Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 16–18

Modification of bidentate bis(*N*-heterocyclic imine) ligands for low-valent main group complexes

Simone V. Hirmer, Florian S. Tschernuth, Franziska Hanusch, Ramona Baierl, Maximilian Muhr and Shigeyoshi Inoue

Content

1 Experimental section

1.1 General methods and instrumentation

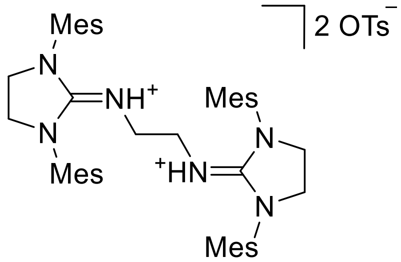
All reactions and manipulations were carried out under dry oxygen-free argon atmosphere using standard Schlenk techniques or in a Labstar glovebox from *MBraun* under argon atmosphere with H_2O and O_2 levels below 0.5 ppm if not stated otherwise. Glassware was heat-dried under vacuum prior to use. Solvents (toluene, THF, MeCN and *n*-hexane) were destilled over sodium/benzophenone under argon, and stored over 3 Å molecular sieve. Pentane was withdrawn from a *MBraun* solvent purification system and stored over 3 Å molecular sieve in a glovebox. Deuterated solvents such as CD_3CN were dried over CaH_2, distilled under argon and stored over 3 Å molecular sieve in the glovebox. THF-d_8 was dried over a potassium mirror, distilled under argon and stored over 3 Å molecular sieve in the glovebox. C_6D_6 was dried over 3 Å molecular sieve in the glovebox. All NMR samples were prepared under argon in J. Young NMR tubes. NMR spectra were recorded on a Bruker Avance 300 MHz, 400 MHz or 500 MHz spectrometer and referenced against the residual proton resonances of the respective deuterated solvent as internal standard (^1H and ^{13}C). ^{29}Si-NMR spectra are referenced to the resonance of tetramethylsilane ($\delta = 0$ ppm) as external standard and the values for the chemical shift (δ) are given in parts per million (ppm). The following abbreviations are used to describe the signal multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, sept = septet, bs = broad singlet, m = multiplet. Melting point measurements were conducted by the microanalytical laboratory of the Catalysis Research Center (Technical University of Munich). Melting Points (m.p.) were determined in glass capillaries, sealed with paraffin wax, under inert gas by a Büchi M-565 melting point apparatus. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.[S1] Electrospray Ionization Mass Spectrometry (ESI-MS) was measured on a Bruker HCT Instrument with a dry gas temperature of 300 °C. The samples were diluted in toluene, acetonitrile or THF and injected under inert atmosphere, the obtained spectra were resolved by mass-to-charge values. Unless otherwise stated, commercially available chemicals were purchased from suppliers and used without further purification. The starting materials $IDipp\rightarrow SiCl_2$,[S2] $GeCl_2$ dioxane,[S3] $SnCl_2$ dioxane,[S4] SIMesNH,[S5] $IMes^{Me}NH$,[S6] and 1,3-dimesitylimidazol-2-ylidene chloride,[S7] were synthesized according to the literature.

1.2 Synthesis and characterization

1.2.1 Ligand syntheses

1.2.1.1 Bis(NHI) ligand L1

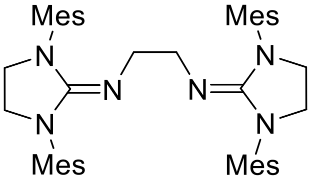
Bis(imidazolidin-2-iminato) ligand precursor L1^{2+} 2[OTs]$^{-}$:



According to a modified procedure of Inoue *et al.*[S8] **SIMesNH** (2.00 g, 6.22 mmol, 2.00 eq.) and 1,2-bis(tosyloxy)ethane (1.15 g, 3.11 mmol, 1.00 eq.) were dried *in vacuo* for 30 min, dissolved in 40 mL toluene and stirred under reflux for 18 h at 110 °C. After cooling to r.t., the reaction mixture was placed in the fridge (1°C) overnight to ensure complete precipitation. Afterwards the brownish solution was decanted, and the orange residue was washed with toluene (2 × 5 mL) and hexane (5 mL) and dried under vacuum. **L1^{2+} 2[OTs]$^{-}$** was obtained as an off-white solid in 63% (3.15 g, 1.97 mmol) yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.84 (bs, 2H, N*H*), 7.48 (d, ^{3}J = 8.1 Hz, 4H, C_6H_4), 7.06 (d, ^{3}J = 7.9 Hz, 4H, C_6H_4), 6.82 (s, 8H, Mes-*H*-3,5), 4.05 (s, 8H, Mes-NCH_2), 2.55 (bs, 4H, C_2H_4), 2.32 (s, 6H, CH_3), 2.32 – 2.25 (m, 24H, Mes-CH_3-2,6), 2.20 (s, 6H, Mes-CH_3-4).

Bis(imidazolidin-2-iminato) ligand L1:



According to a modified procedure of Inoue *et al.*[S9] **L1^{2+} 2[OTs]$^{-}$** (250 mg, 247 µmol, 1.00 eq.) was dried *in vacuo* and dissolved in THF (2 mL). *n*-BuLi in hexane (33.2 mg, 2.50 M, 518 µmol, 2.10 eq.) was added dropwise at 0 °C. After 10 min, the solution was thawed to r.t and stirred for 3 h, then the volatiles were removed. Subsequently, the obtained residue was extracted with toluene (3 × 3.00 mL) and the solution was evaporated. Afterwards the obtained residue was washed with hexane (2 × 2.00 mL). After drying *in vacuo*, **L1** was obtained as an off-white solid in 79% (130 mg, 194 µmol) yield.

^{1}H-NMR (400 MHz, C_6D_6) δ [ppm] = 6.81 (s, 4H, Ar-*H*), 6.66 (s, 4H, Ar-*H*), 3.23 – 2.99 (m, 8H, Mes-NC*H*$_2$), 2.66 (s, 4H, C*H*$_2$), 2.22 – 2.15 (m, 36H, Mes-C*H*$_3$).

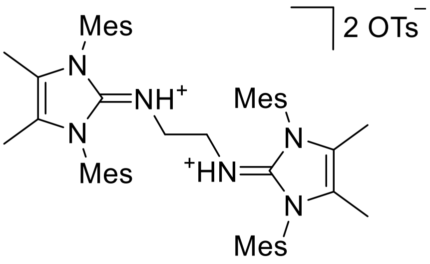
^{13}C-NMR (101 MHz, C_6D_6) δ [ppm] = 147.71 (s, N-*C*-N), 139.20 (s, Mes-*C*-1), 137.67(s, Mes-*C*-2,6),137.61 (s, Mes-*C*-1), 136.30 (s, Mes-*C*-2,6), 135.79 (s, Mes-*C*-4), 135.57 (s, Mes-*C*-4),129.57 (s, Mes-*C*-3,5), 129.26 (s, Mes-C-3,5), 50.63 (s, C=N-*C*H$_2$), 49.02 (s, N-*C*H$_2$-*C*H$_2$-N) 45.84 (s, N-*C*H$_2$-*C*H$_2$-N), 21.13 (s Mes-*C*H$_3$), 21.09 (s, Mes-*C*H$_3$) 18.54 (Mes-*C*H$_3$), 18.20 (Mes-*C*H$_3$).

LIFDI-MS: *m/z* calculated for **L1H^{+}** [$C_{44}H_{57}N_6$] 669.9740, observed 669.461.

m.p.: 205.1 °C.

1.2.1.2 Bis(NHI) ligand L2

Dimethyl-bis(imidazolin-2-iminato) ligand precursor L2^{2+} 2[OTs]$^{-}$:

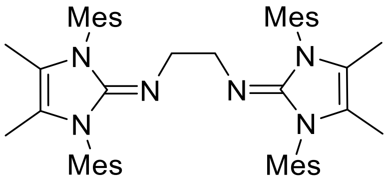


The synthesis was adapted from the literature[S8] **IMes^{Me}NH** (8.58 g, 24.7 mmol, 2.00 eq.) and 1,2-bis(tosyloxy)ethane (4.57 g, 12.4 mmol, 1.00 eq.) were dried under vacuum for 30 min, then dissolved in toluene (300 mL) and stirred under reflux for 18 h at 110 °C. The raw product precipitated while the solution was slowly cooled to r.t. to ensure full precipitation. After decanting the supernatant, the obtained product was washed with toluene (3 × 15 mL). After drying the solid *in vacuo*, **L2^{2+} 2[OTs]$^{-}$** was obtained as an off-white solid in 83% (10.9 g,12.4 mmol) yield.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.54 (d, *J* = 7.9 Hz, 4H, C_6H_4), 7.34 (s, 2H, CN*H*), 7.08 (d, *J* = 7.6 Hz, 2H, C_6H_4), 6.92 (s, 8H, Ar-*H*), 2.58 (bs, 4H, C_2H_4),2.35 (s, 3H, Ar-CH_3) 2.33 (s, 12H, Mes-CH_3-4; 6H, CH_3), 1.98 (s, 24H, Mes-CH_3-2,6), 1.74 (s, 12H, $NCCH_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 143.73 (s, OTs-*C*Ar), 143.12 (s, OTs-*C*Ar), 141.21 (s, N-*C*-N), 138.64 (s, Mes-*C*-1), 136.04 (s, Mes-*C*-2,6), 130.12 (s, Mes-*C*-3,5), 128.17 (s, OTs-*C*H), 127.37 (s, Mes-*C*-4), 126.23 (s, OTs-*C*H), 120.71 (s, N*C*-CH_3), 42.07 (s, C=N-CH_2), 21.37 (s, *p*-Mes-CH_3), 17.61 (s, *o*-Mes-CH_3), 8.53 (s, NC-CH_3).

