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Stable divalent heteroleptic species ArO(X)M [Ar = 2,4,6-Tris(dimethylaminomethyl)phenyl-, M = Ge, Sn, Pb]

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Abstract

The new stable divalent germanium, tin and lead heteroleptic species ArO(X)M [Ar = 2,4,6-[$Me_2NCH_2]_3C_6H_2$; X = Cl, M = Ge (**1**), Sn (**2**); X = N($SiMe_3)_2$, M = Ge (**3**), Sn (**4**), Pb (**5**)] were obtained by ligand redistribution reactions between $(ArO)_2M$ and MCl_2 or $[(Me_3Si)_2N]_2M$, respectively. The coordination behaviour of the *o*-dimethylamino side chains of the ArO ligand was studied by NMR spectroscopy. **1**–**4** show the temperature dependence of their NMR spectra. **1** and **2** exhibit a N···M···N dynamic 'flip-flop' coordination of the *o*-dimethylamino groups to the metal, while a rigid $N \rightarrow M \leftarrow N$ coordination of the two *o*-dimethylamino groups of the ArO ligand which can be lifted at higher temperatures (56°C for **3**, $\Delta G^{\neq} = 68.55$ kJ mol^{-1}) is observed for **3** and **4**. The chemistry of **1**–**5** is illustrated through their reactions with quinones. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Heteroleptic species; Germylenes; Stannylenes; Plumbylenes

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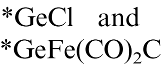
1. Introduction

Only a few heteroleptic germylenes and stannylenes have been characterized until now. In the germanium series, ethylchlorogermylene EtGeCl and phenylchlorogermylene PhGeCl were the first known representatives [1,2] of non-symmetrical divalent species. Subsequently, several RGeX (X = O, N-) [1–4] and $XGeN(R)SiMe_3$ [5] [R = 2,6 $Me_2C_6H_3$, 2,6-$i$$Pr_2C_6H_3$; X = Cl, Br] type compounds, and a few cyclic structures



$$-\overline{\text{GeX(C)}_n\text{X}'}$$

have been described [6]; recently the chlorosupermesitylgermylene Mes*GeCl and the supermesitylferrogermylenes Mes*$GeFe(CO)_2C_5R_5$ (R = H, Me; Mes* = 2,4,6-$t$$Bu_3C_6H_2$) were isolated in a monomeric state [7] while 2,6-$Mes_2C_6H_3$(Cl)Ge was obtained as a dimer in the solid state [8]. A series of semi-sandwich type heteroleptic germylenes has also been obtained from the germylene Me_5C_5GeCl, particularly a germylene with a dimethylamino-substituted cyclopentadienyl ligand $(Me_2NCH_2CH_2)Me_4C_5GeCl$ [9–11]. In the series of heteroleptic dialkylgermylenes, only the germylenes $(Me_3Si)_3CGeCH(SiMe_3)_2$ [12] and Tbt(Tip)Ge [Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl; Tip = 2,4,6-triisopropylphenyl] [13,14] have been isolated in the monomeric state at ambient temperature. In the tin series 2,6-$(Me_2NCH_2)_2C_6H_3$(Cl)Sn [15], several ArO(R_2N)Sn, $R_2N(R'_2N)$Sn, R''_2N(Cl)Sn and 2,6-$(Me_2N)_2C_6H_3$(X)Sn [X = Cl, N$(SiMe_3)_2$] type structures have been described principally by Lappert ([16–19]a). We have recently reported the syntheses and different aspects of the reactivity of stable divalent homoleptic species $(ArO)_2M$ with phenoxy ligands bearing, in the 2,4,6 positions, dimethylaminomethyl groups suitable for intramolecular coordination

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[$Ar = 2,4,6\text{-}(Me_2NCH_2)_3C_6H_2$] [20]. Following these previous studies, we report in this paper, the study of the new heteroleptic species ArO(X)M [X = Cl, M = Ge (**1**), Sn (**2**); $X = N(SiMe_3)_2$, M = Ge (**3**), Sn (**4**), Pb (**5**)] in which the Group 14 metal atom bears the chelating ArO ligand and has a prochiral structure.

2. Results and discussion

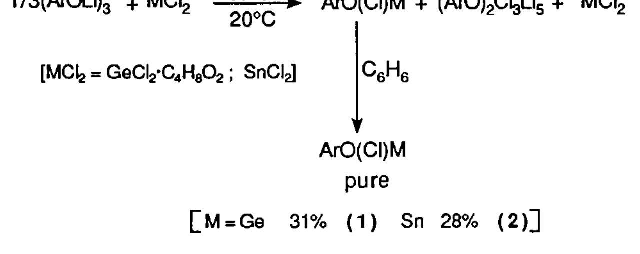
2.1. *Chloro[2,4,6-tris(dimethylaminomethyl)phenoxy]-germylene and stannylene ArO(Cl)M [M = Ge, Sn; Ar = 2,4,6-(Me₂NCH₂)₃C₆H₂]*

2.1.1. *Synthesis*

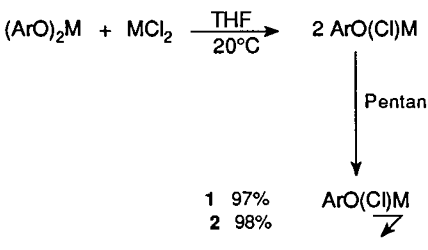
The classical method of alkoxylation of metals from 14 metal–halogen bonds was first considered for the synthesis of the divalent species ArO(Cl)M. The action in diethyl ether of one equivalent of lithium alkoxide [ArOLi] [20] on the divalent species MCl_2 leads to the expected heteroleptic species ArO(Cl)M, but in low yields. These reactions are not quantitative; as we have noticed during the synthesis attempts for the divalent species $(ArO)_2M$ [20], part of the ArOLi reacts with formed LiCl to give the cluster $(ArO)_2Cl_3Li_5$. At the end of these reactions, we only obtain insoluble derivatives in the diethyl ether; however, among all the compounds obtained, only the divalent species are soluble in benzene and thus can be extracted in a pure state (Scheme 1).

