sila[2]alumino-cenophane·(thione) complex 2d
The aluminium trichloride·Lewis base complexes used in the synthesis of **2c**-**d** were generated in situ.
Aluminum trichloride (1.0 g, 7.5 mmol) and carbene (NHC) or thione (NHC=S) (1.35 g, 7.5 mmol NHC; 1.17 g, 7.5 mmol NHC=S) were suspended in 10 ml of toluene and stirred for 15-20 min until all components were completely dissolved. The solution was then used directly in the synthesis of **2c**-**d**.
To a suspension of sila[2]magnesocenophane, **1**, in 150 mL of toluene was added a toluene solution of the corresponding aluminium trichloride·(Lewis base) complex and the mixture was stirred at room temperature overnight. All volatiles were removed under reduced pressure and hexane was added. After filtration, the filtrate was concentrated and stored at -20°C overnight. The colorless crystalline precipitate was collected, washed with small portions of cold hexane and dried in vacuum.
2c: 1,57 mg, 3,23 mmol / 43%; **2d**: 662 mg, 1,2 mmol / 17%.
$AlCl_3$·(NHC):
^{1}H NMR (400 MHz, C_6D_6): δ = 5.72 (s, 2H), 1.69 (s, 6H), 1.14 (d, *J* = 7.0 Hz, 12H);

$^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6): δ = 106, 104 (^{27}Al NMR indicates an equilibrium in solution between $AlCl_3$·NHC and $[AlCl_2{\cdot}(NHC)_2][AlCl_4]$ for this compound).
$AlCl_3$·(NHC=S):
^{1}H NMR (400 MHz, C_6D_6): δ = 5.38 (s, 2H), 1.62 (s, 6H), 1.15 (d, *J* = 7.1 Hz, 12H);
$^{27}Al\{^{1}H\}$ NMR (104 MHz, C_6D_6): δ = 110, 104 (^{27}Al NMR indicates an equilibrium in solution between $AlCl_3$·NHC=S and $[AlCl_2{\cdot}(NHC{=}S)_2][AlCl_4]$ for this compound).
2c:
^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 – 7.24 (m, 2H), 7.02 – 6.90 (m, 2H), 6.83 (d, *J* = 1.2 Hz, 2H), 6.26 (s, 2H), 4.87 (sept, *J* = 7.0 Hz, 2H), 1.41 (s, 6H), 1.09 (d, *J* = 7.0 Hz, 12H), 0.87 (s, 6H), 0.33 (s, 6H);
^{13}C NMR (101 MHz, C_6D_6): δ = 164.0, 134.4, 132.2, 128.6, 126.9, 126.4, 52.0, 21.9, 10.0, -2.0;
^{27}Al NMR (104 MHz, C_6D_6): δ = 124;
^{29}Si NMR(79 MHz, C_6D_6): δ = -21.8.
Elemental analysis for $C_{25}H_{40}AlClN_2Si_2$: found: C: 58.06%, H: 8.73%; calc.: C: 61.63%, H: 8.28% (elemental analysis repeatedly and reproducibly yielded low carbon content, presumably due to the formation of silicon carbide).
2d:
^{1}H NMR (300 MHz, C_6D_6): δ = 7.18 – 7.12 (m, 2H), 7.01 (dt, *J* = 3.1, 1.5 Hz, 2H), 6.72 (dt, *J* = 3.1, 1.4 Hz, 2H), 5.46 (hept, *J* = 7.2 Hz, 2H), 1.34 (s, 6H), 1.07 (d, *J* = 7.1 Hz, 12H), 0.72 (s, 6H), 0.40 (s, 6H);
^{13}C NMR (101 MHz, C_6D_6): δ = 146.27, 129.27, 128.60, 127.35, 125.39, 118.60, 51.18, 20.62, 9.65, -2.29, -2.34.
^{29}Si NMR (79 MHz, C_6D_6): δ = -22.17
Elemental analysis for $C_{25}H_{40}AlClN_2SSi_2$: found: C: 56.19%, H: 8.50%; calc.: C: 57.83%, H: 7.76% (elemental analysis repeatedly and reproducibly yielded low carbon content, presumably due to the formation of silicon carbide).

