The Stable Divalent Homoleptic Species $(ArO)_2M$ (Ar = 2,4,6-Tris((dimethylamino)methyl)phenyl; M = Ge, Sn, Pb)

Jacques Barrau,* Ghassoub Rima, and Tajani El Amraoui

Hétérochimie Fondamentale et Appliquée, UPRES-A 5069 du CNRS, Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

Received July 3, 1997

The synthesis and characterization of new stable divalent germanium, tin, and lead homoleptic species $(ArO)_2M$: (Ar = 2,4,6-$[(CH_3)_2NCH_2]_3C_6H_2$; M = Ge (**2**), Sn (**3**), Pb (**4**)) are described. **2**−**4** were obtained in good yields by alcoholysis of the M−N bonds of the divalent precursors $[(Me_3Si)_2N]_2M$ by ArOH. However, the direct reaction of 2 equiv of [2,4,6-tris((dimethylamino)methyl)phenoxy]lithium trimer (**1**) with the divalent species MCl_2 resulted in the formation of **2**−**4** in lower yields along with the cluster $Li_5(ArO)_2Cl_3$. The coordination behavior of the (dimethylamino)methyl side chains toward the metal atom was studied by variable-temperature NMR spectroscopy; on the NMR time scale **2** in solution exhibits a temperature-dependent N···M···N coordination mode. The chemistry of **2**−**4** is illustrated through their reactions with diphenylethanedione, 1,2- and 1,4-benzoquinones, and triazolinedione.

Introduction

The chemistry of the divalent species R_2M^{II} (M = Ge, Sn, Pb) has made important advances in the recent years,[1−11] and a large number of these species have been isolated in a monomeric state.[12] In particular, various aryloxygermylenes and -stannylenes $(Ar'O)_2M$ (Ar′ = 2,6-t-$Bu_2C_6H_3$, 2,6-t-Bu_2-4-Me-C_6H_2, 2,4,6-t-$Bu_3C_6H_2$) stabilized by electronic and steric effects have been isolated.[13] However, few germylenes stabilized by intramolecular complexation of the germanium atom by a Lewis basic group have been described.[12j,k,14−16] This method of stabilization has been more widely used in the chemistry of tin and silicon; it has been found to be very effective in the case of stannylenes.[17] It has failed so far in all attempts at the stabilization of silylenes, although several precursors with intramolecular coordination of a amino aryl group to silicon have been studied.[18,19] In the present study we have focused on new divalent species of germanium, tin, and lead $(ArO)_2M$ (M = Ge, Sn, Pb) with phenoxy ligands bearing in the 2,4,6 position (dimethylamino)methyl groups suitable for intramolecular coordination (Ar = 2,4,6-$[(CH_3)_2NCH_2]C_6H_2$). Some preliminary aspects of this work have been communicated earlier.[20]

---

(1) Satgé, J.; Massol, M.; Riviére, P. *J. Organomet. Chem.* **1973**, *56*, 1.

(2) Neumann, W. P. The Stannylenes R_2Sn. In *The Organometallic and Coordination Chemistry of Ge, Sn, and Pb*; Gielen, M., Harrison, P., Eds.; Freund: Tel Aviv, 1978; p 51.

(3) Petz, W. *Chem. Rev.* **1986**, *86*, 1099.

(4) Gaspar, P. P. Silylenes. In *Reactive Intermediates III*; Moss, R. A., Jones, M., Eds.; Wiley: New York, **1985**; p 333.

(5) (a) Satgé, J. *Pure Appl. Chem.* **1984**, *56*, 137. (b) Satgé, J. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1985**, *8*, 291.

(6) Riviére, P.; Riviére-Baudet, M.; Satgé, J. *Compr. Organomet. Chem.* **1982**, *2*, 478.

(7) Nefedov, O. M.; Kolesnikov, S. P.; Ioffe, A. I. *J. Organomet. Chem. Libr.* **1977**, *5*, 181.

(8) Satgé, J. *J. Organomet. Chem.* **1990**, *400*, 121.

(9) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267.

(10) Neumann, W. P. *Chem. Rev. (Washington, D.C.)* **1991**, *91*, 311.

(11) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217.

(12) For structurally characterized compounds see the following examples. Ge: (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Lange, L.; Meyer, B.; du Mont, W. W. *J. Organomet. Chem.* **1987**, *329*, C17. (c) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394. (d) Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 1647. (e) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167. (f) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Chem. Lett.* **1995**, *9*, 827. (g) Kira, M.; Iwamoto, T.; Maruyama, T.; Kabuto, C.; Sakurai, H. *Organometallics* **1996**, *15*, 3767. (h) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H. G. *Organometallics* **1996**, *15*, 741. (i) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics*, **1997**, *16*, 1920. (j) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116. (k) Dias H. V. R.; Wang. Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650. Sn: ref 12i and (l) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643. (m) Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23. Lay, U.; Pritzkow, H.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1992**, *260*. (n) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785. (o) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (p) Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846. (q) Klinkhammer, K. W.; Schwartz, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1334. (r) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546. Pb: refs 12i,q and (s) Brooker, S.; Buijink, J. K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25. (t) Tokitoh, N.; Kano, N.; Shibata, K.; Okazaki, R. *Organometallics* **1995**, *14*, 3121.

(13) Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zacorotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

(14) Veith, M.; Lisowsky, R. *Angew. Chem.* 1988, *100*, 1124; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1087.

(15) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351.

(16) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Atwood, J. L.; Roman, E. *Inorg. Chem.* **1992**, *31*, 3871.

(17) Angermand, K.; Jonas, K.; Krüger, C.; Latten, J. L.; Tsay, Y. H. *J. Organomet. Chem.* **1988**, *353*, 17.

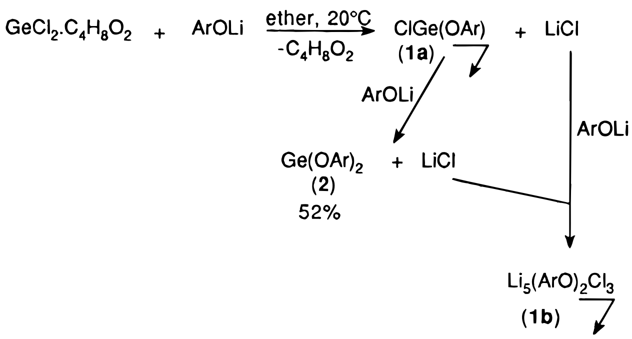
(18) Belzner, J. *J. Organomet. Chem.* **1992**, *430*, C51.

(19) Corriu, R.; Lanneau, G.; Priou, C.; Solairol, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. *J. Organomet. Chem.* **1994**, *466* (1−2), 55.

(20) Barrau, J.; Rima, G.; El Amraoui, T. *Inorg. Chim. Acta* **1996**, *241*, 9.