Numerous exchange reactions between compounds with M–Cl and M–O bonds having been reported, we investigated the redistribution reactions between the divalent metal chlorides MCl_2 and the divalent species $(ArO)_2M$ to obtain ArO(Cl)M structures. These reactions easily lead to **1** and **2** at ambient temperature with a quasi-quantitative yield (Scheme 2).

These divalent species **1**, **2** have also been obtained by redistribution between Ti–Cl and Ge–O bonds by reacting $(ArO)_2M$ with Cp_2TiCl_2. These reactions probably proceed by a radical mechanism since they are notably accelerated by UV irradiation.



Scheme 1.



Scheme 2.

$$(ArO)_2M + Cp_2TiCl_2 \xrightarrow[\substack{20°C\ \ 12\,h\ \ 70\% \\ h\nu\ \ 1\,h\ \ 96\%}]{} ArO(Cl)M + Cp_2Ti(Cl)(OAr) \qquad (1)$$

It is noteworthy that all ArO(Cl)Pb synthesis attempts failed, the reactions resulting in a mixture of derivatives insoluble in common organic solvents.

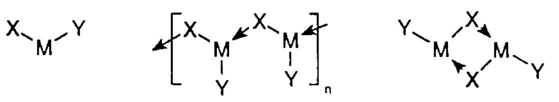
2.1.2. *Physicochemical and structural study*

The heteroleptic species **1** and **2** are air- and moisture-sensitive but particularly thermally stable and they can subjected to temperatures of 120°C without symmetrization by redistribution. Cryoscopic mass determination showed that **1**, **2** are monomeric in benzene solution. Crystals suitable for X ray structural analysis could not be obtained. They were chemically and physicochemically characterized (^1H-, ^{13}C-, ^{119}Sn-NMR and mass spectroscopy) (Table 1).

The ^1H- and ^{13}C-NMR spectra of **1** and **2**, at 25°C, reveal that the four CH_3 groups of the CH_2NMe_2 ligands in the *ortho* position on the benzenic ring are magnetically equivalent (singlet); a singlet also is observed as the signal for the corresponding CH_2N groups.

This equivalence can be explained by:

1. the non-coordination of the *o*-NMe_2 groups to the Group 14 atom; the divalent species ArO(Cl)M being monomeric, dimeric or oligomeric by intermolecular association without intervention of the NMe_2 groups.



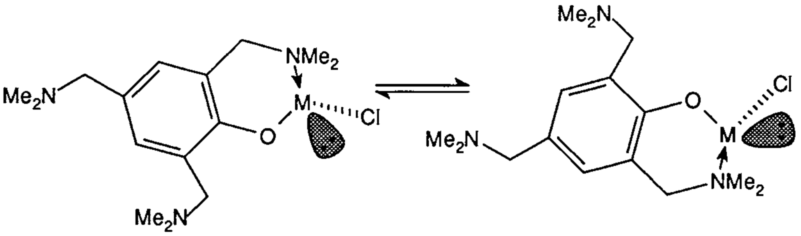
X = Cl, Y = OAr or X = OAr, Y = Cl

2. dynamic N···M···N coordination, with the NMe_2 groups moving quickly (on the ^1H-NMR time scale) from one position to the other as shown in Scheme 3.

The molecular modeling (Insight II, Discover 95, esff forcefield) shows that the limiting forms correspond to the molecular minimun total energy estimated to be 46.4 kJ mol^{-1}.

Table 1
NMR data for **1** and **2**

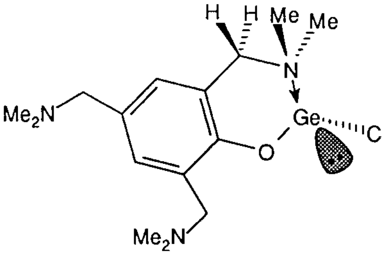
NMR (C_6D_6) (δ ppm)	^1H		^{13}C		^{119}Sn
	1	**2**	**1**	**2**	**2**
p-NMe_2	2.22	2.24	44.61	44.53	−435
o-NMe_2	2.39	2.43	45.73	45.21	
p-CH_2N	3.27	3.48	65.01	64.67	
o-CH2N	3.66	3.79	60.14	59.92	
C_6H_2	7.06	7.08	126.1; 127.9 130.6; 158.2	125.9; 127.2 157.8; 130.3	



Scheme 3.

Such 'flip-flop' coordination modes have already been reported for di- and tetravalent tin and silicon derivatives [19,21–23] and postulated for homoleptic germylenes [20].

