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

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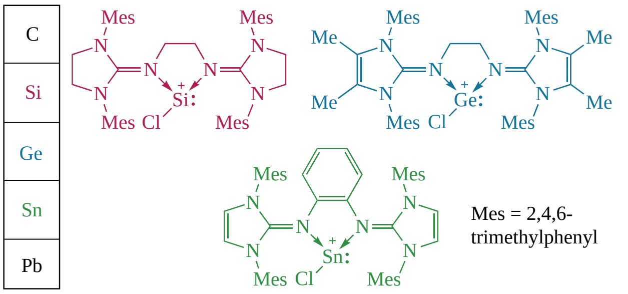
The synthesis of modified neutral bis-NHI (NHI is *N*-heterocyclic imine) ligands and their application for the stabilization of tetryliumylidenes are reported. The ligands' scaffolding consists of either saturated or methylated imidazoline backbones, and the bridge alternated from flexible ethylene to more rigid *o*-phenylene. Transmetalation reactivity of the cationic Sn^{II} compounds was tested towards $LiAlH_4$ and IDipp→$SiCl_2$ [IDipp is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] affording the respective aluminium and silicon complexes.



Keywords: tin, germanium, silicon, *N*-heterocyclic imines, tetryliumylidenes, transmetalation.

In the field of low-valent main group chemistry one of the biggest obstacles is the balance between reactivity and stabilization of the central element. Therefore, the fine-tuning of the ligand systems with adjusted electronic and steric properties is crucial to accomplish desired reactivities.[1] Recently we described the strong π-donating neutral bis-NHI ligand **L0** supported tetryliumylidenes (Figure 1).[2] Tetryliumylidenes, cationic complexes with the central element in the formal oxidation state +II, show unique electronic properties. This qualifies them as potential synthetic building blocks,[1(*c*),3] ligands for transition metals,[2(*d*),4] as well as catalysts.[5] Herein we report the synthesis of three modified bis-NHI ligands and their reactivity towards E^{II} precursors such as ECl_2·dioxane (E = Ge, Sn) and IDipp→$SiCl_2$ [IDipp is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]. We place the focus on the ligands' influence on stability and reactivity of the resulting tetryliumylidene complexes. Whereas variations of *N*-heterocyclic carbenes (NHCs) and the associating donor and acceptor effects are already widely studied, neutral bis-NHIs are less explored.[2(*c*),6] Bis-NHIs offer strong σ- and π-donor abilities combined with a chelating effect, that were already used for the coordination of various metal centers.[2(*c*),7] Recently, we utilized these ligands for stabilizing main group complexes.[2(*a*),(*b*),(*d*)] For a better understanding of the bis-NHI ligand system, more precisely the influence of their steric demand and the effect of suppressed π-back-bonding on group 14 elements, we prepared bis-^{Mes}NHIs containing either a saturated (**L1**) or methylated (**L2**) imidazole backbone or a phenylene bridge (**L3**; see Figure 1).[2(*b*)]

Reactions of various ligand scaffolds **L1**, **L2** and **L3** with ECl_2·dioxane (E = Ge, Sn) afforded the stannyliumylidenes (**1a**[A], **2a**[A], **3a**[A]) and germyliumylidenes (**1b**[A], **2b**[A], **3b**[A]) (A = ECl_3^-, OTf^-).[2(*a*),9] The syntheses of the OTf derivatives **1a**[OTf], **2a**[OTf] and **1b**[OTf], **2b**[OTf] are feasible in the presence of equimolar amounts of TMSOTf, which inhibits the Lewis base mediated auto ionisation forming the ECl_3^- anion (Scheme 1).[2(*a*)]

The isolated stannyliumylidenes were characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{119}Sn, ^{19}F), single crystal X-ray diffraction (SC-XRD) analysis or mass spectrometry with liquid injection field desorption ionization (LIFDI) source.[10] The ^{119}Sn NMR chemical shifts show distinct values for a similar coordination sphere around the central tin(II) cation, which vary from –261.25 ppm for **1a**$^+$, –232.53 ppm for **2a**$^+$ to –154.49 ppm for **3a**$^+$. This indicates a higher degree of shielding at the tin centre for **1a**$^+$ than for **3a**$^+$, which is affected by delocalization of electron density within the conjugated

