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Tetrylenes Chelated by Hybrid Amido–Amino Ligand: Derivatives of 2-[(*N*,*N*-Dimethylamino)methyl]aniline

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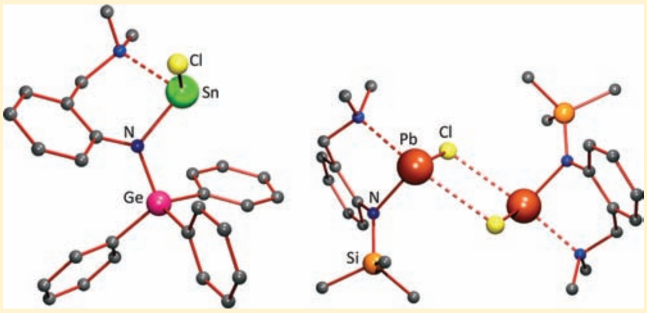
S *Supporting Information*



ABSTRACT: Reaction of 2-[(dimethylamino)methyl]aniline with butyllithium, followed by conversion with trimethylsilyl, triphenylsilyl, triphenylgermyl, trimethylstannyl, or tri-*n*-butylstannyl chloride, gives the corresponding substituted aniline. These compounds were further deprotonated by butyllithium and reacted with germanium, tin, and lead dichlorides, respectively, in both stoichiometric ratios 2:1 and 1:1, providing the target homo- ($[2\text{-}(Me_2NCH_2)C_6H_4(YR_3)N]_2M$) and heteroleptic ($[2\text{-}(Me_2NCH_2)C_6H_4(YR_3)N]MCl$) germylenes and stannylenes, where M = Ge, Sn, Y = Si, Ge, and R = Me, Ph. Unlike all of these cases, the heteroleptic plumbylene can only be obtained with this reaction when the amide is substituted by a trimethylsilyl moiety. Anilines substituted by trimethyltin or tri-*n*-butyltin moieties gave transmetalation products after the second deprotonation by butyllithium. The trimethyltin-substituted stannylenes could likewise not be obtained by hexamethyldisilazane elimination of (trimethylstannyl)-2-[(dimethylamino)-methyl]aniline with 0.5 mol equiv of either bis[bis(trimethylsilyl)amido]tin or {bis[bis(trimethylsilyl)amido]tin chloride}. Products of these reactions are heterocubanes with compositions $\{[2\text{-}(Me_2NCH_2)C_6H_4N]Sn\}_4$ and $[2\text{-}(Me_2NCH_2)C_6H_4N]_2\text{-}(\mu^2\text{-}SnMe_2)_2$, respectively, and Me_4Sn or Me_3SnCl. The structures of trimethylsilyl- and triphenylgermyl-substituted germylenes, stannylenes, and plumbylenes, as well as a number of their precursors, in the crystalline state, were investigated by X-ray diffraction and NMR spectroscopy in solution. Density functional theory methods were used for evaluation of the structures of several compounds.

INTRODUCTION

Tetrylenes, low-valent group 14 compounds including carbenes, silylenes, germylenes, stannylenes, and plumbylenes, are a subject of growing research interest.[1] In particular, metal amides are among the most studied and used compounds in catalysis and new materials preparation.[2] The heavier elements of group 14 metal amides with the metal atom in a lower oxidation state are widely accepted as carbene[3] $[M(NR_2)]$, radical[4] $[M(NR_2)_3]$, or alkyne[5] analogues. Special attention has been paid to the reactivity of $M(NR_2)_2$ compounds in oxidative addition reactions,[6] in the activation of small molecules,[7] in the use as carbene analogues for complexation[8] of transition-metal complexes, and in reductions to metal clusters.[9] Even though the first work on these groups of metal amides was reported by Lappert in 1974[3a] and many compounds were prepared and structurally characterized, amides containing both group 14 metals and an amino functionality remain rather uncommon (Figure 1).[10]

Such compounds are nearly restricted to pyridine derivatives with the intramolecular donor interaction from the amino nitrogen atom to the metal (Figure 1B). The successful stabilization of

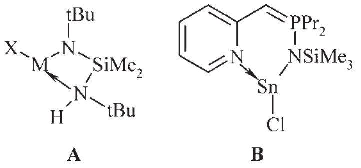


Figure 1. Examples of amino-group-chelated amidotetrylenes (M = Ge, Sn, Pb).

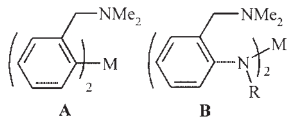


Figure 2. C,N- and N,N-chelated homoleptic tetrylenes.

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Table 1. Selected Crystallographic Data for **3′**, **8a**, **8b**, **12**, and **14**−**18**

	3′·1.5$C_4H_8O_2$	**8a**	**8b**	**12**	**14**·3.5C_6D_{12}
formula	$C_{36}H_{66}Li_2N_4O_6Si_2$	$C_{24}H_{42}GeN_4Si_2$	$C_{24}H_{42}GeN_4Si_2$	$C_{24}H_{42}N_4Si_2Sn$	$C_{54}H_{54}Ge_2N_4Sn$
cell setting	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\,2_1/c$	$P\,\bar{1}$	Cc	$P\,2_1/c$	$P\bar{1}$
a (Å)	9.6670(5)	9.8378(9)	17.7691(9)	13.7200(11)	10.5760(7)
b (Å)	14.0810(5)	10.6822(8)	10.0000(8)	14.4010(12)	14.4601(14)
c (Å)	16.6901(14)	14.9001(8)	15.4009(6)	18.5601(7)	23.856(2)
α (deg)	90	77.456(5)	90	90	80.329(7)
β (deg)	115.567(7)	86.819(6)	92.782(12)	129.951(5)	86.883(7)
γ (deg)	90	86.819(6)	90	90	70.892(7)
Z	2	2	4	4	2
V (Å^3)	2049.4(2)	1404.1(2)	2733.4(3)	2811.2(3)	3398.3(5)
total (R_{int})^a	4593 (0.067)	6379 (0.0673)	5721 (0.0673)	6440 (0.0632)	15458 (0.0826)
max/min τ (e/Å^3)	0.460/−0.321	0.478/−0.472	2.099/−1.451	0.420/−0.692	5.342/−1.042
GOF^b	1.160	1.091	1.132	1.105	1.123
R^c/wR^c	0.0669/0.1142	0.0373/0.0844	0.0690/0.1617	0.0306/0.0563	0.0883/0.2050

	15	**16**	**17**	**18**
formula	$C_{27}H_{27}ClGeN_2Sn$	$C_{24}H_{42}Cl_2N_4Pb_2Si_2$	$C_{36}H_{48}N_8Sn_4$	$C_{22}H_{36}N_4Sn_2$
cell setting	monoclinic	monoclinic	tetragonal	triclinic
space group	$C\,2/c$	$P\,2_1/c$	$I\bar{4}$	$P\bar{1}$
a (Å)	34.1866(9)	6.8431(4)	14.0430(9)	7.6861(4)
b (Å)	8.4024(11)	12.7100(7)	14.0430(8)	8.8950(3)
c (Å)	19.1884(7)	19.6427(12)	9.6569(7)	9.0669(3)
α (deg)	90	90	90	105.140(3)
β (deg)	111.428(11)	110.055(5)	90	91.336(3)
γ (deg)	90	90	90	99.662(4)
Z	8	2	2	1
V (Å^3)	5130.9(8)	1604.85(17)	1904.4(4)	588.41(4)
total (R_{int})^a	5738 (0.0496)	3567 (0.0622)	2164 (0.0298)	2682 (0.0198)
max/min τ (e/Å^3)	0.498/−0.497	1.735/−2.166	0.284/−0.307	0.395/−0.640
GOF^b	1.105	1.145	1.079	1.129
R^c/wR^c	0.0314/0.0544	0.0409/0.0819	0.0224/0.0427	0.0161/0.0394

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$. [b] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data. [c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

low-valent group 14 metals and the special chemical behavior of compounds containing a [2-(dimethylamino)methyl]phenyl ligand (Figure 2A)[11] prompted us to explore the chemistry of lower-valent complexes of heavier group 14 metals with [2-(dimethylamino)methyl]aniline as a ligand (Figure 2B). Thus, this ligand contains both the amido functionality, prone to strong nitrogen-to-metal covalent bonds, and the pendant amino group for the formation of a weaker intramolecular donor−acceptor interaction, which together give rise to a six-membered diazametalla ring, similar to related β-diketiminato ligand-substituted tetrylenes.[12] The steric protection at the amido functionality is expected to be very variable and, together with the hemilabile coordination of the amino group, would give rise to structure fine-tuning, which is the main goal of this paper.