Dimethyl-bis(imidazolin-2-iminato) ligand L2:



According to a modified procedure of Inoue *et al.*[S9], **L2^{2+} 2[OTs]$^-$**(400 mg, 375 µmol, 1.00 eq.) was dried *in vacuo.* NaHMDS (203 mg, 1.11 mmol, 2.95 eq.) was added, the mixture was dissolved in THF (5 mL) and stirred at r.t. for 4 h. Subsequently, the solvent was removed under reduced pressure, and extracted with toluene (3 × 5.00 mL). The solvent was evaporated, and the obtained precipitate was washed with hexane (2 × 2.00 mL). After drying, **L2** was obtained as a colourless solid in 59% (160 mg, 222 µmol) yield.

^{1}H-NMR (400 MHz, C_6D_6) δ [ppm] = 6.74 (s, 8H, Ar-*H*), 2.79 (s, 4H, C_2H_4), 2.19 (s, 12H, *p*-Mes-C*H*$_3$), 2.17 (s, 24H, *o*-Mes-C*H*$_3$), 1.45 (s, 12H, NCC*H*$_3$).

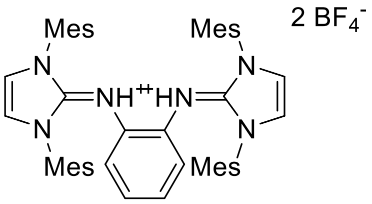
^{13}C-NMR (101 MHz, C_6D_6) δ [ppm] = 142.85 (s, N-*C*-N), 138.00 (s, Mes-*C*-1), 136.82 (s, Mes-*C*-2,6), 128.80 (s, Mes-*C*-3,5), 127.96 (s, Mes-*C*-4), 114.37 (s, N*C*-CH$_3$), 50.63 (s, C=N-*C*H$_2$), 21.23 (s, *p*-Mes-*C*H$_3$), 18.37 (s, *o*-Mes-*C*H$_3$), 9.17 (s, NC-*C*H$_3$).

LIFDI-MS: *m/z* calculated for [$C_{48}H_{60}N_6$] 721.4958, observed 721.493.

m.p.: 343.9 °C

1.2.1.3 Bis(NHI) ligand L3

Dimethyl-bis(imidazolin-2-iminato) ligand precursor L3^{2+} 2[BH$_4$]$^-$:



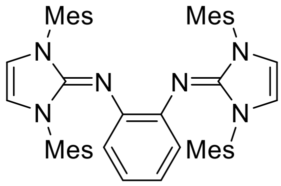
According to a modified synthesis Tamm *et al.*,[S10] to a mixture of 2-chloro-1,3-dimesitylenimidazolium tetrafluoroborate (18.3 g, 42.8 mmol, 2.00 eq.), *o*-phenylenediamine (2.32 g, 20.5 mmol, 1.00 eq.) and KF (7.15 g, 123 mmol, 6.00 eq.) was suspended in 240 ml acetonitrile. Triethylamine (8.57 mL, 61.5 mmol, 3.00 eq.) was added and the reaction mixture was stirred overnight at room temperature. Afterwards, chloroform (240 ml) was added, and the precipitate was filtrated off. The solid residue was washed with 60 mL chloroform and the combined organic layers were extracted with 120 ml aqueous NaBF$_4$ solution (2.00 M) and 120 mL aqueous sodium hydroxide solution (1.25 M). The organic layer was dried with MgSO$_4$, filtered, and stripped from solvents *in vacuo*. The obtained brown and highly viscous residue was dissolved in a little chloroform and precipitated by the addition of Et$_2$O. The crystalline and off-white product **L3^{2+} 2[BF$_4$]$^{2-}$** was obtained through filtration in 23% yield.

^{1}H-NMR (400 MHz, CDCl$_3$): δ [ppm] = 6.78 (s, 4H, C*H*$_2$), 6.77 (s, 8H, Mes-*H*), 5.98 (s, 4H, Ar-*H*), 2.22 (s, 12H, *p*-Mes-C*H3*), 1.95 (s, 24H, *o*-Mes-C*H3*).

^{13}C-NMR (101 MHz, CDCl$_3$): δ [ppm] = 143.77 (s, N*C*N), 139.75 (s, Mes-*C*-1),134.90 (s, Mes-*C*-2,6), 134.25 (s, Ph-*C*), 130.84 (s, Mes-*C*-4) 129.4 (s, Mes-*C*-3,5), 120.48 (s, Ph-*C*H), 118.14 (s, Ph-*C*H), 117.41 (s, *C*H=*C*H), 20.94 (s, *p*-Mes-*C*H$_3$), 17.66 (s, *o*-Mes-*C*H$_3$).

^{11}B-NMR (128 MHz, CDCl$_3$): δ [ppm] = -0.92.

Dimethyl-bis(imidazolin-2-iminato) ligand L3:



The synthesis was adapted from the literature.[S10] To solution of **L3^{2+} 2[BF$_4$]$^{2-}$** (1.00 g, 1.13 mmol, 1.00 eq.) in THF (15 mL) was stirred at 0 °C and a solution of KOtBu (265 mg, 2.36 mmol, 2.10 eq.) in 12 mL THF was added dropwise over a period of 30 min. The resulting mixture was slowly warmed to room temperature and stirred for 2 more hours. All volatiles were removed *in vacuo*, giving an off-white solid, which was extracted with Et_2O (2 x 15 mL). After solvent removal, a brown shiny foam was obtained. Mechanical crushing yielded **L3** as an off-white solid in 96% yield.

^{1}H-NMR (400 MHz, C_6D_6) δ [ppm] = 6.68 (s, 8H, Mes-H-3,5), 6.39 – 6.33 (m, 2H, Ph-H), 6.25 – 6.20 (m, 2H, Ph-H), 5.67 (s, 4H, N-C*H*-C*H*-N), 2.25 (s, 24H, *o*-Mes-CH3), 2.08 (s, 12H, *p*-Mes-CH3).

^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 143.37 (s, N-*C*-N), 142.68 (s, Mes-*C*-1),136.74 (s, Mes-*C*-2,6), 134.78 (s, Ph-*C*), 129.15 (s, Mes-*C*-4) 128.79 (s, Mes-*C*-3,5), 121.33 (s, Ph-*C*H), 118.90 (s, Ph-*C*H), 113.61 (s, *C*H=*C*H), 21.03 (s, *p*-Mes-*C*H$_3$), 18.66 (s, *o*-Mes-*C*H$_3$).

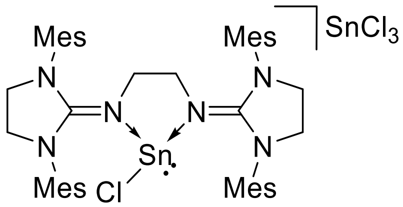
LIFDI-MS: *m/z* calculated for [$C_{48}H_{52}N_6$] 712.4253, observed 712.423.

m.p.: 125.0 °C

1.2.2 Tetryliumylidenes

1.2.2.1 Stannyliumylidenes

Stannyliumylidene 1a[$SnCl_3$]:



According to the literature[S11] **L1** (300 mg, 448 µmol, 1.00 eq) and $SnCl_2$ · dioxane (249 mg, 897 µmol, 2.00 eq) were dissolved in THF (4 mL) and the reaction mixture was stirred at r.t. for 24 h. Then, the solvent was removed under reduced pressure and the hereby-obtained brown residue was washed with a 1:1 pentane/toluene mixture (3 ×1.5 mL). The product was obtained as an off-white solid in 70% (328 mg, 313 µmol) yield.

^{1}H-NMR (400 MHz, THF-*d₈*) δ [ppm] = 6.92 (s, 8H, Ar-*H*), 3.92 (s, 8H, Mes-NCH_2), 2.84 – 2.47 (m, 4H, CH_2), 2.39 – 2.18 (m, 36H, Mes-CH_3).

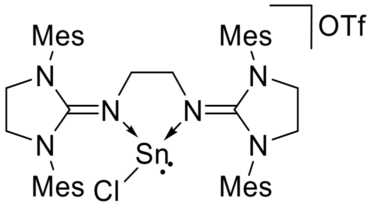
^{13}C-NMR (101 MHz, THF-d_8) δ [ppm] = 159.38(s, N-*C*-N), 136.88(s, Mes-*C*-1), 130.42(s, Mes-*C*-3,5), 129.72 (s. Mes-*C*-2,6), 128.95 (s, Mes-*C*-4), 50.54 (s, C=N-CH_2), 48.40 (s, N-CH_2-CH_2-N), 21.26 (s, *p*-Mes-CH_3), 18.57 (s, *o*-Mes-CH_3).

^{119}Sn-NMR (149 MHz, THF-d_8) δ [ppm] = 7.11 (s, $SnCl_3^-$), -261.25 (s, Sn^+).

ESI-MS: *m/z* calculated for $[C_{44}H_{56}ClN_6Sn]^+$ 823.13, observed 823.4.

m.p.: 272.9 °C

Stannyliumylidene 1a[OTf]:



The synthesis of **1a[OTf]** was conducted according to the literature.[S11] Therefore, **L1** (150 mg, 224 μmol, 1.00 eq) and $SnCl_2$ · dioxane (62.3 mg, 224 μmol, 1.00 eq) were dissolved in THF (4 mL) and cooled to 0 °C. Then, a solution of TMSOTf (49.8 mg, 0.25 M, 224 μmol, 1.00 eq) in toluene was added dropwise within 15 min. Then, the solution was warmed to r.t. and stirred for 18 h. The precipitate was separated via filtration and subsequently washed with THF (3 × 1.5 mL). **1a[OTf]** was obtained as a colourless powder in 20% (43 mg, 44.2 μmol) yield.

^{1}H-NMR (400 MHz, CD_3CN) δ [ppm] = 6.92 (s, 8H, Ar-*H*), 3.81 (s, 8H, Mes-NCH_2), 2.51 (bs, 4H, CH_2), 2.29 (s, 12H, Mes-CH_3-4), 2.19 (s, 24H, Mes-CH_3-2,6).