S0276-7333(97)00566-9 CCC: $15.00

Scheme 1



Results and Discussion

I. Synthesis and Structural Characterization of the Divalent Species $(ArO)_2M$ (M = Ge, Sn, Pb). I.1. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]germylene, $(ArO)_2Ge$ (Ar = 2,4,6-$[(CH_3)_2NCH_2]_3$-C_6H_2). We first tried to prepare bis[2,4,6-tris((dimethylamino)methyl)phenoxy]germylene employing the classical method of synthesis of germylated ether, the alkoxylation of germanium−halogen bonds, by carrying out the reaction of [2,4,6-tris((dimethylamino)methyl)phenoxy]lithium with $GeCl_2{\cdot}C_4H_8O_2$.

[2,4,6-Tris((dimethylamino)methyl)phenoxy]lithium was prepared by the action of *n*-BuLi with the corresponding alcohol in diethyl ether; it is soluble in diethyl ether but can be isolated in the pure state as crystals by precipitation at −20 °C from an ether/pentane (50/50) solution. Cryoscopic molecular weight measurements in benzene indicated the presence of a trimer, $(ArO)_3Li_3$, in solution. Its mass spectrum displays the same cluster structure $(ArO)_3Li_3$ also in the gas phase. The electron impact results in the formation of the radical cation $(ArO)_2Li_3{}^{\bullet+}OAr$, which loses NMe_2; the mass spectrum shows six fragment ions corresponding to $[(ArO)_2Li_3]^+$, $[(ArO)Li_2]^+$, Li^+ and $[ArO_3Li_3 - NMe_2]^+$, $[(ArO)_2Li_2 - NMe_2]^+$, $[ArOLi - NMe_2]^+$; the most abundant species is $[(ArO)Li_2]^+$. Thus the fragmentations lead to the related species $Li_x(ArO)_x$, which lose a NMe_2 group.

A suspension of $GeCl_2{\cdot}C_4H_8O_2$ was treated with $(ArOLi)_3$ at room temperature. The yield of $(ArO)_2Ge$ was high (52%), but along with germylene **2**, which is insoluble in diethyl ether, we extracted a solid phase which mass spectrometric analysis showed to be a mixture of the germylene ClGeOAr and the cluster $Li_5(ArO)_2Cl_3$. The action of $(ArOLi)_3$ on $GeCl_2{\cdot}C_4H_8O_2$ thus can be summarized by Scheme 1.

Chloro[2,4,6-tris((dimethylamino)methyl)phenoxy]germylene (**1a**) was identified by comparing its properties with those of an authentic sample prepared by a ligand redistribution reaction between $GeCl_2{\cdot}C_4H_8O_2$ and $(ArO)_2Ge$.[21] The cluster $Li_5(ArO)_2Cl_3$ (**1b**) was identified by comparison with an authentic sample obtained by mixing lithium chloride and the lithium phenolate in diethyl ether.

The low yield of $(ArO)_2Ge$ and the difficulties arising from the formation of byproducts which cannot be isolated very easily led us to explore an alternate method of preparing $(ArO)_2Ge$. The known extreme sensitivity of the germanium−nitrogen bond to alcoholysis prompted us to carry out the reaction of Lappert's germylene $Ge[N(SiMe_3)_2]_2$[38] with the phenol in benzene. The rapid reaction is exothermic and proceeds nearly quantitatively. At −30 °C in pentane a white, analytically pure, air-sensitive solid, $(ArO)_2Ge$ (**2**), precipitated. This product was fully characterized by NMR, IR, UV, and mass spectroscopy.

$$[(Me_3Si)_2N]_2Ge + 2\,ArOH \xrightarrow[20°C]{C_6H_6} \underset{(\mathbf{2})}{(ArO)_2Ge} + 2\,(Me_3Si)_2NH \qquad (1)$$

I.2. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]stannylene and -plumbylene, $(ArO)_2M$ (M = Sn, Pb). Following the same approach, we prepared the divalent tin and lead species $(ArO)_2M$ (**3** and **4**, respectively) by reaction of the corresponding divalent compounds $M[N(SiMe_3)_2]_2$ with the phenol. These reactions, as in the germanium case, gave high yields of the expected products as white solids.

$$[(Me_3Si)_2N]_2M + 2\,ArOH \xrightarrow[20°C]{C_6H_6} (ArO)_2M + 2\,(Me_3Si)_2NH \qquad (2)$$

$$M = Sn\ (\mathbf{3})\ ;\ M = Pb\ (\mathbf{4})$$

We have also investigated the organolithium route, in the tin case, in the reaction of $SnCl_2$ with ArOLi species **1**. As in the germanium case, this reaction resulted in a mixture of homoleptic and heteroleptic species $(ArO)_2Sn$ (**3**) and (ArO)SnCl (**3a**),[21] along with the cluster $Li_5(ArO)_2Cl_3$ and insoluble unidentified products.

The divalent species $(ArO)_2M$ (**2**−**4**) are stable under an argon atmosphere but are very sensitive to atmospheric oxygen and moisture. Thus, bis[2,4,6-tris((dimethylamino)methyl)phenoxy]germanium, -tin, and -lead oxides are formed when dry oxygen is bubbled in solutions of **2**, **3**, and **4**. Hydrolysis results in formation of oxides via intermediates that are difficult to isolate and identify. These divalent species are very soluble in common organic solvents. The nature of solvent (hexane, tetrahydrofuran, dioxane) does not influence the chemical behavior of these divalent species in solution, which points to a loss of Lewis acidity of the M(II) centers.

I.3. Physicochemical and Structural Study of the Divalent Species $(ArO)_2M$ (M = Ge, Sn, Pb). Cryoscopic mass determination showed that **2**−**4** are monomeric in benzene solution. Compounds **2**−**4** have been characterized by ^1H and ^{13}C NMR, IR, UV, and mass spectroscopy and, for stannylene **3,** also by ^{119}Sn NMR and Mössbauer spectroscopy. Spectroscopic data are reported in Table 1. ^1H NMR spectra of **2**−**4** at

---

[21] Improved detailed procedures for the syntheses of **1a** and **3a** will be reported in a publication currently underway. **1a**: mp 123−125 °C. ^1H NMR (C_6D_6): 2.22 (s, 6H), 2.39 (s, 12H), 3.27 (s, 2H), 3.66 (s, 4H), 7.06 (s, 2H). ^{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 $[M]^{\bullet+}$. Anal. Calcd for $C_{15}H_{26}N_3OGeCl$: C, 48.43; H, 6.99; N, 11.30. Found: C, 48.26; H, 6.72; N, 10.94. **3a**: mp 120−122 °C. $^{119}Sn\{^1H\}$ NMR (C_6D_6): −435.2. ^1H NMR (C_6D_6): 2.24 (s, 6H), 2.43 (s, 12H), 3.48 (s, 2H), 3.79 (s, 4H), 7.08 (s, 2H). ^{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 $[M]^{\bullet+}$. Anal. Calcd for $C_{15}H_{26}N_3OSnCl$: C, 43.08; H, 6.22; N, 10.05. Found: C, 42.68; H, 6.06; N, 9.87.

