Novel Hypervalent Complexes of Main-Group Metals by Intramolecular Ligand→Metal Electron Transfer*

Matthias Driess,* Nicoleta Dona, and Klaus Merz[a]

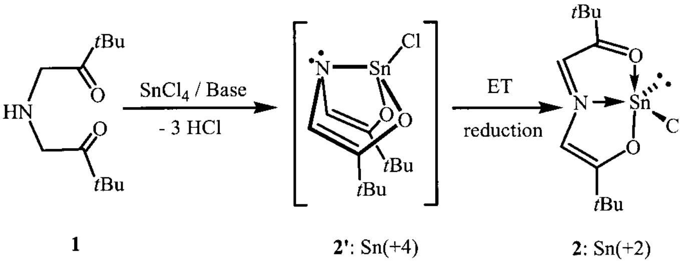
Abstract: New fascinating electronic features of the simple diketoamine chelate ligand HN[CH$_2$C(*t*Bu)=O]$_2$ (**1**) are described. Unexpectedly, the corresponding trianionic amido-dienolate form of **1** is capable of reducing main-group metal atoms M after initial coordination and intramolecular L→M two-electron transfer and of stabilizing main-group elements in unusual low oxidation states. This is impressively shown by the synthesis and structural characterization of the novel Ge and Sn complexes **4–6** by redox reactions of lithiated **1** with the corresponding metal halides GeCl$_4$ and MCl$_2$ (M = Ge, Sn). Surprisingly, conversion of tris-lithiated **1** with GeCl$_4$ readily consumes two molar equivalents of GeCl$_4$ and results in the formation of the neutral GeCl$_3$ complex **4** and GeCl$_2$. The former represents the second example of a structurally characterized neutral octahedrally coordinated germanium compound. Reaction of dilithiated **1** with GeCl$_2$ does not lead to the expected ClGe(+2) complex but affords the novel dimeric germylene **5**, whereas similar reaction using SnCl$_2$ furnishes the monomeric stannylene (ClSn(+2) complex) **2** and elemental tin due to the higher oxidation potential of Sn(+2). Unexpectedly, a similar redox reaction of dilithiated **1** with PbCl$_2$ furnishes the first air- and water-stable lithium 1,2-diketoimine–enolate **7** and elemental lead. Compound **7** is tetrameric in the solid state and consists of a strongly distorted Li$_4$O$_4$ cubic core with trigonal-bipyramidal coordinated Li$^+$ ions.

Keywords: carbene homologues · charge-transfer complexes · hypervalent compounds · lithium enolates · N,O ligands

Introduction

Intramolecular electron-transfer (ET) processes in coordination compounds ML$_n$ are strongly dependent on the ratio of the redox states between the coordination center M and ligands L. Complexes containing unsaturated, polyanionic chelate ligands L are predestined for intramolecular ligand→metal (L→M) ET, as impressively shown for Schiff bases, several 2,2′-diphenolamines,[1] and related systems.[2] While this is widespread in the coordination chemistry of transition metals, leading to important tools for catalysis,[3] such processes are much less common in main-group chemistry. Some years ago, Arduengo et al. reported on the astonishing coordination chemistry of the simple diketoamine HN[CH$_2$C(O)*t*Bu]$_2$ (**1**),[4] which can function simultaneously as a tridentate ligand and an intramolecular two-electron reducing agent toward the heavier Group 15 elements (phosphorus, arsenic, and antimony), leading to unusual hypervalent (10 valence electrons (VE)) compounds with trigonal-planar coordinate E atoms (10-E-3 systems) in the oxidation state +1.[5] The latter results prompted us to investigate the coordination and reduction ability of **1** toward the more electropositive Group 14 metals, germanium, tin, and lead. There has been only one report on tin, showing that SnCl$_4$ reacts with **1** exclusively to give the hypervalent stannylene **2** (10-Sn-4 system, Scheme 1).[6]

We report here the unusual reactivity of **1** and its lithiated enolate derivatives toward GeCl$_4$ and the Group 14 metal dichlorides MCl$_2$ (M = Ge, Sn, Pb), respectively, which leads to the four novel types of hypervalent main-group metal di-



Scheme 1. Synthesis of the hypervalent stannylene **2**.