The low temperature ^1H-NMR study of the germanium derivatives seems to confirm this latter hypothesis. At −75°C, the two methyl groups on one o-nitrogen atom are not equivalent. The spectrum of **1** exhibits three broadened singlet signals for the o-NMe_2 groups [$\delta = 2.37(6H)$; 2.55(3H); 2.77(3H)] and a poorly resolved system between $\delta = 3.3$ and 4.2 ppm for the corresponding o-CH_2N groups. This could be explained by a static conformation with one only o-NMe_2 group coordinated to the germanium atom.



The coalescence (a single broad signal $\delta = 2.52$ ppm) of the three o-NMe_2 signals occurs at −56°C; a large broadening for the o-CH_2N methylenic protons is observed at this temperature. Based on this hypothesis, we can evaluate the activation energy of the N···Ge coordination-decoordination process to be 44.6 kJ mol^{-1} at this temperature.

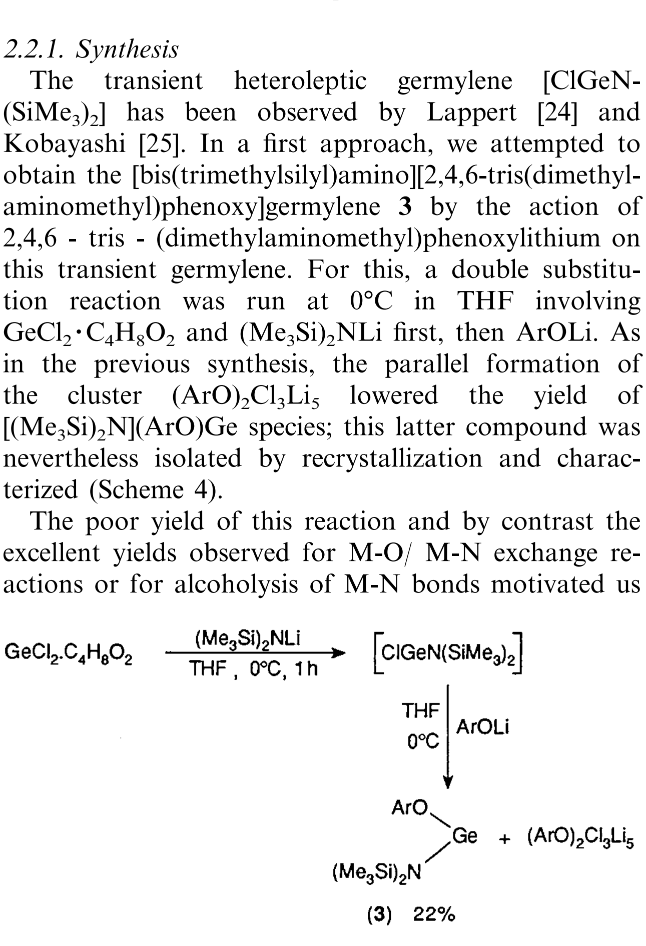
We cannot exclude the possibility that the non equivalence of the two types of o-NMe_2 observed at −75°C may also result from coexistence at this low temperature of conformers resulting from intermolecular associations.

2.2. *[Bis(trimethylsilyl)amino][2,4,6-tris(dimethylaminomethyl)phenoxy]germylene, stannylene and -plumbylene [$(Me_3Si)_2N$](ArO)M [M = Ge, Sn, Pb; Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$]*

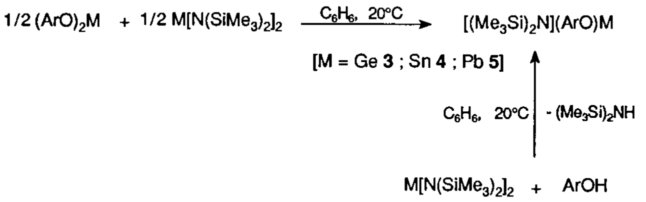
2.2.1. *Synthesis*

The transient heteroleptic germylene [$ClGeN(SiMe_3)_2$] has been observed by Lappert [24] and Kobayashi [25]. In a first approach, we attempted to obtain the [bis(trimethylsilyl)amino][2,4,6-tris(dimethylaminomethyl)phenoxy]germylene **3** by the action of 2,4,6 - tris - (dimethylaminomethyl)phenoxylithium on this transient germylene. For this, a double substitution reaction was run at 0°C in THF involving $GeCl_2 \cdot C_4H_8O_2$ and $(Me_3Si)_2NLi$ first, then ArOLi. As in the previous synthesis, the parallel formation of the cluster $(ArO)_2Cl_3Li_5$ lowered the yield of [$(Me_3Si)_2N$](ArO)Ge species; this latter compound was nevertheless isolated by recrystallization and characterized (Scheme 4).

The poor yield of this reaction and by contrast the excellent yields observed for M-O/ M-N exchange reactions or for alcoholysis of M-N bonds motivated us



Scheme 4.



Scheme 5.

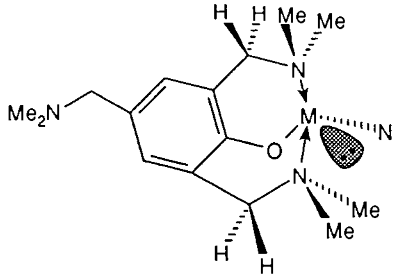
to apply these latter methods to the corresponding bis-(dimethylsilylamino) substituted divalent species (Scheme 5).