^{13}C-NMR (101 MHz, CD_3CN) δ [ppm] = 159.32 (s, N-*C*-N), 139.10 (s, Mes-*C*-1), 136.87 (s, Mes-*C*-2,6), 130.43 (s, Mes-*C*-3,5), 50.49 (s, C=N-*C*H_2), 48.18 (s, N-*C*H_2-*C*H_2-N), 21.21 (s, *p*-Mes-*C*H_3), 18.38 (s, *o*-Mes-*C*H_3). *(Note: C-OTf and Mes-C-4 not observed.)*

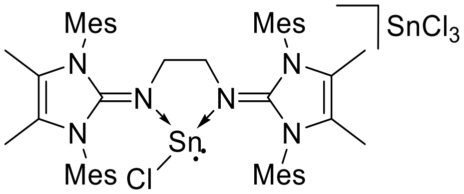
^{19}F-NMR (400 MHz, CD_3CN) δ [ppm] = -79.32 (s, CF_3).

^{119}Sn-NMR (112 MHz, CD_3CN) δ [ppm] = -269.81. (s, Sn^+).

LIFDI-MS: *m/z* calculated for $[C_{44}H_{56}ClN_6Sn]^+$ 823.1340, observed 823.316.

m.p.: 340.9 °C

Stannyliumylidene 2a[SnCl$_3$]:



According to the literature,[S11] **L2** (160 mg, 222 µmol, 1.00 eq) and SnCl$_2$ · dioxane (123 mg, 444 µmol, 2.00 eq) were dissolved in THF (3 mL) and stirred at r.t. for 24 h. After removing the solvent *in vacuo*, the hereby-obtained yellow residue was washed with pentane/toluene (3 ×1 mL, 1:1). **2a[SnCl$_3$]** was obtained as an off-white solid in 64% (156 mg, 142 µmol) yield.

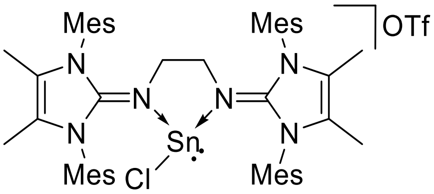
^{1}H-NMR (400 MHz, THF-d_8) δ [ppm] = 7.04 (s, 8H, Ar-*H*), 2.69 (s, 4H, C*H*$_2$), 2.37 (s, 12H, Mes-C*H*$_3$-4), 2.08 (s, 24H, Mes-C*H*$_3$-2,6), 1.72 (s, 12H, NCC*H*$_3$).

^{13}C-NMR (101 MHz, THF-d_8) δ [ppm] = 149.26 (s, N-*C*-N), 141.93 (s, Mes-*C*-1), 138.38 (s, Mes-*C*-2,6), 131.29 (s, Mes-*C*-3,5), 128.66 (s, Mes-*C*-4), 120.00 (s, N*C*-CH$_3$), 48.98 (s, C=N-*C*H$_2$), 21.50 (s, *p*-Mes-*C*H$_3$), 18.48 (s, *o*-Mes-*C*H$_3$), 8.95 (s, NC-*C*H$_3$).

^{119}Sn-NMR (149 MHz, THF-d_8) δ [ppm] = 18.04 (s, *Sn*Cl$_3^-$), -232.53 (s, *Sn*$^+$).

ESI-MS: *m/z* calculated for $[C_{48}H_{60}ClN_6Sn]^+$ 875.36, observed 875.4.

Stannyliumylidene 2a[OTf]:



The synthesis of **6[OTf]** was conducted according to the literature.[S11] Therefore, **L2** (200 mg, 277 µmol, 1.00 eq) and $SnCl_2$ · dioxane (77.0 mg, 277 µmol, 1.00 eq) were dissolved THF (in 16 mL) and cooled to 0 °C. Then, a solution of TMSOTf (61.7 mg, 0.25 M, 277 µmol, 1.00 eq) in toluene was added dropwise within15 min. Afterwards, the solution was warmed to r.t. and stirred for 18 h. After removal of the solvent *in vacuo,* **2a[OTf]** was obtained as an off-white powder in 86% (244 mg, 238 µmol) yield.

^{1}H-NMR (400 MHz, CD_3CN) δ [ppm] = 7.01 (s, 8H, Ar-*H*), 2.85 - 2.43 (bs, 4H, C*H*$_2$), 2.36 (s, 12H, Mes-C*H*$_3$-4), 2.01 (s, 24H, Mes-C*H*$_3$-2,6), 1.65 (s, 12H, NCC*H*$_3$).

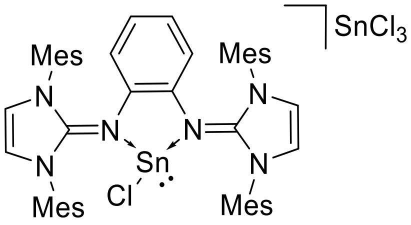
^{13}C-NMR (101 MHz, THF-*d*$_8$) δ [ppm] = 149.23 (s, N-*C*-N), 141.97 (s, Mes-*C*-1), 137.45 (s, Mes-*C*-2,6), 131.30 (s, Mes-*C*-3,5), 128.66 (s, Mes-*C*-4), 119.99 (s, N*C*-CH_3), 48.88 (s, C=N-*C*H$_2$), 21.49 (s, *p*-Mes-*C*H$_3$), 17.96 (s, *o*-Mes-*C*H$_3$), 8.79 (s, NC-*C*H$_3$).

^{19}F-NMR (400 MHz, CD_3CN) δ [ppm] = -79.35 (s, C*F*$_3$).

^{119}Sn-NMR (149 MHz, CD_3CN) δ [ppm] = -230.56 (s, *Sn*$^+$).

ESI-MS: *m/z* calculated for $[C_{48}H_{60}ClN_6Sn]^+$ 875.36, observed 875.4.

Stannyliumylidene 3a[SnCl$_3$]:



The synthesis of **3a[SnCl$_3$]** was conducted according to the literature.[S11] Therefore, **L3** (350 mg, 491 µmol, 1.00 eq.) and SnCl$_2$ · dioxane (273 mg, 982 µmol, 2.00 eq.) were dissolved in THF (5 mL) and stirred for 18 h at r.t.. After evaporation of the solvent the obtained brownish solid was washed with a 3:1 hexane: toluene (3 ×1.5 mL). Subsequent drying in *vacuo* gives 3a[SnCl$_3$] as an off-white solid in 95% (509 mg, 466 µmol) yield.

^{1}H-NMR (400 MHz, CD$_3$CN) δ [ppm] = 6.96 (s, 4H, N-C*H*-C*H*-N), 6.92 (s, 8H, Mes-*H*-3,5), 6.48 – 6.40 (m, 2H, Ph-*H*), 6.24 – 6.17 (m, 2H, Ph-*H*), 2.28 (s, 12H, *p*-Mes-C*H*3), 2.14 (s, 24H, *o*-Mes-C*H*3).

^{13}C NMR (101 MHz, CD$_3$CN) δ [ppm] = 148.54 (s, N-*C*-N), 141.52 (s, Mes-*C*-1), 136.83 (s, Mes-*C*-2,6), 131.85 (s, Mes-*C*-4), 131.19 (s, Mes-*C*-3,5), 129.22 (s, Ph-*C*), 120.90 (Ph-*C*H), 119.72 (s, *C*H=*C*H), 118.27 (Ph-*C*H), 21.26 (s, *p*-Mes-*C*H$_3$), 19.07 (s, *o*-Mes-*C*H$_3$).

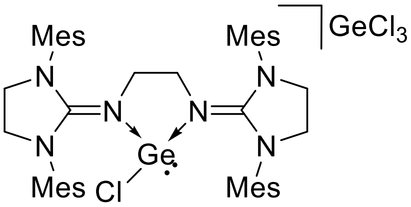
^{119}Sn-NMR (112 MHz, CD$_3$CN) δ [ppm] = -20.81 (s, *Sn*$^-$), -154.69.(s, *Sn*$^+$).

LIFDI-MS: *m/z* calculated for [C$_{48}$H$_{52}$ClN$_6$Sn]$^+$ 867.2964 observed 867.289.

m.p.: 134.7 °C

1.2.2.2 Germyliumylidenes

Germyliumylidene 1b[GeCl$_3$]:



The synthesis of **1b[GeCl$_3$]** was conducted according to the literature.[S11] **L1** (100 mg, 150 µmol, 1.00 eq) and GeCl$_2$ · dioxane (69.3 mg, 299 µmol, 2.00 eq) were dissolved in THF (2 mL) and stirred at r.t. for 24 h. Thereafter, the solvent was removed under reduced pressure and the off-white residue was washed with a 1:1 mixture of pentane/toluene (2 ×0.5 mL). The product was obtained as a colorless powder in 86% (48.3 mg, 47.9 µmol) yield.

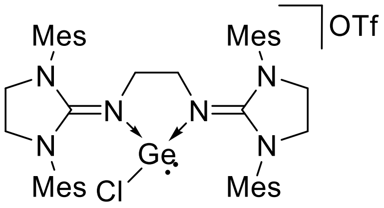
^{1}H-NMR (400 MHz, THF-*d$_8$*) δ [ppm] = 6.91 (bs, 8H, Ar-H), 3.95 (s, 8H, Mes-NCC*H*$_2$), 2.90 – 2.82 (m, 2H, C*H*$_2$), 2.57 – 2.50 (m, 2H, C*H*$_2$), 2.30 (s, 12H, Mes-C*H*$_3$-4), 2.28 – 2.20 (bs, 24H, Mes-C*H*$_3$-2,6).

