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Preliminary Communication

# New bivalent germanium, tin and lead compounds with M–O bond

J. Barrau *, G. Rima, T. El Amraoui

*Laboratoire d'Hétérochimie Fondamentale et Appliquée, URA No. 477 du CNRS, Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France*

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## Abstract

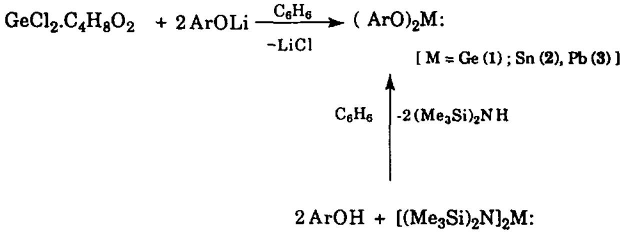
The syntheses of new stable bivalent germanium, tin and lead homoleptic species $(ArO)_2M$: ($ArO = 2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2O$; M = Ge (**1**), Sn (**2**), Pb (**3**)), $Ge(OSO_2CF_3)_2 \cdot C_4H_8O_2$ (**4**) and heteroleptic species $M(OAr)[N(SiMe_3)_2]$ (M = Ge (**5**), Sn (**6**)) are described. New organometallic heterocycles, stable metalla-imines and germathione $(ArO)_2M{=}X$ ($X = NSiMe_3$, S) and metal(II)–transition metal complexes are obtained starting from **1** and **2**.

*Keywords:* Germanium complexes; Tin complexes; Lead complexes; Bivalent complexes

There has been remarkable progress over the last few years in the preparation of bivalent species $R_2M(II)$ (M = Ge, Sn, Pb) and of their transition metal complexes [1–4] and a large number of monomeric species have been described; in particular divalent metal aryl-oxides $M(OAr')_2$ ($Ar' = 2,6\text{-}Bu^t{}_2\text{-}4\text{-}CH_3\text{-}C_6H_2\text{-}$) stabilized by steric effect were isolated [5]. However as compared with tin species the knowledge of germanium(II) complexes stabilized by intramolecular base coordination is limited.

We report here the details of synthesis and characterization of (i) new bivalent germanium, tin and lead compounds $(ArO)_2M$: with phenoxy groups having in the 2,4,6 position $(CH_3)_2NCH_2\text{-}$ groups suitable for intramolecular coordination that could facilitate stabilization [6,7] ($Ar = 2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2$; M = Ge (**1**), Sn (**2**), Pb (**3**)) and (ii) $Ge(OSO_2CF_3)_2 \cdot C_4H_8O_2$ (**4**). These bivalent $M^{14}$ compounds are potential precursors of various stable organometallic complexes, heterocycles and doubly bonded $M^{14}$ derivatives; these chemical properties are currently being investigated.

Bis[2,4,6-tris(dimethylaminomethyl)phenoxy]-germylene (**1**) was first synthesized from $GeCl_2 \cdot C_4H_8O_2$ by reaction with LiOAr. It was also observed that this germylene (**1**) and the tin and lead analogues **2** and **3** are readily obtained by cleavage of the M–N bonds of $[(Me_3Si)_2N]_2M$ with ArOH.



$$GeCl_2.C_4H_8O_2 + 2\,ArOLi \xrightarrow[-LiCl]{C_6H_6} (ArO)_2M: \quad [M = Ge\,(1);\ Sn\,(2),\ Pb\,(3)]$$

$$2\,ArOH + [(Me_3Si)_2N]_2M: \xrightarrow[-2(Me_3Si)_2NH]{C_6H_6} (ArO)_2M:$$

The bivalent species **1**–**3** were characterized by MS, IR, NMR spectroscopies and elemental analysis. Selected analytical data for **1**–**3**: **1**: m.p. 159–160 °C. $^1H$ NMR ($C_6D_6$) $\delta$ (ppm): 2.16 (s, 24H, $NMe_2$); 2.18 (s, 12H, $NMe_2$); 3.35 (s, 4H, $CH_2$); 3.57 (s, 8H, $CH_2$); 7.20 (s, 4H, $C_6H_2$). $^{13}C$ NMR ($C_6D_6$) $\delta$ (ppm): 44.88 ($NMe_2$); 45.46 ($NMe_2$); 60.25 ($CH_2$); 64.48 ($CH_2$); 125.86, 129.33, 131.04, 151.48 (aromatics). Mass spectrum: $m/z = 602$ ($M^+$). **2**: m.p. 139–140 °C. $^1H$ NMR ($C_6D_6$) $\delta$ (ppm): 2.13 (s, 24H, $NMe_2$); 2.16 (s, 12H, $NMe_2$); 3.32 (s, 4H, $CH_2$); 3.54 (s, 8H, $CH_2$); 7.14 (s, 4H, $C_6H_2$). $^{13}C$ NMR ($C_6D_6$) $\delta$ (ppm): 44.70 ($NMe_2$); 45.37 ($NMe_2$); 60.57 ($CH_2$); 64.49 ($CH_2$); 126.46, 131.46, 159.51. $^{119}Sn$ NMR ($C_6D_6$) $\delta$ (ppm): −529.80. Mass spectrum: $m/z$: 648 ($M^+$). **3**: $^1H$ NMR ($C_6D_6$) $\delta$ (ppm): 2.18 (s, 24H, $NMe_2$); 2.20 (s, 12H, $NMe_2$); 3.37 (s, 8H, $CH_2$); 3.38 (s, 4H, $CH_2$); 7.20 (s, 4H, $C_6H_2$). Mass spectrum: $m/z = 736$ ($M^+$).