These reactions are quasi-quantitative and compounds **3**, **4** and **5** were isolated by crystallization in pentane.

2.2.2. Structural and physicochemical study

The air-sensitive mixed derivatives **3–5**, which are monomeric in benzene solution (cryoscopic mass determination), were characterized by ^{1}H-, ^{13}C-, ^{119}Sn-NMR and spectroscopic values are given in Table 2. Crystals suitable for X ray structural analysis could not be obtained.

The ^{1}H-NMR spectra at ambient temperature of compounds **3–5** exhibit, in the three cases, an AX system $J_{HH} = 12$ Hz, for the methylenic protons of the two groups o-CH_2NMe_2 while two singlets are observed for the methylic protons o-NMe_2. The non-equivalence of the methylenic and the methylic protons, respectively can be explained by static coordination of the two nitrogen atoms of the two o-NMe_2 groups to the Group 14 atom.



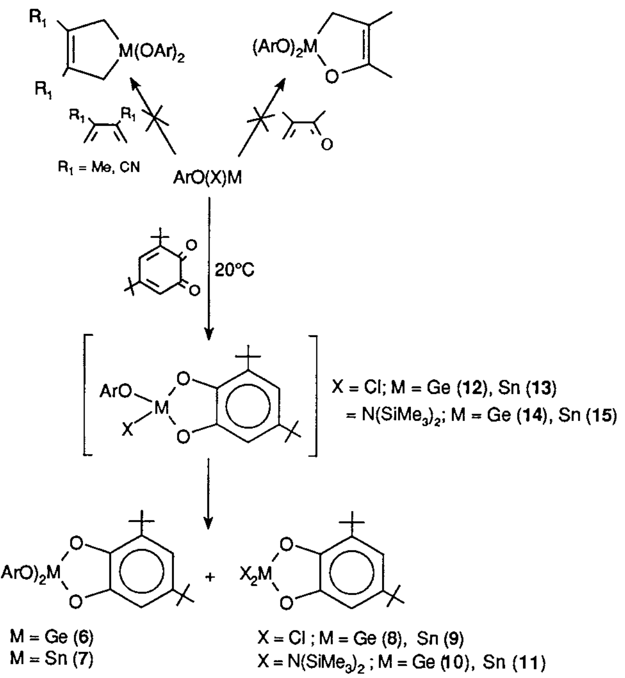
We investigated the tin derivative using variable temperature ^{1}H-NMR spectroscopy. At 65°C, the ^{1}H-NMR spectrum of **4** exhibits a sharp singlet ($\delta = 2.06$ ppm) for the methylic protons of the o-CH_2NMe_2 groups along with a sharp singlet ($\delta = 3.60$ ppm) for the corresponding methylenic protons. This indicates, at this temperature, the non-coordination of the o-NMe_2 groups ($\delta = 2.05$ ppm) or their dynamic coordination to the metal atom. Coalescence of the o-NMe_2 groups is observed at 56°C, which permits us to evaluate the activation energy $\Delta G^{\neq}$ of the 'opening–closing' process of the coordination bond N···Sn to be 68.55 kJ mol^{-1}.

2.3. Chemical reactivity of the divalent species **1–5**

The chemical properties of these heteroleptic divalent species are quite similar to those of the corresponding homoleptic species. All attempts of reaction with diene and carbonyl conjugated compounds failed. Thus the presence of the dimethylaminomethyl groups on the benzenic cycle of these divalent species clearly differentiates them from free divalent species and this observed loss of reactivity towards conjugated dienes or heterodienes supports the idea of the N···M···N intramolecular coordination. With 1,3-quinones we observed easy heterocyclisation reactions in very mild experimental conditions. These reactions are very similar to those ones already observed from corresponding homoleptic divalent Group 14 species [20] and the ones reported by Kobayashi [26–28], and probably also proceed by single electron transfer. However, they only allow isolation of the 2-metalla-1,3-dioxolanes **6–11** that are formally the adducts of the $(ArO)_2M$ or X_2M homoleptic divalent species with quinones. Some of these metalladioxolanes have been previously described but essentially as the adducts with bidendate neutral donors [29–32]. The expected ArO(X)M heteroleptic divalent species-quinones adducts (**12–15**) are transient and were only characterized by mass spectroscopy and ^{119}Sn-NMR analysis for the tin species (Scheme 6).

Table 2
NMR data for **3** and **4**

NMR (C_6D_6) (δ, ppm)	^{1}H		^{13}C		^{119}Sn
	3	**4**	**3**	**4**	**4**
$[Me_3Si]_2N$	0.43	0.41	6.31	5.78	−52
p-NMe_2	2.21	2.16	44.55	43.64	
o-NMe_2	2.06; 2.07	2.01; 2.02	45.51	44.53	
p-CH_2N	3.38	3.34	64.41	63.47	
o-CH_2N	2.80 (d, 2H)	2.78 (d, 2H)	59.69	59.54	
	4.00 (d, 2H)	3.94 (d, 2H)			
C_6H_2	7.16	7.16	125.6	126.7	
			127.5	127.5	
			130.2	129.8	
			157.4	158.9	



Scheme 6.