^{13}C-NMR (101 MHz, THF-*d$_8$)* δ [ppm] = 158.79 (s, N-*C*-N), 140.22 (s, Mes-*C*-1), 130.86 (s, Mes-*C*-3,5), 129.03 (s, Mes-*C*-2,6), 128.95 (s, Mes-*C*-4), 49.78 (s, C=N-*C*H$_2$), 47.89 (s, N-*C*H$_2$-*C*H$_2$-N), 21.27 (s, *p*-Mes-*C*H$_3$), 18.56 (s, *o*-Mes-*C*H$_3$).

LIFDI-MS: *m/z* calculated for $[C_{44}H_{56}ClN_6Ge]^+$ 777.3467, observed 777.342.

m.p.: 269.6 °C

Germyliumylidene 1b[OTf]:



The synthesis of **1b[OTf]** was conducted according to the literature.[S11] **L1** (80 mg, 120 µmol, 1.00 eq) and $GeCl_2$ · dioxane (27.7 mg, 119 µmol, 1.00 eq) were dissolved in THF (2 mL) and cooled to 0°C. A solution of TMSOTf (26.6 mg, 0.25 M, 119 µmol, 1.00 eq) in toluene was added dropwise over a period of 10 min. After warming to r.t the mixture was stirred for 18 h. The reaction mixture was concentrated to the point of crystalisation and placed at -35 °C over night. The colourless crystals were washed with pentane (2 × 0.5 mL). However, the ^{1}H-NMR confirms, that 1b[$GeCl_3$] is also formed. SC-XRD analysis of crystals grown from the reaction mixture, confirm the mixed anion composition. Due to that position disorder, the data could not be refined to a satisfactory level. However, the connectivity of the cation and the presence of $GeCl_3$/OTf mixed anion can be confirmed (see Chapter 2,Figure S7).

^{1}H-NMR (400 MHz, CD_3CN) δ [ppm] = δ 7.03 (s, 8H, Ar-*H*), 3.99 (s, 8H, Mes-NC*H*$_2$), 2.87 – 2.70 (m, 4H, C*H*$_2$), 2.53 – 2.40 (m, 4H, C*H*$_2$), 2.34 (s, 12H, Mes-C*H*$_3$-4), 2.16 (s, 24H, Mes-C*H*$_3$-2,6).

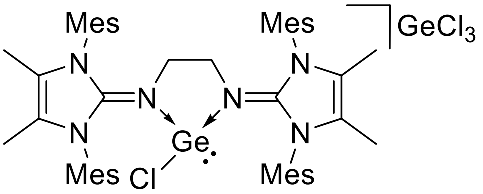
^{13}C-NMR (101 MHz, CD_3CN) δ [ppm] = 141.64 (s, N-C-N), 137.76 (s, Mes-C-1), 131.15 (s, Mes-*C*-3,5), 49.42 (s, C=N-*C*H$_2$), 47.71 (s, N-*C*H$_2$-*C*H$_2$-N), 21.23 (*p*-Mes-*C*H$_3$), 17.83 (s, *o*-Mes-*C*H$_3$). Less intense signal of Mes-*C*$_4$ was not observed.

^{19}F-NMR (376 MHz, CD_3CN) δ [ppm] = -79.10 (s, C*F*$_3$).

LIFDI-MS: *m/z* calculated for $[C_{44}H_{56}ClN_6Ge]^+$ 777.3467, observed 777.338.

m.p.: 264.2 °C

Germyliumylidene 2b[GeCl$_3$]:

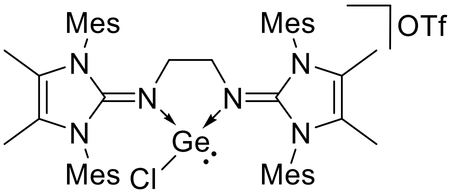


The synthesis of **2b[GeCl$_3$]** was conducted according to the literature.[S11] **L2** (75 mg, 104 µmol, 1.00 eq) and GeCl$_2$ · dioxane (48.2 mg, 208 µmol, 2.00 eq) were suspended in THF (2 mL) and stirred at r.t. for 24 h. Thereafter, the solvent was removed under reduced pressure and the white residue was washed with a 1:1 mixture of pentane/toluene (2 ×1.5 mL). The product was obtained as a colorless powder in 59% (61.3 mg, 60.8 µmol) yield.

^{1}H-NMR (400 MHz, CDCl$_3$) δ [ppm] = 7.02 (s, 8H, Ar-*H*), 2.55-2.51 (m, 4H, C*H*$_2$), 2.39 (s, 12H, Mes-C*H*$_3$-4), 2.01 (s, 24H, Mes-C*H*$_3$-2,6), 1.77 (s, 12H, NCC*H*$_3$).

^{13}C-NMR (101 MHz, CDCl$_3$) δ [ppm] = 136.07 (s, Mes-*C*-2,6), 130.37 (s, Mes-*C*-3,5), 127.71 (s, Mes-*C*-4), 42.72 (s, C=N-*C*H$_2$), 21.54 (s, *p*-Mes-*C*H$_3$), 17.95 (s, *o*-Mes-*C*H$_3$), 8.76 (s, NC-*C*H$_3$). (Due to the decreased solubility, less intense signals were not observed in this spectrum. For comparison of the cation please see ^{13}C-NMR of **2b[OTf]**.)

Germyliumylidene 2b[OTf]:



The synthesis of **2b[OTf]** was conducted according to the literature.[S11] **L2** (51.2mg, 71.0 µmol, 1.00 eq) and $GeCl_2$ · dioxane (15.8 mg, 71.0 µmol, 1.00 eq) were dissolved in THF (2 mL) and cooled to 0°C. A solution of TMSOTf (1.8 mg, 0.25 M, 71.0 µmol, 1.00 eq) in toluene was added dropwise over a period of 10 min. After warming to r.t the mixture was stirred for 18 h. The reaction mixture was concentrated to the point of crystalisation and placed at -35 °C overnight. The colourless crystals were washed with pentane (2 × 0.5 mL) and **2b[OTf]** was obtained as a white powder in 63% (48.5 mg, 44.5 µmol) yield.

^{1}H-NMR (400 MHz, THF-d_8) δ [ppm] = 7.10 (s, 8H, Ar-H), 2.57 – 2.22 (m, 4H, CH_2), 2.38 (s, 12H, Mes-CH_3-4), 2.04 (s, 24H, Mes-CH_3-2,6), 1.79 (s, 12H, $NCCH_3$).

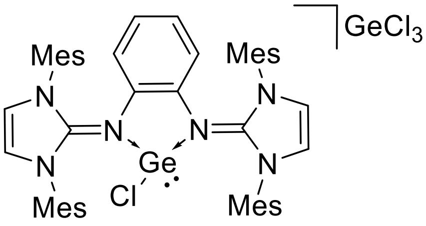
^{13}C-NMR (101 MHz, THF-*d*$_8$) δ [ppm] = 144.38 (s, N-*C*-N), 142.02 (s, Mes-*C*-1), 137.40 (s, Mes-*C*-2,6), 131.11 (s, Mes-*C*-3,5), 129.04 (s, Mes-*C*-4), 121.84 (s, N*C*-CH_3), 43.59 (s, C=N-*C*H_2), 21.55 (s, *p*-Mes-*C*H_3), 18.08 (s, *o*-Mes-*C*H_3), 8.57 (s, NC-*C*H_3).

^{19}F-NMR (376 MHz, THF-*d*$_8$) δ [ppm] = -79.05.

LIFDI-MS: *m/z* calculated for $[C_{48}H_{60}N_6GeCl]^+$ 829.3780, observed 829.369.

m.p.: 107.3 °C

Germyliumylidene 3b[GeCl$_3$]:



The synthesis of **3b[GeCl$_3$]** was conducted according to the literature.[S11] **L3** (350 mg, 491 µmol, 1.00 eq) and GeCl$_2$ · dioxane (227 mg, 982 µmol, 2.00 eq) were dissolved in THF (5 mL) and stirred at r.t. for 24 h. Subsequently, the solvent was removed in *vacuo* and the off-white residue was washed with a 4:1 mixture of hexane/toluene (3 ×1.0 mL). The product was obtained as a colourless powder in 92% (452 mg, 452 µmol) yield.

1H NMR (400 MHz, CD$_3$CN) δ [ppm] = 6.98 (s, 4H, C*H*=C*H*), 6.97 – 6.79 (br, 8H, Mes-*H*), 6.49 – 6.39 (m, 2H, Ph-C*H*), 6.33 – 6.24 (m, 2H, Ph-C*H*), 2.27 (s, 12H, *p*-Mes-CH_3), 2.34 – 1.78 (br, 24H, *o*-Mes-CH_3).

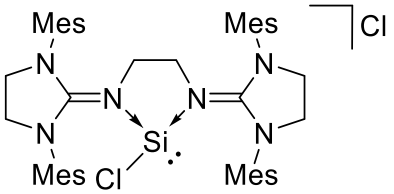
^{13}C NMR (101 MHz, CD$_3$CN) δ [ppm] = 146.37 (s, N-*C*-N), 141.46 (s, Mes-*C*-1), 137.23 (s, Mes-*C*-2,6), 131.87 (s, Mes-*C*-4) 130.73 (s, Mes-*C*-3,5), 130.59 (s, Ph-*C*), 121.24 (s, Ph-*C*H), 120.71 (s, *C*H=*C*H), 117.68 (s, Ph-*C*H), 21.25 (s, *p*-Mes-*C*H$_3$), 19.90 (s, *o*-Mes-*C*H$_3$).

LIFDI-MS: *m/z* calculated for $[C_{48}H_{52}ClN_6Ge]^+$ 821.3154, observed 821.31.

m.p.: 275.0 °C

1.2.2.3 Silyliumylidenes

Chlorosilyliumylidene 1c[Cl]:



In order to synthesize chlorosilyliumylidene **1c[Cl],** IDipp$\rightarrow SiCl_2$ (94.8 mg, 194 µmol, 1.30 eq) was dissolved in toluene (5 mL). After stirring for 20 min, the precipitated imidazoline salt (IDipp · HCl) was separated *via* filtration and the filtrate was added dropwise to a solution of **L1** (100 mg, 149 µmol, 1.00 eq) in toluene (1.5 mL). The reaction mixture was stirred for 18 h at r.t. Subsequent concentration of the reaction mixture and cooling to -35 °C ensured product precipitation. Afterwards, the solid was filtrated and washed with *n*-hexane (3 × 1 mL). The colorless product was obtained in 52% (60.1 mg, 78.3 µmol) yield.