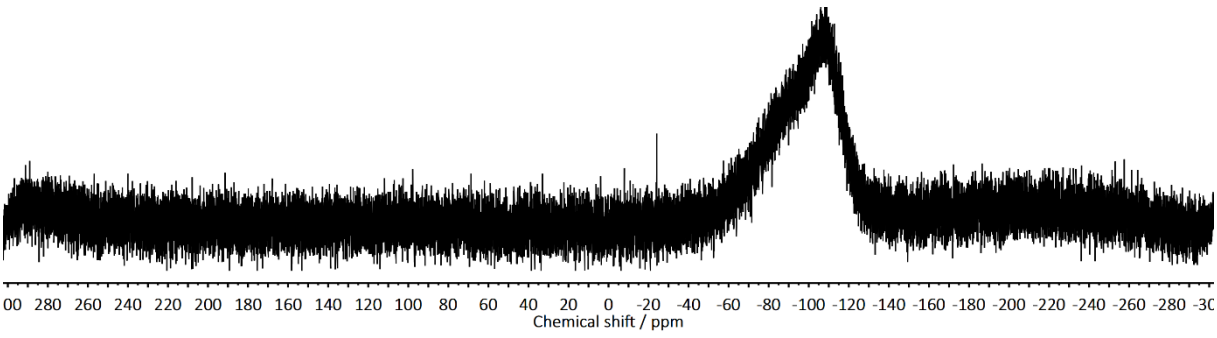
2. NMR spectra



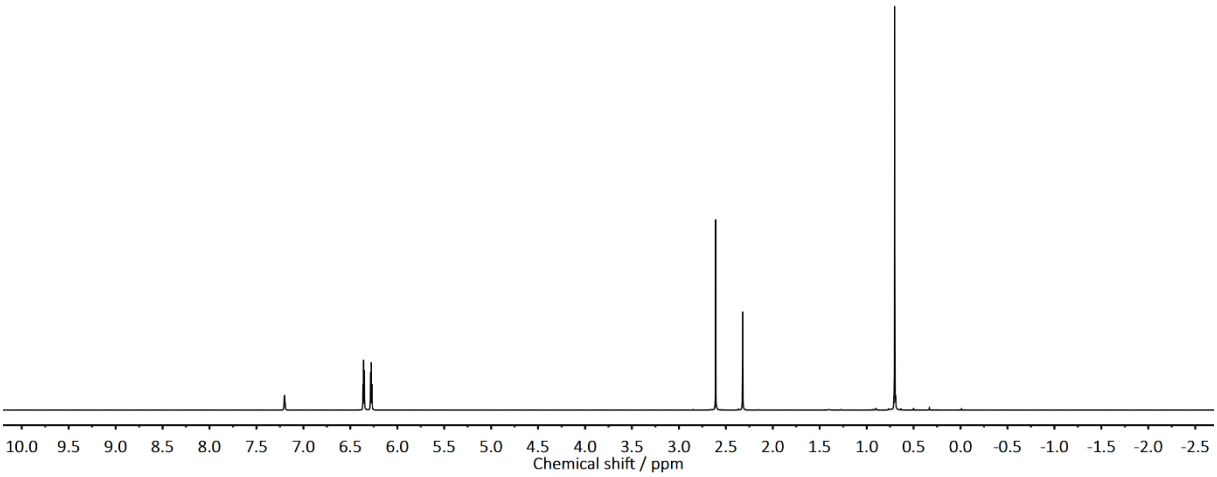
^{1}H NMR (C_6D_6) spectrum of **1b**



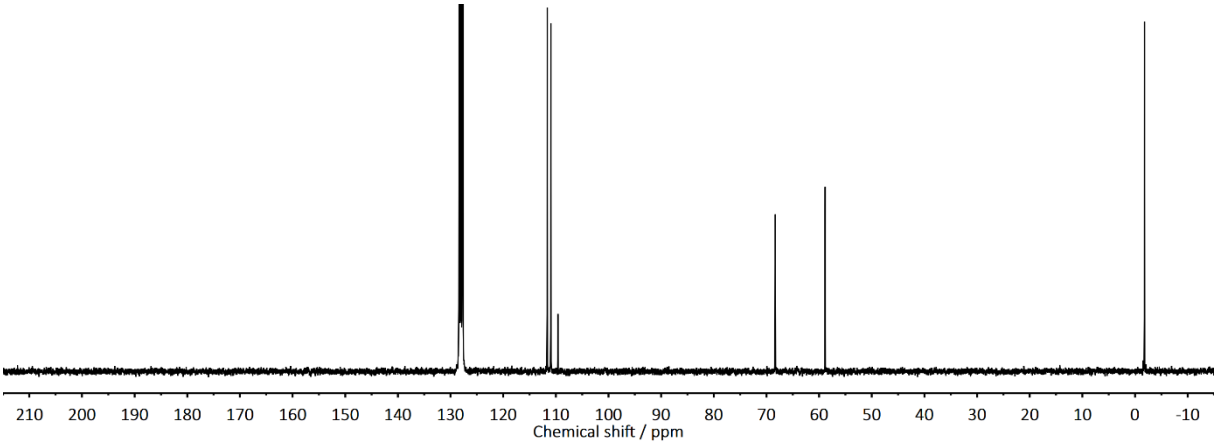
^{13}C{^{1}H} NMR (C_6D_6) spectrum of **1b**



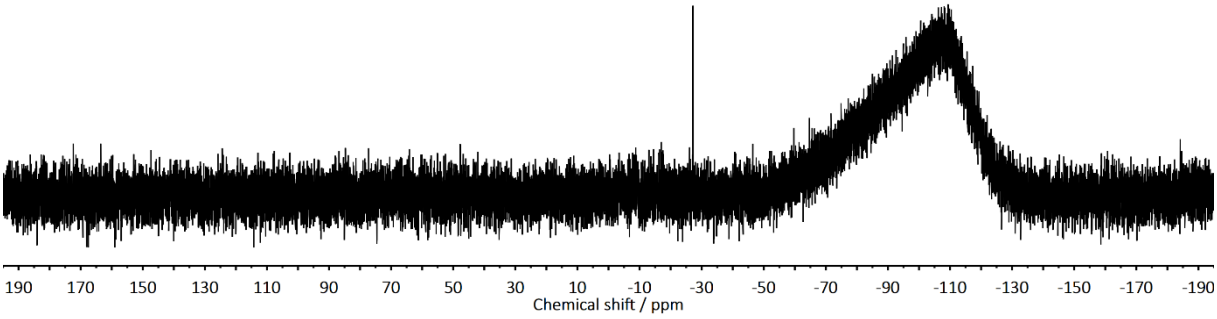
^{29}Si{^{1}H} NMR (C_6D_6) spectrum of **1b**



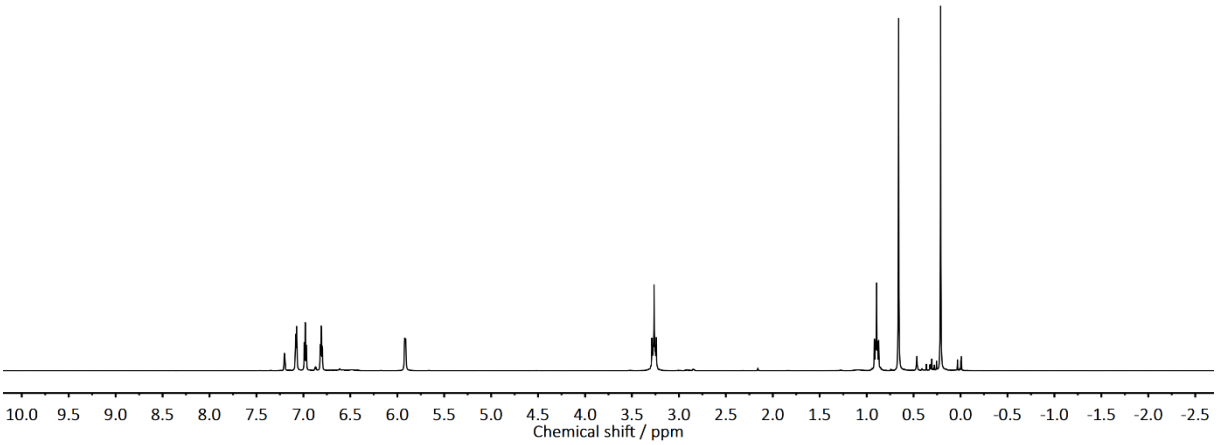
^{1}H NMR (C_6D_6) spectrum of **1b**·DME



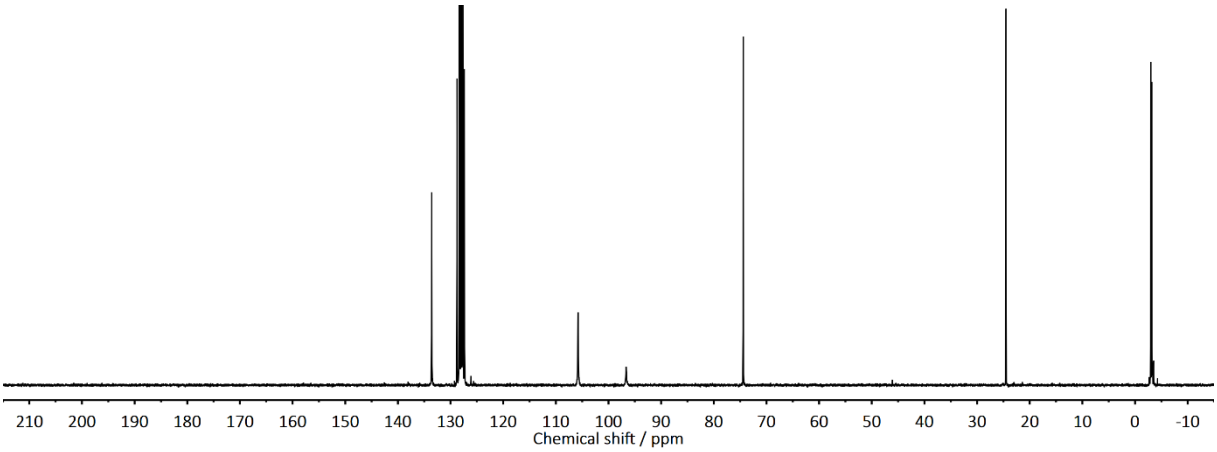
^{13}C{^{1}H} NMR (C_6D_6) spectrum of **1b**·DME