3. Experimental section

All the compounds described are sensitive to oxygen and moisture. All manipulations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk and high vacuum-line techniques. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium benzophenone before use. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are given in ppm (δ) relative to Me_4Si) or on a AC 200 MHz spectrometer (VT NMR studies), ^{13}C spectra on a AC 200 MHz spectrometer; the multiplicity of the ^{13}C-NMR signals was determined by the APT technique and quoted as: (+) for CH_3 or CH, (−) for CH_2 and (C_{quat}) for quaternary carbon atoms. ^{1}H-decoupled ^{119}Sn-NMR spectra were recorded on a Bruker AC 200 or 400 MHz (chemical shifts are reported in ppm (δ) relative to external Me_4Sn as reference). Mass spectra were recorded on a Nermag R10-10H or a Hewlett Packard 5989 instrument operating in the electron impact mode at 70 eV and 30 eV, and samples were contained in glass capillaires under argon or in the chemical ionization mode (CH_4). IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrophotometer. Irradiation was carried out at 25°C by using a low-pressure mercury immersion lamp in a quartz tube. Melting points were taken on a hot-plate microscope apparatus Leitz Biomed. Elemental analyses (C, H, N) were performed at the Laboratory at the Ecole Nationale Supérieure de Chimie de Toulouse.

*3.1. Chloro[2,4,6-tris(dimethylaminomethyl)phenoxy]-germanium(II) ArO(Cl)Ge (**1**)*

To a solution of 2,4,6-tris(dimethylaminomethyl) phenoxylithium (0.12 g, 0.44 mmol) in 20 ml of diethyl ether was added a suspension of $GeCl_2 \cdot C_4H_8O_2$ (0.1 g, 0.44 mmol) in diethyl ether (20 ml). The resulting reaction mixture was stirred at r.t. for 16 h. The volatile materials were then removed under reduced pressure and the residue extracted with 50 ml of benzene. The solution was filtered to remove the white lithium chloride precipitate and 50 ml of pentane was added to the filtrate. Filtration, followed by drying in vacuo gave **1** (0.04 g, 31%).

1: M.p. 123–125°C. ^{1}H-NMR (C_6D_6): 2.22 (s, 6H, NMe), 2.39 (s, 12H, NMe), 3.27 (s, 2H, CH_2), 3.66 (s, 4H, CH_2), 7.06 (s, 2H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.61(+), 45.73(+), 60.14 (−), 65.01 (−), 126.1 (C_{quat}), 127.9(+), 130.6 (C_{quat}), 158.2 (C_{quat}). MS: $m/z = 373$ $[M]^+$. Anal. Found: C, 48.31; H, 6.92; N, 11.14. $C_{15}H_{26}N_3OGeCl$. Calc.: C, 48.37; H, 6.99; N, 11.29.

A solution of $(ArO)_2Ge$ (0.89 g, 1.4 mmol) in 30 ml of THF was added dropwise to a stirred solution of $GeCl_2 \cdot C_4H_8O_2$ (0.35 g, 1.4 mmol) in 30 ml of THF. The solution was stirred at r.t. for 12 h. After addition of pentane (ca. 60 ml) filtration afforded **1** (0.16 g, 70%).

A mixture of $(ArO)_2Ge$ (0.39 g, 0.65 mmol) and Cp_2TiCl_2 (0.162 g, 0.65 mmol) in 60 ml of THF was irradiated for 1 h in a quartz tube. After which time 60 ml of pentane was added to the solution, filtration afforded **1** (0.16 g, 96%).

*3.2. Chloro[2,4,6-tris(dimethylaminomethyl)phenoxy]-tin(II) ArO(Cl)Sn (**2**)*

2,4,6-Tris(dimethylaminomethyl)phenoxylithium (0.16 g, 0.59 mmol) in diethyl ether (20 ml) was added to a stirred suspension of anhydrous $SnCl_2$ (0.11 g, 0.59 mmol) in 20 ml of diethyl ether. The mixture was stirred at r.t. for 16 h, then the solvent was removed in vacuo. The residue was extracted with 60 ml of benzene and the white lithium chloride precipitate was filtered off. After removal of the solvent by pumping off in vacuo, **2** was isolated as a white solid (0.07 g, 28%).

2: M.p. 120–122°C. ^{119}Sn{^{1}H}-NMR (C_6D_6): −435.2. ^{1}H-NMR (C_6D_6): 2.24 (s, 6H, NMe), 2.43 (s, 12H, NMe), 3.48 (s, 2H, CH_2), 3.79 (s, 4H, CH_2), 7.08 (s, 2H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.53 (+), 45.21 (+), 59.92 (−), 64.67 (−), 125.97(C_{quat}), 127.2 (+), 130.3 (C_{quat}), 157.86 (C_{quat}). MS: $m/z = 419[M]^+$. Anal. Found: C, 42.98; H, 6.12; N, 9.87. $C_{15}H_{26}N_3OSnCl$. Calc.: C, 43.04; H, 6.22; N, 10.04.

To a suspension of anhydrous $SnCl_2$ (0.14 g, 0.75 mmol) in 25 ml of THF was added a solution of

(ArO)$_2$Sn (0.49 g, 0.75 mmol) in 30 ml of THF. The mixture was stirred at r.t. for 20 h, then 70 ml of pentane was added. Filtration afforded **2** as a white powder (0.3 g, 96%).

A solution of (ArO)$_2$Sn (0.40 g, 0.62 mmol) in 25 ml of THF was added to Cp$_2$TiCl$_2$ (0.15 g, 0.62 mmol) in 25 ml of THF. After stirring 20 h at r.t. 60 ml of pentane was added to the raction mixture. Filtration gave **2** (0.24 g, 94%).