■ EXPERIMENTAL SECTION

NMR Spectroscopy. NMR spectra were recorded at 295 K from solutions in benzene-d_6 and/or tetrahydrofuran (THF)-d_8 on a Bruker Avance 500 spectrometer, equipped with a z-gradient 5-mm probe, operating at 500.13 MHz for ^1H and 186.50 MHz for ^{119}Sn nuclei and on a Bruker Avance II 400 spectrometer operating at 400.13 MHz for ^1H and 81.49 MHz for ^{207}Pb nuclei. All deuterated solvents were degassed and then stored over a potassium or sodium mirror under an argon atmosphere. Solutions were obtained by dissolving approximately 40 mg of each compound in 0.5 mL of a deuterated solvent. Values of ^1H chemical shifts were calibrated to internal standard tetramethylsilane [$\delta(^1H)$ = 0.00] or to residual signals of benzene [$\delta(^1H)$ = 7.16] and THF [$\delta(^1H)$ = 3.58 or 1.73]. The ^{119}Sn and ^{207}Pb chemical shifts are referred to external neat tetramethylstannane (δ = 0.0) and tetraethyllead (δ = 0.0), respectively, and measured using the inverse-gated proton broad-band decoupling mode.

Crystallography. The X-ray diffraction data (Tables 1 and S1−S3 in the Supporting Information) obtained from colorless crystals of compounds **1**, **3′**, **4**, **5**, **8a**, **8b**, **12**, and **14**−**18** and 1-(chloromethyl)-2-nitrobenzene were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å), a graphite monochromator, and the ϕ- and χ-scan mode. Data reductions were performed with DENZO-SMN.[13] The absorption was corrected by integration methods.[14] Structures were solved by direct methods (*SIR92*)[15] and refined by full-matrix least squares based on F^2 (*SHELXL97*).[16] Hydrogen atoms were mostly located on a difference Fourier map; however, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}$(pivot atom) or $1.5U_{\mathrm{eq}}$ for the methyl moiety, using C−H bond distances of 0.96, 0.97, and 0.93 Å for methyl, methylene, and aromatic hydrogen atoms, respectively, and 0.86 Å for N−H bonds.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre (825147−825159). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk, or www http://www.ccdc.cam.ac.uk).

Synthetic Procedures. Standard Schlenk techniques were used for all manipulations under argon. *n*-Butyllithium (1.6 M in hexanes, Sigma-Aldrich), trimethylsilyl chloride (98%, Sigma-Aldrich), triphenylsilyl chloride (96% Sigma-Aldrich), triphenylgermyl chloride (99%, Sigma-Aldrich), trimethylstannyl chloride (97%, Sigma-Aldrich), tributyltin chloride (97%, Fluka), tin(II) chloride (99.9%, anhydrous, Strem Chemicals), a 1:1 germanium(II) chloride−dioxane complex (Sigma-Aldrich), and lead(II) chloride (p.a., Lachema) were used without further purification. Diethyl ether and *n*-hexane were dried over and distilled from a potassium−sodium alloy, degassed, and stored under argon over a potassium mirror. High-purity deuterated solvents were distilled from a potassium mirror, degassed, and stored over a sodium mirror. Compounds **1**, bis[bis(trimethylsilyl)amido]tin(II), bis[bis(trimethylsilyl)amido]lead(II), and bis[bis(trimethylsilyl)amidotin(II) chloride] were obtained by published methods.[17,18] For the preparation of **3**−**7**, see the Supporting Information.

Compositional analyses were determined under an inert atmosphere of argon on an EA 1108 automatic analyzer by Fisons Instruments.

Preparation of {{2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{SiMe_3}$)N}$_2$Ge (8). *n*-Butyllithium (1.6 M solution in hexanes, 0.74 mL, 1.19 mmol) was added dropwise to a stirred solution of **3** (272 mg, 1.19 mmol) in 20 mL of hexane at room temperature, causing the immediate precipitation of a white powder, which was washed with 10 mL of hexane. Afterward, the solvent was evaporated and the resulting product was dissolved in 20 mL of diethyl ether and added dropwise to a suspension of the 1:1 germanium(II) chloride−dioxane complex (138 mg, 0.595 mmol) in 15 mL of diethyl ether. The reaction mixture was stirred overnight and filtered away from lithium chloride. The solution was reduced to a half of the volume in vacuo. Single crystals of **8b** were obtained from diethyl ether at −28 °C (211 mg, yield 67%) and those of polymorph **8a** from toluene at −28 °C. Mp: 132 °C (dec). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.31 (d, ^3J = 7.0 Hz, 2H, H6′), 6.83 (t, ^3J = 7.4 Hz, 2H, H5′), 6.66 (t, ^3J = 7.6 Hz, 2H, H4′), 6.00 (d, ^3J = 7.9 Hz, 2H, H3′), 3.71, 3.11 (AX spin system Δδ = 0.60 ppm = 300.1 Hz, 13.2 Hz, 4H, C7′), 2.18 (s, 12H, $\mathrm{NMe_2}$), 0.25 (s, 18H, $\mathrm{SiMe_3}$). ^{13}C{^{1}H} NMR (125 MHz, $\mathrm{C_6D_6}$, ppm): δ 149.75 (C1′), 133.64 (C2′), 129.02 (C6′), 128.93 (C5′), 128.00 (C4′), 121.76 (C3′), 62.05 (C7′), 46.36 ($\mathrm{NMe_2}$), 3.22 ($\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{24}H_{42}Ge_2N_4Si_2}$: C, 55.93; H, 8.21; N, 10.87. Found: C, 55.8; H, 8.1; N, 10.8.

The compound {{2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{SiMe_3}$)NLi($\mathrm{C_4H_8O_2}$)}$_2$-($\mathrm{C_4H_8O_2}$) (**3′**) was obtained as a minor product from the second crop of crystallization.

Preparation of {2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{SiMe_3}$)NGeCl (9). A workup similar to that for **8** was used except that the stoichiometric ratio of the starting compounds was 1:1 (272 mg, 1.19 mmol of **3** corresponds to 276 mg, 1.19 mmol of the 1:1 germanium(II) chloride−dioxane complex; 227 mg, yield 60%). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.14 (t, ^3J = 7.7 Hz, 1H, H5′), 6.95 (d, ^3J = 7.3 Hz, 1H, H6′), 6.87 (d, ^3J = 8.0 Hz, 1H, H3′), 6.72 (d, ^3J = 7.4 Hz, 1H, H4′), 3.00, 2.51 (AX spin system 248.9 Hz, 11.8 Hz, 2H, $\mathrm{CH_2}$), 1.96 (s, 6H, $\mathrm{N(CH_3)_2}$), 0.26 (s, 9H, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125 MHz, $\mathrm{C_6D_6}$, ppm): δ 149.09 (C1′), 128.56 (C2′), 129.77 (C6′), 129.56 (C5′), 126.00 (C4′), 120.46 (C3′), 61.21 (C7′), 46.58 ($\mathrm{NMe_2}$), 2.28 ($\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{C_{12}H_{21}ClGeN_2Si}$: C, 43.75; H, 6.43; N, 8.50. Found: C, 43.8; H, 6.5; N, 8.5.