^{1}H-NMR (400 MHz, CD_3CN) δ [ppm] = 6.90 (d, *J* =8.4 Hz, 8H, Ar-*H*), 3.97 – 3.69 (m, 8H, Mes-N$C\mathit{H}_2$), 2.89 – 2.82 (m, 2H, $C\mathit{H}_2$), 2.51 – 2.47 (m, 2H, $C\mathit{H}_2$), 2.29 (bs, 12H, Mes-$C\mathit{H}_3$-2,6), 2.17 – 2.08 (m, 24H, Mes-$C\mathit{H}_3$-4).

^{13}C-NMR (126 MHz, CD_3CN) δ [ppm] = 147.88 (s, N-C-N), 141.60 (s, Mes-*C*-1), 137.14(s, Mes-*C*-3,5), 132.59 (s. Mes-*C*-2,6), 130.17 (s, Mes-*C*-4), 66.25 (s, C=N-$\mathit{C}H_2$), 47.26 (s, N-$\mathit{C}H_2$-$\mathit{C}H_2$-N), 21.24 (s, *p*-Mes-$\mathit{C}H_3$), 18.32 (s, *o*-Mes-$\mathit{C}H_3$).
^{29}Si-NMR (99 MHz, CD_3CN) δ [ppm] = -1.43.

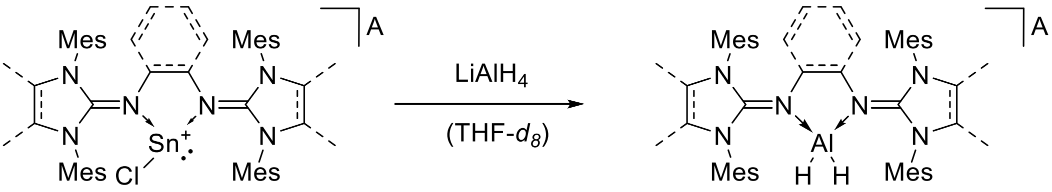
LIFDI-MS: molecule peak of **1c$^+$** was not observed, due to decomposition to free **L1** during MS measurement.

m.p.: 134.3 °C

1.3 Transmetalation experiments

1.3.1 Transmetalation with $LiAlH_4$

General procedure:

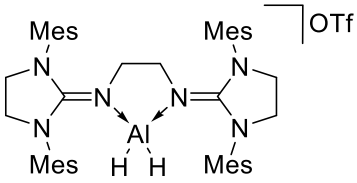


$1a^+$, $2a^+$, $3a^+$ **$L_1AlH_2^+$, $L_2AlH_2^+$, $L_3AlH_2^+$**

Scheme S1: General transmetalation reaction of stannyliumylidenes **$1a^+$**, **$2a^+$**, **$3a^+$** with $LiAlH_4$.

In NMR scale experiments, at -78 °C to a solution of the stannyliumylidenes **$1a^+$**,**$2a^+$**, **$3a^+$** in THF-d_8 (0.2 mL) was added a slight excess of $LiAlH_4$ in THF-d_8 (0.2 mL). A colour change from yellow to brown and precipitation of elemental tin was detected immediately upon warming to room temperature. Monitoring ^1H- ^{13}C-NMR evidences the formation of the dialuminiumhydride species **$LxAlH_2^+$** (x = 1,2,3).

$L1AlH_2^+$:



1a[OTf] (16.0 mg, 16.5 µmol, 1.00 eq), $LiAlH_4$ (579 µg, 15.3 µmol, 1.00 eq)

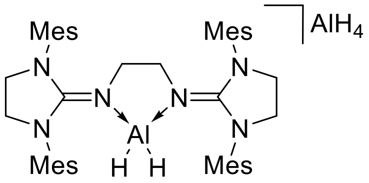
*Note: reaction was carried out in MeCN-d_3 due to insolubility of **1a[OTf]** in THF.*

^{1}H-NMR (400 MHz, CD_3CN) δ [ppm] = 6.92 (s, 8H Ar-*H*), 3.81 (s, 8H, NCH_3), 2.51 (s, 4H CH_2), 2.29 (s, 12H Mes-CH_3-4), 2.19 (s, 24H Mes-CH_3-2,6).

^{13}C-NMR (101 MHz, CD_3CN) δ [ppm] = 159.33 (s, N-*C*-N), 137.94 (s, Mes-*C*-1), 137.5 (s, Mes-*C*-4), 136.91 (s, Mes-*C*-2,6), 130.30 (s, Mes-*C*-3,5), 130.12 (s, Mes-*C*-3,5), 48.70 (s, N-CH_2-CH_2-N), 48.18 (s, C=N-CH_2), 21.21 (s, *p*-Mes-CH_3), 18.33 (s, *o*-Mes-CH_3).

^{19}F-NMR (376 MHz, CD_3CN) δ [ppm] = -79.31.

$L1AlH_2^+$:



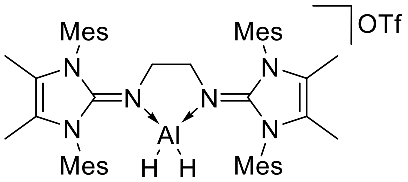
1a[$SnCl_3$] (22.0 mg, 21.0 µmol, 1.00 eq); $LiAlH_4$ (797 µg, 21.0 µmol, 1.00 eq.)

^{1}H-NMR (300 MHz, THF-*d₈*) δ [ppm] = 6.82 (s, 8H Ar-*H*), 3.90 (s, 8H, NCH_3), 2.33 (s, 2H, AlH_2), 2.30 (s, 4H CH_2), 2.25 (s, 12H Mes-CH_3-4), 2.16 (s, 24H Mes-CH_3-2,6).

^{13}C-NMR (75 MHz, THF-*d₈*) δ [ppm] = 160.01 (s, N-*C*-N), 130.67 (s, Mes-*C*-1), 129.68 (s, Mes-*C*-2,6), 129.51 (s, Mes-*C*-4), 128.93 (s, Mes-*C*-3,5), 126.86 (s, Mes-*C*-3,5), (NC-CH_2, not observed), 46.54 (s, N-CH_2-CH_2-N), 21.36 (s, *p*-Mes-CH_3), 21.28 (s, *p*-Mes-CH_3), 18.40 (s, *o*-Mes-CH_3).

Note: No ^{119}Sn-NMR signal visible; counter anion AlH_4^- confirmed via SC-XRD.

$L2AlH_2^+$:

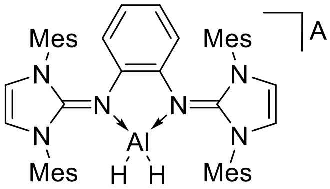


2a[OTf] (8.00 mg, 21.0 µmol, 1.00 eq); $LiAlH_4$ (301 µg, 21.0 µmol, 1.00 eq.)

^{1}H-NMR (400 MHz, THF-*d₈*) δ [ppm] = 6.97 (s, 8H, Ar-*H*), 2.41 (s, 4H, CH_2), 2.35 (s, 12H, Mes-CH_3-4), 2.01 (s, 24H, Mes-CH_3-2,6), 1.70 (s, 12H, NCCH_3).

^{19}F-NMR (376 MHz, THF-*d₈*) δ [ppm] = -79.14 (s, CF_3).

$L3AlH_2^+$:



3a[$SnCl_3$] (23.0 mg, 21.1 µmol, 1.00 eq); $LiAlH_4$ (800 µg, 21.1 µmol, 1.00 eq.)

^{1}H-NMR (400 MHz, THF-d₈) δ [ppm] = 7.07 (s, 4H, N-C*H*-C*H*-N), 6.87 (s, 8H Ar-*H*), 6.10 – 6.06 (m, 2H, Ph-*H*), 6.00 – 5.94 (m, 2H, Ph-*H*), 2.37 (s, 2H, AlH_2), 2.22 (s, 12H, *p*-Mes-C*H*3), 2.01 (s, 24H, *o*-Mes-C*H*3).

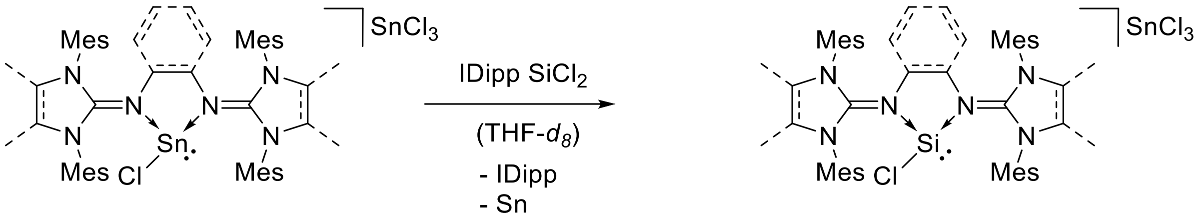
^{13}C-NMR (101 MHz, THF-d₈) δ [ppm] = 144.86 (s, N-*C*-N), 140.38 (s, Mes-*C*-1), 137.02 (s, Mes-*C*-2,6), 132.17 (s, Ph-*C*), 130.57 (s, Mes-*C*-4), 130.28 (s, Mes-*C*-3,5), 121.07 (s, Ph-*C*), 119.06 (s, Ph-*C*), 118.60 (s, N-*C*H=*C*H-N), 21.03 (s, *p*-Mes-CH_3), 18.15 (s, *o*-Mes-CH_3).

Note: No ^{119}Sn-NMR signal visible, but no SC-XRD available so counter anion A^- not confirmed.