*3.3. [Bis(trimethylsilyl)amino][2,4,6-tris(dimethylaminomethyl)phenyl]germanium(II) [(Me$_3$Si)$_2$ N](ArO)Ge (**3**)*

GeCl$_2$·C$_4$H$_8$O$_2$ (1 g, 4.32 mmol) in solution in 10 ml THF was added to a solution of bis(trimethylsilyl)aminolithium (0.72 g, 4.32 mmol) cooled to 0°C in THF (20 ml). The mixture was stirred at 0°C for 1 h, then 2,4,6-tris(dimethylaminomethyl)phenoxylithium (1.17 g, 4.32 mmol) in THF (20 ml) was added. After 12 h, lithium chloride was separated by filtration. 30 ml of pentane was added to the filtrate; cooling to −30°C for 6 days afforded **3** (0.47 g, 22%) as yellow crystals.

3 M.p. 130–132°C. ^{1}H-NMR (C$_6$D$_6$): 0.43 (s, 18H, SiMe), 2.06 (s, 6H, NMe), 2.07 (s, 6H, NMe), 2.21 (s, 6H, NMe), 3.38 (s, 2H, CH$_2$), 2.81 and 3.97 (AX system, 4H, $J_{AX} = 12$ Hz), 7.16(s, 2H, C6H2). ^{13}C-NMR (C6D6): 6.31 (+), 44.55 (+), 45.51 (+), 59.69 (−), 64.41 (−), 125.6 (C$_{quat}$), 127.5 (+), 130.2 (C$_{quat}$), 157.41 (C$_{quat}$). MS: $m/z = 498[M]^{+\bullet}$. Anal. Found: C, 50.66; H, 8.79; N, 11.12. C$_{21}$H$_{44}$N$_4$Si$_2$OGe. Calc.: C, 50.74; H, 8.86; N, 11.27.

A solution of ArOH (0.33 g, 1.2 mmol) in 10 ml of pentane was added dropwise with stirring to bis[-bis(trimethylsilyl)amino]germanium(II) (0.5 g, 1.2 mmol) in 20 ml of pentane. The mixture was further stirred at room temperature for 2 h. The volatiles were removed in vacuo; the resulting yellow paste, dissolved in pentane (ca. 30 ml) and cooled to −30°C, afforded **3** (0.53 g, 89%) as a yellow solid.

The mixture of bis[bis(trimethylsilyl)amino]-germanium(II) (0.36 g, 0.9 mmol) and bis[2,4,6-tris-(dimethylaminomethyl)phenoxy]germanium(II) (0.55 g, 0.9 mmol) in 30 ml of pentane was stirred at r.t. for 2 h. **3** crystallized from pentane at −30°C (0.42 g, 94%).

*3.4. [Bis(trimethylsilyl)amino][2,4,6-tris(dimethylaminomethyl)phenoxy] tin(II) [(Me$_3$Si)$_2$N](-ArO)Sn (**4**)*

To a solution of bis[bis(trimethylsilyl)amino]tin(II) (0.16 g, 0.36 mmol) in 20 ml of pentane was added dropwise a solution of ArOH (0.096 g, 0.36 mmol) in 10 ml of pentane. The reaction mixture was stirred at r.t. for 2 h. The volatile material was removed in vacuo; the residue, dissolved in pentane (ca. 30 ml) and cooled to −30°C, afforded **4** (0.18 g, 91%) as a yellow solid.

4: M.p. 110–112°C. ^{119}Sn{^{1}H}-NMR (C$_6$D$_6$): −52.6. ^{1}H-NMR (C$_6$D$_6$): 0.41 (s, 18H, SiMe), 2.01 (s, 6H, NMe), 2.02 (s, 6H, NMe), 2.16 (s, 6H, NMe), 2.81 and 3.97 (AX system, 4H, $J_{AX} = 12$ Hz), 3.34 (s, 2H, CH$_2$), 7.16 (s, 2H, C$_6$H$_2$). ^{13}C-NMR (C$_6$D$_6$): 5.78 (+), 43.66 (+), 44.53 (+), 59.54 (−), 63.47 (−), 126.7 (C$_{quat}$), 127.5 (+), 129.9 (C$_{quat}$), 158.95 (C$_{quat}$). MS: $m/z = 544$ $[M]^{+\bullet}$. Anal. Found: C, 46.36; H, 7.96; N, 10.22. C$_{21}$H$_{44}$N$_4$Si$_2$OSn. Calc.: C, 46.43; H, 8.11; N, 10.32.

By a similar procedure, a mixture of bis[bis-(trimethylsilyl)amino]tin(II) (0.4 g, 0.9 mmol) and bis-[2,4,6-tris(dimethylaminomethyl)phenoxy)tin(II) (0.59 g, 0.9 mmol) in 30 ml of pentane yielded **4** (0.45 g, 92%).

*3.5. [Bis(trimethylsilyl)amino][2,4,6-tris(dimethylaminomethyl)phen oxy]lead(II) [(Me3Si)$_2$N](ArO)Pb (**5**)*

A solution of 2,4,6-tris(dimethylaminomethyl)phenol (0.42 g, 1.6 mmol) in 10 ml of pentane was added dropwise to a suspension of bis[bis(trimethylsilyl)amino]lead(II) in 20 ml of pentane. The reaction mixture was stirred at r.t. for 2 h. The volatiles were removed in vacuo; the resulting yellow paste was dissolved in pentane (ca. 30 ml) and cooled to −30°C, affording the yellow solid **5** (0.82 g, 82%).