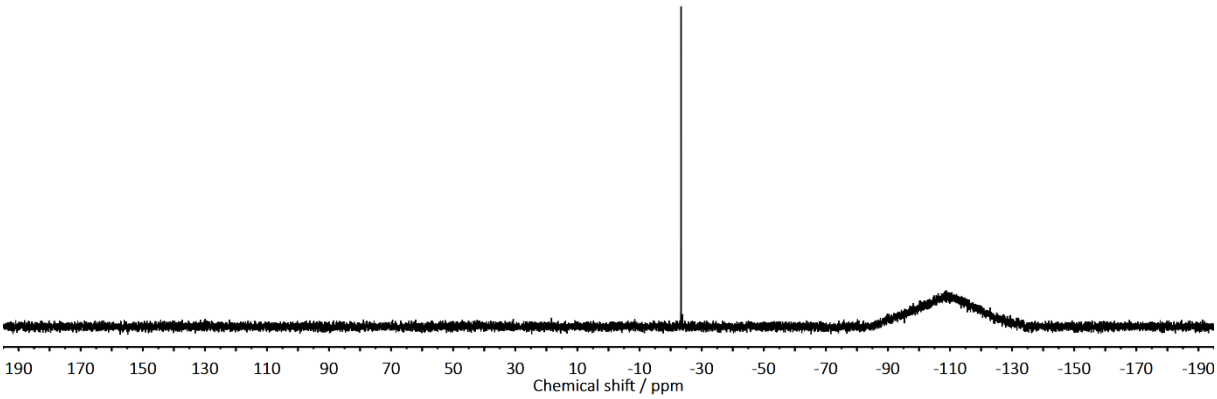
^{29}Si{^{1}H} NMR (C_6D_6) spectrum of **1b**·DME



^{1}H NMR (C_6D_6) spectrum of **2a**



^{13}C{^{1}H} NMR (C_6D_6) spectrum of **2a**



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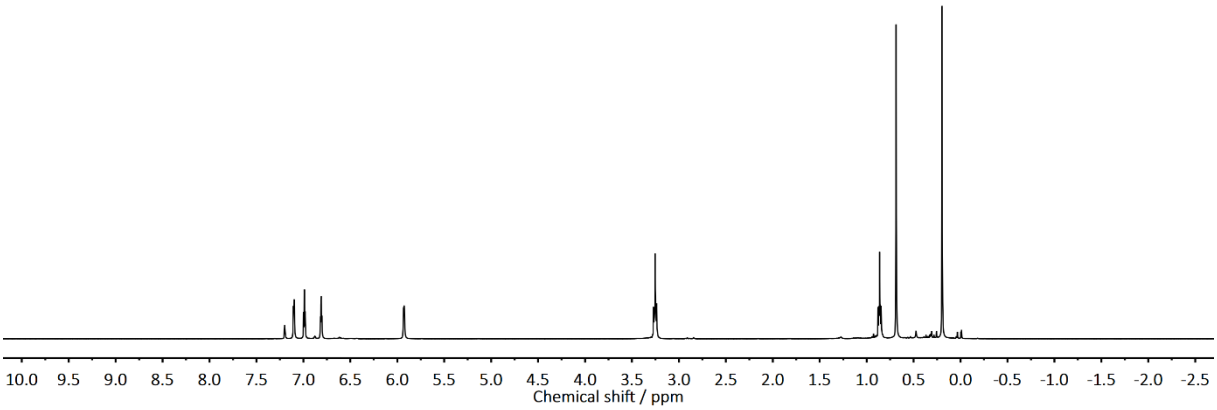
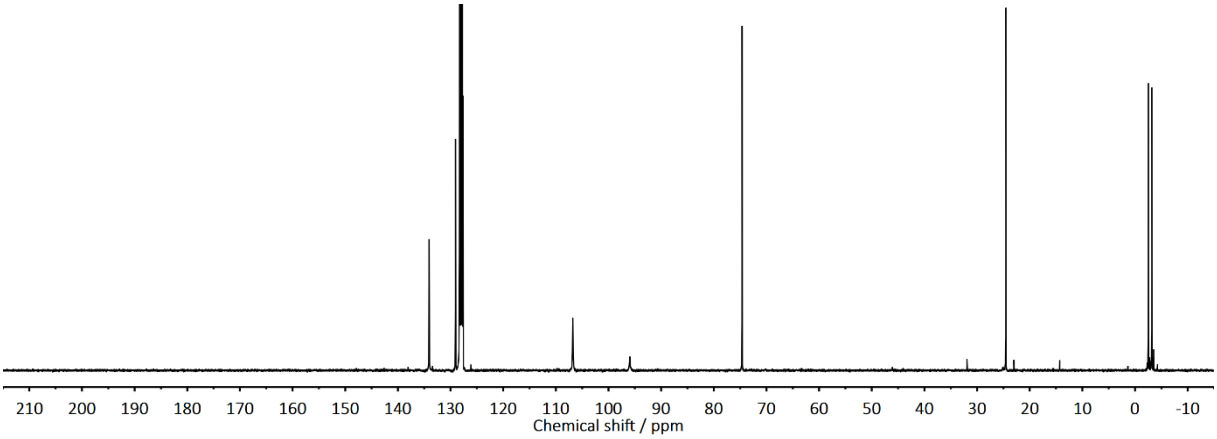
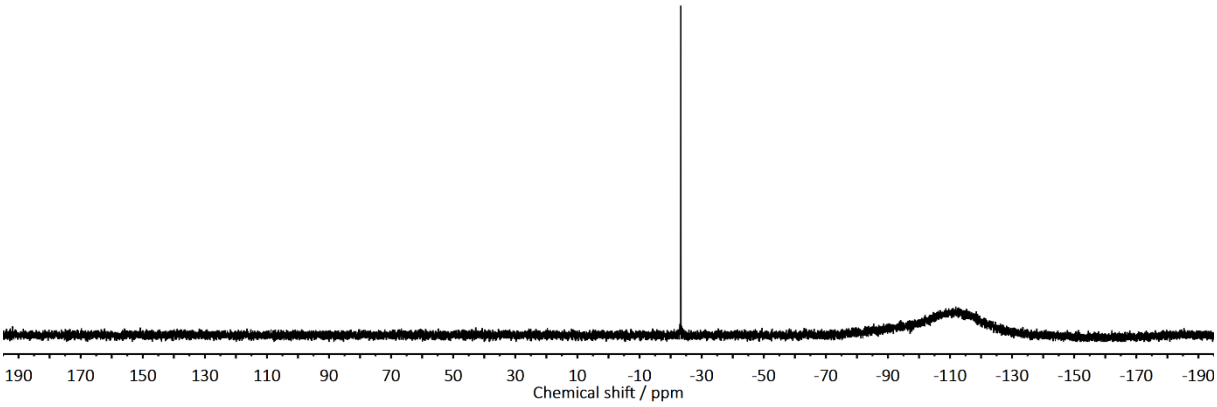