LIFDI-MS: *m/z* calculated for $[C_{48}H_{52}N_6AlH_2]^+$ 741.4225, observed 741.413.

1.3.2 Transmetalation with IDipp→SiCl$_2$

General Procedure:

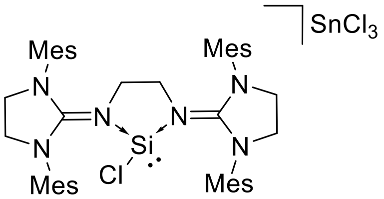


1a[SnCl$_3$], 2a[SnCl$_3$], 3a[SnCl$_3$] **1c[SnCl$_3$], 2c[SnCl$_3$], 3c[SnCl$_3$]**

Scheme S 2: General transmetalation reaction of stannyliumylidenes **1a$^+$**, **2a$^+$**, **3a$^+$** with IDipp→SiCl$_2$.

In NMR scale experiments, to a solution of stannyliumylidenes **1a[SnCl$_3$]**, **2a[SnCl$_3$]**, **3a[SnCl$_3$]**, in THF-*d*$_8$ (0.4 mL) was added IDipp→SiCl$_2$. The reaction was heated to 60 °C for 48 h and elemental tin precipitated. In the ^{1}H- ^{29}Si- and ^{119}Sn-NMR the formation of **1c[SnCl$_3$],2c[SnCl$_3$],3c[SnCl$_3$]** can was observed.

1c[SnCl$_3$]:



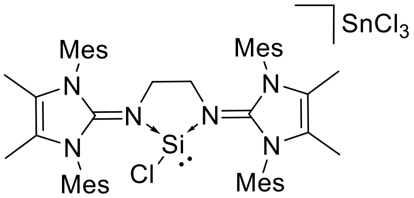
1a[SnCl$_3$] (20.0 mg, 19.3 µmol, 1.00 eq.) IDipp→SiCl$_2$ (14.3 mg, 29.3 µmol, 1.52 eq.).

^{1}H-NMR (400 MHz, THF-*d*$_8$) δ [ppm] = 6.90 (s, 8H, Ar-*H*), 4.17 – 3.79 (m, 8H, Mes-NCH_2), 2.29 (bs, 4H, CH_2), 2.29 (s, 12H, Mes-CH_3-4), 2.20 (s, 24H, Mes-CH_3-2,6). IDipp: δ [ppm] = 8.37 (d, ^3J = 1.6 Hz, 2H, NC*H*), 7.62 (t, ^3J = 7.1 Hz, 2H, Ar-H_{para}), 7.31 (d, ^3J = 7.7 Hz, 4H, Ar-H_{meta}), 2.75 (sept, ^3J = 6.9 Hz, 4H, Dipp-CC*H*), 1.31 (dd, ^3J = 6.8 Hz, 24H, Dipp-CH_3).

^{29}Si-NMR (79 MHz, THF) δ [ppm] = -1.61.

^{119}Sn-NMR (149 MHz, THF) δ [ppm] = 8.53.

2c[SnCl₃]:



2b[SnCl₃] (20.0 mg, 18.4 µmol, 1.00 eq.) ;IDipp→$SiCl_2$ (11.2 mg, 22.9 µmol, 1.25 eq.)

^{1}H-NMR (400 MHz, THF-d_8) δ [ppm] = 7.00 (s, 8H, Ar-*H*), 2.94 (bs, 4H, CH_2), 2.35 (s, 12H, Mes-CH_3-4), 2.01 (s, 24H, Mes-CH_3-2,6), 1.73 (s, 12H, Mes-NCH_2). IDipp: δ [ppm] = 8.36 (d, ^{3}J = 1.6 Hz, 2H, NC*H*), 7.62 (t, ^{3}J = 7.8 Hz, 2H, Ar-H_{para}), 7.30 (d, ^{3}J = 7.8 Hz, 4H, Ar-H_{meta}), 2.77 (sept, ^{3}J = 6.9 Hz, 4H, Dipp-CC*H*), 1.31 (d, ^{3}J = 6.8 Hz, 12H, Dipp-CH_3), 1.27 (d, ^{3}J = 6.8 Hz, 12H, Dipp-CH_3).

^{29}Si-NMR (79 MHz, THF-d_8) δ [ppm] = 2.32.

^{119}Sn-NMR (149 MHz, THF-d_8) δ [ppm] = 13.72.

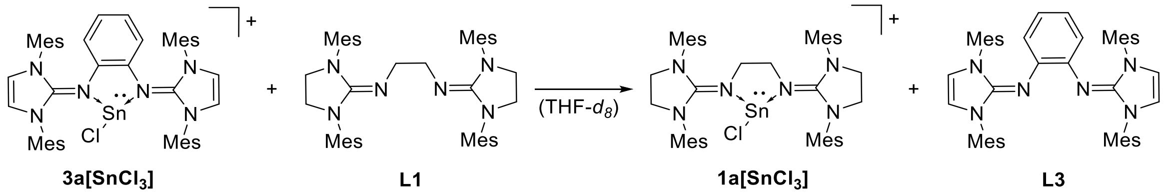
.

1.4 Ligand exchange reactions

General Procedure:

A)

In an NMR scale experiment, to a solution of **3a[SnCl$_3$]** (10,0 mg, 9.16 µmol, 1.00 eq.) in THF-*d$_8$* (0.4 mL) L1 (6.12 mg, 9.16 µmol, 1.00 eq.) was added at r.t.. After 10 minutes, full conversion to **1a[SnCl$_3$]** and free ligand L3 was visible, confirmed *via* ^{1}H-NMR.



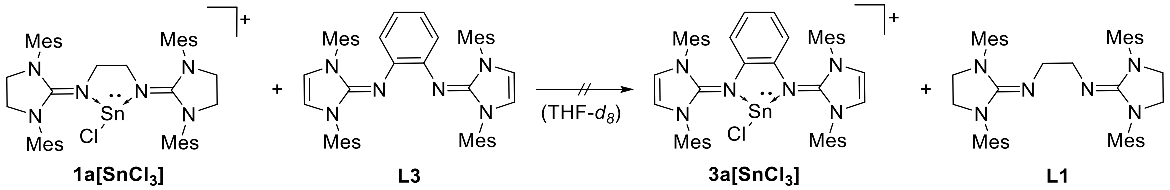
Scheme S 3: Ligand exchange reaction of **3a[SnCl$_3$]** with **L1** resulting in **1a[SnCl$_3$]** and **L3**.

1a[SnCl$_3$]: ^{1}H-NMR (400 MHz, THF-*d$_8$*) δ [ppm] = 6.92 (bs, 8H, Ar-*H*), 3.93 (s, 8H, Mes-NC*H$_2$*), 2.66 (bs, 4H, C*H$_2$*), 2.33 – 2.22 (m, 36H, Mes-C*H$_3$*).

L3: ^{1}H-NMR (400 MHz, THF-*d$_8$*) δ [ppm] = 6.61 (s, 8H, Mes-H-3,5), 6.16 (s, 4H, NCH$_2$), 5.90 (m, 2H, Ph-H), 5.69 (m, 2H, Ph-H), 2.13 (s, 12H, *p*-Mes-CH3), 2.06 (s, 3H, *o*-Mes-CH3).

B)

In NMR scale experiments, at r.t. to a solution of stannyliumylidenes **1a[SnCl$_3$]** (10.0 mg, 9.54 µmol, 1.00 eq.) in THF-*d$_8$* (0.4 mL) L3 (6.80 mg, 9.54 µmol, 1.00 eq.) was added. After 48 h of heating at 60 °C no reaction occurred, and no changes in ^{1}H-NMR are visible.



Scheme S 4: Attempts of ligand exchange reaction of **1a[SnCl$_3$]** with **L3** showed no reaction.

2 Crystallographic Data

General:

The X-ray intensity data were recorded on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator, a Mo IMS microsource (λ = 0.71073 Å) and a Cu IMS microsource (λ = 1.54178 Å). The data collection was performed, using the APEX III software package[S12] on single crystals coated with Fomblin ® Y as perfluorinated ether. The single crystal was picked on a MiTiGen MicroMount microsampling tool, transferred to the diffractometer and measured frozen under a stream of 100 K cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S13] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS[S13]. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the APEX III software in conjunction with SHELXL-2014[S14] and SHELXLE[S15]. H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and Uiso(H) = 1.2·Ueq(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2\text{-}Fc^2)^2$ with the SHELXL weighting scheme[S16]. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S17] The images of the crystal structures were generated by Mercury[S18]. The CCDC numbers CCDC-2105732 (**L1**), CCDC-2105733 (**L2**), CCDC-2105734 (**1a[SnCl3]**), CCDC-2105735 (**3a[SnCl3]**), CCDC-2105736 (**3b[GeCl3]**), CCDC-2105737 (**L1AlH$_2^+$**), and CCDC-2105738 (**1a[A]**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Table S1: Crystal data and structure refinement details for compound L1, L2, 1a[SnCl3].