Preparation of {{2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{GePh_3}$)N}$_2$Ge (10). *n*-Butyllithium (1.6 M solution in hexanes, 0.29 mL, 0.46 mmol) was added dropwise to a stirred solution of **5** (210 mg, 0.46 mmol) in 15 mL of hexane at room temperature, causing the immediate precipitation of a white powder, which was washed with 10 mL of hexane. Afterward, the solvent was evaporated and the resulting product was dissolved in 15 mL of diethyl ether and added dropwise to a suspension of the 1:1 germanium(II) chloride−dioxane complex (54 mg, 0.23 mmol) in 15 mL of diethyl ether. The reaction mixture was stirred overnight and filtered away from lithium chloride. The solution was reduced to half of its volume in vacuo (118 mg, yield 52%). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.61−7.59 (m, 18H, Ph), 7.50 (d, ^3J = 6.4 Hz, 2H, H6′), 7.13−7.06 (m, 24H, Ph, H3′, H4′, H5′), 3.73, 2.92 (AX spin system Δδ = 0.81 ppm = 405.1 Hz, 13.4 Hz, 4H, $\mathrm{CH_2}$), 1.83 (broad signal, 12H, $\mathrm{N(CH_3)_2}$). ^{13}C{^{1}H} NMR (125 MHz, $\mathrm{C_6D_6}$, ppm): δ 150.88 (C1′), 139.16 (Ph), 136.98 (C2′), 136.76 (Ph), 135.80 (C6′), 135.28 (Ph), 130.84 (C5′), 129.50 (C4′), 128.59 (Ph), 128.55 (C3′), 65.01 (C7′), 44.83 ($\mathrm{NMe_2}$). Anal. Calcd for $\mathrm{C_{54}H_{54}Ge_3N_4}$: C, 66.40; H, 5.57; N, 5.74. Found: C, 66.5; H, 5.6; N, 5.8.

Preparation of {2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{GePh_3}$)NGeCl (11). A workup similar to that for **10** was used except that the stoichiometric ratio of the starting compounds was 1:1 (210 mg, 0.46 mmol of **5** corresponds to 108 mg, 0.46 mmol of the 1:1germanium(II) chloride dioxane complex; 151 mg, yield 58%). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.14−7.10 (m, 15H, Ph), 6.80 (d, ^3J = 7.4 Hz, 1H, H6′), 6.61−6.57 (m, 2H, H4′, H5′), 6.32 (d, ^3J = 8.0 Hz, 1H, H3′), 3.26, 3.11 (AB spin system Δδ = 0.15 ppm = 75.0 Hz, 12.1 Hz, 2H, C7′), 1.91 (broad signal, 6H, $\mathrm{NMe_2}$). ^{13}C{^{1}H} NMR (125 MHz, $\mathrm{C_6D_6}$, ppm): δ 150.16 (C1′), 136.26 (Ph), 135.41 (Ph), 134.90 (C2′), 134.51 (C6′), 134.10 (Ph), 130.13 (C5′), 129.76 (C4′), 129.43 (C3′), 128.57 (Ph), 61.39 (C7′), 44.11 ($\mathrm{NMe_2}$). Anal. Calcd for $\mathrm{C_{27}H_{27}Ge_2N_2Cl}$: C, 57.89; H, 4.86; N, 5.00. found: C, 58.0; H, 4.9; N, 5.0.

Preparation of {{2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{SiMe_3}$)N}$_2$Sn (12). *n*-Butyllithium (1.6 M solution in hexanes, 8.96 mL, 14.34 mmol) was added dropwise to a stirred solution of **3** (3.19 g, 14.34 mmol) in 40 mL of hexane at room temperature, causing the immediate precipitation of a white powder, which was washed with 10 mL of hexane. Afterward, the solvent was evaporated and the resulting product was dissolved in 35 mL of diethyl ether and added dropwise to a suspension of tin(II) chloride (1.36 g, 7.17 mmol) in 40 mL of diethyl ether. The reaction mixture was stirred overnight and filtered away from lithium chloride. The solution was reduced to a half of its volume in vacuo. Single crystals of **12** were obtained from diethyl ether at −28 °C (2.98 g, yield 74%). Mp: 113 °C (dec). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.29 (t, ^3J = 7.7 Hz, 1H, H5′), 7.16 (d, ^3J = 7.1 Hz, 2H, H6′), 6.83 (d, ^3J = 7.9 Hz, 2H, H3′), 6.78 (t, ^3J = 7.4 Hz, 2H, H4′), 3.72, 2.52 (AX spin system Δδ = 1.20 ppm = 599.4 Hz, 11.2 Hz, 4H, $\mathrm{CH_2}$), 2.00 (s, 12H, $\mathrm{N(CH_3)_2}$), 0.32 (s, 18H, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$, ppm): δ 152.38 (C1′), 133.90 (C2′), 130.84 (C6′), 130.63 (C5′), 129.47 (C4′), 120.87 (C3′), 63.74 (C7′), 46.12 ($\mathrm{NMe_2}$), 2.72 ($\mathrm{SiMe_3}$). ^{119}Sn{^{1}H} NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ −115.6. ^{119}Sn{^{1}H} NMR (500 MHz, THF-d_8, ppm): δ −118.0. Anal. Calcd for $\mathrm{C_{24}H_{42}Si_2N_4Sn}$: C, 51.34; H, 7.54; N, 9.98. Found: C, 51.4; H, 7.6; N, 9.9.

Preparation of {2-[$(\mathrm{CH_3})_2\mathrm{NCH_2}$]$\mathrm{C_6H_4}$}($\mathrm{SiMe_3}$)NSnCl (13). A workup similar to that for **12** was used except that the stoichiometric ratio of the starting compounds was 1:1 (3.19 g, 14.34 mmol of **3** corresponds to 2.72 g, 14.34 mmol of tin(II) chloride; 4.47 g, yield 83%). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, ppm): δ 7.26 (t, ^3J = 7.6 Hz, 1H, H5′), 7.06 (d, ^3J = 8.0 Hz, 1H, H6′), 6.99 (d, ^3J = 7.3 Hz, 1H, H3′), 6.83 (t, ^3J = 7.3 Hz, 1H, H4′), 3.12, 2.54 (AX spin system Δδ = 0.58 ppm = 288.2 Hz, 2H, C7′), 2.06 (s, 6H, NMe_2), 0.37 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 151.56 (C1′), 131.49 (C2′), 130.32 (C6′), 128.83 (C5′), 127.62 (C4′), 120.52 (C3′), 62.07 (C7′), 45.49 (NMe_2), 3.59 ($SiMe_3$). $^{119}Sn\{^1H\}$ NMR (500 MHz, C_6D_6, ppm): δ −51.2. $^{119}Sn\{^1H\}$ NMR (500 MHz, THF-d_8, ppm): δ −64.6. Anal. Calcd for $C_{12}ClH_{21}SiSnN_2$: C, 38.38; H, 5.64; N, 7.46. Found: C, 38.5; H, 5.7; N, 7.4.

Preparation of $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}(GePh_3)N\}_2Sn$ (14). *n*-Butyllithium (1.6 M solution in hexanes, 2.59 mL, 4.15 mmol) was added dropwise to a stirred solution of **5** (1.88 g, 4.15 mmol) in 35 mL of hexane at room temperature, causing the immediate precipitation of a white powder, which was washed with 10 mL of hexane. Afterward, the solvent was evaporated and the resulting product was dissolved in 35 mL of diethyl ether and added dropwise to a suspension of tin(II) chloride (393 mg, 2.075 mmol) in 25 mL of diethyl ether. The reaction mixture was stirred overnight and filtered away from lithium chloride. The solution was reduced to half of its volume in vacuo. Compound **14** was crystallized from toluene at −28 °C (1.29 g, yield 61%). Single crystals of **14** were obtained from deuterated cyclohexane in a vacuum-sealed NMR tube. ^1H NMR (500 MHz, C_6D_6, ppm): δ 7.72−7.56 (m, 12H, Ph), 7.14−7.08 (m, 20H, H4′ + Ph), 6.94 (d, ^3J = 7.4 Hz, 2H, H6′), 6.72 (t, ^3J = 7.4 Hz, 2H, H5′), 6.43 (d, ^3J = 7.8 Hz, 2H, H3′), 3.54, 2.12 (AX spin system 503.3 Hz, 10.2 Hz, 4H, C7′), 1.93 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 154.38 (C1′), 139.65 (Ph), 136.47 (Ph), 135.71 (C2′), 134.43 (C6′), 131.47 (C5′), 129.35 (Ph), 128.86 (C4′), 128.68 (Ph), 121.43 (C3′), 64.98 (C7′), 44.82 (NMe_2). $^{119}Sn\{^1H\}$ NMR (500 MHz, C_6D_6, ppm): δ −124.5. $^{119}Sn\{^1H\}$ NMR (500 MHz, THF-d_8, ppm): δ −128.6. Anal. Calcd for $C_{54}H_{54}Ge_2N_4Sn$: C, 63.40; H, 5.32; N, 5.48. Found: C, 63.5; H, 5.3; N, 5.5.