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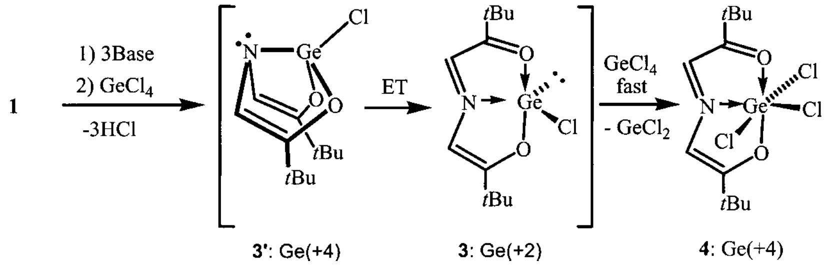
ketoimino–enolate complexes **4**–**7**, respectively (see Scheme 2–4).

Results and Discussion

Synthesis and crystal structure of the $GeCl_3$ complex 4: In contrast to the reactivity of **1** towards $SnCl_4$, the chelate ligand **1** reacts readily with two molar equivalents of $GeCl_4$ in the presence of NEt_3 as an auxiliary base to afford $GeCl_2$ and the neutral $GeCl_3$ complex **4** with a hexacoordinate Ge(+4) atom (Scheme 2).



Scheme 2. Synthesis of the germanium complex **4**.

The composition and structure of **4** was elucidated by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction analysis. The latter revealed that **4** consists of a Ge(+4) center, which adopts a distorted octahedral coordination geometry, surrounded by the monoanionic, tridentate C_4NO_2-diketoimine–enolate ligand and three Cl ligands (Figure 1). Compound **4** is the second example of a neutral octahedrally coordinated germanium compound in which a $GeCl_3$ moiety has been characterized structurally.[7]

Each of the almost identical ring C–C (av 143 pm), C–N (av 132 pm), and C–O distances (av 126 pm) for the C_4NO_2 skeleton is in accordance with full π-resonance stabilization of the 1,2-diketoimine–enolate ligand. Notably, the Ge–Cl distances are considerably different (Ge1–Cl2 (214.4(2) pm) versus Ge1–Cl1 (225.9(2) pm) and Ge1–Cl3 (228.1(2) pm), reflecting the electron redistribution around the Ge atom and the different donor ability of the donor atoms.[8] The elongated Ge1–Cl3 distance is partially due to the close proximity of the Cl3A atom and the H2AB atom of a neighboring molecule (278 pm versus 297 pm for the sum of van der Waals radii), leading to a infinite chain with attractive Cl···H interactions (Figure 1 b).[8] Although no intermediate could be detected, we assume that the formation of **4** occurs via **3′** and **3** as transient species (Scheme 2). The latter are formed in analogy to the stannylene homologue **2**. Remarkably and in contrast to the Sn(+2) atom in **2**, the Ge(+2) atom in **3** is readily oxidized even by the relatively weak chlorinating reagent $GeCl_4$ to afford **4** and $GeCl_2$ (Scheme 2). The same products result from the conversion of the corresponding trilithium bis(enolate)amide derivative of **1**, irrespective of the molar ratio of the components (1:1 or 1:2). This suggests that the electron-rich Ge atom in **3** shows a more hypervalent germanide- than a germylene-like reactivity. Noteworthy are also the results of the conversion of dilithiated **1** with the Group 14 metal dichlorides MCl_2 (E = Ge, Sn, Pb).

Synthesis of the novel carbene-homologues 5 and 6: Because of its remarkable ability to stabilize main-group elements in low oxidation states, we have extensively studied the reactivity of the dilithiated ligand **1** toward the Group 14 dichlorides, with the aim of isolating new hypervalent carbene-homologues. Whereas the conversion of $GeCl_2$·dioxane with dilithiated **1** affords the novel hypervalent germylene **5**, the same reaction pathway using $SnCl_2$ does not lead to the expected tin-homologue **6**, but solely to the Sn(+2) complex **2** and elemental tin (Scheme 3). The different reactivity of $SnCl_2$ is due to its higher oxidation