Table 1. Spectroscopic Data for Compounds 2−4

NMR (C_6D_6; δ ppm)

	^1H			^{13}C			
	Ge (**2**)	Sn (**3**)	Pb (**4**)	Ge (**2**)	Sn (**3**)	Pb (**4**)	Sn (**3**)
p-NMe_2	2.18 (s)	2.16 (s)	2.18 (s)	44.88	44.70	44.69	−529.8
o-NMe_2	2.16 (s)	2.13 (s)	2.00 (s)	44.45	45.37	45.44	
p-CH_2N	3.35 (s)	3.32 (s)	3.40 (s)	60.25	60.57	60.54	
o-CH_2N	3.57 (s)	3.54 (s)	3.37 (s)	64.08	64.49	64.48	
C_6H_2	7.28 (s)	7.28 (s)	7.20 (s)	125.86	126.46	125.77	
				129.33	129.24	129.61	
				131.04	131.46	131.59	
				151.48	159.58	159.61	

UV (C_6H_{12}; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}))

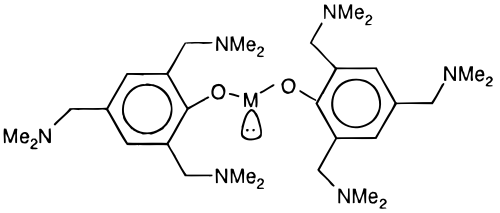
2	3	4
385 (360)[a]	372 (390)[a]	360 (420)[a]

[a] Erroneous values due to the particular sensitivity of **2**−**4** to hydrolysis.

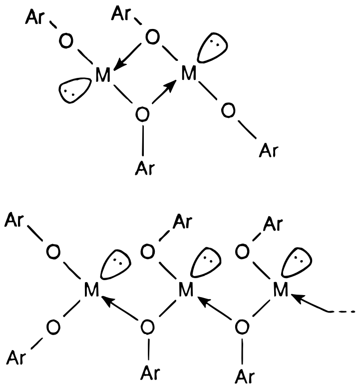
ambient temperature exhibit in all cases the equivalence of the four *o*-NMe_2 groups (broad singlet); a singlet also is observed as the signal for the corresponding CH_2N groups.

Three explanations are possible for the magnetic equivalence of the *o*-NMe_2 groups of compounds **2**−**4**.

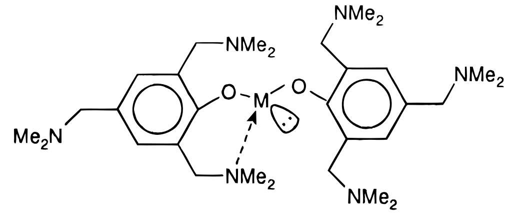
(1) The structure is monomeric, without intramolecular interaction between the *o*-NMe_2 groups and the Group 14 atom and no intermolecular interactions, thus allowing inversion of the nitrogen atom.



(2) The structure, in which the monomeric species (also without intramolecular interactions between the *o*-NMe_2 groups and the group 14 atom) are linked by coordination of the oxygen lone pair of ArO groups to a vacant p orbital of the group 14 metal.



(3) There is a dynamic N···M···N coordination−decoordination process involving the four donor functions in 2,6-positions of the phenoxy groups. Such "flip-flop" coordination modes have already been reported for tetravalent tin and silicon derivatives.[22−24]



Molecular modeling (Insight II, Discover 95, esff force field) allowed us to obtain the four equivalent limiting forms resulting from this dynamic coordination process corresponding to a molecular minimum total energy estimated to be 31.5 kcal mol^{-1}.

The idea of such a coordination is lent support by the unusual thermal stability of these divalent entities (no polymerization even at 200 °C) and also by their chemical properties, which clearly differentiate them from the noncomplexed divalent species.

We were not able to define the nature of the interaction between the NMe_2 groups and the group 14 atom since crystals suitable for X-ray structural analysis could not be obtained.

To obtain information concerning the nature and strength of coordination of the nitrogen atoms to the metal atom, we conducted a variable-temperature ^1H NMR study with the germylene **2**.

The ^1H NMR spectrum of **2** at −60 °C exhibits three resonances of equal intensity for the *N*-methyl protons (^1H NMR (CD_2Cl_2): δ 2.11 (s, 12H), 2.12 (s, 12H), 2.21 (s, 12H)). The observed nonequivalence of these protons at low temperature indicates that the flip-flop coordination process is slow enough so that we can observe two types of *o*-dimethylamino groups, along with the *p*-dimethylamino group. One type probably corresponds to two free *o*-dimethylamino groups far from the germanium atom and the other to the two groups in dynamic coordination, consistent with the two limiting forms represented in Scheme 2. The two coordinated nitrogens probably originate from two different ArO ligands as shown, not from the same ArO ligand. The structure corresponding to the latter possibility should give four distinct NMe_2 signals in the NMR spectrum, and this is not what was observed.

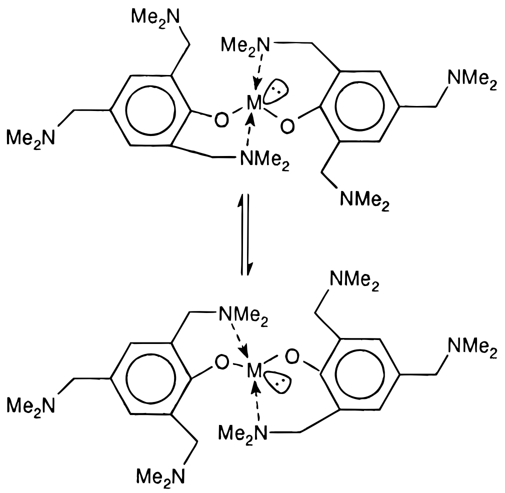
---

[22] van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Speck, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *184*, 233.

[23] Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blümel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162.

[24] Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1097.

Scheme 2



On further lowering the temperature (−75 °C), we did not observe demixing of signals of the *o*-NMe$_2$ and *o*-NCH$_2$ atoms which whould be characteristic of their static arrangement with all the *o*-NMe$_2$ groups coordinated to the metal atom.

We cannot exclude the possibility that the nonequivalence of the two types of *o*-NMe$_2$ groups observed at −60 °C may also result from hindrance to O−Ge−O rotation or from formation of stereoisomers resulting from static six-membered chelating geometries at this low temperature.