5: M.p. 104–106°C. ^{1}H-NMR (C$_6$D$_6$): 0.39 (s, 18H, SiMe), 2.02 (s, 12H, NMe), 2.15 (s, 6H, NMe), 2.80 and 3.97 (AX system, 2H, $J_{AX} = 12$ Hz, CH$_2$), 3.37 (s, 2H), 7.15 (s, 2H, C$_6$H$_2$). ^{13}C-NMR (C$_6$D$_6$): 5.66 (+), 43.42 (+), 44.39 (+), 59.46(−), 63.42(−), 126.5 (C$_{quat}$), 127.3 (+), 129.8 (C$_{quat}$), 158.7 (C$_{quat}$). MS: $m/z = 632[M]^{+\bullet}$. Anal. Found: C, 39.86; H, 6.90; N, 8.79. C$_{21}$H$_{44}$N$_4$Si$_2$OPb. Calc.: C, 39.92; H, 6.97; N, 8.87.

*3.6. Reaction of **1** with 3,5-di-tert-butyl-1,2-benzoquinone*

To a solution of **1** (0.15 g, 0.4 mmol) in 40 ml of benzene was added dropwise a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.08 g, 0.4 mmol) in 10 ml of benzene. Immediately, the colour of the reaction mixture turned to yellow. The mixture was then stirred at r.t. for 4 h. Pentane was added (ca. 40 ml) and the precipitate isolated by filtration. Yield (0.2 g, 84%). ^{1}H-NMR and mass spectroscopy analyses of the precipitate showed that compounds **6** [20] and **8** were present in relative amounts of 52 and 48%, respectively.

6: M.p. 133–135°C. ^{1}H-NMR (C$_6$D$_6$): 1.34 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu), 1.90 (s, 3H, NMe), 2.07 (s, 3H, NMe), 2.18 (s, 12H, NMe), 2.76 (s, 6H, NMe), 2.23 (s, 6H, NMe), 2.60 (s, 3H, NMe), 2.71 (s, 3H, NMe), 3.13 and 3.61 (AB system, 2H, $^2J_{HH} = 12$ Hz, CH$_2$), 3.94 (s, 4H, CH$_2$), 3.51 (s, 2H, CH$_2$), 3.54 (s, 2H, CH$_2$), 4.03 and 4.65 (AB system, 2H, $^2J_{HH} = 12$ Hz, CH$_2$), 6.81 and 7.58 (dd, 4H, C_6H_2), 6.9 (d, 1H, $^4J_{HH} = 2.4$ Hz), 7.23 (d, 1H, $^4J_{HH} = 2.4$ Hz). ^{13}C-NMR (C_6D_6): 30.10 (+), 32.32 (+), 34.59 (C_{quat}), 35.18 (C_{quat}), 44.01 (+), 47.09 (+), 59.06 (−), 64.05 (−), 109.6 (+), 111.9 (+), 127.73 (C_{quat}), 132.1 (+), 132.5 (C_{quat}), 139.0 (C_{quat}), 146.9 (C_{quat}), 151.2 (C_{quat}), 159.01 (C_{quat}), 159.1 (C_{quat}). MS: $m/z = 822$ $[M]^{+\bullet}$. Anal. Calcd for $C_{44}H_{72}N_6O_4Ge$: C, 64.34; H, 8.77; N, 10.23. Found: C, 64.22; H, 8.71; N, 10.12.

8: M.p. 144–145°C. ^{1}H-NMR ($CDCl_3$): 1.22 (s, 9H, *t*-Bu), 1.42 (s, 9H, *t*-Bu), 6.62 (d, 1H, 2.3 Hz), 6.78 (d, 1H, 2.3 Hz). ^{13}C-NMR ($CDCl_3$): 29.30 (+), 29.87 (+), 33.66 (C_{quat}), 33.86 (C_{quat}), 109.12 (+), 111.19 (+), 132.37 (C_{quat}), 138.12 (C_{quat}), 146.30 (C_{quat}), 150.23 (C_{quat}). MS: $m/z = 364$ $[M]^+$.

When the reaction was monitored by mass spectroscopy the transient formation of **12** was observed ($m/z = [593-123]^+$).

3.7. Reaction of **2** with 3,5-di-tert-butyl-1,2-benzoquinone

A solution of **2** (0.22 g, 0.52 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.11 g, 0.52 mmol) in benzene (60 ml) was stirred at r.t. for 4 h. After addition of pentane (60 ml), the precipitate was separated by filtration. Yield (0.28 g, 85%). ^{119}Sn{^{1}H}-NMR and mass spectroscopy analyses of the precipitate showed the presence of compounds **7** [20] and **9** (relative amounts ca. 50/50).