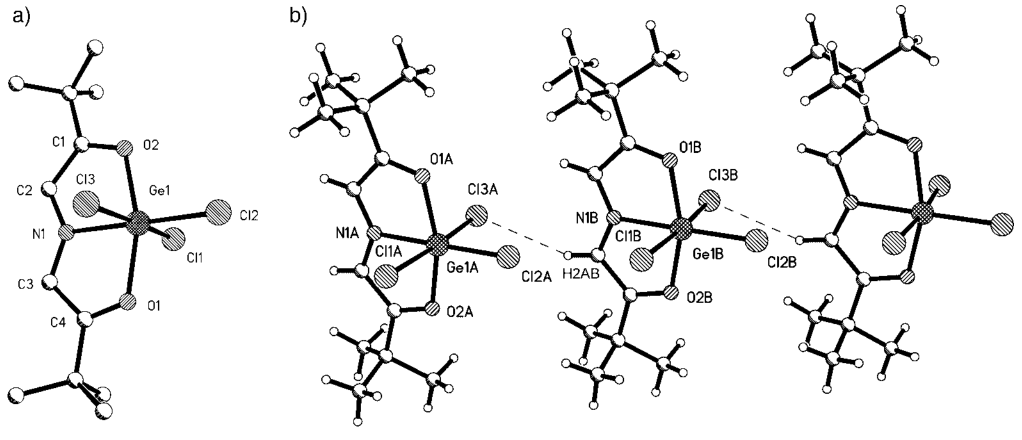
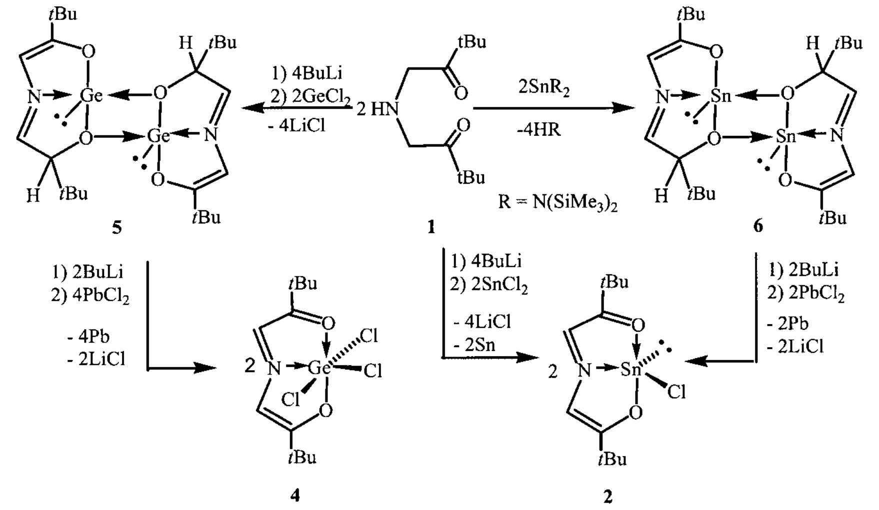


Figure 1. a) Molecular structure of **4**; H atoms are omitted for clarity. Selected distances [pm] and angles [°]: Ge1–O1 193.6(6), Ge1–O2 196.7(6), Ge1–N1 201.9(6), Ge1–Cl1 225.9(2), Ge1–Cl2 214.4(2), Ge1–Cl3 228.1(2), C1–O2 127.0(11), C4–O1 125.4(11), C1–C2 142.6(13), C3–C4 143.4(12); O1-Ge1-O2 160.7(2), O1-Ge1-N1 80.3(3), O2-Ge1-N2 80.4(3), N1-Ge1-Cl2 179.0(2), Cl1-Ge1-Cl3 173.0(1). b) Intermolecular Cl···H interactions of **4** in the crystal.



Scheme 3. Synthesis and conversion of the complexes **5** and **6**.

potential toward dilithiated **1** which favors a two-electron oxidation of the ligand. However, the Sn(+2) homologue **6** is accessible in almost quantitative yield by reaction of the "free" ligand **1** with the less-oxidizable Sn(+2) amide $[Sn\{N(SiMe_3)_2\}_2]$. According to the similar NMR spectroscopic data (^1H, ^{13}C) of **5** and **6** and their mass spectra, the complexes represent novel heteroleptic carbene-homologue dimers.