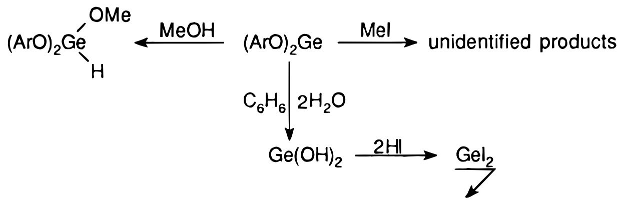
In UV−vis spectroscopy, absorption maxima due to **2**−**4** were observed at 385, 372, and 360 nm, respectively. As previously observed for germylene donor complexes,[25] these bands are shifted to shorter wavelengths compared to those of nonelectronically stabilized divalent species of group 14 metals (M$_{14}$). It is also noteworthy that the $\lambda_{\max}$ values decrease on going from germylene to plumbylene, in contrast with what is usually observed for free divalent M$_{14}$ species, except for some sterically overcrowed diaryl species.[12i] These results probably indicate that the monomeric divalent units are coordinated with lone-pair electrons of the (dimethylamino)methyl side chains. The position of the absorption maxima probably provides an indication of the strength of the M···N interaction. However, correlation between $\lambda_{\max}$ and the nature of the M···N coordination does not provide a full explanation, since additional effects such as the bond angle at the metal and the presence of an aryloxy group may play a role.

The tin-119 Mössbauer spectroscopy data are as follows: isomer shift IS, 2.88; quadrupole splitting QS, 1.82.

The isomer shift confirms the tin oxidation state +II, since it is known that all the tin compounds with an isomer shift greater than 2.03 mm/s are Sn(II) compounds[12l,26] and the quadrupole splitting reflects the asymmetrical electron density at the tin nucleus.

Compounds **2**−**4** change color on heating; they turn into yellow-orange solids after being heated to 120 °C and become more sensitive to hydrolysis and oxidation. This change of color probably reflects intramolecular (or intermolecular) N···M$_{14}$ coordination changes (reduction) in the solid phase. After the samples are heated for 1 h at 120 °C, their spectroscopic analyses still correspond to the structure of divalent species. The ^{119}Sn NMR analysis of the stannic compound, for instance, notably exhibits three signals at δ −529.5, −532.1, and −534.5 ppm. These only slightly different chemical shifts can be attributed to identical or very similar fundamental structures (divalent species), probably with different coordinations at the central metal atom.

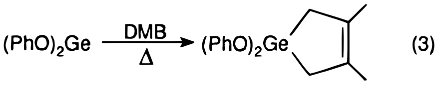
Scheme 3



II. Chemical Reactivity of the Divalent Species (ArO)$_2$M (M = Ge, Sn, Pb). Due to their “carbene-like” character, the free divalent species R$_2$M have a high potential for applications in organometallic chemistry. Insertion into various σ-bonds, addition or cycloaddition to nonconjugated alkenes, alkynes or conjugated dienes, heterodienes, trienes and complexation (by donors or acceptors) reactions are characteristic[1−11] of these divalent species.

II.1. Behavior toward σ-bonds. We did not observe any insertion reactions of the divalent species (ArO)$_2$M into σ-bonds, in contrast to the behavior of the free divalent species. Addition of methyliodide to (ArO)$_2$Ge results in the quaternization of the nitrogen atoms and the formation of various insoluble solids whose nature is still obscure (Scheme 3). An attempt to obtain insertion products of (ArO)$_2$Ge with methanol failed; the action of water leads, via hydrolysis of the Ge−O bonds of (ArO)$_2$Ge, to Ge(OH)$_2$. The latter, which is yellow-orange and precipitates while cold, was characterized by reaction with hydroiodic acid.[27]

II.2. Behavior toward Unsaturated Systems. II.2.1. 1,3-Dienes. (ArO)$_2$M compounds react neither with electron-poor or -rich 1,3-dienes nor with oxadienes, again in contrast to the case for the free divalent species. The germylene (PhO)$_2$Ge reacts readily in a classical way by 1,4 cycloaddition with 2,3-dimethylbuta-1,3-diene (DMB):



(3)

The presence of the dimethylamino groups on the phenyl group, thus seems to be responsible for the loss of this characteristic chemistry of free germylenes (with both electrophilic Lewis-acid and nucleophilic Lewis-base character) (Scheme 4).

II.2.2. Diketones and Quinones. Various heterocyclization reactions have been observed for **2** and **3** with nonenolizable ketones and also with 1,2-quinones.

II.2.2.1. Diphenylethanedione and 1,2-Benzoquinone. Germylenes and stannylenes (ArO)$_2$M for example react immediately at ambient temperature

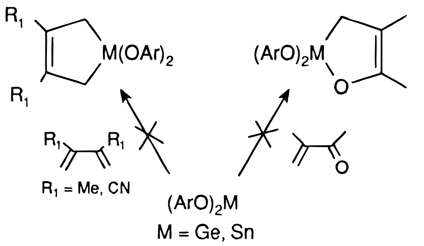
---

[25] Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

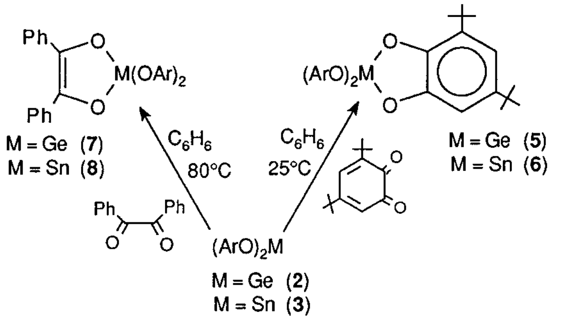
[26] Corvan, J. P.; Zuckerman, J. J. *Inorg. Chim. Acta Lett.* **1979**, L256.

[27] Jolley, W. L.; Latimer, W. M. *J. Am. Chem. Soc.* **1952**, *74*, 5752.

Scheme 4



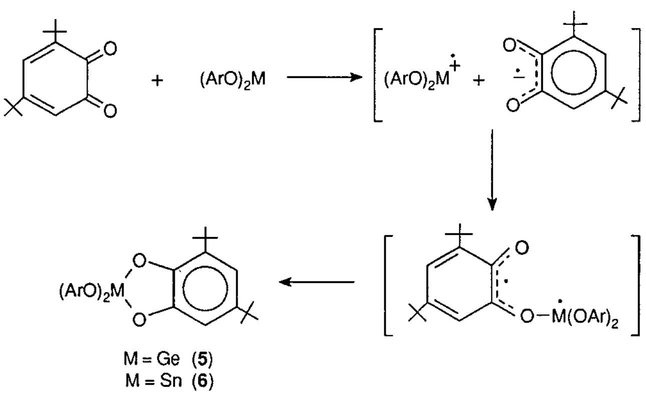
Scheme 5



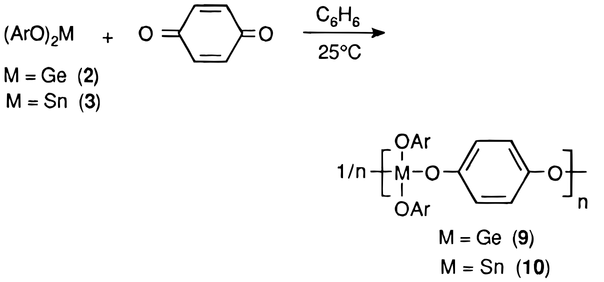
with 3,5-di-*tert*-butyl-1,2-benzoquinone and only at 80 °C with diphenylethanedione, leading to the new heterocycles **5**−**8**, respectively, in good yields (Scheme 5).