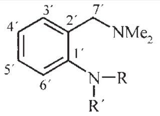
Preparation of $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}(GePh_3)NSnCl$ (15). The solution of **5** (186 mg, 0.41 mmol) in diethyl ether (15 mL) was added to a suspension of bis{bis[bis(trimethylsilyl)amido]tin(II) chloride} (129 mg, 0.21 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred overnight and then filtered. Single crystals of **15** were obtained from diethyl ether at room temperature (139 mg, yield 56%). Mp: 79 °C. ^1H NMR (400 MHz, C_6D_6, ppm): δ 7.81−7.80 (m, 5H, Ph), 7.29 (d, ^3J = 8.1 Hz, 1H, H6′), 7.16−7.10 (m, 10H, Ph), 6.88 (t, ^3J = 7.6 Hz, 1H, H4′), 6.59 (d, ^3J = 7.4 Hz, 1H, H3′), 6.88 (t, ^3J = 7.3 Hz, 1H, H5′), 3.36, 2.57 (AX spin system Δδ = 0.79 ppm = 314.6 Hz, 11.6 Hz, 2H, CH_2), 1.79 (s, 3H, $N(CH_3)_2$), 1.52 (s, 3H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8, ppm): δ 153.42 (C1′), 137.78 (Ph), 135.08 (Ph), 130.91 (C6′), 129.43 (Ph), 128.84 (C5′), 128.22 (Ph), 127.24 (C2′), 124.73 (C4′), 115.89 (C3′), 67.37 (C7′), 43.94 (NMe_2). $^{119}Sn\{^1H\}$ NMR (500 MHz, C_6D_6, ppm): δ −85.8. $^{119}Sn\{^1H\}$ NMR (500 MHz, THF-d_8, ppm): δ −89.7. Anal. Calcd for $C_{27}H_{27}ClGe_2N_2Sn$: C, 53.48; H, 4.49; N, 4.62. Found: C, 53.5; H, 4.5; N, 4.7.

Preparation of $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}(SiMe_3)NPbCl\}_2$ (16). *n*-Butyllithium (1.6 M solution in hexanes, 0.70 mL, 1.12 mmol) was added dropwise to a stirred solution of **3** (249 mg, 1.12 mmol) in 15 mL of hexane at room temperature, causing the immediate precipitation of a white powder, which was washed with 10 mL of hexane. Afterward, the solvent was evaporated and the resulting product was dissolved in 20 mL of diethyl ether and added dropwise to a suspension of lead(II) chloride (311 mg, 1.12 mmol) in 20 mL of diethyl ether. The reaction mixture was stirred overnight and filtered away from lithium chloride. The solution was reduced to half of its volume in vacuo. Single crystals of **16** were obtained from diethyl ether at room temperature. (379 mg, yield 73%). Mp: 128 °C (dec). ^1H NMR (500 MHz, C_6D_6, ppm): δ 7.09 (t, ^3J = 7.0 Hz, 1H, H4′), 7.02 (d, ^3J = 7.1 Hz, 1H, H6′), 6.72 (t, ^3J = 7.3 Hz, 1H, H5′), 6.06 (broad signal., 1H, H3′), 3.85 (broad signal, 1H, C7′), 2.59 (broad signal, 1H, C7′), 2.11 (s, 6H, NMe_2), 0.09 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, ppm): δ 153.40 (C1′ broad), 134.12 (C6′), 132.41 (C2′), 131.13 (C5′), 129.42 (C4′), 120.63 (C3′), 63.59 (C7′), 45.95 (NMe_2), 3.33 ($SiMe_3$). $^{207}Pb\{^1H\}$ NMR (81 MHz, C_6D_6, ppm): δ 1816.3. Anal. Calcd for $C_{12}H_{21}ClN_2PbSi$: C, 31.06; H, 4.56; N, 6.04. Found: C, 31.2; H, 4.6; N, 6.0.

Chart 1

1	$Ar^{N}NH_2$	**10**	$[Ar^{N}N(GePh_3)]_2Ge$
2	$Ar^{N}NHLi$	**11**	$Ar^{N}N(GePh_3)GeCl$
3	$Ar^{N}N(SiMe_3)H$	**12**	$[Ar^{N}N(SiMe_3)]_2Sn$
4	$Ar^{N}N(SiPh_3)H$	**13**	$Ar^{N}N(SiMe_3)SnCl$
5	$Ar^{N}N(GePh_3)H$	**14**	$[Ar^{N}N(GePh_3)]_2Sn$
6	$Ar^{N}N(SnMe_3)H$	**15**	$Ar^{N}N(GePh_3)SnCl$
7	$Ar^{N}N(SnBu_3)H$	**16**	$Ar^{N}N(SiMe_3)PbCl$
8	$[Ar^{N}N(SiMe_3)]_2Ge$	**17**	$[Ar^{N}NSn]_4$
9	$Ar^{N}N(SiMe_3)GeCl$	**18**	$[Ar^{N}NSnMe_2]_2$

$Ar^{N}NRR' =$



Preparation of $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}NSn\}_4$ (17). A solution of **6** (232 mg, 0.37 mmol) in diethyl ether (15 mL) was added to a suspension of bis[bis(trimethylsilyl)amido]tin(II) (163 mg, 0.19 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred overnight and then filtered. Single crystals of the unexpected product **17** were obtained from a diethyl ether solution at room temperature (91 mg, yield 46%). Mp: >330 °C. ^{13}C CP/MAS NMR: δ 142, 133, 130, 127, 125, 124, 61, 45, 44. ^{119}Sn MAS NMR (ppm): δ −139.9. Anal. Calcd: C, 40.50; H, 4.53; N, 10.50. Found: C, 40.6; H, 4.6; N, 10.5. Me_4Sn was identified in the mother liquors by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy [δ(^{119}Sn) = −1.4 ppm].[19]

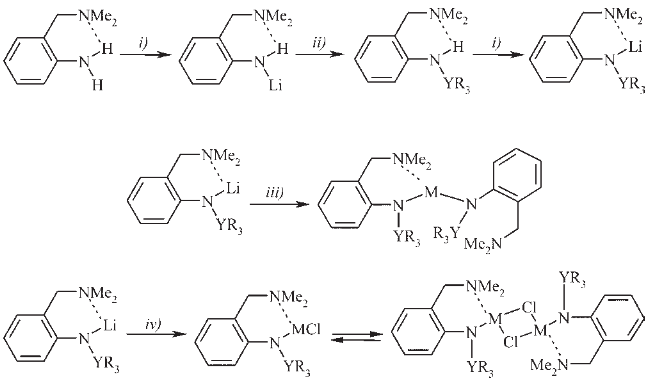
Alternative Preparation of 17. A solution of **6** (226 mg, 0.72 mmol) in diethyl ether (15 mL) was added to a suspension of bis{bis[bis(trimethylsilyl)amido]tin(II) chloride} (227 mg, 0.36 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred overnight and then filtered. Single crystals of **17** were obtained from diethyl ether at room temperature (62 mg, yield 32%). Me_3SnCl was identified in the mother liquors by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy [δ(^{119}Sn) = −156.0 ppm].[19]

Preparation of $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}NSnMe_2\}_2$ (18). Compound **18** was obtained from the reaction of bis[bis(trimethylsilyl)-amido]tin(II) and **6** as a minor product. Single crystals of **18** were obtained from hexane extraction at room temperature (31 mg, yield 7%). Mp: 165 °C (dec). ^1H NMR (500 MHz, THF-d_8, ppm): δ 6.82 (t, ^3J = 7.2 Hz, 1H, H4′), 6.70 (d, ^3J = 7.6.6 Hz, 1H, H3′), 6.30 (d, ^3J = 8.2 Hz, 1H, H6′), 6.14 (t, ^3J = 7.2 Hz, 1H, H5′), 4.18 (broad signal, 1H, C7′), 2.89 (broad signal, 1H, C7′), 2.18 (broad signal, 6H, NMe_2), 0.62 (broad signal, 6H, $SnMe_2$). $^{119}Sn\{^1H\}$ NMR (500 MHz, THF-d_8, ppm): δ −123.8. Anal. Calcd for $C_{12}H_{21}ClN_2PbSi$: C, 44.49; H, 6.11; N, 9.43. Found: C, 44.5; H, 6.2; N, 9.4.