The molecular structure of **6** was elucidated by a single-crystal X-ray diffraction analysis (Figure 2), which revealed that each stannylene unit consists of a new tautomeric form of dianionic **1** that coordinates the Sn(+2) atom in a tridentate fashion. Apparently, this tautomeric form is preferred by C=C–N=C π conjugation. The two stannylene units are *cis*-oriented to each other and linked through two intermolecular O(donor)–Sn(acceptor) bonds, leading to a 10-Sn-4 system with pseudo-trigonal-bipyramidal-coordinate Sn atoms. Its structure displays for each Sn atom two relatively short Sn–O distances (Sn1–O1 207.6(14), Sn1–O3 216.9(12) pm) and one longer Sn–O bond (Sn1–O4 241.0(13) pm), reflecting the different O-donor ability, the geometric constraints, and the electronic saturation at tin. Similar distinctly different Sn(+2)–O distances have been observed in related hypervalent stannylenes.[9]

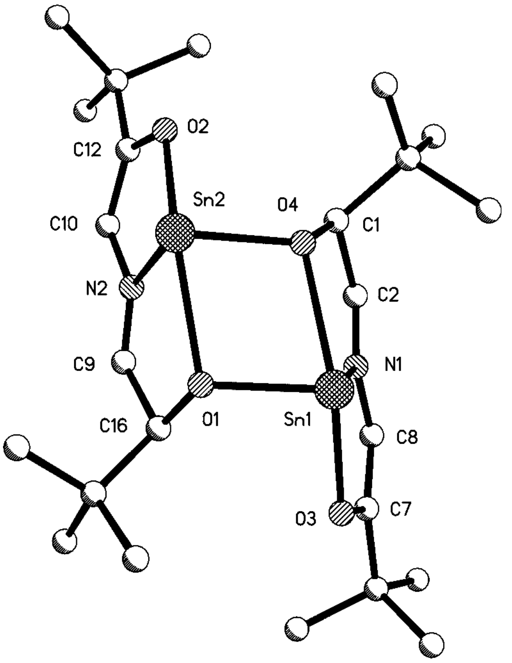


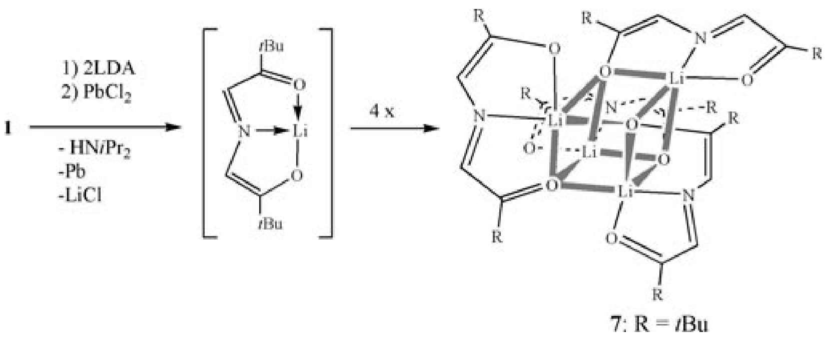
Figure 2. Molecular structure of **6**; H atoms are omitted for clarity. Selected distances [pm] and angles [°]: Sn1–O1 207.6(14), Sn1–O3 216.9(12), Sn1–O4 241.0(13), Sn1–N1 227.1(16), Sn2–O1 237.9(13), Sn2–O2 215.5(15), Sn2–O4 205.7(15); O1-Sn1-O3 92.6(5), O1-Sn1-N1 93.6(5), O3-Sn1-N1 73.5(5), O1-Sn1-O4 75.0(5), O3-Sn1-O4 140.2(4).

The Sn–N distances (av 227 pm) are shorter than those in **2** and related hypervalent stannylenes.[9] Complex **6** can be selectively converted to the stannylene **2** by oxidation of the ligand backbone with $PbCl_2$ in the presence of a base, whereas under similar conditions **5** undergoes oxidation of the ligand and of the Ge(+2) atom at the same time, affording solely the $GeCl_3$ complex **4**. This again confirms the higher sensitivity of the Ge(+2) atom even toward gentle oxidation reagents (Scheme 3).