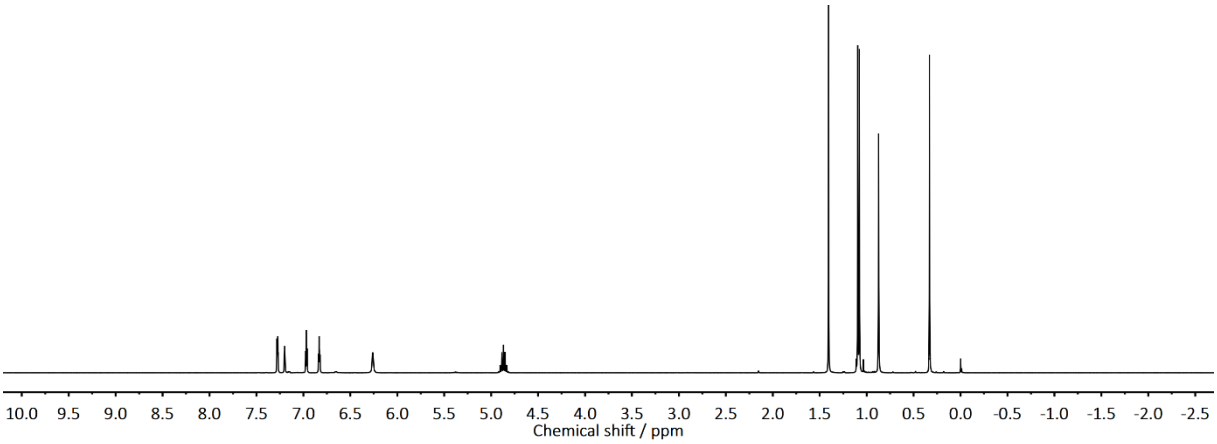
^{1}H NMR (C_6D_6) spectrum of **2b**



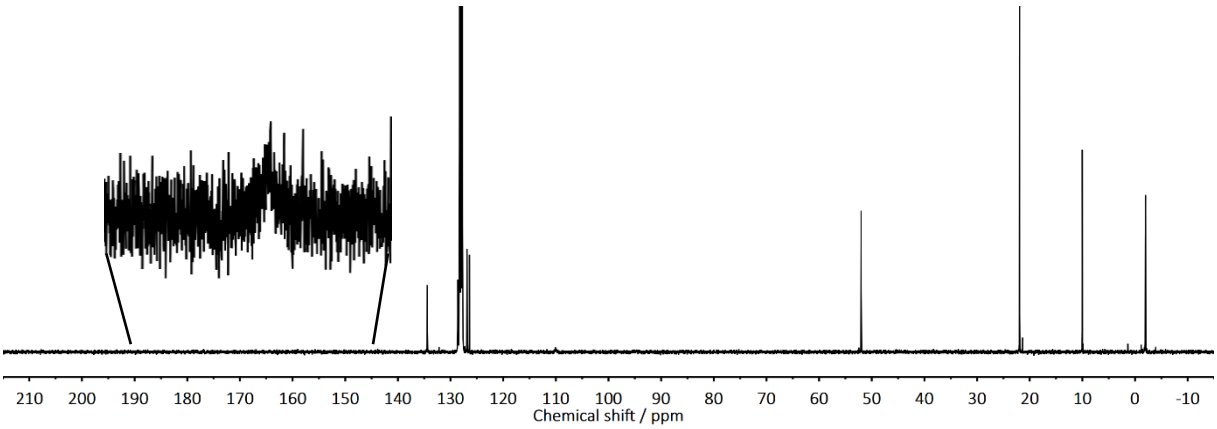
^{13}C{^{1}H} NMR (C_6D_6) spectrum of **2b**



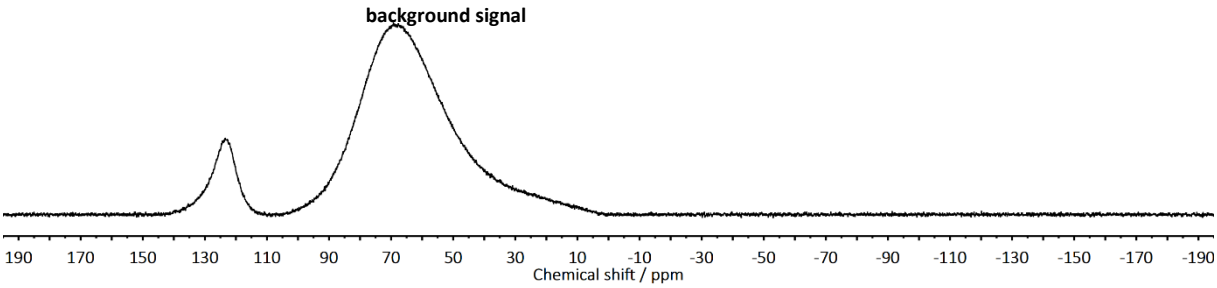
^{29}Si{^{1}H} NMR (C_6D_6) spectrum of **2b**



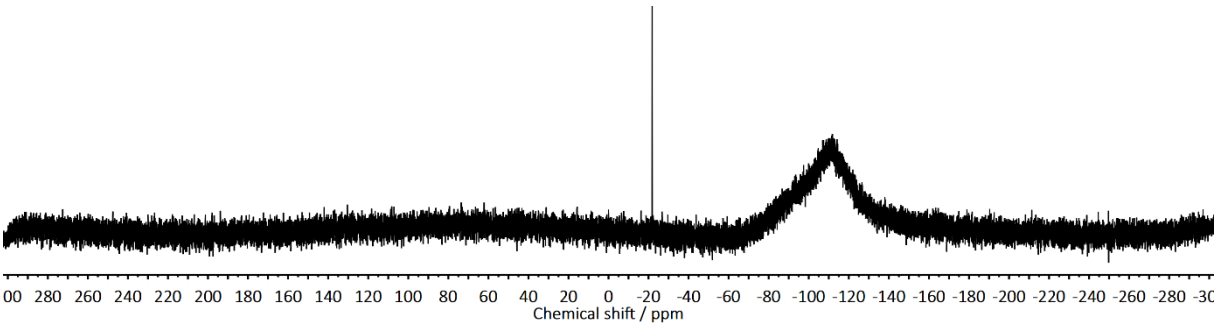
^{1}H NMR (C_6D_6) spectrum of **2c**



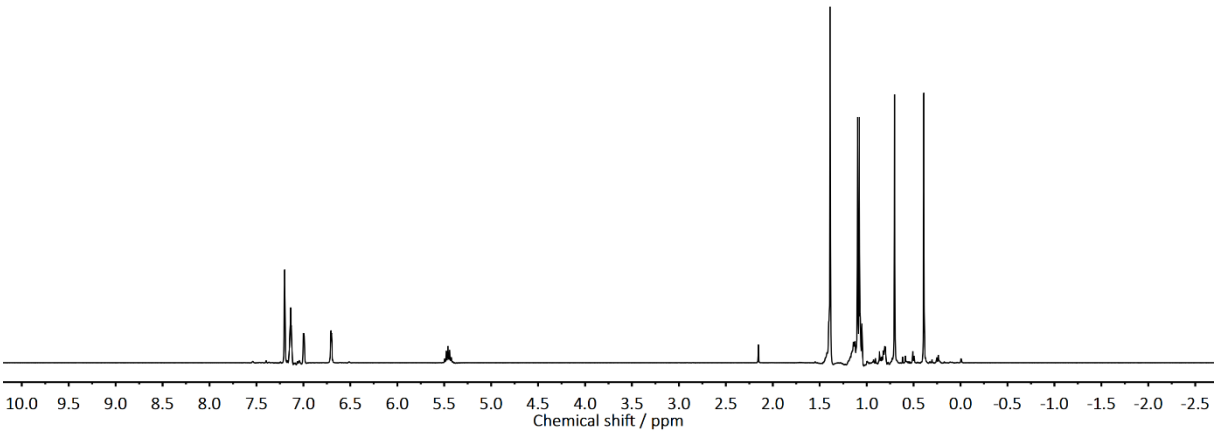
^{13}C{^{1}H} NMR (C_6D_6) spectrum of **2c**