■ COMPUTATIONAL DETAILS

All calculations were performed with the *Gaussian 09* program.[20] Density functional theory (DFT)[21] geometry optimizations of the molecules were done using a hybrid B3LYP functional[22] and a Pople 6-311++g(d,p) basis set[23] on all atoms, with a LANL2DZ ECP pseudopotential[24] for tin and lead atoms. The cubane **16** was optimized with the Dunning-type basis set cc-pVDZ[25] on carbon, hydrogen, and nitrogen and the cc-pVDZ-PP[26] basis set on tin. Frequency calculations were carried out to confirm that the obtained structures correspond to minima on the potential energy surface.

Scheme 1. Preparation of Target Compounds[a]



[a] Reagents and conditions: (i) *n*-BuLi; (ii) YR_3Cl, where Y = Si, Ge, Sn and R = Me, *n*-Bu, Ph; (iii) $^1/_2MCl_2$, where M = Ge, Sn, Pb; (iv) MCl_2, where M = Ge, Sn, Pb.

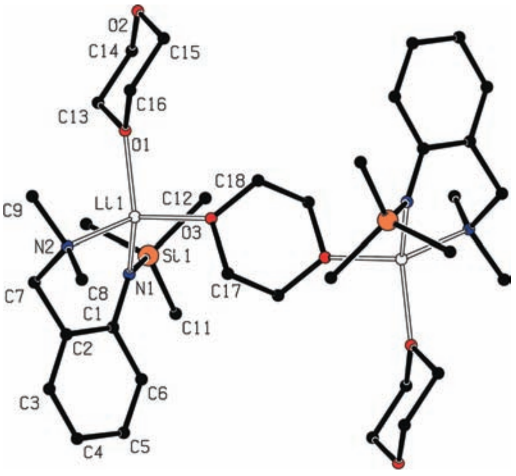


Figure 3. Molecular structure of **3′** ({[$Ar^N(SiMe_3)Li(diox)]_2$-μ^2-diox]}) in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): O1−Li1 2.023(5), O3−Li1 1.994(5), N2−Li1 2.140(5), N1−Li1 1.993(5); N1−Li1−O3 112.2(2), N1−Li1−O1 125.5(3), O3−Li1−O1 99.0(2), N1−Li1−N2 101.1(2), O3−Li1−N2 112.5(2), O1−Li1−N2 106.6(2), C1−C2−C7−N2 71.6(3).

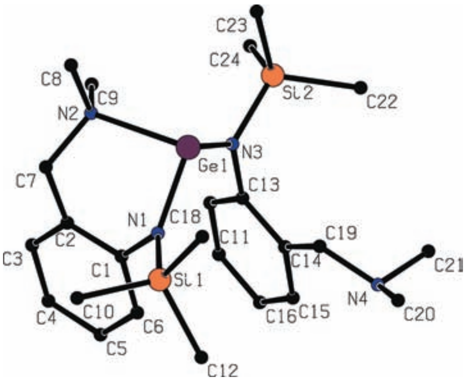


Figure 4. Molecular structure of **8a** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ge1−N1 1.9166(19), Ge1−N3 1.9137(18), Ge1−N2 2.290(2), Ge1−N4 4.996(2), Si1−N1 1.733(2); N1−Ge1−N2 89.95(8), N1−Ge1−N3 101.08(8), N3−Ge1−N4 59.08(7), Si1−N1−Ge1 121.39(11), C1−C2−C7−N2 66.5(3), C13−C14−C19−N4 157.5(2).

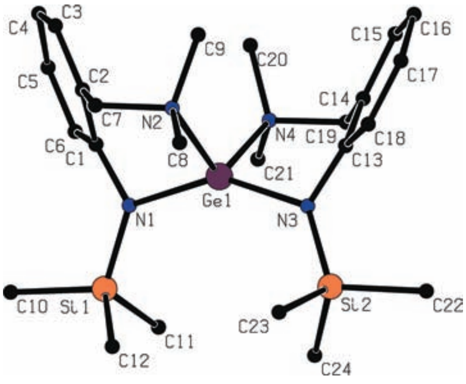


Figure 5. Molecular structure of **8b** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ge1−N1 1.979(6), Ge1−N3 1.975(6), Ge1−N2 2.176(5), Ge1−N4 2.178(5), Si1−N1 1.713(6), N1−Ge1−N2 95.3(2); N1−Ge1−N3 147.3(2), N2−Ge1−N4 113.9(2), Si1−N1−Ge1 127.1(3), C1−C2−C7−N2 73.5(8).

■ RESULTS AND DISCUSSION

Synthesis. The ligand ArN^NH_2 (**1**; Chart 1) was prepared according to the literature,[17] where it was used for amidoxime ligand preparation. In our present work, it is used for the first time as such.

Compound **1** can be converted with 1 mol equiv of *n*-butyllithium for single deprotonation to lithium anilide, in which, in turn, lithium gets electrophilically substituted by an YR_3 moiety, with Y a group 14 element in the oxidation state IV+ [$YR_3 = SiMe_3$, $SiPh_3$, $GePh_3$, $SnMe_3$, and Sn(n-Bu)$_3$; see Scheme 1, compounds **1** and **3**−**7**]. Descriptions of the preparation, structures, and properties of **1**−**7** are located in the Supporting Information.

All the compounds substituted with a YR_3 moiety (**3**−**7**) can be deprotonated by butyllithium to produce the corresponding lithium salt, except the triphenylsilyl-substituted compound **4**, which is probably caused by the high steric hindrance of the Ph_3Si group on the NH one.

The trimethylsilyl-substituted lithium amide **3′** was obtained as a minor byproduct of the reaction of lithiated (trimethylsilyl)-amide **3** with $GeCl_2$·diox. The yellow, extremely air-sensitive crystals were suitable for X-ray diffraction. The crystal structure of **3′** (Figure 3) is composed by two trimethylsilyl-substituted lithium amides, which are connected by one dioxane molecule, while each lithium atom is coordinated by one additional dioxane molecule. The second oxygen donor atom of these two dioxane molecules remains uncoordinated (Figures 3 and S5 in the Supporting Information). The lithium atom centers are four-coordinated with a tetrahedral vicinity configuration and can be compared directly to the monomeric species [(pmdeta)-$LiN(SiMe_3)_2$][27] or lithium amidinate coordinated by two THF molecules.[28]

Homoleptic Tetrylenes. The conversion of lithium salts with trimethylsilyl and triphenylgermyl substituents with 0.5 mol equiv of $GeCl_2$·diox or $SnCl_2$ provides the corresponding homoleptic

Table 2. Selected Interatomic Measured/Calculated Distances (Å) and Angles (deg) of a Selection of Compounds

	8a	8b	12	14	15	16
d[M−N(YR$_3$)]	1.9166(19)/ 1.9513	1.979(6)/ 2.235	2.131(2)/ 2.144	2.151(6)	2.107(2)	2.221(6)
	1.9137(18)/ 1.9409	1.975(6)/ 2.235	2.134(2)/ 2.144	2.145(6)		
d[M−N(Me$_2$)]	2.290(2)/ 2.4641	2.176(5)/ 2.386	2.640(2)/ 2.828	2.638(8)	2.349(2)	2.509(6)
	4.996(2)/ 5.071	2.178(5)/ 2.386	2.668(2)/ 2.8281	2.497(8)		
N$_{\text{amido}}$−M−N$_{\text{amido}}$	101.08(8)	147.3(2)	103.41(8)	93.3(2)		
N$_{\text{amino}}$−M−N$_{\text{amino}}$		113.9(2)	160.98(7)	172.7(2)		

germylenes (**8** and **10**) and stannylenes (**12** and **14**), respectively. Attempts to prepare related homoleptic plumbylenes were undertaken, but all experiments reveal almost the same results: (i) the trimethylsilyl-substituted plumbylene **18** was the only isolated product to be soluble, independent of the molar ratio of the starting lithium salt and PbCl$_2$, and (ii) in all experiments with triphenylgermyl-substituted lithium amide and lead dichloride, the starting triphenylgermyl-substituted aniline **5** was isolated after the reaction. The reaction of 2 mol equiv of [bis(trimethylsilyl)amido]lead(II) with substituted anilines **3** and **5** did not lead to the desired products under standard conditions (overnight stirring at room temperature).