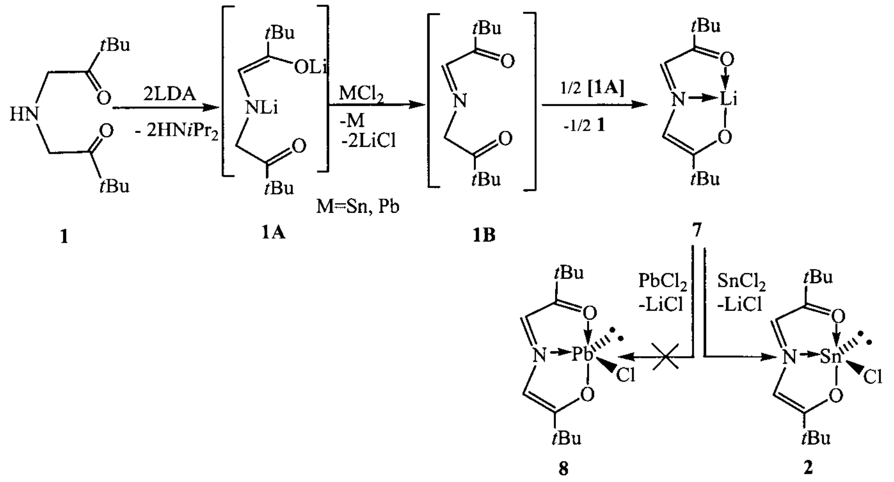
Synthesis and crystal structure of the Li_4O_4 enolate cluster 7: The convenient access to the hypervalent stannylene **2** as described in the previous section prompted us to apply similar redox reactions for the synthesis of the plumbylene homologue. However, attempts to synthesize a hypervalent plumbylene through conversion of dilithiated **1** with $PbCl_2$ in THF/hexane failed but led us to the first lithium 1,2-diketoimine-enolate **7** and elemental lead (Scheme 4).

The formation can be explained by the fact that the oxidation potential of Pb(+2) is higher than that of Ge(+2) and Sn(+2) toward polyanionic **1**. However, it seems peculiar that **7** does not react with $PbCl_2$ even in boiling toluene or THF, probably because the Pb(+2) complexation is much weaker than that of Li^+ or Sn(+2) (Scheme 3 and Scheme 5).

The composition and constitution of **7** was confirmed by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction studies. The tetramer crystallizes in the orthorhomic space group *P*ccn and consists of a strongly distorted Li_4O_4 cubic core with trigonal-bipyramidal-coordinated Li^+ ions (Figure 3). The range of different Li–O distances is tremendous, and varies from 192 to 266 pm due to different coordination numbers (2 and 4) of the oxygen atoms, geometric constraints, and steric congestion. Less distorted geometrical features around lithium and oxygen have been observed for chelated lithium phenolates[10] and other related compounds.[11] The slightly different pairs of C–O, C–C, and C–N distances suggest undisturbed π-resonance stabili-



Scheme 4. Synthesis of the tetrameric Li_4O_4 enolate cluster **7**.



Scheme 5. Formation of **2** and **7** by oxidation of lithiated **1** (**1A**) with MCl_2 (M = Sn, Pb).

zation within each C_4NO_2 ligand framework despite aggregation. The tetrameric structure of **7** is retained in aromatic solvents (^{1}H, ^{13}C NMR, osmometric measurements) but dissociates in donor solvents (e.g., THF and MeCN). Surprisingly, solutions of **7** in aprotic donor solvents are air- and water-stable (^{1}H NMR), in contrast to the high sensitivity of other keto- or imino-substituted lithium enolates.[11]

This can be explained by the substantial π-resonance stabilization of the negative charge and tight chelate coordination of the Li^+ ion. However, the Li^+ ions can be replaced by reaction of **7** with $SnCl_2$ and $GeCl_4$ in THF (molar ratio of 1:4), affording the expected hypervalent stannylene **2** and the $GeCl_3$ complex **4**, respectively. The lithium complex **7** seems to be the perfect precursor for the synthesis of the Ge(+2) homologue **3.** Unfortunately, the synthesis of the monomeric germylene-homologue **3** from **7** and $GeCl_2$·dioxane, failed because of its high sensitivity, although no $GeCl_4$ was present to oxidize the hypervalent germylene **3**.