Galvinoxyl, which is a very efficient inhibitor of radical chain processes, has no effect on the rate of the reactions between quinones and divalent species **2** and **3**. (It is noteworthy that galvinoxyl is inert toward quinones but reactive toward **2** and **3**.) Additionally, these reactions cannot be induced photochemically; at high dilution and at −40 °C the thermal process is strongly slowed but the reaction cannot be accelerated at this temperature by UV irradiation. Therefore, it is reasonable to assume that these reactions proceed by single electron transfer with the formation of a pair of radical ions in the first step. The ESR study of the reaction mixture (in the case of germanium) clearly shows the transient formation of a paramagnetic species with a semi-quinonic structure. The ESR spectrum ($g = 2.0018$, $a^H = 3.5$ G) of the green solution at −40 °C, resulting from the mixture of the 3,5-di-*tert*-butyl-1,2-benzoquinone and the divalent species in toluene, is quite comparable to the *o*-semiquinone spectrum obtained in other ways.[28−30] Thus, divalent species **2** and **3**, which are singlets in the ground state, behave like electron donors, allowing immediate electron transfer to the quinone. These results agree with previous studies[31−35] and demonstrate that germylenes, known so far for their electrophilic and nucleophilic properties, can also be involved in a single electron-transfer process in accord with recent electrochemical and theoretical studies of germylenes, stannylenes, and their complexes with Lewis bases.[36,37] The reactions leading to adducts **5** and **6** are summarized in Scheme 6.

Scheme 6



II.2.2.2. 1,4-Benzoquinones. With 1,4-benzoquinone, the $(ArO)_2M$ species initiate and participate in copolymerization reactions. These reactions are initiated by simply mixing $(ArO)_2M$ and 1,4-benzoquinone solutions in the absence of a catalyst. The copolymer structures **9** and **10** were determined by ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis. These copolymers are thermally stable and melt without decomposition.



(4)

With 2,6-di-*tert*-butyl-1,4-benzoquinone, 1/1 copolymerization does not occur, probably because of the steric hindrance due to the two *tert*-butyl groups. The reaction of 1 equiv of $(ArO)_2Ge$ with 1 equiv of 2,6-di-*tert*-butyl-1,4-benzoquinone mainly results in germadioxolane **11**, with substitued cyclohexadienone groups (Scheme 7). In this reaction, various oligomers with paracyclophane bridges have been detected by mass spectrometry. These results are in agreement with those of Kobayashi.[33−35]

II.2.2.3. Triazolinedione. The $(ArO)_2M$ species (**2**, **3**) react at room temperature with the N═N double bond of *N*-methyltriazolinedione to yield the corresponding [2 + 1] addition products **13** and **14** (Scheme 8). To our knowledge, these metalladiaziridines are the first three-membered rings with M−N−N catenation.

These divalent group 14 compounds **2**−**4** are also potential precursors of various stable doubly bonded derivatives $(ArO)_2M{=}Y$ (Y = $NSiMe_3$, S, Se, Te) and of

---

(28) Rivière-Baudet, M.; Rivière, P.; Khallaayoun, A.; Satgé, J.; Rauzy, K. *J. Organomet. Chem.* **1988**, *358*, 77.

(29) Ryba, O.; Pilar, J.; Petrânek, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 26.

(30) Razuvaev, G. A.; Abakumov, G. A.; Klimov, E. S. *Dokl. Akad. Nauk* SSSR **1971**, *201*, 624 (Russ.); *Dokl. Chem. (Transl. of Dokl. Akad. Nauk)* **1971**, *201* (3), 968.

(31) Rivière, P.; Castel, A.; Guyot, D.; Satgé, J. *J. Organomet. Chem.* **1986**, *315*, 157.

(32) Rivière, P.; Rivière-Baudet, M.; Castel, A. *Main Group Met. Chem.* **1994**, *17*, 679.

(33) Kobayashi, S.; Iwata, S.; Abe, M.; Shoda, S. *J. Am. Chem. Soc.* **1990**, *112*, 1625.

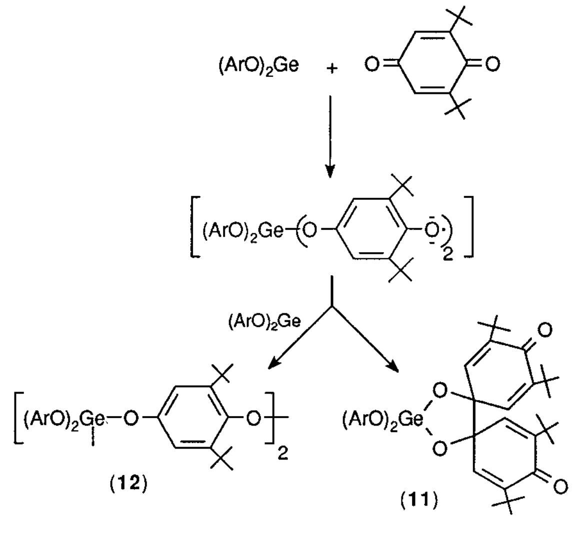
(34) Kobayashi, S.; Iwata, S.; Abe, M.; Shoda, S. *J. Am. Chem. Soc.* **1995**, *117*, 2187.

(35) Kobayashi, S.; Shoda, S.; Iwata, S.; Abe, M.; Yajima, K.; Yagi, K.; Hiraishi, M. *Pure Appl. Chem.* **1994**, *A31* (11), 1835.

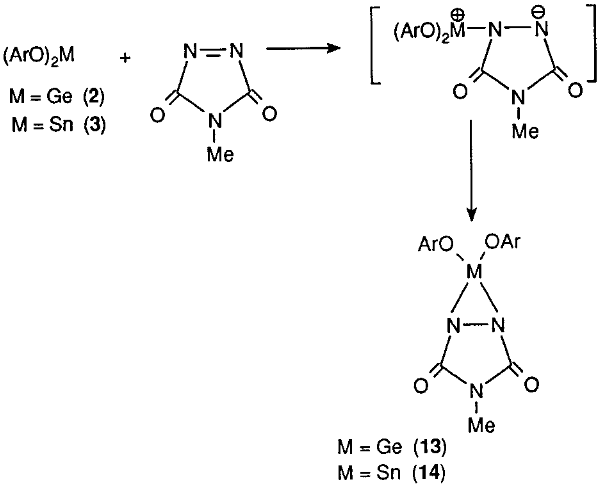
(36) Egorov, M. P.; Galminas, A. M.; Basova, A. A.; Nefedov, O. M. *Dokl. Akad. Nauk* **1993**, *329*, 594.