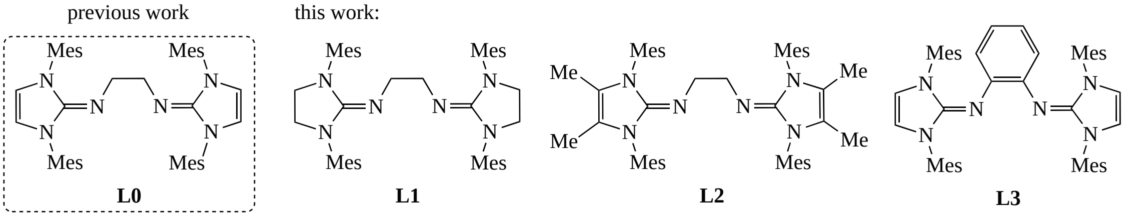
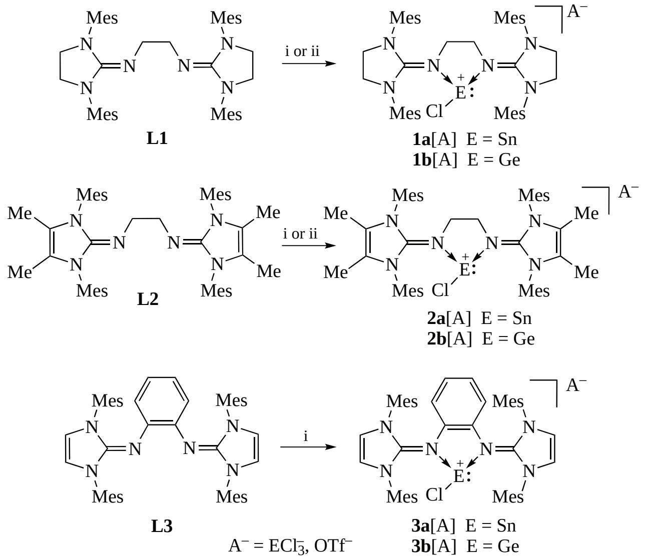


Figure 1 Isolated neutral bis-NHI ligand systems **L1**–**L3**, synthesized by a modified procedure adapted from previously reported[8] **L0**.



Scheme 1 *Reagents and conditions*: i, ECl_2·dioxane (E = Ge, Sn, 2 equiv.), THF, room temperature, 24 h; ii, ECl_2·dioxane (E = Ge, Sn, 1 equiv.), TMSOTf, THF, 0 °C → room temperature, 18 h.

π-system and the complex geometry of the phenylene-bridged **L3**. Due to the unsaturated backbone in the imidazole moiety, **L2** and bis-NHI **L0** may be referred to as pseudo-conjugated π-systems.[2(*d*)] Hence, the same trend is apparent for **2a**$^+$ and **L0a**[A], that exhibit similar ^{119}Sn NMR signals at –232.53 and –240.42 ppm, respectively. In contrast, **1a**$^+$, that lacks an enlarged conjugated π-system, resonates at higher fields (–261.25 ppm) indicating enhanced shielding of the tin(II) unit.