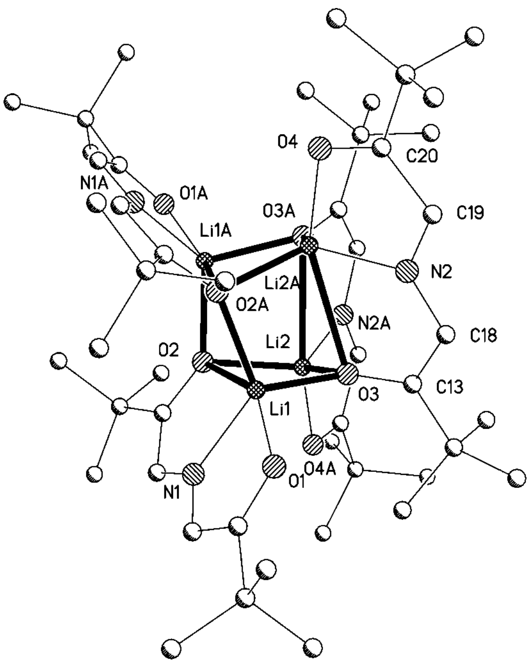


Figure 3. Molecular structure of **7**; H atoms are omitted for clarity. Selected distances [pm] and angles [°]: Li1–O1 203.6(9), Li1–O2 266.4(9), Li1–O3 193.0(9), Li2–O3 192.1(8), Li2–O2 192.5(9), Li1A–O2 192.0(8), Li1–N1 203.0(9), Li2–N2A 203.3(9), O1–C1 122.2(5), O2–C8 127.5(5), C1–C2 144.9(7), C7–C8 139.7(6); O1-Li1-N1 81.1(3), O1-Li1-O2 149.6(4), O2-Li1-N1 68.7(3), O2-Li1-O3 83.2(3).

Conclusion

The simple diketoamine ligand **1** allows quite unusual reduction processes even toward the electropositive Group 14 metals in different oxidation states. Surprisingly, the lithiated, electron-rich ligand **1** is able to transfer two electrons from its trianionic amido-bis(enolate) chelate skeleton to M(+4) and M(+2) ions (M = Ge, Sn, Pb), leading to unusual germanium and tin complexes and the first water-stable lithium enolate. Since the direction and completeness of the electron transfer between ligand and metal is strongly dependent on the redox potential of the metal ion, it is a feasible objective to synthesize novel redox-active catalysts with transition metals in low-oxidation states. Such investigations are currently in progress in our laboratory.

Experimental Section

General remarks: All manipulations were carried out under anaerobic conditions in dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. NMR spectra were recorded on a Bruker Avance250 spectrometer at 250.1 MHz (^1H), 63 MHz (^{31}C), 93.2 MHz (^{119}Sn) and 97.2 MHz (^7Li). The chemical shifts are reported relative to TMS at $\delta=0.00$ ppm (^1H), $CDCl_3$ at 77 ppm (^{13}C), 1 M LiCl at 0.00 ppm (^7Li) and $SnMe_4$ at 0.00 ppm (^{119}Sn). The starting ligand 5-aza-2,2,8,8-tetramethylnonane-3,7-dione (**1**) was prepared by the established literature procedure.[4]

4: BuLi (0.93 g, 14.22 mmol) in hexane was added to a stirring solution of diisopropylamine (1.48 g, 14.22 mmol) in THF (10 mL) at −70 °C. The solution was allowed to warm up to room temperature and stirred for 0.5 h. To this solution of lithium diisopropylamide (LDA) a solution of **1** (1.02 g, 4.74 mmol) in THF (10 mL) was added dropwise over 10 min at −20 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. All volatile components were removed in vacuo (10^{-3} Torr), and the red solid of threefold-lithiated **1** was redissolved in THF. This solution was slowly treated with $GeCl_4$ (2.02 g, 9.48 mmol) diluted in THF (10 mL) at −30 °C. After the reaction mixture had been stirred overnight at room temperature, the solvent was removed in vacuo and the residue redissolved in CH_2Cl_2 (30 mL) to afford a red solution. After filtration and evaporation of the solvent, the residue was recrystallized from solutions in Et_2O (10 mL) to afford **4** (1.11 g; 60 % yield) in the form of a yellow powder. M.p. 160 °C (decomp). ^1H NMR (250 MHz, $CDCl_3$, 298 K): $\delta=1.44$ (s, 18 H; CH_3), 7.64 ppm (s, 2 H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): $\delta=27.28$ (s; CH_3), 40.8 (s; *C*CH_3), 111.47 (s; CN), 200.4 ppm (s; CO); MS (70 eV): *m*/*z* (%): 354 (17) [M^+-Cl]; elemental analysis calcd (%) for $C_{12}H_{20}Cl_3NO_2Ge$ (389.2): C 37.01, H 5.15, N 3.60; found: C 36.66, H 5.60, N 3.21.