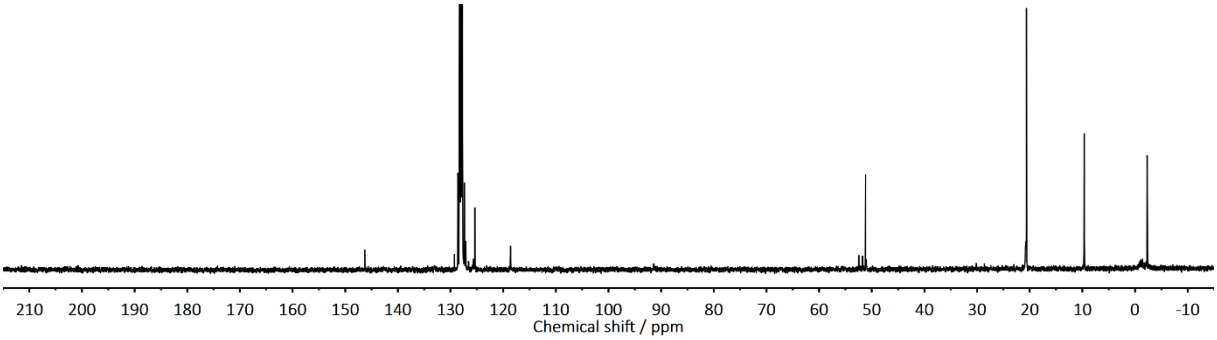
^{27}Al{^{1}H} NMR (C_6D_6) spectrum of **2c**



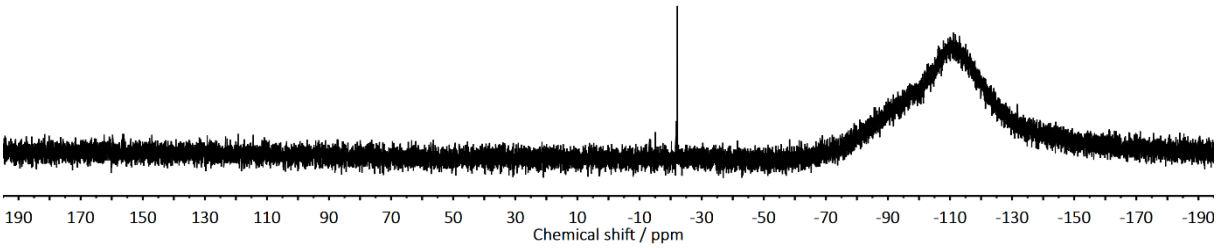
^{29}Si{^{1}H} NMR (C_6D_6) spectrum of **2c**



^{1}H NMR (C_6D_6) spectrum of **2d**



^{13}C{^{1}H} NMR (C_6D_6) spectrum of **2d**



^{29}Si{^{1}H} NMR (C_6D_6) spectrum of **2d**

3. XRD data

Crystal structure data of 1b·DME

CCDC code:	1849427	
Empirical formula:	$C_{18}H_{30}MgO_2Si_2$	
Formula weight:	358.91	
Temperature:	142(2) K	
Wavelength :	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 11.3620(6) Å	a= 90°
	b = 13.9388(7) Å	b= 103.8625(19)°
	c = 13.4716(6) Å	g = 90°
Volume:	2071.39(18) $Å^3$	
Z:	4	
Density (calculated):	1.151 Mg/m^3	
Absorption coefficient:	0.208 mm^{-1}	
F(000):	776	
Crystal size:	0.270 x 0.176 x 0.092 mm^3	
Theta range for data collection:	2.111 to 27.886°	
Index ranges:	-14<=h<=14, -18<=k<=17, -17<=l<=11	
Reflections collected:	20320	
Independent reflections:	4945 [R(int) = 0.0370]	
Completeness to theta = 25.242°:	100.0 %	
Absorption correction:	semi-empirical from equivalents	
Max. and min. transmission:	0.7456 and 0.7264	
Refinement method:	full-matrix least-squares on F^2	
Data / restraints / parameters:	4945 / 0 / 328	
Goodness-of-fit on F^2:	1.008	
Final R indices [I>2sigma(I)]:	R1 = 0.0344, wR2 = 0.0776	
R indices (all data):	R1 = 0.0502, wR2 = 0.0850	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.318 and -0.216 $e.Å^{-3}$	

Crystal structure data of 2a

CCDC code:	1849424	
Empirical formula:	$C_{18}H_{28}AlClOSi_2$	
Formula weight:	379.01	
Temperature:	152(2) K	
Wavelength:	0.71073 Å	
Crystal system:	triclinic	
Space group:	P-1	
Unit cell dimensions:	a = 9.1113(2) Å	a= 71.9090(10)°
	b = 10.3235(2) Å	b= 85.5720(10)°
	c = 11.3696(2) Å	g = 84.1350(10)°
Volume:	1010.07(4) $Å^3$	
Z:	2	
Density (calculated):	1.246 Mg/m^3	
Absorption coefficient:	0.353 mm^{-1}	
F(000):	404	
Crystal size:	0.450 x 0.371 x 0.340 mm^3	
Theta range for data collection:	1.886 to 33.260°	
Index ranges:	-14<=h<=14, -15<=k<=15, -17<=l<=17	
Reflections collected:	28872	
Independent reflections:	7554 [R(int) = 0.0202]	
Completeness to theta = 25.242°:	100.0 %	
Absorption correction:	semi-empirical from equivalents	
Max. and min. transmission:	0.7465 and 0.7228	
Refinement method:	full-matrix least-squares on F^2	
Data / restraints / parameters:	7554 / 51 / 307	
Goodness-of-fit on F^2:	1.042	
Final R indices [I>2sigma(I)]:	R1 = 0.0307, wR2 = 0.0883	
R indices (all data):	R1 = 0.0364, wR2 = 0.0921	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.479 and -0.537 $e.Å^{-3}$	

Crystal structure data of 2b

CCDC code:	1849423	
Empirical formula:	$C_{18}H_{28}AlBrOSi_2$	
Formula weight:	423.47	
Temperature:	152(2) K	
Wavelength:	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 9.3142(4) Å	a= 90°
	b = 16.0816(7) Å	b= 95.313(2)°
	c = 14.3879(6) Å	g = 90°
Volume:	2145.86(16) $Å^3$	
Z:	4	
Density (calculated):	1.311 Mg/m^3	
Absorption coefficient:	2.070 mm^{-1}	
F(000):	880	
Crystal size:	0.241 x 0.202 x 0.054 mm^3	
Theta range for data collection:	1.904 to 29.720°	
Index ranges:	-12<=h<=8, -22<=k<=22, -19<=l<=19	
Reflections collected:	22822	
Independent reflections:	6007 [R(int) = 0.0504]	
Completeness to theta = 25.242°:	99.6 %	
Absorption correction:	semi-empirical from equivalents	
Max. and min. transmission:	0.7459 and 0.6385	
Refinement method:	full-matrix least-squares on F^2	
Data / restraints / parameters:	6007 / 81 / 245	
Goodness-of-fit on F^2:	1.012	
Final R indices [I>2sigma(I)]:	R1 = 0.0453, wR2 = 0.0971	
R indices (all data):	R1 = 0.0885, wR2 = 0.1099	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.555 and -0.435 $e.Å^{-3}$	