SC-XRD measurements confirmed the molecular structures of **1a**[$SnCl_3$] and **3b**[$GeCl_3$], with the central E^{II} being embedded in a five-membered EN_2C_2-ring (Figure 2).[†] The trigonal-pyramidal orientation of the central element implies the existence of a lone pair of electrons.[2(*a*),(*d*)] The metallate anions are separated from the corresponding cations by 3.08 and 2.80 Å for **1a**[$SnCl_3$] and **3b**[$GeCl_3$], respectively. Compared to free ligand **L1** the endocyclic C_{carb}–N_{im} distance is slightly elongated, indicating a less pronounced double bond character of the respective bond for **1a**[$SnCl_3$] (1.32 to 1.34 Å). For the analogous Sn complexes **1a**$^+$, **3a**$^+$, and **L0a**$^+$, determination of bond lengths C_{carb}–N_{im}, N_{im}–C_{bridge} (**L0a**$^+$: 1.32, 1.48; **1a**$^+$: 1.33, 1.51; **3a**$^+$: 1.35, 1.41 Å) and angles C_{Mes}–E–C_{Mes} (**L0a**$^+$: 46.09, **1a**$^+$: 52.69, **3a**$^+$: 43.76°) indicates that the bonding properties of the ligands are influenced by the increasing size of the π-system **L1** < **L0** < **L3** and their steric demand (*e.g.* rigidness of phenylene bride in **L3**), among others. However, the distinctions in the solid state are rather insignificant, resulting in comparable complex solid-state structures. Ligand exchange and transmetalation reactions were performed to gain further insight into the ligand properties of **L1** to **L3** and resulting complex characteristics of the respective stannyliumylidenes. Upon reaction of **L1** with an equimolar amount of **3a**$^+$, complete conversion to **1a**$^+$ and free **L3** was observed within minutes at room temperature. No equilibrium was detected and attempts of the reverse reaction remained unsuccessful even at elevated temperature, indicating stronger donor abilities of **L1** in comparison to **L3** (see Online Supplementary Materials, Schemes S3 and S4). Transmetalation of **1a**[$SnCl_3$] with $LiAlH_4$ resulted in the corresponding derivative of **L0**AlH_2^+ (Scheme 2).[2(*a*)] Whereas the transmetalation product **L1**AlH_2^+ of **1a**$^+$ was confirmed by SC-XRD (see Online Supplementary Materials, Figure S6), the reaction of **2a**$^+$ and **3a**$^+$ was monitored *via* ^{1}H NMR affording respective **L2**AlH_2^+ and **L3**AlH_2^+.

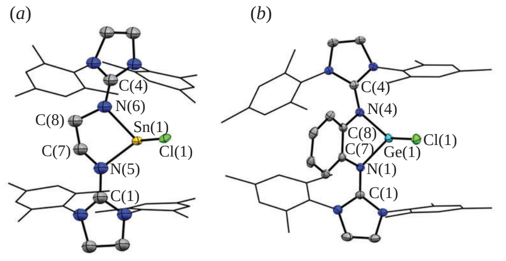


Figure 2 Molecular structure of (*a*) **1a**[$SnCl_3$] and (*b*) **3b**[$GeCl_3$]. Thermal ellipsoids are set to 50% probability level. Hydrogen atoms, counter anions and solvent molecules are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. Selected bond lengths (Å) and angles (°) for **1a**[$SnCl_3$]: Sn(1)–Cl(1) 2.497(8), Sn(1)–N(5) 2.244(8), N(6)–C(4) 1.323(9), N(5)–C(1) 1.337(9), Cl(1)–Sn(1)–N(5) 91.8(3), Cl(1)–Sn(1)–N(6) 90.5(3), N(5)–Sn(1)–N(6) 76.3(3); for **3b**[$GeCl_3$]: Ge(1)–Cl(1) 2.2806(10), Ge(1)–N(1) 2.000(3), N(4)–C(4) 1.346(4), N(1)–C(1) 1.356(4), Cl(1)–Ge(1)–N(4) 92.28(8), Cl(1)–Ge(1)–N(1) 97.08(8), N(1)–Ge(1)–N(4) 80.69(11).

While heavier tetryliumylidenes of **L1** to **L3** were obtained from direct conversion with readily available $GeCl_2$·dioxane and $SnCl_2$·dioxane, the corresponding strategy for silyliumylidenes makes use of base-stabilized IDipp→$SiCl_2$ as stable and accessible precursor.