5: A solution of **1** (0.8 g, 3.75 mmol) in THF (10 mL) was slowly treated with a solution of BuLi (0.48 g, 7.51 mmol) in hexane at −80 °C. The solution was allowed to warm up to room temperature and stirred for 3 h. The latter solution was treated with $GeCl_2$·dioxane (0.86 g, 3.75 mmol) dissolved in THF (10 mL) at −40 °C. The reaction mixture was allowed to warm up to room temperature and stirred for additional 3 h. After evaporation of the solvents in vacuo, the residue was redissolved in toluene (30 mL) to afford a slightly green suspension. The salt was filtered off and the clear solution concentrated in vacuo to about 10 mL. Cooling at −20 °C furnished **5** (1.05 g; 100 % yield) in the form of a colorless powder. M.p. 210–212 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): $\delta=0.79$ (s, 18 H; CH_3), 1.03 (s, 18 H; CH_3), 4.09 (d, $^{sp}J(H,H)=2.51$ Hz, 2 H; CH), 6.18 (s, 2 H; CH), 7.67 (d, $^{sp}J(H,H)=2.51$ Hz, 2 H; CH); ^{13}C NMR (62.9 MHz, CD_2Cl_2, 298 K): $\delta=26.54$ (s; CH_3), 28.19 (s; CH_3), 35.43 (s; *C*CH_3), 37.57 (s; *C*CH_3), 79.64 (s; *C*HO), 107.60 (s; *C*N), 159.32 (s; CN=), 176.08 ppm (s; *C*O); MS (70 eV): *m*/*z* (%): 567 (7) [M^+]; elemental analysis calcd (%) for $C_{24}H_{42}N_2O_4Ge_2$ (567.2): C 50.07, H 7.40, N 4.93, found: C 50.31, H 7.43, N 4.74.

6: A solution of bis[bis(trimethylsilyl)amino]stannylene (4.6 g, 10.5 mmol) in n-pentane (20 mL) was added to a solution of **1** (2.21 g, 10.5 mmol) in n-pentane (50 mL) under stirring. The reaction mixture was stirred at room temperature for 14 h. The brown precipitate was filtered off to afford **6** (2.16 g). The filtrate was concentrated to a volume of 20 mL to give at −20 °C additionally 1.05 g of **6** in the form of colorless crystals (3.21 g, 93 %). M.p. 138–140 °C. ^1H NMR (250 MHz, $CDCl_3$, 298 K): $\delta=0.93$ (Sn sat., $J(Sn,H)=63.1$ Hz, 18 H; CH_3), 1.18 (Sn sat., $J(Sn,H)=63.1$ Hz, 18 H; CH_3), 4.67 (d, $^{sp}J(H,H)=2.51$ Hz, 2 H; CH), 6.46 (s, 2 H; CH), 7.84 ppm (d, $^{sp}J(H,H)=2.51$ Hz, Sn sat. $J(Sn,H)=9.73$ Hz, 2 H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): $\delta=26.73$ (s; CH_3), 28.64 (s; CH_3), 35.57 (s; *C*CH_3), 37.34 (s; *C*CH_3), 80.94 (s; *C*HO), 106.38 (s; CN), 156.80 (s; CN=), 177.58 ppm (s; CO); ^{119}Sn NMR (93.2 MHz, $CDCl_3$, 298 K): $\delta=-348.98$; MS (70 eV): *m*/*z* (%): 660 (30) [M^+]; elemental analysis (%) calcd for $C_{24}H_{42}N_2O_4Sn_2$ (659.98): C 43.60, H 6.36, N 4.24; found: C 43.24, H 6.58, N 4.38.

7: A solution of BuLi (0.87 g, 13.70 mmol) in hexane at −80 °C was added dropwise to a solution of **1** (1.46 g, 6.85 mmol) in THF (30 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. This solution was added dropwise to a stirred suspension of $PbCl_2$ (1.23 g, 4.56 mmol) in THF (20 mL) at −20 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The black precipitate (Pb) was filtered off and the solvent was removed in vacuo. The residue was redissolved in toluene (60 mL) and filtered to give a clear yellow solution. Crystallization from concentrated solutions (10 mL) afforded **7** (0.95 g; 95 % yield) in the form of a bright yellow powder. M.p. 238–240 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): $\delta=1.04$ (s, 72 H; CH_3), 1.17 (s, 72 H; CH_3), 7.10 (s, 4 H; CH), 7.57 ppm (s, 4 H; CH); ^{13}C NMR (62.9 MHz, CD_2Cl_2, 298 K): $\delta=27.07$ (s; CH_3), 28.19 (s; CH_3), 40.06 (s; *C*CH_3), 41.19 (s; *C*CH_3), 118.02 (s; CN), 127.49 (s; CN), 199.12 (s; CO), 204.15 ppm (s; CO); ^1H NMR ([D_8]THF): $\delta=1.04$ (s, 18 H; CH_3), 7.23 ppm (s, 2 H; CH); ^{13}C NMR ([D_8]THF): $\delta=27.64$ (s; CH_3), 40.19 (s; *C*CH_3), 118.52 (s; CN), 199.54 ppm (s, CO); ^7Li NMR (97.2 MHz, CD_2Cl_2, 298 K) $\delta=-0.98$ ppm; ^7Li NMR ([D_8]THF): $\delta=-1.23$ ppm; elemental analysis calcd (%) for $C_{48}H_{80}N_4O_8Li_4$ (868.0): C 66.36, H 9.21, N 6.45, Li 3.22; found: C 65.51, H 9.55, N 7.13, Li 2.90.