Crystal structure data of 2c

CCDC code:	1849425	
Empirical formula:	$C_{25}H_{40}AlClN_2Si_2$	
Formula weight:	487.20	
Temperature:	102(2) K	
Wavelength:	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 9.7469(17) Å	a= 90°
	b = 20.074(4) Å	b= 97.939(6)°
	c = 14.418(3) Å	g = 90°
Volume:	2794.0(9) $Å^3$	
Z:	4	
Density (calculated):	1.158 Mg/m^3	
Absorption coefficient:	0.269 mm^{-1}	
F(000):	1048	
Crystal size:	0.587 x 0.086 x 0.039 mm^3	
Theta range for data collection:	1.750 to 26.777°	
Index ranges:	-12<=h<=12, -25<=k<=24, -18<=l<=18	
Reflections collected:	23827	
Independent reflections:	5967 [R(int) = 0.0821]	
Completeness to theta = 25.242°:	100.0 %	
Absorption correction:	semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.6532	
Refinement method:	full-matrix least-squares on F^2	
Data / restraints / parameters:	5967 / 0 / 293	
Goodness-of-fit on F^2:	1.032	
Final R indices [I>2sigma(I)]:	R1 = 0.0585, wR2 = 0.1261	
R indices (all data):	R1 = 0.1077, wR2 = 0.1451	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.559 and -0.349 $e.Å^{-3}$	

Crystal structure data of 2d

CCDC code:	1849426	
Empirical formula:	$C_{25}H_{40}AlClN_2SSi_2$	
Formula weight:	519.26	
Temperature:	102(2) K	
Wavelength:	0.71073 Å	
Crystal system:	orthorhombic	
Space group:	Pnma	
Unit cell dimensions:	a = 11.6832(5) Å	a= 90°
	b = 17.3962(10) Å	b= 90°
	c = 13.8225(8) Å	g = 90°
Volume:	2809.3(3) $Å^3$	
Z:	4	
Density (calculated):	1.228 Mg/m^3	
Absorption coefficient:	0.343 mm^{-1}	
F(000):	1112	
Crystal size:	-	
Theta range for data collection:	1.882 to 31.422°	
Index ranges:	-14<=h<=17, -21<=k<=25, -20<=l<=20	
Reflections collected:	20489	
Independent reflections:	4770 [R(int) = 0.0378]	
Completeness to theta = 25.242°:	99.9 %	
Absorption correction:	semi-empirical from equivalents	
Max. and min. transmission:	0.7462 and 0.6940	
Refinement method:	full-matrix least-squares on F^2	
Data / restraints / parameters:	4770 / 0 / 231	
Goodness-of-fit on F^2:	1.028	
Final R indices [I>2sigma(I)]:	R1 = 0.0333, wR2 = 0.0770	
R indices (all data):	R1 = 0.0477, wR2 = 0.0840	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.436 and -0.255 $e.Å^{-3}$	

4. Computational Details

All calculations were performed using the Gaussian 09, Revision D.01 package of programs.[4] All geometry optimizations have been carried out at the B3LYP-D3/6-311+G(d,p)(C,H,Cl,O,S,Si);SDD(Br)[5] level of theory, starting from the corresponding crystal structures. Every optimized structure was confirmed to be a minimum on the potential energy surface by a subsequent frequency analysis (all positive eigenvalues).

Optimized geometry of 2a

1	14	0	1.813297	-1.551526	0.423162
2	14	0	2.818389	0.290749	-0.678676
3	6	0	-0.070108	-1.422695	0.086739
4	6	0	2.421147	-3.234439	-0.193094
5	6	0	2.122220	-1.425088	2.285130
6	6	0	1.623384	1.720167	-0.481499
7	6	0	3.079245	-0.081975	-2.520503
8	6	0	4.472007	0.747322	0.118428
9	13	0	-0.617647	0.497467	0.353963
10	6	0	-0.482092	-1.756507	-1.292752
11	6	0	-0.959183	-2.248186	0.922039
12	6	0	0.218345	1.768900	-0.976990
13	6	0	1.835788	2.901402	0.203757
14	17	0	-0.710821	1.109777	2.409327
15	8	0	-2.489953	0.524418	-0.089449
16	6	0	-1.520500	-2.654048	-1.255332
17	6	0	-1.819491	-2.956027	0.118188
18	6	0	-0.274471	3.107209	-0.637517
19	6	0	0.682397	3.749979	0.103772
20	6	0	-3.013788	0.680754	-1.456334
21	6	0	-3.567845	0.136593	0.843386
22	6	0	-4.707132	-0.279817	-0.072254
23	1	0	3.476870	-3.384083	0.054323
24	1	0	1.844545	-4.040023	0.271815
25	1	0	2.307559	-3.322545	-1.276179
26	1	0	1.637524	-2.249688	2.816756
27	1	0	3.195629	-1.477516	2.491576
28	1	0	1.740629	-0.488061	2.696743
29	1	0	3.536319	0.775627	-3.024095
30	1	0	3.731133	-0.949457	-2.661689
31	1	0	2.130114	-0.295019	-3.020790
32	1	0	5.198964	-0.062533	0.006282
33	1	0	4.351718	0.944380	1.187099
34	1	0	4.892592	1.643967	-0.347365
35	1	0	-0.014176	-1.365106	-2.187774
36	1	0	-0.926219	-2.270030	2.003319
37	1	0	-0.012026	1.344054	-1.956708
38	1	0	2.733830	3.151250	0.755202
39	1	0	-2.026313	-3.077803	-2.114423
40	1	0	-2.590809	-3.637206	0.456166
41	1	0	-1.253367	3.495505	-0.889368
42	1	0	0.581410	4.723528	0.565302
43	1	0	-2.623742	1.618544	-1.849234
44	1	0	-2.638507	-0.162107	-2.037482
45	6	0	-4.526287	0.648534	-1.282994
46	1	0	-3.177712	-0.661633	1.469594
47	1	0	-3.794876	1.015462	1.448366
48	1	0	-4.582268	-1.324209	-0.368146
49	1	0	-5.677627	-0.165741	0.412560
50	1	0	-5.024552	0.281929	-2.181396
51	1	0	-4.909083	1.648313	-1.060739

Optimized geometry of 2b

1	35	0	0.738153	-1.607222	2.015323
2	13	0	0.582881	-0.415107	0.025704
3	8	0	2.442694	-0.291528	-0.477800
4	6	0	-0.012753	1.494333	0.247596
5	6	0	-1.661112	-1.459451	-1.020553
6	6	0	-0.273963	-1.341452	-1.552726
7	6	0	2.881494	-0.050528	-1.861015
8	6	0	3.565973	-0.092307	0.467314
9	14	0	-1.890722	1.496942	0.657306
10	6	0	0.883602	2.140350	1.222186
11	6	0	0.331323	2.155111	-1.029541
12	14	0	-2.891954	-0.061776	-0.822532
13	6	0	-1.826598	-2.781643	-0.655411
14	6	0	0.257291	-2.707606	-1.581065
15	6	0	4.202903	0.682058	-1.704975