This well-established method was successful for **L1** resulting in the formation of silyliumylidene **1c**[Cl], analogously to

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[†] Crystals of compounds **1a**[$SnCl_3$] and **3b**[$GeCl_3$] were grown from concentrated THF solutions at – 30 °C under argon atmosphere.

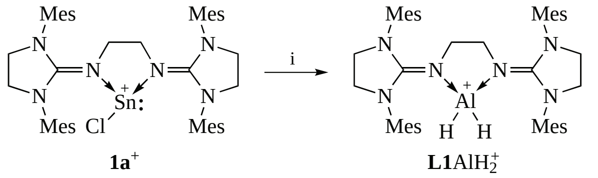
Crystal data for **1a**[$SnCl_3$]. [$C_{44}H_{56}ClN_6Sn$][$SnCl_3$], M = 1048.12, monoclinic, space group $C2/c$, 100 K, a = 36.5247(14), b = 15.7548(6) and c = 18.4624(6) Å, β = 100.052(1)°, Z = 8, V = 10460.9(7) Å^3, d_{calc} = 1.331 g cm^{-3}, F(000) = 4240. A clear colourless crystal fragment with dimensions 0.243 × 0.211 × 0.194 mm was selected and intensities of 44530 reflections were measured using a Bruker D8 Venture Duo IMS system diffractometer (ω and φ scans, frozen in perfluorinated ether, λ[MoKα] = 0.71073 Å, μ = 1.192 mm^{-1}, $2\theta_{max}$ = 25.68°). After merging of equivalents and absorption correction, 9930 independent reflections (R_{int} = 0.0756) were used for the structure solution and refinement. Final R factors: R_1 = 0.0686 [8747 reflections with $I > 2\sigma(I)$], wR_2 = 0.1694 (all refractions), GOF = 1.017.

Crystal data for **3b**[$GeCl_3$]. [$C_{48}H_{52}ClN_6Ge$][$GeCl_3$], M = 999.98, monoclinic, space group $P21/c$, 100 K, a = 24.651(5), b = 13.602(3) and c = 32.916(7) Å, β = 110.472(7)°, Z = 8, V = 10340(4) Å^3, d_{calc} = 1.285 g cm^{-3}, F(000) = 4112. A clear colorless crystalline block with dimensions 0.368 × 0.152 × 0.109 mm was selected and intensities of 228336 reflections were measured using a Bruker D8 Venture Duo IMS system diffractometer (ω and φ scans, frozen in perfluorinated ether, λ[MoKα] = 0.71073 Å, μ = 1.192 mm^{-1}, $2\theta_{max}$ = 25.35 °). After merging of equivalents and absorption correction, 18884 independent reflections (R_{int} = 0.0601) were used for the structure solution and refinement. Final R factors: R_1 0.0448 [15254 reflections with $I > 2\sigma(I)$], wR_2 = 0.1191 (all refractions), GOF = 1.023.

The X-ray data were collected using the APEX III software package.[11] The single crystals were frozen under 100 K cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged using SAINT. Absorption corrections were performed using SADABS.[12] Space group assignments were based upon systematic absences, E statistics, and successful refinement. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the APEX III software in conjunction with SHELXL-2014[13] and SHELXLE.[14] 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 $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2–Fc^2)^2$ with the SHELXL weighting scheme.[15]

See Online Supplementary Materials for the crystal data of **L1**, **L2**, **3a**[$SnCl_3$], **L1**AlH_2^+ and **1a**[A].

CCDC 2105732–2105738 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



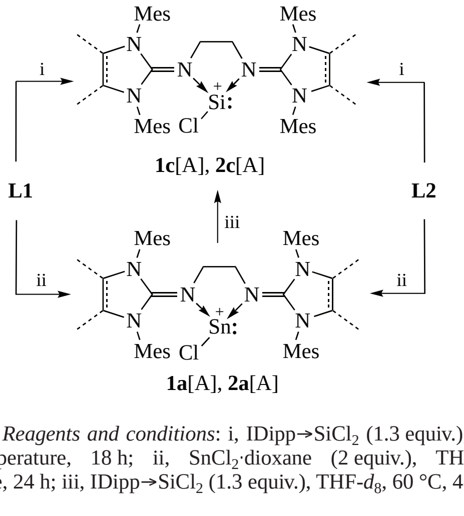
Scheme 2 *Reagents and conditions*: i, $LiAlH_4$ (1 equiv.) in THF-d_8 (0.2 ml), –78 °C to room temperature, 10 min.