4 from 5: A solution of BuLi (0.05 g, 0.818 mmol) in hexane at −80 °C was added dropwise to a solution of **5** (0.27 g, 0.409 mmol) in THF (15 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. This solution was added dropwise to a stirred suspension of $PbCl_2$ (0.44 g, 1.630 mmol) in THF (10 mL) at −20 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 3 h. The black precipitate (Pb) was filtered off and the solvent was removed in vacuo. The residue was redissolved in CH_2Cl_2 (30 mL) to afford a white solid and a yellow solution. After filtration and evaporation of the solvent, the residue was recrystallized from solutions in Et_2O (10 mL) to afford **4** (0.20 g; 56 % yield). The NMR data of **4** synthesized by this route are identical with that for the product synthesized from trilithiated ligand and $GeCl_4$.

2 from 6: A solution of BuLi (0.05 g, 0.818 mmol) in hexane at −80 °C was added dropwise to a solution of **6** (0.27 g, 0.409 mmol) in THF (15 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. This solution was added dropwise to a stirred suspension of $PbCl_2$ (0.22 g, 0.818 mmol) in THF (5 mL) at −20 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 3 h. The black precipitate (Pb) was filtered off and the solvent was removed in vacuo. The residue was dissolved in Et_2O (10 mL) and crystallized at −30 °C to afford **2** (0.25 g; 86 % yield) as a orange solid. Its NMR data are identical with that of authentic samples.

X-ray crystal structure analyses

4 ($C_{12}H_{20}Cl_3NO_2Ge$): Orthorhombic, *Pna2₁*, $a=23.345(5)$, $b=11.571(2)$, $c=6.524(1)$ Å, $V=1762.3(6)$ Å^3, $\rho_{calcd}=1.467$ g cm^{-3}, $Z=4$, $\mu=2.190$ mm^{-1}, 6394 collected reflections ($2\theta_{max}=50.1°$), 2639 independent [$I>2\sigma(I)$], 2136 observed ($F_0>4\sigma(F_0)$), 172 parameters, $R1=0.0481$ (observed reflections), $wR2$ (all data) $=0.1235$.

6 ($C_{24}H_{42}N_2O_4Sn_2$): Monoclinic, $P2_1/c$, $a=21.67(2)$, $b=11.139(9)$, $c=11.870(8)$ Å, $\beta=97.61(2)°$, $V=2841(4)$ Å^3, $\rho_{calcd}=1.543$ g cm^{-3}, $Z=4$, $\mu=1.787$ mm^{-1}, 3259 collected ($2\theta_{max}=50.36°$), 3259 independent [$I>2\sigma(I)$], 2266 observed ($F_0>4\sigma(F_0)$), 289 parameters, $R1=0.0960$ (observed reflections), $wR2$ (all data) $=0.2563$.

7 ($C_{48}H_{80}Li_4N_4O_8$) Orthorhombic, *Pccn*, $a=22.985(7)$, $b=11.829(4)$, $c=19.739(7)$ Å, $V=5367(3)$ Å^3, $\rho_{calcd}=1.075$ g cm^{-3}, $Z=4$, $\mu=0.071$. 15 595 collected reflections ($2\theta_{max}=45.0°$), 3424 independent [$I>2\sigma(I)$], 2152 observed ($F_0 > 4\sigma(F_0)$), 289 parameters, $R1=0.0795$, $wR2$ (all data) $=0.2202$.

The intensities were measured with a Bruker-axs-SMART diffractometer ($Mo_{K\alpha}$ radiation, $\lambda=0.71707$ Å, ω-scan, The structures were solved by direct methods (SHELXS 97). Refinements were carried out with the SHELXL-97 package.[12] All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode. All refinements were made by full-matrix least-squares on F^2.

CCDC-237516 (**4**), CCDC-237517 (**6**), and CCDC-237518 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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