16	6	0	4.786349	0.050588	-0.432011
17	6	0	-2.539057	3.264032	0.456292
18	6	0	-2.147393	0.956450	2.450769
19	6	0	1.683545	3.052020	0.578297
20	6	0	1.340799	3.061505	-0.818355
21	6	0	-3.225930	0.739488	-2.509620
22	6	0	-4.504771	-0.749641	-0.113616
23	6	0	-0.660282	-3.544137	-1.001768
24	1	0	-0.090168	-0.678220	-2.400977
25	1	0	2.108019	0.536529	-2.351215
26	1	0	2.986668	-1.025284	-2.342276
27	1	0	3.342235	0.815011	1.027216
28	1	0	3.578160	-0.953525	1.130971
29	1	0	0.899562	1.903590	2.277630
30	1	0	-0.166876	1.968969	-1.973106
31	1	0	-2.698939	-3.189055	-0.159414
32	1	0	1.235133	-2.987587	-1.951469
33	1	0	4.014198	1.747297	-1.552291
34	1	0	4.842724	0.557435	-2.579670
35	1	0	5.219638	-0.928822	-0.652555
36	1	0	5.554879	0.667942	0.034822
37	1	0	-1.953307	3.953345	1.072277
38	1	0	-3.585538	3.333168	0.769780
39	1	0	-2.469474	3.599692	-0.581106
40	1	0	-1.630740	1.634587	3.136886
41	1	0	-1.775213	-0.053673	2.632168
42	1	0	-3.213265	0.977405	2.698619
43	1	0	2.445807	3.667945	1.039597
44	1	0	1.793155	3.695715	-1.570994
45	1	0	-2.299525	1.094768	-2.970494
46	1	0	-3.900084	1.596372	-2.416511
47	1	0	-3.682588	0.017015	-3.193362
48	1	0	-4.921427	-1.517524	-0.772852
49	1	0	-5.253794	0.039792	-0.001201
50	1	0	-4.340867	-1.199321	0.869422
51	1	0	-0.523780	-4.599506	-0.805596

Optimized geometry of 2c

1	13	0	-0.193394	-0.117384	-0.453216
2	17	0	-0.322638	-1.300378	-2.282335
3	6	0	1.840178	0.085507	-0.022424
4	6	0	-1.103324	-1.073241	1.094165
5	6	0	-0.987099	1.739419	-0.834300
6	7	0	2.856119	-0.694167	-0.473453
7	7	0	2.439605	1.191908	0.496373
8	6	0	2.650570	-2.094266	-0.935725
9	6	0	1.699560	2.189868	1.310654
10	14	0	-2.981158	-1.244072	0.756688
11	6	0	-0.748985	-0.280709	2.285924
12	6	0	-0.343679	-2.320871	1.271700
13	6	0	-2.390834	1.444099	-1.234666
14	6	0	-0.327973	2.217910	-2.060979
15	6	0	4.085007	-0.062847	-0.284086
16	6	0	3.822323	1.128140	0.330038
17	6	0	3.095410	-2.299884	-2.381966
18	6	0	3.247502	-3.096141	0.055884
19	6	0	1.774432	3.604735	0.737586
20	6	0	2.099533	2.107210	2.786458
21	14	0	-3.732777	0.835560	-0.086292
22	6	0	-3.828087	-1.736286	2.379117
23	6	0	-3.282001	-2.608519	-0.517066
24	6	0	0.144393	-0.985329	3.057629
25	6	0	0.398932	-2.248896	2.426853
26	6	0	-2.462127	1.616259	-2.599513
27	6	0	-1.201383	2.090408	-3.105434
28	6	0	5.402244	-0.578531	-0.765765
29	6	0	4.781203	2.220614	0.675877
30	6	0	-5.357602	0.655464	-1.040181
31	6	0	-3.969645	2.077798	1.331507
32	1	0	1.573880	-2.226316	-0.906055
33	1	0	0.669326	1.851958	1.255921
34	1	0	-0.853165	2.320993	0.079642
35	1	0	-1.166918	0.689091	2.528100
36	1	0	-0.377936	-3.153786	0.581642
37	1	0	0.700881	2.546443	-2.132291
38	1	0	2.639142	-1.549575	-3.029092
39	1	0	2.751729	-3.280597	-2.718716
40	1	0	4.180210	-2.269438	-2.495890
41	1	0	4.338533	-3.106281	0.050427
42	1	0	2.907723	-4.099171	-0.213619
43	1	0	2.898237	-2.879752	1.066460
44	1	0	1.069303	4.242069	1.276748
45	1	0	1.496361	3.618412	-0.316281
46	1	0	2.766527	4.044533	0.849273
47	1	0	3.096092	2.508436	2.975936
48	1	0	2.057192	1.073744	3.130114
49	1	0	1.390781	2.692305	3.377684
50	1	0	-3.375355	-2.648314	2.780597
51	1	0	-4.894952	-1.925344	2.222546
52	1	0	-3.726794	-0.952615	3.133985
53	1	0	-4.355574	-2.725311	-0.695892
54	1	0	-2.896061	-3.566893	-0.155925
55	1	0	-2.795750	-2.382379	-1.467650

56	1	0	0.575395	-0.656473	3.995026
57	1	0	1.062230	-3.015474	2.807914
58	1	0	-3.329329	1.408715	-3.214502
59	1	0	-0.979936	2.283710	-4.147284
60	1	0	6.211786	0.008143	-0.331867
61	1	0	5.485478	-0.502931	-1.853494
62	1	0	5.569425	-1.619235	-0.491610
63	1	0	4.657725	2.580346	1.696972
64	1	0	4.668691	3.076663	0.004573
65	1	0	5.804939	1.860067	0.578630
66	1	0	-6.160815	0.303141	-0.386068
67	1	0	-5.255009	-0.060013	-1.860622
68	1	0	-5.665781	1.615815	-1.465467
69	1	0	-3.026844	2.257500	1.856553
70	1	0	-4.694704	1.715132	2.066540
71	1	0	-4.323961	3.038625	0.944832