recently reported **L0c**[Cl].[2(*d*)] However, the sterically more demanding **L2** and **L3** showed no reactivity towards $\text{IDipp}\rightarrow\text{SiCl}_2$. To achieve formation of silyliumylidenes $\mathbf{2c}^+$ and $\mathbf{3c}^+$, transmetalation of the corresponding stannyliumylidenes **2a**[$SnCl_3$] and **3a**[$SnCl_3$] was tested. Within 3 days at 60 °C the successful transfer of the central element was confirmed for **2c**[$SnCl_3$], accompanied by precipitation of elemental Sn. Intriguingly, silyliumylidene **3c**[A] could not be obtained *via* transmetalation of **3a**[$SnCl_3$] with $\text{IDipp}\rightarrow\text{SiCl}_2$, decomposition took place releasing free ligand **L3**. To the best of our knowledge, reactions of stannyliumylidenes leading to silyliumylidenes are not documented; however, we found species $\mathbf{1a}^+$ and $\mathbf{2a}^+$ to be prone for transmetalation (Scheme 3).

In contrast, germyliumylidenes **1b**[A], **2b**[A], or **3b**[A] did not undergo transmetalation into the corresponding Si^{II} compounds.

These results indicate that complex formation starting from **L2** and **L3** is kinetically hindered due to the sterical demand of the IDipp moiety and the obstructed coordination cavity of **L2** and **L3**. Seemingly, the pre-orientated tin(II) complexes facilitate the complexation of the Si(II) synthon in case of **L2** and reveal a new synthetic application of chlorostannyliumylidenes as building blocks. As expected, the ^{29}Si NMR chemical shifts for the synthesized silyliumylidenes reinforce the observed trend for the analogous Sn^{II} complexes. For the silyliumylidenes **2c**[$SnCl_3$] and **L0c**[Cl] the chemical shifts were found at 2.32 ppm and 1.54 ppm, respectively, which is comparable to **1c**[Cl] (^{29}Si –1.43 ppm) with saturated imidazole backbone. This further reinforces the assumed ligand suitability sequence of **L1** > **L2** > **L3**.

In conclusion, we report a series of bis-NHI ligands **L1–L3**, that were tailor made to differ from previously reported bis-NHI ligands in electronic properties and steric demand. As a result of the predicted enhanced donor properties, ligand **L1** showed increased shielding of the central tin(II) cation for the isolated complexes. The transmetalation of synthesized stannyliumylidenes with $LiAlH_4$ was upheld, forming the corresponding aluminium complexes. Enlargement of the steric demand, such as introducing a methylated backbone **L2** or rigid phenylene bridge **L3**, affects the reactivity substantially. In consequence, silyliumylidene $\mathbf{1c}^+$ was isolated by reaction of **L1** and $\text{IDipp}\rightarrow\text{SiCl}_2$, which is inhibited for sterically demanding **L2** and **L3**. In an alternative approach, the transmetalation of cationic Sn^{II} complexes $\mathbf{1a}^+$ and $\mathbf{2a}^+$ gave access to the corresponding silyliumylidene $\mathbf{2c}^+$.



Scheme 3 *Reagents and conditions*: i, $\text{IDipp}\rightarrow\text{SiCl}_2$ (1.3 equiv.), toluene, room temperature, 18 h; ii, $SnCl_2\cdot$dioxane (2 equiv.), THF, room temperature, 24 h; iii, $\text{IDipp}\rightarrow\text{SiCl}_2$ (1.3 equiv.), THF-d_8, 60 °C, 48 h.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.004.

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