(37) Lee, V. Ya.; Basova, A. A.; Matchkarovskaya, I. A.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Rakhimov, R. D.; Butin, K. P. *J. Organomet. Chem.* **1995**, *499*, 27.

Scheme 7



Scheme 8



organometallic complexes $(ArO)_2M{=}M'L_n$ ($M'L_n$ = $Fe(CO)_4$, $W(CO)_5$, $Cr(CO)_5$, $Pt(PPh_3)_2$); these chemical properties and the syntheses of the heteroleptic species ArO(X)M: (X = $NSiMe_3$, Cl), in which the metal has a prochiral structure, will be reported in future publications.

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. ^1H NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in parts per million relative to internal Me_4Si as reference) and ^{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. ^1H-decoupled ^{119}Sn NMR spectra were recorded on a Bruker AC 200 or 400 MHz (chemical shifts are reported in parts per million relative to external Me_4Sn as reference). Mass spectra under electron impact (EI) or chemical ionization (CH_4) conditions at 70 and 30 eV were obtained on Hewlett-Packard 5989 and Nermag R10-10H spectrometers. IR and UV spectra were recorded on Perkin-Elmer 1600 FT-IR and Lambda-17 spectrophotometers. EPR spectra were obtained on a Bruker ER 200 equipped with a Gauss probe and an EiP frequency probe. Melting points were taken uncorrected on a Leitz Biomed hot-plate microscope apparatus. Elemental analyses (C,H,N) were performed at the "Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse".

[2,4,6-Tris((dimethylamino)methyl)phenoxy]lithium, Trimer, $(ArOLi)_3$ (1). n-BuLi (0.04 mmol, 25 mL of a 1.6 M solution in hexane) was added to 2,4,6-tris((dimethylamino)methyl)phenol (10.6 g, 0.04 mmol) in dry diethyl ether (100 mL). The solution was cooled to 0 °C for 30 min. The mixture was stirred for a further 2 h at room temperature and the solvent was removed in vacuo. The residue was extracted with an 1/1 ether/pentane solution (80 mL); after cooling to −20 °C for 12 h **1** was filtered off as white crystals and dried in vacuo (9.8 g, 90%).

1: mp 168−170 °C. ^7Li NMR (C_6D_6): 0.78. ^1H NMR (C_6D_6): 1.92 (s, 36H, NMe), 2.23 (s, 18H, NMe), 3.33 (s, 12H, CH_2), 3.42 (s, 6H, CH_2), 7.14 (s, 6H, CH_2). ^{13}C (C_6D_6): 45.38 (+), 45.92 (+), 63.90 (−), 65.03 (−), 121.38 (C_{quat}), 126.42 (+), 131.53 (C_{quat}), 167.12 (C_{quat}). MS: *m/z* 813 $[M]^{\bullet+}$. Anal. Calcd for $C_{45}H_{78}N_9O_3Li_3$: C, 66.42; H, 9.59; N, 15.49. Found: C, 66.22; H, 9.54; N, 15.44.

Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]germanium(II), $(ArO)_2Ge$ (2). 1. A solution of 2,4,6-tris((dimethylamino)methyl)phenol (2.54 g, 9.58 mmol) in 30 mL of pentane was added dropwise to a stirred solution of bis[bis(trimethylsilyl)amino]germanium(II)[38] (1.88 g, 4.79 mmol) in 20 mL of pentane. The mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue was extracted with pentane (ca. 30 mL). On cooling (−30 °C, 48 h) **2** separated as a white precipitate which was filtered off and dried in vacuo (2.76 g, 96%).

2: mp 158−160 °C. ^1H NMR (C_6D_6): 2.16 (s, 24H, NMe), 2.18 (s, 12H, NMe), 3.35 (s, 4H, CH_2), 3.57 (s, 8H, CH_2), 7.20 (s, 4H, C_6H_2). ^{13}C (C_6D_6): 44.88 (+), 45.46 (+), 60.25 (−), 64.48 (−), 125.86 (C_{quat}), 129.33 (+), 131.04 (C_{quat}), 151.48 (C_{quat}). MS: *m/z* 602 $[M]^{\bullet+}$. UV(C_6H_{12}): λ_{max} 385 nm. IR (C_6H_6, cm^{-1}): ν_{Ge-O} 1040. Anal. Calcd for $C_{30}H_{52}N_6O_2Ge$: C, 59.94; H, 8.65; N, 13.98. Found: C, 59.96; H, 8.68; N, 14.02.

2. To a suspension of $GeCl_2$−dioxane (0.17 g, 0.7 mmol) in diethyl ether (20 mL) was added a solution of [2,4,6-tris((dimethylamino)methyl)phenoxy]lithium (0.4 g, 1.46 mmol) in diethyl ether (40 mL). The mixture was stirred at room temperature for 10 h. Filtration yielded a white precipitate; the filtrate was concentrated in vacuo, and the residue was redissolved in pentane (ca. 30 mL) and cooled (−30 °C) to afford white crystals of **2** (0.23 g, 52%). The white precipitate obtained above was analyzed by mass spectroscopy; analysis showed that it was a mixture of (ArO)ClGe (**1a**) and $Li_5(ArO)_2Cl_3$ (**1b**). **1a**: *m/z* 373 $[M]^{\bullet+}$. **1b**: *m/z* 668 $[M]^{\bullet+}$. **1a** and **1b** were respectively identified by comparison of the spectral data with those of authentic samples. (See ref 21 for **1a**. **1b**: To a suspension of ArOLi (0.54 g, 2 mmol) in 50 mL of diethyl ether was added LiCl (0.13 g, 3 mmol). After stirring for 18 h at room temperature, filtration gave **1b** as a white powder. MS: *m/z* 668 $[M]^{\bullet+}$. Anal. Calcd for $C_{30}H_{52}N_6O_2Li_5Cl_3$: C, 53.82; H, 7.77; N, 12.55. Found: C, 53.45; H, 7.82; N, 12.36.

Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]tin(II) $(ArO)_2Sn$ (3). 1. A solution of 2,4,6-tris((dimethylamino)methyl)phenol (1.88 g, 7.1 mmol) in 30 mL of pentane was added dropwise to a stirred solution of bis[bis(trimethylsilyl)amino]tin(II)[38] (1.56 g, 3.55 mmol) in 20 mL of pentane. After stirring was continued at room temperature for 2 h, the solution was concentrated in vacuo (ca. 20 mL) and cooled to −30 °C. Filtration, followed by drying in vacuo, afforded **3** (2.2 g, 96%).