The typical pattern of ^{1}H NMR spectra is one set of signals, except for the diastereotopic benzylic protons, which give rise to AX spin systems for all prepared homoleptic tetrylenes (~400 Hz for germylenes and ~550 Hz for stannylenes). The ^{119}Sn chemical shift in C$_6$D$_6$ at room temperature is −115.6 and −124.5 ppm for **12** and **14**, respectively. Nearly the same values (−118.0 and −128.6 ppm) were found in THF-d_8, clearly indicating coordination hampering of THF units toward the tin atom.

Single crystals of homoleptic germylene **8** and stannylenes **12** and **14** suitable for structure determination by X-ray methods were obtained.

In the case of **8**, single crystals of two different polymorphs, **8a** and **8b**, were found to be suitable for X-ray diffraction: **8a** crystallized from toluene and **8b** from diethyl ether.

The germanium atom in the first polymorph, **8a** (Figure 4), reveals the coordination geometry of the trigonal pyramid with two amido nitrogen atoms and a single of the chelating amino nitrogen atoms in the basement of the pyramid. With the lone pair at its top, the electron domain structure of **8a** is that of a strongly distorted tetrahedron. The second amino group is even expelled from the primary coordination sphere of the germanium atom. On the other hand, the germanium atom is four-coordinated in **8b** (Figure 5) with pseudo-trigonal-bipyramidal structure deviation from the ideal tetrahedral geometry (Ψ-trigonal bipyramid), where the amido nitrogen atoms (N1 and N3) occupy axial positions and the coordinating amino groups (N2 and N4) and the lone electron pair equatorial positions. This coordination geometry is reflected in a strongly reduced N1−Ge1−N3 angle of 147.3(2)° compared to the axial bond angle of 180° of an ideal trigonal bipyramid and a N2−Ge1−N4 angle of 113.9(2)° compared to the ideal 120° equatorial bond.

The Ge−N bonds are significantly shorter for the amido nitrogen atoms, 1.979(6) and 1.975(6) Å, than for the amino ones, 2.176(5) and 2.178(5) Å. This is confirmed by DFT calculations. Thus, Table 2 reveals that the calculated Ge−amido N bond distance (2.235 Å) is again shorter than the Ge−amino N one (2.386 Å). Nevertheless, the latter bond length indicates a strong coordination of the amino group to the germanium atom and, hence, a high stabilization of the germylene **8b**.

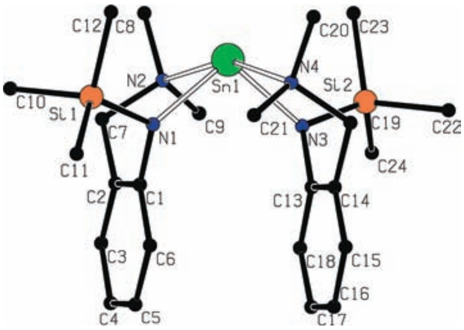


Figure 6. Molecular structure of **12** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn1−N1 2.131(2), Sn1−N3 2.134(2), Sn1−N2 2.640(2), Sn1−N4 2.668(2), Si1−N1 1.723(2); N1−Sn1−N2 80.39(9), N1−Sn1−N3 103.41(8), N2−Sn1−N4 160.98(7), Si1−N1−Sn1 121.74(11), C1−C2−C7−N2 68.2(5).

The bonds between the germanium atom and amido nitrogen atoms are shorter by ca. 0.06 Å (DFT calculated: 0.28 Å) than those in the first polymorph **8a**, but the amino N−Ge distance increased by ca. 0.12 Å (DFT calculated: 0.08 Å). The calculated energy difference between **8a** and **8b** is 24.4 kcal/mol, with compound **8a** being the low-energy isomer, which is in agreement with the shorter (calculated) Ge−N amido distances in **8a** (see values in Table 2).

The coordination polyhedra around the tin atoms in trimethylsilyl- (**12**) and triphenylgermyl-substituted (**14**) homoleptic stannylenes (Figures 6 and 7) are distorted Ψ-trigonal bipyramids similar to that of the germylene **8b**. The main difference between these structures is that in stannylenes the amido nitrogen atoms occupy the equatorial positions, together with the lone electron pair. The weakly coordinated amino groups are located in the axial positions. The amino N−Sn−N interatomic angles are 160.98(7) and 172.7(2)° (for **12** and **14**); in germylene **8b**, these atoms are in pseudoequatorial positions (Scheme 2).

The bond distances between the amido nitrogen atoms and the tin atoms are slightly larger by 0.01−0.02 Å in **14** than in **12** and by ca. 0.04 Å compared to, for example, bis[*N*-(trimethylsilyl)-*N*-(2,6-diisopropylphenyl)amido]tin(II)[29] [2.095(3)Å]. The calculated Sn−amido N distances of stannylene **12** (Table 2) are in very good agreement with the experimental values. The intramolecularly coordinating amino groups in **12** and **14** display only quite weak coordination to the tin atom compared to the similar germylene **8b**. On the other hand, the Sn−N distances are similar to the corresponding distances in the C,N-chelated stannylene.[11b] Structures of **12** and **14** also differ in the orientation of the ligands,

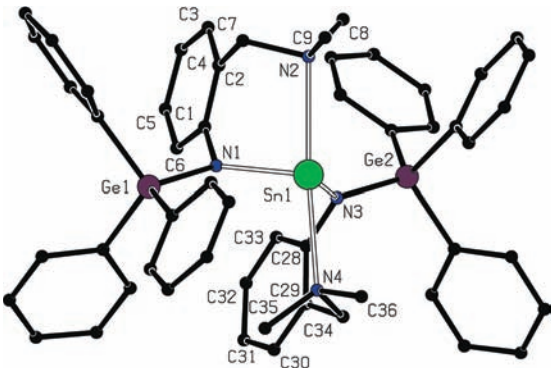
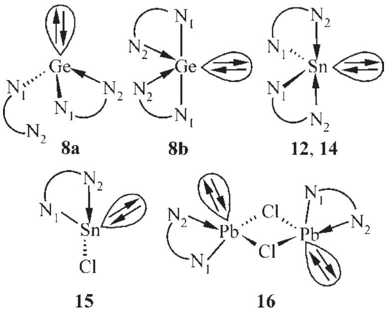


Figure 7. Molecular structure of $\mathbf{14} \cdot 3.5C_6D_{12}$ in a PLUTON representation. Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn1−N1 2.151(6), Sn1−N3 2.145(6), Sn1−N2 2.638(8), Sn1−N4 2.597(8), Ge1−N1 1.836(6); N1−Sn1−N3 93.3(2), N2−Sn1−N4 172.7(2), N1−Sn1−N2 83.8(2), N1−Sn1−N4 101.8(2), Ge1−N1−Sn1 128.6(3), C1−C2−C7−N2 77.2(8).

Scheme 2. Structural Differences within the Group of Compounds Studied[a]



[a] An elliptical arc means a ligand, N_1 an amido nitrogen atom, and N_2 an amino nitrogen atom.

with **12** displaying a π−π-stacking interaction between the aromatic rings. The aromatic rings of the ligand in **14** are also coplanar, but one of them is twisted away, as a likely consequence of sterical strain.

Heteroleptic Tetrylenes. Heteroleptic germylenes (**9** and **11**), stannylenes (**13** and **15**), and plumbylene (**18**) were prepared by a method similar to that of the homoleptic analogues using the molar ratio of reactants 1:1.

The resonance patterns in the ^{1}H NMR spectra of all germylenes and stannylenes are quite similar to those of the homoleptic tetrylenes, with the AX (or AB) spin pattern characteristic for the diastereotopic benzylic protons with separations of ∼300 Hz in all spectra except the case of the triphenylgermyl-substituted germylene **11** with a strongly coupled AB system and a separation of only 75 Hz.

In the ^{119}Sn NMR spectra of stannylenes **13** and **15**, the chemical shifts of −51.2 and −85.8 ppm were found in C_6D_6 at room temperature. Similar values of −64.6 and −89.7 ppm were detected in THF-d_8, revealing further that these species are monomeric with no additional coordination in solutions of both coordinating and noncoordinating solvents.

The ^{207}Pb chemical shift in the NMR spectrum of **18** is 1816 ppm, which corresponds to plumbylenes with a coordination number at the lead atom higher than 2.[30] For comparison, the ^{207}Pb chemical shift of the C,N-chelated plumbylene $[2\text{-}(Me_2NCH_2)C_6H_4]_2Pb$,[31] with the coordination geometry of Ψ-trigonal bipyramid at 2624 ppm.