7: M.p. 124–125°C. ^{119}Sn{^{1}H}-NMR (C_6D_6): −566.08. ^{1}H-NMR (C_6D_6): 1.39 (s, 9H, *t*-Bu), 1.55 (s, 9H, *t*-Bu), 1.80 (s, 3H, NMe), 2.01 (s, 3H, NMe), 2.16 (s, 6H, NMe), 2.18 (s, 12H, NMe), 2.23 (s, 6H, NMe), 2.58 (s, 3H, NMe), 2.69 (s, 3H, NMe), 3.05 and 3.06 (AB system, 2H, $^2J_{HH} = 12$ Hz, CH_2), 3.34 (s, 4H, CH_2), 3.51 (s, 2H, CH_2), 3.55 (s, 2H, CH_2), 3.9 and 4.6 (AB system, 2H, $^2J_{HH} = 12$ Hz, CH_2), 6.8 and 7.67 (dd, 4H, C_6H_2), 6.9 (d, 1H, $^4J_{HH} = 2.4$ Hz), 7.26 (d, 1H, $^4J_{HH} = 2.4$ Hz), 7.26 (d, 1H, $^4J_{HH} = 2.4$ Hz).^{13}C-NMR (C_6D_6): 30.15 (+), 32.15 (+), 34.62 (C_{quat}), 35.22 (C_{quat}), 44.01 (+), 47.10 (+), 59.05 (−), 64.09 (−), 109.69 (+), 112 (+), 132.1 (+), 132.5 (C_{quat}), 133.92 (C_{quat}), 139.06 (C_{quat}), 146.96 (C_{quat}), 151.23 (C_{quat}), 159.05 (C_{quat}), 159.13 (C_{quat}). MS: $m/z = 868[M]^{+\bullet}$. Anal. Calcd for $C_{44}H_{72}N_6O_4Sn$: C, 60.92; H, 8.30; N, 9.69. Found: C, 60.87; H, 8.22; N, 9.57.

9: 218–220°C (dec.). ^{119}Sn{^{1}H}-NMR (C_6D_6): −477.70. ^{1}H-NMR (C_6D_6): 1.39 (s, 9H, *t*-Bu), 1.56 (s, 9H, *t*-Bu), 6.83 (d, 1H, 2.3Hz), 6.96 (d, 1H, 2.3Hz). ^{13}C-NMR (C_6D_6): 29.26 (+), 29.47 (+), 33.62 (C_{quat}), 33.72 (C_{quat}), 108.32 (+), 110.09 (+), 132.14 (C_{quat}), 137.07 (C_{quat}), 145.89 (C_{quat}), 149.72 (C_{quat}). MS: $m/z = 410[M]^{+\bullet}$.

When the reaction was monitored by ^{119}Sn-NMR and mass spectroscopy the transient formation of **13** was observed (^{119}Sn{^{1}H}-NMR $(CD_3)_2SO$: −522.11. MS: $m/z = [639-88]^+$).

3.8. Reaction of **3** with 3,5-di-tert-butyl-1,2-benzoquinone

To a solution of **3** (0.26 g, 0.52 mmol) in 40 ml of benzene was added a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.14 g, 0.67 mmol) in 60 ml of benzene, in a similar procedure as above. Yield (0.34 g, 91%). ^{1}H-NMR and mass spectroscopy analyses of the precipitate showed presence of compounds **6** and **10** [32] in 50/50 relative amounts.

10: M.p. 84–86°C. ^{1}H-NMR (C_6D_6): 0.28 (s, 18H, SiMe), 1.31 (s, 9H, *t*-Bu), 1.39 (s, 9H, *t*-Bu), 6.74 (d, 1H, 2.3 Hz), 6.81 (d, 1H, 2.3 Hz). ^{13}C-NMR (C_6D_6): 5.1 (+), 30.12 (+), 31.93 (+), 34.57 (C_{quat}), 34.66 (C_{quat}), 109.31 (+), 113.82 (+), 134.35 (C_{quat}), 142.12 (C_{quat}), 143.79 (C_{quat}), 148.28 (C_{quat}). MS: $m/z = [614]^+$.

When the raction was monitored by mass spectroscopy the transient formation of **14** was observed ($m/z = [718-161]^+$).

3.9. Reaction of **4** with 3,5-di-tert-butyl-1,2-benzoquinone

By a similar procedure, this reaction was carried out with **4** (0.28 g, 0.67 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.14 g, 0.67 mmol) in 60 ml of benzene. Yield (0.44 g, 87%). ^{119}Sn{^{1}H}-NMR and mass spectroscopy analyses of the precipitate showed presence of compounds **7** [20] and **11** (ca. 50/50).

11: M.p. 110–115°C. ^{119}Sn{^{1}H}-NMR ($CDCl_3$): −150.00. ^{1}H-NMR ($CDCl_3$): 0.26 (s, 18H, SiMe), 1.27 (s, 9H, *t*-Bu), 1.42 (s, 9H, *t*-Bu), 6.69 (d, 1H, 2.3 Hz), 6.85 (d, 1H, 2.3 Hz). ^{13}C-NMR ($CDCl_3$): 4.93 (+), 30.04 (+), 31.96 (+), 34.51 (C_{quat}), 34.99 (C_{quat}), 111.12 (+), 113.34 (+), 135.68 (C_{quat}), 140.78 (C_{quat}), 145.35 (C_{quat}), 149.28 (C_{quat}). MS: $m/z = 660[M]^{+\bullet}$.

When the reaction was monitored by ^{119}Sn-NMR and mass spectroscopy the transient formation of **15** was observed (^{119}Sn-NMR (C_6D_6): −382.15. MS: $m/z = [764-161]^+$).

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