---

(38) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

3: mp 139−140 °C. ^{119}Sn{^{1}H} NMR (C_6D_6): −529.80. ^{1}H NMR (C_6D_6): 2.13 (s, 24H, NMe), 2.16 (s, 12H, NMe), 3.32 (s, 4H, CH_2), 3.54 (s, 8H, CH_2), 7.14 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 44.70 (+), 45.37 (+), 60.57 (−), 64.49 (−), 126.46 (C_{quat}), 129.24 (+), 131.46 (C_{quat}), 159.51 (C_{quat}). MS: *m/z* 648 $[M]^{\bullet+}$. UV(C_6H_{12}): λ_{max} 372 nm. Anal. Calcd for $C_{30}H_{52}N_6O_2Sn$: C, 55.66; H, 8.04; N, 12.98. Found: C, 55.73; H, 8.07; N, 13.03.

2. A suspension of anhydrous tin(II) chloride (0.095 g, 0.5 mmol) and [2,4,6-tris((dimethylamino)methyl)phenoxy]lithium (0.27 g, 1 mmol) in diethyl ether (50 mL) was stirred at room temperature for 10 h. Filtration yielded a white solid, which was analyzed by ^{1}H and ^{119}Sn NMR and mass spectroscopy; it is a mixture of (ArO)SnCl (**3a**), $(ArO)_2SnLiCl$ (**3b**), and $Li_5(ArO)_2Cl_3$ (**1b**). **1b** and **3a**[21] were identified by comparison of the spectral data with those of authentic samples; **3b** was chemically characterized (see next reaction). The filtrate was concentrated in vacuo, and the residue was extracted with pentane (ca. 30 mL) and cooled (−30 °C) to give compound **3** (0.1 g, 31%). **3a**: *m/z* 419 $[M]^{\bullet+}$. **1b**: *m/z* 668 $[M]^{\bullet+}$. **3b**: *m/z* 690 $[M]^{\bullet+}$.

Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]lead(II), $(ArO)_2Pb$ (4). 2,4,6-Tris((dimethylamino)methyl)phenol (1.21 g, 4.56 mmol) in pentane (30 mL) was added dropwise to a stirred solution of bis[bis(trimethylsilyl)amino]lead(II)[38] in 20 mL of pentane. The mixture was stirred at room temperature for 2 h and the solvent removed by evaporation under reduced pressure. The resulting yellow solid product, **4**, was recrystallized from pentane at −30 °C. Yield: 1.6 g, 96%.

4: mp 110−111 °C. ^{1}H NMR (C_6D_6): 2.00 (s, 24H, NMe), 2.18 (s, 12H, NMe), 3.37 (s, 8H, CH_2), 3.40 (s, 4H, CH_2), 7.20 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 44.69 (+), 45.44 (+), 60.54 (−), 64.48 (−), 125.77 (C_{quat}), 129.61 (+), 131.59 (C_{quat}), 159.61 (C_{quat}). MS: *m/z* 736 $[M]^{\bullet+}$. UV (C_6H_{12}): λ_{max} 360 nm. Anal. Calcd for $C_{30}H_{52}N_6O_2Pb$: C, 48.96; H, 7.07; N, 11.42. Found: C, 48.88; H, 7.16; N, 11.36.

Reaction of 2 with 3,5-Di-*tert*-butyl-1,2-benzoquinone. To a solution of **2** (0.25 g, 0.41 mmol) in 80 mL of benzene was added a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.09 g, 0.41 mmol) in benzene (10 mL). The mixture was stirred at room temperature for 4 h. To this solution was added 20 mL of pentane; a yellow precipitate immediately appeared. Filtration afforded **5** (0.3 g, 90%).

5: mp 133−135 °C. ^{1}H NMR (C_6D_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.

Reaction of 3 with 3,5-Di-*tert*-butyl-1,2-benzoquinone. 3,5-Di-*tert*-butyl-1,2-benzoquinone (0.2 g, 0.92 mmol) in 15 mL of benzene was added dropwise to a stirred solution of **3** (0.6 g, 0.92 mmol) in 5 mL of benzene. The mixture was stirred at room temperature for 4 h. Addition of 20 mL of pentane, filtration, and drying in vacuo gave **6** as yellow crystals (0.75 g, 94%).

6: mp 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, 4 H, C_6H_2), 6.9 (d, 1 H, $^4J_{HH}$ = 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.

Reaction of 2 with Diphenylethanedione. To a solution of diphenylethanedione (0.15 g, 0.7 mmol) in 10 mL of benzene was added dropwise a solution of **2** (0.42 g, 0.7 mmol) in 15 mL of benzene. The mixture was refluxed with stirring for 2 h. Concentration in vacuo afforded the crude product which was recrystallized from pentane/toluene (1/1, 30 mL) (−20 °C). Filtration gave **7** as yellow crystals (0.46 g, 81%).

7: mp 105−106 °C. ^{1}H NMR (C_6D_6): 2.11 (s, 24H, NMe), 2.20 (s, 12H, NMe), 3.37 (s, 8H, CH_2), 3.58 (s, 4H, CH_2), 6.80−7.80 (m, 14H, C_6H_2,C_6H_5), ^{13}C NMR (C_6D_6): 44.54 (+), 45.18 (+), 60.20 (−), 64.20 (−), 123.78 (C_{quat}) 127.80 (+), 128.34 (+), 130.14 (C_{quat}), 132.14 (+), 133.74 (C_{quat}), 134.5 (+), 151.20 (C_{quat}), 154.20 (C_{quat}). MS: *m/z* 812 $[M]^{\bullet+}$. IR (C_6H_6, cm^{-1}): ν_{Ge-O} = 680. Anal. Calcd for $C_{44}H_{62}N_6O_4Ge$: C, 65.14; H, 7.65; N, 10.36. Found: C, 65.25; H, 7.68; N, 10.45.

Reaction of 3 with Diphenylethanedione. Using the same operating conditions as in the previous preparation, **8** was obtained from **3** (0.55 g, 0.85 mmol) and diphenylethanedione (0.18 g, 0.85 mmol). Yield: 0.6 g, 82%.

8: mp 110−112 °C. ^{119}Sn{^{1}H} NMR (C_6D_6): −129. ^{1}H NMR (C_6D_6): 2.04 (s, 24H, NMe), 2.17 (s, 12H, NMe), 3.34 (s, 8H, CH_2), 3.51 (s, 4H, CH_2), 6.8−8.02 (m, 14H, C_6H_2, C_6H_5). ^{13}C NMR (C_6D_6): 44.80 (+), 45.50 (+), 60.76 (−), 64.82 (−), 123.81 (C_{quat}), 129.10 (+), 129.33 (+), 130.04 (C_{quat}), 130.24 (+), 133.74 (C_{quat}), 134.49 (+), 152.06 (C_{quat}), 154.44 (C_{quat}). MS: *m/z* 858 $[M]^{\bullet+}$. IR (C_6H_6, cm^{-1}): ν_{Sn-O} 670. Anal. Calcd for $C_{44}H_{62}N_6O_4Sn$: C, 61.63; H, 7.23; N, 9.80. Found: C, 61.71; H, 7.28; N, 9.88.