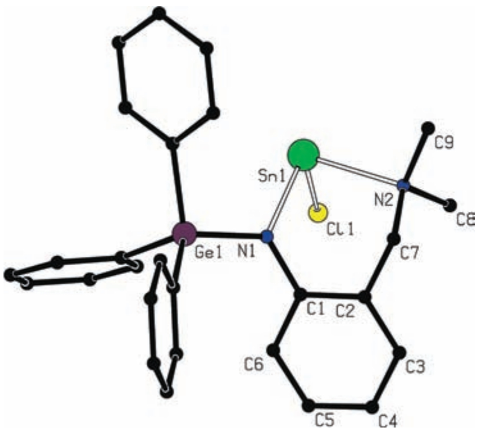


Figure 8. Molecular structure of **15** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn1−N1 2.107(2), Sn1−Cl1 2.4642(8), Sn1−N2 2.349(2), Ge1−N1 1.835(2); N1−Sn1−N2 86.71(9), N1−Sn1−Cl1 92.89(7), Ge1−N1−Sn1 118.29(12), C1−C2−C7−N2 71.1(4), Sn1···Cl1a 4.053(2).

The structure determination of the triphenylgermyl-substituted heteroleptic stannylene **15** by X-ray diffraction reveals its monomeric structure in the crystalline state (Figure 8). Thus, the chlorine atom of the adjacent molecule is too remote from the primary coordination sphere of the tin central atom [4.053(2)Å] to consider a dimeric structure. The monomeric nature of **15** is further reflected by the short bond distance Sn1−Cl1 of 2.4642(8) Å, shorter by about 0.1 Å than that in typical dimeric amides like, for example, $[\{Sn(N(C_6H_3\mathit{i}Pr_2\text{-}2,6)(SiMe_3))(\mu\text{-}Cl)\}_2]$[9a] having no extra coordination. Similar monomeric stannylenes containing bidentate ligands were described in the literature[14b−e,f,34] for β-diketiminates, amidinates, guanidinates, or bidentate amides. The nearly pyramidal configuration of the tin atom consists of the chlorine atom, the amino nitrogen atom, which is much more strongly coordinated [2.349(2)Å] than that in the homoleptic species **12** and **14**, and the amido nitrogen atom, with almost the same Sn−N distance as that in **12** or **14**.

The structure of **16** is dimeric, with the lead atoms being connected by nonsymmetrical chlorine bridges (Figure 9), similar to that in three lead amidinates and guanidinates[33] and pyridyl-substituted[34] ones; on the other hand, the β-diketiminate-substituted plumbylene is virtually monomeric.[12g] The lead atom in **16** is virtually five-coordinated with the coordination geometry of a Ψ-trigonal bipyramid, in which the trimethylsilyl-substituted amido nitrogen and one of the chlorine atoms occupy, together with the lone electron pair, the three equatorial positions. The adjacent chlorine and nitrogen atoms from the coordinated amino group are located in the axial positions. The amido group N1−Pb1 bond distance of 2.221(6) Å (DFT calculated: 2.194 Å) is comparable to the corresponding bond distance in another trimethylsilyl-substituted amide, $[(2,6\text{-}{}^iPr_2C_6H_3)N(SiMe_3)]_2Pb$ [2.204(3) Å].[31] The Pb1−N2 atom bond distance of 2.509(6) Å (DFT calculated: 2.626 Å) is shorter than that in $[2\text{-}(Me_2NCH_2)C_6H_4]_2Pb$,[31] ca. 2.7 Å. The strong contrast between the Pb−Cl contact distances, 2.620(2) Å (DFT calculated: 2.647 Å) for the Pb1−Cl1 distance and 3.167(2) Å

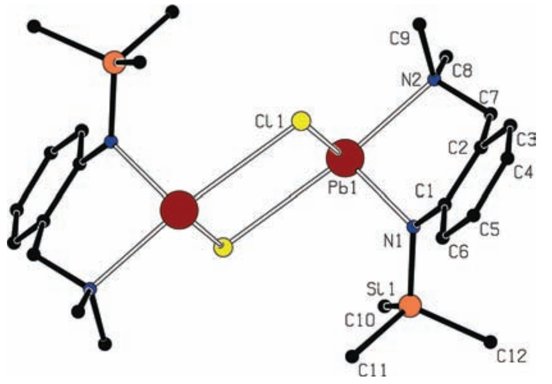


Figure 9. Molecular structure of **16** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Pb1−N1 2.221(6), Pb1−Cl1 2.620(2), Pb1−Cl1a 3.167(2), Pb1−N2 2.509(6), N1−C1 1.415(8), Si1−N1 1.718(6); N1−Pb1−N2 84.11(19), Pb1−Cl1−Pb1a 99.34(6), N2−Pb1−Cl1a 168.96(15), N1−Pb1−Cl1 92.82(16), Si1−N1−Pb1 119.1(3), C1−C2−C7−N2 74.8(8).

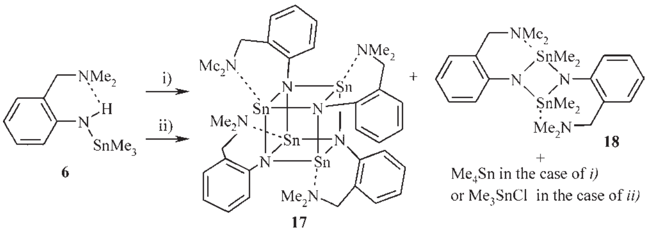
(theory: 3.205 Å) for the Pb1−Cl1a distance, is comparable to the findings of Junk et al.[33] and could be explained by the sterical strain induced by the ligand. A direct comparison of the heteroleptic stannylene **15** and plumbylene **16** reveals mainly structural similarities at the level of the M−Cl and M−amido N bond distances, the higher values of which in **16** are caused by either the higher covalent radius of the lead atom or the bridging nature of the chlorine atoms. The axial angle N2−Pb1−Cl1a of 168.96(15)° is close to the 180° ideal value, in spite of the equatorial lone-pair repulsion (Scheme 2).

The possible monomer−dimer equilibrium of plumbylene **16** was investigated by DFT computations. The complexation or dimerization energy of two monomer molecules amounts to −11.6 kcal/mol, indicating a stabilizing interaction. The Gibbs free energy difference ΔG is found to be 0.09 kcal/mol. The calculated equilibrium constant for this monomer−dimer equilibrium, estimated using Boltzmann's statistical thermodynamics, is 0.61. More details are given in the Supporting Information.

Quest for a Stannyl-Substituted Amido Stannylene. Because of the general interest in compounds containing two metals of the same element, but with different oxidation states in the same molecule, attempts to prepare trimethyltin- or tributyltin-substituted stannylenes were undertaken. A plethora of synthetic attempts, including the inorganic salt elimination as in the preparation of stannylenes **12**−**15** discussed above, invariably resulted in inseparable mixtures of unknown composition, similar to previously reported attempts using tributyltin- or triphenyltin-substituted 2,6-diisopropylaniline.[35] On the other hand, reactions of **6** with bis[bis(trimethylsilyl)amido]tin(II) or bis{bis[bis(trimethylsilyl)amido]tin(II) chloride} gave the unexpected heterocubane structure (Scheme 2), together with [2-(Me_2NCH_2)C_6H_4N]$_2$(μ^2-$SnMe_2$)$_2$ and Me_4Sn, in the case of reaction with [bis(trimethylsilyl)amido]tin(II), or Me_3SnCl, in the second reaction, as the main products. All compounds generated were identified by ^{1}H and ^{119}Sn NMR, and the structures of **17** and **18** were determined by X-ray diffraction (Scheme 3).