Compound #	**L1**	**L2**	**1a[SnCl3]**
Chemical formula	C44 H56 N6, C4 H8 O	C48 H60 N6	C44 H56 Cl N6 Sn, Cl3 Sn
Formula weight	741.05 g/mol	721.02 g/mol	1048.17 g/mol
Temperature	100 K	100 K	100 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	1.0 x 0.8 x 0.4 mm	0.276 x 0.249 x 0.221 mm	0.243 x 0.211 x 0.194 mm
Crystal habit	clear colorless fragment	clear colorless fragment	clear colorless fragment
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P -1	C 2 2 21	C 2/c
Unit cell dimensions	a = 11.2899(6) Å; α = 106.384(2)°	a = 14.4071(13) Å; α = 90°	a = 36.5247(14) Å; α = 90°
	b = 11.8831(5) Å; β = 96.607(2)°	b = 20.3447(13) Å; β = 90°	b = 15.7548(6) Å; β = 100.052(1)°
	c = 17.8196(8) Å; γ = 108.700(2)°	c = 14.2314(10) Å; γ = 90°	c = 18.4624(6) Å; γ = 90°
Volume	2116.23(18) Å^3	4171.3(5) Å^3	10460.9(7) Å^3
Z	2	4	8
Density (calculated)	1.163 g/cm^3	1.148 g/cm^3	1.331 g/cm^3
Radiation source	IMS microsource	IMS microsource	IMS microsource
Theta range for data collection	1.96 to 25.73°	2.25 to 25.33°	2.13 to 25.68°
Index ranges	-13<=h<=13, -14<=k<=14, -21<=l<=21	-17<=h<=17, -24<=k<=24, -17<=l<=17	-42<=h<=44, -19<=k<=19, -22<=l<=17
Reflections collected	117861	33435	44530
Independent reflections	8069	3823	9930
Completeness	0.997	0.999	0.999
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.7453 and 0.7024	0.7452 and 0.7125	0.7453 and 0.6252
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2
Data / restraints / parameters	8069 / 0 / 508	3823 / 0 / 252	9930 / 2463 / 986
Goodness-of-fit on F^2	1.012	1.006	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1199	R1 = 0.0349, wR2 = 0.0915	R1 = 0.0686, wR2 = 0.1639
R indices (all data)	R1 = 0.0544, wR2 = 0.1262	R1 = 0.0364, wR2 = 0.0927	R1 = 0.0756, wR2 = 0.1694
Largest diff. peak and hole	0.474 and -0.353 eÅ^{-3}	0.222 and -0.221 eÅ^{-3}	1.907 and -1.305 eÅ^{-3}

Table S2: Crystal data and structure refinement details for compound 3a[SnCl3], 3b[GeCl3], and L1AlH$_2^+$.

Compound #	3a[SnCl3]	3b[GeCl3]	L1AlH$_2^+$
Chemical formula	C48 H52 Cl N6 Sn, Cl3 Sn	C48 H52 Cl Ge N6, Cl3 Ge	C44 H58 Al N6, C4 H8 O, Al H4
Formula weight	1092.18 g/mol	999.98 g/mol	801.06 g/mol
Temperature	100 K	100 K	100 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.148 x 0.092 x 0.091 mm	0.368 x 0.152 x 0.109 mm	0.763 x 0.660 x 0.530 mm
Crystal habit	clear colorless fragment	clear colorless fragment	clear colorless fragment
Crystal system	triclinic	monoclinic	orthorhombic
Space group	P -1	P 21/c	P b c a
Unit cell dimensions	a = 12.4305(9) Å; α = 74.440(2)°	a = 24.651(5) Å; α = 90°	a = 21.7014(10) Å; α = 90°
	b = 14.6316(10) Å; β = 85.291(2)°	b = 13.602(3) Å; β = 110.472(7)°	b = 18.3758(8) Å; β = 90°
	c = 20.0663(15) Å; γ = 71.039(2)°	c = 32.916(7) Å; γ = 90°	c = 23.4218(10) Å; γ = 90°
Volume	3325.0(4) Å^3	10340(4) Å^3	9340.2(7) Å^3
Z	2	8	8
Density (calculated)	1.091 g/cm^3	1.285 g/cm^3	1.139 g/cm^3
Radiation source	TXS rotating anode	IMS microsource	IMS microsource
Theta range for data collection	2.06 to 25.35°	1.99 to 25.35°	1.98 to 25.36°
Index ranges	-14<=h<=14, -17<=k<=17, -24<=l<=24	-29<=h<=29, -16<=k<=13, -39<=l<=39	-26<=h<=26, -22<=k<=22, -28<=l<=28
Reflections collected	94008	228336	174416
Independent reflections	12169	18884	8554
Completeness	0.999	0.997	0.999
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.7452 and 0.6438	0.7452 and 0.6581	0.7452 and 0.6975
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2	Σ w(F$_o^2$ - F$_c^2$)^2
Data / restraints / parameters	12169 / 739 / 755	18884 / 474 / 1203	8554 / 0 / 550
Goodness-of-fit on F^2	1.037	1.023	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1398	R1 = 0.0448, wR2 = 0.1102	R1 = 0.0413, wR2 = 0.1052
R indices (all data)	R1 = 0.0851, wR2 = 0.1570	R1 = 0.0601, wR2 = 0.1191	R1 = 0.0508, wR2 = 0.1124
Largest diff. peak and hole	1.413 and -0.879 eÅ^{-3}	2.420 and -1.248 eÅ^{-3}	0.341 and -0.297 eÅ^{-3}

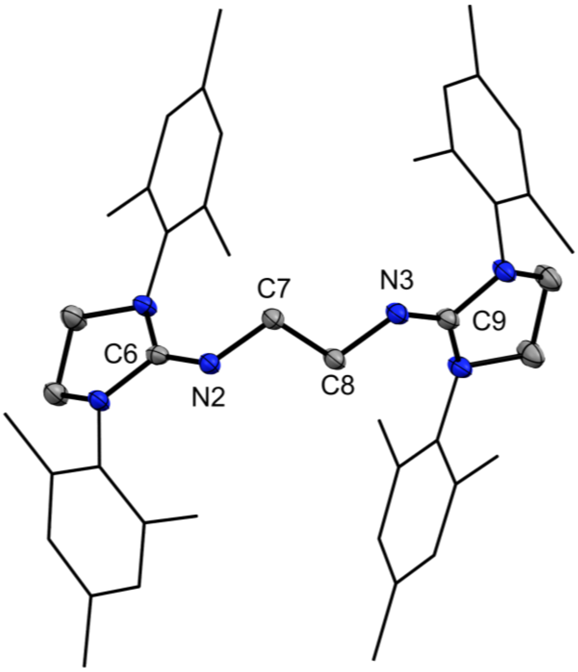


Figure S1: Molecular structure of **L1** thermal ellipsoids are set to 50% probability level. Hydrogen atoms and lattice solvent (THF) are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity.

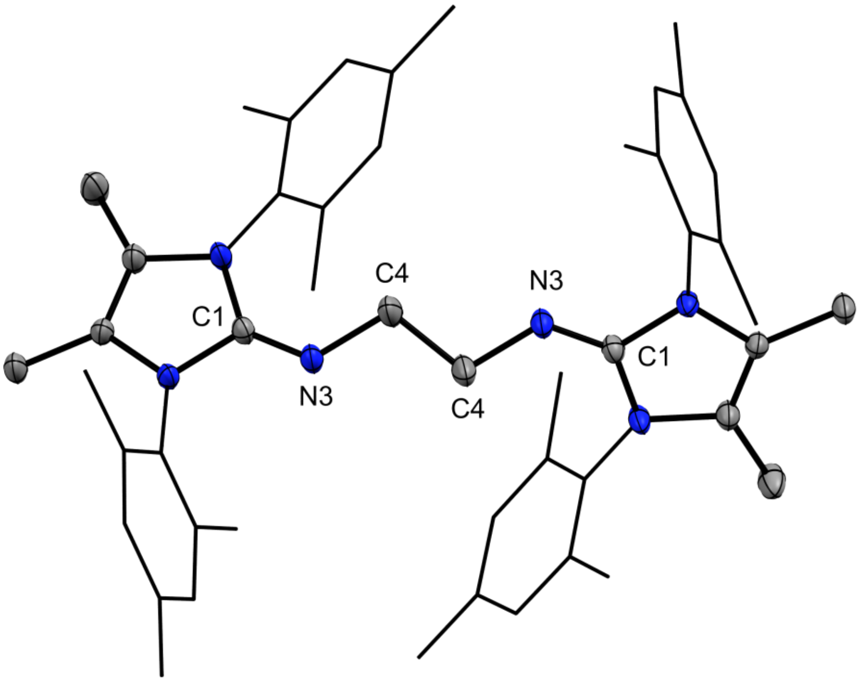


Figure S2: Molecular structure of **L2** thermal ellipsoids are set to 50% probability level. Hydrogen atoms are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity.

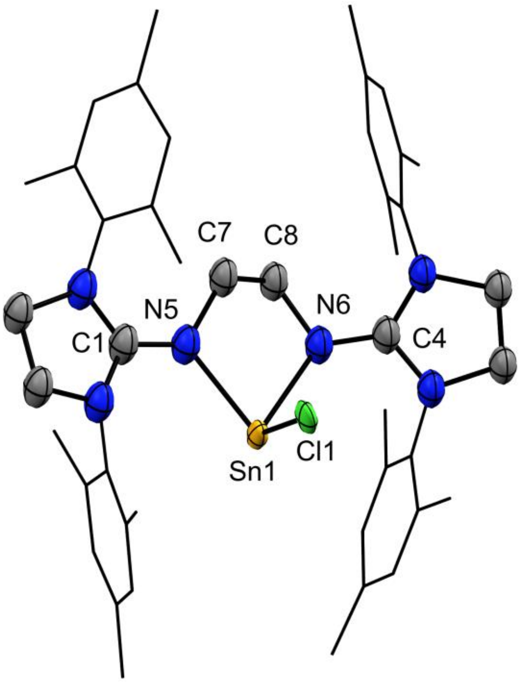


Figure S3: Molecular structure of **1a[SnCl$_3$]** thermal ellipsoids are set to 50% probability level. Hydrogen atoms and counter anion are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. The cation was modelled as an over-lying two-part disorder. The second part was omitted for clarity.