Optimized geometry of 2d

1	14	0	-3.437972	1.191237	0.667381
2	14	0	-3.437962	-1.191245	0.667394
3	6	0	-1.904661	1.652335	-0.383867
4	6	0	-4.990721	1.980107	-0.070922
5	6	0	-3.174719	1.829677	2.428969
6	6	0	-1.904658	-1.652334	-0.383866
7	6	0	-4.990713	-1.980133	-0.070882
8	6	0	-3.174684	-1.829658	2.428988
9	13	0	-0.745642	0.000001	-0.173004
10	6	0	-1.112605	2.833998	-0.013375
11	6	0	-2.086078	1.794547	-1.841956
12	6	0	-1.112598	-2.833998	-0.013387
13	6	0	-2.086089	-1.794538	-1.841954
14	17	0	0.207235	-0.000003	1.814087
15	16	0	1.011970	-0.000001	-1.704622
16	6	0	-0.828913	3.565724	-1.140499
17	6	0	-1.431399	2.920517	-2.273916
18	6	0	-0.828916	-3.565718	-1.140518
19	6	0	-1.431414	-2.920507	-2.273926
20	6	0	2.354636	0.000000	-0.593823
21	7	0	2.987998	1.092482	-0.104227
22	7	0	2.987998	-1.092482	-0.104227
23	6	0	4.047753	0.682910	0.703134
24	6	0	2.535122	2.481231	-0.383628
25	6	0	4.047753	-0.682910	0.703134
26	6	0	2.535123	-2.481231	-0.383631
27	6	0	4.964571	1.604139	1.438127
28	6	0	2.277715	3.268445	0.901185
29	6	0	3.472625	3.177640	-1.369730
30	6	0	4.964573	-1.604138	1.438127
31	6	0	2.277723	-3.268450	0.901181
32	6	0	3.472622	-3.177635	-1.369740
33	1	0	-4.856765	3.062655	-0.158098
34	1	0	-5.199405	1.587440	-1.069174
35	1	0	-5.865836	1.790787	0.558813
36	1	0	-3.138461	2.923081	2.443950
37	1	0	-3.988276	1.506161	3.085310
38	1	0	-2.236934	1.448575	2.841095
39	1	0	-4.856762	-3.062683	-0.158030
40	1	0	-5.199399	-1.587491	-1.069144
41	1	0	-5.865826	-1.790794	0.558850
42	1	0	-3.138411	-2.923060	2.443986
43	1	0	-3.988239	-1.506142	3.085331
44	1	0	-2.236901	-1.448536	2.841099
45	1	0	-0.799552	3.060130	0.996353
46	1	0	-2.653726	1.119573	-2.467734
47	1	0	-0.799535	-3.060134	0.996337
48	1	0	-2.653744	-1.119561	-2.467722
49	1	0	-0.244980	4.477725	-1.178103
50	1	0	-1.371771	3.265359	-3.298246
51	1	0	-0.244983	-4.477719	-1.178132
52	1	0	-1.371797	-3.265344	-3.298258
53	1	0	1.573137	2.346794	-0.875358
54	1	0	1.573136	-2.346792	-0.875355
55	1	0	5.268523	2.454172	0.827093
56	1	0	4.501008	1.991997	2.348858
57	1	0	5.868322	1.068871	1.730163
58	1	0	1.700722	2.667435	1.606095
59	1	0	3.195498	3.609939	1.381246
60	1	0	1.684862	4.149272	0.647942
61	1	0	3.571982	2.590725	-2.285365
62	1	0	3.052088	4.150766	-1.634219
63	1	0	4.468316	3.345129	-0.952426
64	1	0	5.268517	-2.454177	0.827097
65	1	0	4.501013	-1.991988	2.348864
66	1	0	5.868327	-1.068872	1.730153
67	1	0	1.700737	-2.667442	1.606098
68	1	0	3.195509	-3.609949	1.381234
69	1	0	1.684867	-4.149274	0.647938
70	1	0	3.571972	-2.590717	-2.285374
71	1	0	3.052087	-4.150762	-1.634227
72	1	0	4.468317	-3.345121	-0.952442

Optimized geometry of donor-free chloro aluminocenophane

1	13	0	-1.279586	-0.005377	-0.121935
2	17	0	-3.055224	-0.133402	1.018386
3	6	0	0.005673	-1.716352	-0.109055
4	6	0	-0.966170	1.803135	-1.256637
5	14	0	1.756324	-1.150356	0.306995
6	6	0	-0.673005	-1.578898	-1.419248
7	6	0	-0.733998	-2.721888	0.580472
8	6	0	-0.049084	1.717781	-0.097004
9	6	0	-2.022491	2.673186	-0.907128
10	14	0	1.767809	1.177603	-0.145377
11	6	0	3.014496	-2.130850	-0.709338
12	6	0	2.028831	-1.452503	2.153911
13	6	0	-1.735825	-2.514248	-1.451689
14	6	0	-1.766991	-3.203256	-0.232139
15	6	0	-0.655274	2.538573	0.906282
16	6	0	-1.828347	3.115144	0.409647
17	6	0	2.703604	2.130601	1.191055
18	6	0	2.466351	1.577010	-1.857499
19	1	0	-0.714616	1.499248	-2.265155
20	1	0	-0.239056	-1.099765	-2.289797
21	1	0	-0.553535	-3.017740	1.605137
22	1	0	-2.863316	2.916554	-1.541979
23	1	0	2.918290	-3.202300	-0.509749
24	1	0	4.038594	-1.829901	-0.466944
25	1	0	2.862915	-1.973586	-1.780830
26	1	0	3.018392	-1.104513	2.463540
27	1	0	1.958475	-2.518341	2.390843
28	1	0	1.284155	-0.923880	2.755824
29	1	0	-2.429467	-2.639272	-2.271928
30	1	0	-2.513445	-3.927818	0.061662
31	1	0	-0.275457	2.656731	1.912267
32	1	0	-2.511365	3.735777	0.972308
33	1	0	3.757571	1.837708	1.212837
34	1	0	2.284518	1.934159	2.181622
35	1	0	2.651290	3.207725	1.008095
36	1	0	1.926460	1.042971	-2.644888
37	1	0	3.519737	1.289621	-1.926729
38	1	0	2.388820	2.648291	-2.065970

Optimized geometry of donor-free bromo aluminocenophane

1	35	0	-2.924608	-0.517672	0.765859
2	13	0	-0.936630	-0.121907	-0.289362
3	6	0	0.484688	-1.509343	-0.255437
4	6	0	-0.030899	1.829714	-0.388303
5	6	0	-0.724808	1.450497	-1.646498
6	14	0	1.925686	-0.685745	0.701208
7	6	0	0.015027	-2.811297	0.253974
8	6	0	0.734323	-1.769614	-1.700841
9	14	0	1.807453	1.578293	0.009189
10	6	0	-0.951023	2.664156	0.298239
11	6	0	-1.976378	2.131856	-1.660743
12	6	0	3.546981	-1.584235	0.352133
13	6	0	1.507203	-0.760730	2.547081
14	6	0	-0.021499	-3.716749	-0.770565
15	6	0	0.421665	-3.073063	-1.979464
16	6	0	2.815283	1.942693	-1.548628
17	6	0	2.271778	2.769093	1.399709
18	6	0	-2.109853	2.855456	-0.477112
19	1	0	-0.224595	1.066708	-2.527750
20	1	0	-0.281810	-2.990767	1.277916
21	1	0	1.138767	-1.050296	-2.401816
22	1	0	-0.792631	3.061894	1.291893
23	1	0	-2.715880	2.049419	-2.445306
24	1	0	3.452475	-2.644687	0.603369
25	1	0	4.365583	-1.163475	0.944057
26	1	0	3.815364	-1.511731	-0.704520
27	1	0	1.451824	-1.797994	2.889650
28	1	0	0.545207	-0.286290	2.765943
29	1	0	2.270705	-0.249340	3.140430
30	1	0	-0.346350	-4.746212	-0.695286
31	1	0	0.500294	-3.548554	-2.948548
32	1	0	2.530410	1.281683	-2.371862
33	1	0	3.883954	1.798862	-1.363563
34	1	0	2.659767	2.974720	-1.876911
35	1	0	2.102301	3.806676	1.097370
36	1	0	3.327351	2.661359	1.666204
37	1	0	1.681577	2.575372	2.299570
38	1	0	-2.985710	3.409698	-0.171015

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