Reaction of 2 with 1,4-Benzoquinone. **2** (0.22 g, 0.36 mmol) in 20 mL of benzene was added dropwise to a stirred solution of 1,4-benzoquinone (0.04 g, 0.36 mmol) in 10 mL of benzene. The mixture was stirred at room temperature for 2 h. Addition of 20 mL of pentane, filtration and drying in vacuo afforded **9**. Yield 0.23 g, 90%.

9: mp >300 °C. ^{1}H NMR (C_6D_6): 2.05 (s, 12 H, NMe), 2.17 (s, 24H, NMe), 3.34 (s, 8H, CH_2), 3.51 (s, 4H, CH_2), 6.00 (s, 4H, C_6H_4), 7.23 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 44.64 (+), 45.50 (+), 60.51 (−), 64.60 (−), 123.20 (+), 129.40 (C_{quat}), 129.60 (+), 134.90 (C_{quat}), 150.10 (C_{quat}), 156.20 (C_{quat}). IR (C_6H_6, cm^{-1}): ν 1462.3, 1220.2, 840. Anal. Calcd for $(C_{36}H_{56}N_6O_4Ge)_n$: C, 60.96; H, 7.90; N, 11.85. Found: C, 60.88; H, 7.86; N, 11.73.

Reaction of 3 with 1,4-Benzoquinone. In a similar way the reaction of **3** (0.28 g, 0.43 mmol) with 1,4-benzoquinone (0.046 g, 0.43 mmol) afforded **10** as a red solid product (0.29 g, 89%).

10: mp >300 °C. ^{119}Sn{^{1}H} NMR (C_6D_6): −693.44. ^{1}H NMR (C_6D_6): 2.05 (s, 12H, NMe), 2.16 (s, 24H, NMe), 3.32 (s, 8H, CH_2), 3.49 (s, 4H, CH_2), 6.04 (s, 4H, C_6H_4), 7.22 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 44.80 (+), 45.40 (+), 60.22 (−), 64.30 (−), 123.74 (+), 129.22 (C_{quat}), 129.65 (+), 135.89 (C_{quat}), 149.47 (C_{quat}), 155.90 (C_{quat}). IR (C_6H_6, cm^{-1}): ν 1459, 1214.9, 780. Anal. Calcd for $(C_{36}H_{56}O_4\,N_6Sn)_n$: C, 57.24; H, 7.42; N, 11.13. Found: C, 57.16; H, 7.38; N, 11.06.

Reaction of 2 with 2,6-Di-*tert*-butyl-1,4-benzoquinone. A benzene solution (20 mL) of 2,6-di-*tert*-butyl-1,4-benzoquinone (0.56 g, 2.56 mmol) was added to **2** (1.54 g, 2.56 mmol) in 10 mL of benzene. The solution turned red. The resulting reaction mixture was stirred at room temperature for 4 h. The ^{1}H NMR analysis indicates the formation of **11** in amounts corresponding to the coupling of 42% of **2** with 84% of quinone. Addition of 30 mL of pentane, filtration, and drying in vacuo afforded pure **11** (0.22 g, 8.4%).

11: ^{1}H NMR (C_6D_6): 1.18 (s, 36H, *t*-Bu), 2.10 (s, 24H, NMe), 2.18 (s, 12H, NMe), 3.36 (s, 8H, CH_2), 3.56 (s, 4H, CH_2), 6.46 (d, 4H, $^4J_{HH} = 2.9$ Hz, C_6H_2), 7.25 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 29.60 (+), 35.35 (C_{quat}), 44.52 (+), 45.16 (+), 60.17 (−), 64.19 (−), 80.90 (+), 127.80 (+), 128.34 (+), 132.14 (C_{quat}), 140.11 (C_{quat}), 151.20 (C_{quat}), 185.90 (C_{quat}). IR (C_6H_6, cm^{-1}): ν 1659, 1636. MS: *m*/*z* 1042 $[M]^{\bullet+}$.

12 was detected as impurities by mass spectroscopy: *m*/*z* 1642 $[M]^{\bullet+}$.

Reaction of 2 with 4-Methyl-1,2,4-triazoline-3,5-dione. A benzene solution (2 mL) of 4-methyl-1,2,4-triazolidione (0.02 g, 0.17 mmol) was added dropwise to a stirred solution of **2** (0.1 g, 0.17 mmol) in 5 mL of benzene. The reaction mixture was then stirred at room temperature for 2 h, and the volatiles were removed in vacuo. After addition of pentane (15 mL) to the crude material, filtration and drying in vacuo gave **13** as a pale yellow powder (0.11 g, 91%).

13: mp 136−138 °C. ^{1}H NMR (C_6D_6): 2.14 (s, 24H, NMe), 2.18 (s, 12H, NMe), 2.88 (s, 3H, NMe), 3.35 (s, 8H, CH_2), 3.52 (s, 4H, CH_2), 7.18 (s, 4H, C_6H_2). ^{13}C NMR (C_6D_6): 21.13 (+), 45.34 (+), 45.75 (+), 61.01 (−), 64.57 (−), 128.69 (+), 130.16 (+), 156.46 (C_{quat}), 160.01 (C_{quat}). MS: *m*/*z* 715 $[M]^{\bullet+}$. IR (C_6H_6, cm^{-1}): ν_{CO} 1676, 1728. Anal. Calcd for $C_{33}H_{55}N_9O_4Ge$: C, 55.49; H, 7.70; N, 17.65. Found: C, 55.31; H, 7.62; N, 17.56.

Reaction of 3 with 4-Methyl-1,2,4-triazolidine-3,5-dione. In a similar fashion the reaction of 4-methyl-1,2,4-triazolinedione (0.02 g, 0.17 mmol) with **3** (0.11 g, 0.17 mmol) afforded **14** (0.11 g, 85%).

14: mp 124−126 °C. ^{119}Sn{^{1}H} NMR (C_6D_6): −448.03. ^{1}H NMR (C_6D_6): 2.20 (s, 24H, NMe), 2.27 (s, 12H, NMe), 2.69 (s, 3H, NMe), 3.45 (s, 8H, CH_2), 3.66 (s, 4H, CH_2), 7.20 (s, 4H, CH_2). ^{13}C NMR (C_6D_6): 21.10 (+), 44.95 (+), 45.50 (+), 60.46 (−), 64.52 (−), 128.49 (+), 130.19 (+), 158.10 (C_{quat}), 160.30 (C_{quat}). MS: *m*/*z* 761 $[M]^{\bullet+}$. IR (C_6H_6, cm^{-1}): ν_{CO} 1651, 1717. Anal. Calcd for $C_{33}H_{55}O_4N_9Sn$: C, 52.12; H, 7.24; N, 16.58. Found: C, 51.88; H, 6.94; N, 16.42.

OM9705665