The heterocubane **17** is, in fact, the tetramer of the tin imide of composition [2-(Me_2NCH_2)C_6H_4N]Sn (Figure 9). Its crystal structure was determined by X-ray diffraction as well as by ^{13}C and ^{119}Sn CP/MAS NMR spectroscopy. The chemical shift values of the signals in the ^{13}C CP MAS NMR spectrum are found in the expected chemical shift ranges (see the Experimental Section); two distinct signals were found for the diastereotopic methyl carbon atoms. The heterocubane geometry (Figure 10) reveals a strongly distorted cube structure, with the distances of faces' centroids being 2.143(2) Å, while the deviation of the fourth atom of each face defined by three other atoms is about 0.47 Å. The cube is composed of four tin atoms and four imido nitrogen atoms with distances of 3.417(3) Å (DFT calculated: 3.488 Å) between the tin atoms of each face. The coordination sphere configuration of each tin atom is that of a strongly distorted Ψ-trigonal bipyramid with the lone electron pair and two imido nitrogen atoms in equatorial positions, while a third imido nitrogen atom and the coordinated amino group are located in axial positions. The contact distance between the amino group nitrogen and the tin atoms [2.527(3) Å)] (DFT calculated: 2.752 Å) lies in the range defined by the corresponding distance in the heteroleptic [2.349(2) Å in **15**] and the homoleptic stannylene [2.640(2) and 2.668(2) for **12** and 2.638(8) Å for **14**]. The bond distances between each tin atom and the imido nitrogen atoms are similar for both equatorial substituents [2.162(2) and 2.179(3) Å] (DFT calculated: 2.227 and 2.254 Å) but are quite different for the axial imido nitrogen

Scheme 3. Preparation of Compounds 17 and 18[a]



[a] Reagents and conditions: (i) bis[bis(trimethylsilyl)amido]tin(II), in Et_2O, at RT; (ii) bis[bis(trimethylsilyl)amidotin(II) chloride], in Et_2O, at RT.

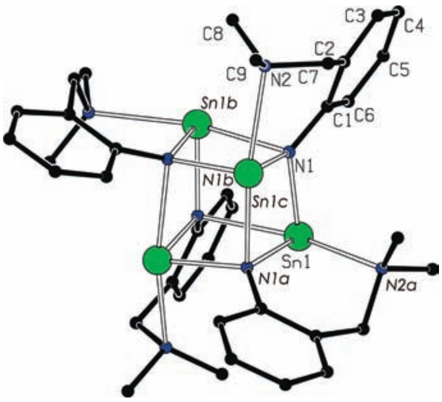


Figure 10. Molecular structure of **17** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn1−N1a 2.162(2), Sn1−N1 2.179(3), Sn1−N1b 2.466(3), Sn1−N2a 2.527(3); N1−Sn1−N1b 83.42(12), N1a−Sn1−N1b 76.93(11), N1−Sn1−N1a 82.50(12), N1a−Sn1−N2a 82.35(11), N1−Sn1−N2a 93.95(12), N1b−Sn1−N2a 159.24(10), Sn1−N1−Sn1c 103.82(12), Sn1b−N1−Sn1c 94.94(11), Sn1−N1−Sn1b 96.28(11).

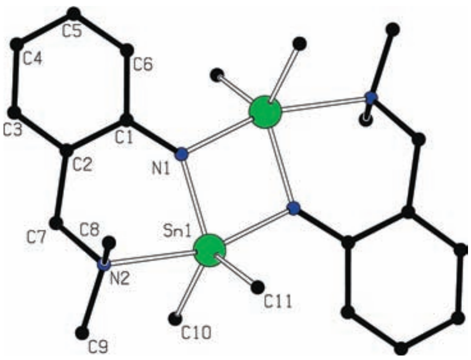


Figure 11. Molecular structure of **18** in a PLUTON representation. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn1−N1 2.0428(15), Sn1−N1a 2.1339(15), Sn1−C10 2.1366(19), Sn1−C11 2.1393(19), Sn1−N2 2.4921(15), Sn1−Sn1a 3.2255(2); N1−Sn1−N1a 78.91(6), N1−Sn1−N2 84.39(5), Sn1−N1−Sn1a 101.09(6), C10−Sn1−C11 118.70(8), C10−Sn1−N1 121.52(7), N1−Sn1−C11 121.52(7), N1a−Sn1−N2 162.79(5), C1−C2−C7−N2 58.7(2).

atom [2.466(3) Å] (DFT calculated: 2.431 Å). The N−Sn−N angles between the core atoms of the distorted cube are smaller than the angles of the ideal cube, and, accordingly, the Sn−N−Sn angles are larger, with an extreme value for the Sn1−N1−Sn1c angle of 103.82(12)° (DFT calculated: 101.6°). The angles between the imido nitrogen atom, the tin one, and the coordinated amino nitrogen one in axial positions of the distorted Ψ-trigonal bipyramid of each tin atom differ significantly from the ideal value of 180° [for example, N1b−Sn1−N2a 159.24(10)°].

A DFT optimization of the heterocubane **17** geometry has been performed in order to assess the structure distortion. Virtually identical structures were found in silico and in the crystalline state. The coordinates are given in the Supporting Information.

Compound **18** is rather unique, with two similar structures having been obtained by Roesky and Schuh for bis(μ^2-2,6-diisopropylamidophenyl)tetramethylditin(IV) and 1,1,2,3,3,4-hexa-*tert*-butyl-1,3-distanna-2,4-diazacyclobutane.[36] The formation of this compound through the metathetical exchange mechanism from a trimethylstannyl-substituted amide is obviously taking place. The ^{1}H NMR spectrum of **18** in THF-d_8 reveals a pair of broad resonances for the NCH_2 moiety and single, likewise broad resonances for the NCH_3 as well as the $Sn(CH_3)_2$ groups. By contrast, the aromatic resonances are sharp and display the usual homonuclear coupling splittings. In the ^{119}Sn NMR spectrum, a broad signal was found at −123.0 ppm, indicating that in solution the tin atom is pentacoordinated, similar to **17** or [2-[(*N*,*N*-dimethylamino)methyl]phenyl]dimethyltin(IV) chloride and its hydrolysis products.[37]

The structure of **18** (Figure 11) is probably the result of dimerization of the dimethyltin(IV) imide, 2-(Me_2NCH_2)-$C_6H_4N{=}SnMe_2$, displaying a nearly perfect planar arrangement of all heteroatoms and also the carbon atoms C1 and C1a. The core four-membered Sn_2N_2 ring reveals rather different Sn−N distances, with Sn1−N1 being 2.0428(15) Å and Sn1−N1a being 2.1339(15) Å, while the smaller one is comparable to those found in $[(t\text{-}Bu_2Sn)\text{-}\mu^2\text{-}N(t\text{-}Bu)_2]_2$ (2.059 and 2.055 Å) and $[(t\text{-}Bu_2Sn)\text{-}\mu^2\text{-}(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$ (2.047 and 2.059 Å). The longer Sn1−N1a bond is caused by the trans effect of the rather strong intramolecular coordination of the amino group [Sn1−N2 2.4921(15) Å]. The tin coordination spheres display distorted trigonal-bipyramidal configurations with almost perfect equatorial bond angles. Also, the axial angle [162.79(5)°] is closer to the ideal value than that in the cubane **17**. Interestingly, the N1−Sn1−N1a angle 78.91(6)° is much smaller than the Sn1−N1−Sn1a angle [101.09(6)°].

■ CONCLUSIONS

The group 14 metal anilinates containing groups with a broad variety of steric strain were prepared and characterized in solution and in the crystalline state. Some of these compounds can be further deprotonated and substituted by low-valent group 14 organometallic substituents. All germylenes and stannylenes are monomeric in solutions of coordinating and noncoordinating solvents as well as in the crystalline state. Main structural differences were observed for homoleptic germylenes and stannylene, where three motifs were found (see Scheme 2). The amido nitrogen atoms can be present in both the equatorial and axial positions of the Ψ-trigonal bipyramid. The distances between metal and amino nitrogen atoms, delimiting the intramolecular interaction strength responsible for stabilization of compounds, are found in a large range of values from the very strong ones, such as, for example, in the case of monomeric heteroleptic stannylene **15**, to uncoordinated ones, such as those for one of the amino nitrogen atoms in **8a**. For plumbylenes, only the heteroleptic compound containing the smallest ligand, the trimethylsilyl-substituted one, could be obtained and was characterized as a dimer in the crystalline state. Attempts to prepare stannylenes substituted by tin(IV) moieties afforded a heterocubane and dimethyltin(IV) derivative, both containing an imido ligand.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data in CIF format, extensive figures of compounds **3**−**16** (Figures S1−S12), experimental details as well as discussion, Tables S1−S10 with all of the crystallographically related data and DFT optimizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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