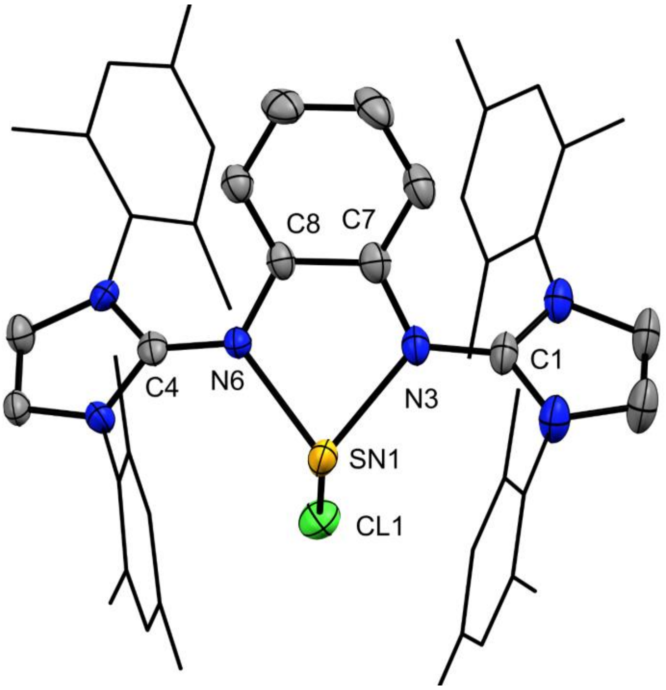


Figure S4: Molecular structure of **3a[SnCl$_3$]** thermal ellipsoids are set to 50% probability level. Hydrogen atoms and counter anion are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. A two-part disorder of two mesityl-wings was modelled the second part was omitted for clarity

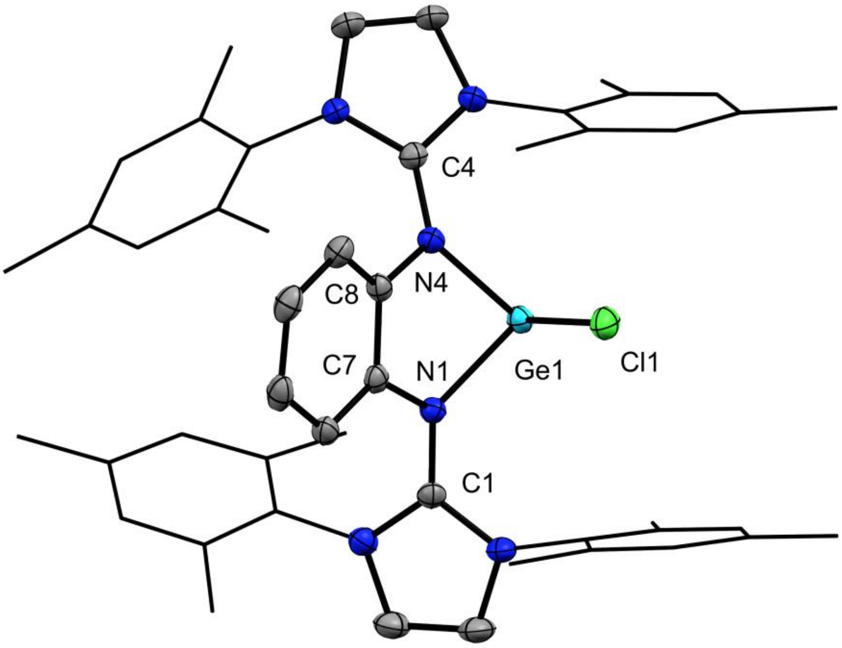


Figure S5: Molecular structure of **3b[GeCl₃]** thermal ellipsoids are set to 50% probability level. Hydrogen atoms and counter anion are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity.

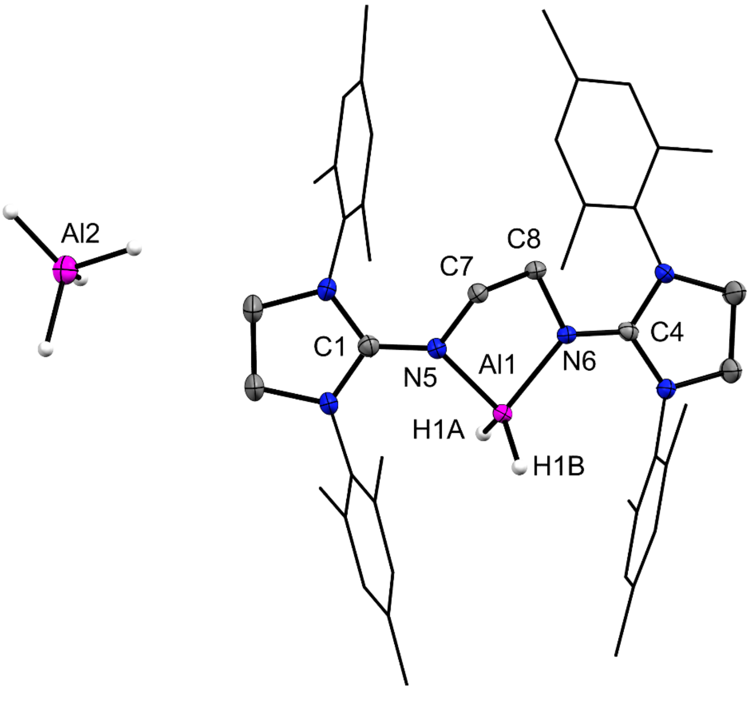


Figure S6: Molecular structure of **L1AlH₂[AlH4]** thermal ellipsoids are set to 50% probability level. Hydrogen atoms and lattice solvent (THF) are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity.

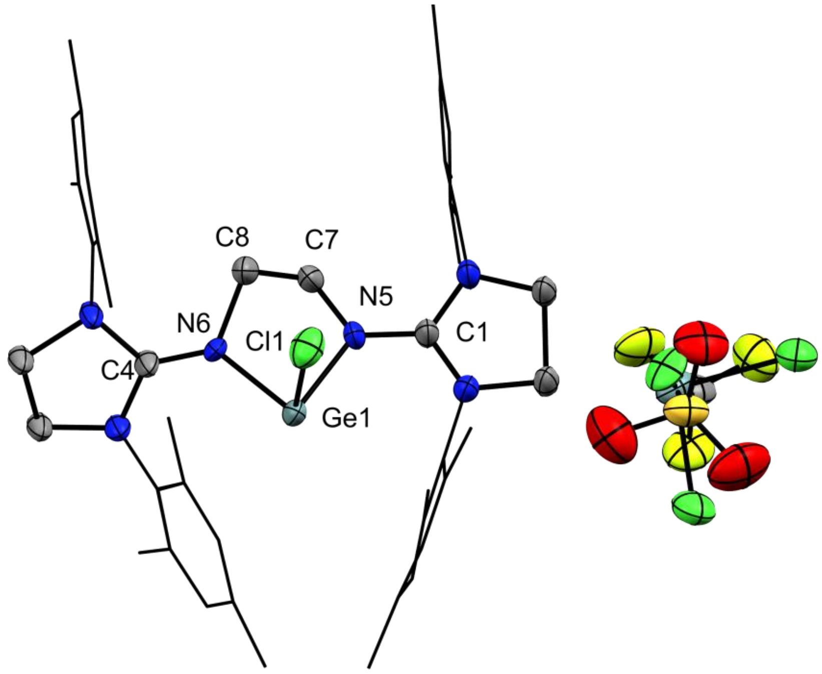


Figure S7: Molecular structure of **1b[A]** thermal ellipsoids are set to 50% probability level. Hydrogen atoms are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. Due to low diffracting quality of the rather small crystal, twinning and position disorder, a satisfactory refinement could not be achieved. However, the connectivity of the cation and the presence of mixed $GeCl_3$/OTf anion can be confirmed.

3 References

S1 M. Muhr, P. Heiß, M. Schütz, R. Bühler, C. Gemel, M. H. Linden, H. B. Linden, R. A. Fischer, *Dalton Trans.* 2021, **50**, 9031.

S2 R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem. Int. Ed.* 2009, **48**, 5683.

S3 T. Gar, O. Dombrova, D. Ivashchenko, V. Mironov, *Russian Chemical Bulletin* 1993, **42**, 1717.

S4 E. Hough, D. G. Nicholson, *Journal of the Chemical Society, Dalton Transactions* 1976, 1782.

S5 J. Tönnemann, R. Scopelliti, K. Severin, *Eur. J. Inorg. Chem.* 2014, **2014**, 4287.

S6 F. W. Seidel, I. Tomizawa, K. Nozaki, *Angew. Chem. Int. Ed.* 2020, **59**, 22591.

S7 M. L. Cole, C. Jones, P. C. Junk, *New Journal of Chemistry* 2002, **26**, 1296.

S8 D. Franz, E. Irran, S. Inoue, *Angew. Chem. Int. Ed.* 2014, **53**, 14264.

S9 D. Franz, T. Szilvási, A. Pöthig, F. Deiser, S. Inoue, *Chem. Eur. J.* 2018, **24**, 4283.

S10 J. Volbeda, P. G. Jones, M. Tamm, *Inorg. Chim. Acta* 2014, **422**, 158.

S11 F. S. Tschernuth, F. Hanusch, T. Szilvási, S. Inoue, *Organometallics* 2020, **39**, 4265.

S12 *APEX suite of crystallographic software, APEX 3 2015.5-2*, Bruker AXS Inc, Madison, Wisconsin, USA, 2015.

S13 *SAINT and SADABS, 7.56a and 2008/1*, Bruker AXS Inc, Madison, Wisconsin, USA, 2008.

S14 G. M. Sheldrick, *SHELXL-2014*, University of Göttingen, Göttingen, Germany, 2014.

S15 C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* 2011, **44**, 1281.

S16 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1998.

S17 A. J. C. Wilson, V. Geist, *International Tables for Crystallography. Volume C: Mathematical, Physical and Chemical Tables.,* Tables 6.1.1.4 (pp 500-502), 4.2.6.8 (pp. 219-222) and 4.2.4.2 (pp. 193-199), Kluwer Academic Publishers (published for the International Union of Crystallography), Dordrecht/Boston/London, 1992.

S18 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* 2008, **41**, 466.