These new germylene, stannylene and plumbylene complexes were isolated in the solid state at ambient temperature. In solution a dynamic N···M···N 'flip-flop' coordination

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* Corresponding author.

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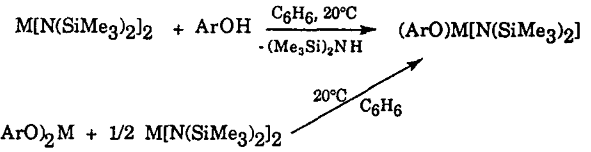
mode [8] involving the four donor functions in 2,6 position on the phenoxy groups — two amine donors displacing two other ones — could explain the $^1$H NMR data (**1** ($CD_2Cl_2$): two singlets 2.17 (24H), 2.25 (12H) for the all twelve methyl groups at 298 K and three singlets 2.11 (12H), 2.12 (12H), 2.21 (12H) at 238 K).

The germanium compound $Ge(OSO_2CF_3)_2 \cdot C_4H_8O_2$ was synthesized conveniently by reacting $GeCl_2 \cdot C_4H_8O_2$ with an excess of $HOSO_2CF_3$ analogously to the synthesis of $Sn(OSO_2CF_3)_2$ [9].

$$GeCl_2 \cdot C_4H_8O_2 + 2HOSO_2CF_3 \xrightarrow[-2\,HCl]{20\ ^\circ C} \underset{\mathbf{4}}{Ge(OSO_2CF_3)_2 \cdot C_4H_8O_2}$$

**4**: m.p. 69–70°C. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 3.2 (s, 8H). $^{13}$C NMR ($CDCl_3$): 66.58, 66.59 ($C_4H_8O_2$); 119 (q, $CF_3$, $J_{CF} = 953.3$ Hz). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): −0.55. Mass spectrum: $m/z = 460$ ($M^+$).

The reaction of $M[N(SiMe_3)_2]_2$ with ArOH in a 1/1 ratio in benzene resulted in the formation of the novel heteroleptic [10] compounds **5** and **6**, $M(OAr)[N(SiMe_3)_2]$ (M = Ge (**5**) or Sn (**6**)), obtained also by redistribution reaction between $M[N(SiMe_3)_2]_2$ and $M(OAr)_2$.



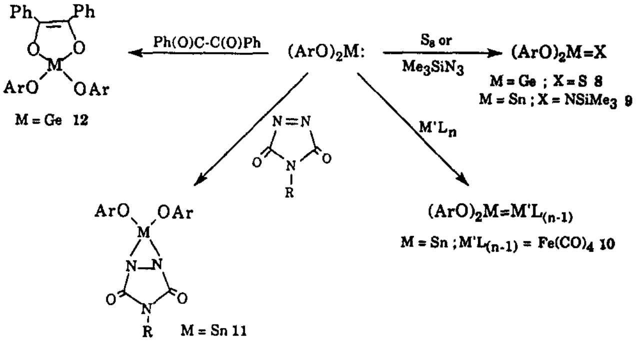
**5**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 0.48 (s, 18H, $SiMe_3$); 2.10 (s, 12H, $NMe_2$); 2.25 (s, 6H, $NMe_2$); 3.44 (s, 6H, $CH_2$). **6**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 0.47 (s, 18H, $SiMe_3$); 2.07 (s, 12H, $NMe_2$); 2.23 (s, 6H, $NMe_2$); 3.41 (s, 6H, $CH_2$). $^{119}$Sn NMR ($C_6D_6$) $\delta$ (ppm): −52.96.

It is noteworthy that **6** was surprisingly inert to redistributive symmetrization at 80 °C.

A rather different reaction was observed when $Ge[N(SiMe_3)_2]_2$ was reacted with $HOSO_2CF_3$ in a 1/1 ratio, the major (> 80%) germylated isolated product of this reaction being the oligomer $[GeNSiMe_3]_4$ (**7**) [11].

All these bivalent compounds (**1**–**6**) exhibit high potential in organometallic synthesis. They can lead to new organometallic heterocycles as well to new stable metalla-imines and germathione $(ArO)_2M{=}X$ (X = S, $NSiMe_3$) [12]; some examples are reported in Scheme 1.

Selected analytical data for **8**–**12**: **8**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 2.03 (s, 24H, $NMe_2$); 2.19 (s, 12H, $NMe_2$); 3.36 (s, 4H, $CH_2$); 3.52 (s, 8H, $CH_2$); 7.24 (s, 4H, $C_6H_2$). $^{13}$C NMR ($C_6D_6$) $\delta$ (ppm): 44.87 ($NMe_2$); 45.42 ($NMe_2$); 60.34 ($CH_2$); 64.45 ($CH_2$), 127.57, 128.05, 129.36, 151.2 (aromatics). Mass spectrum: $m/z = 634$ ($M^+$). **9**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 0.25 (s, 9H, $SiMe_3$); 2.08 (s, 24H, $NMe_2$); 2.19 (s, 12H, $NMe_2$); 3.36 (s, 4H, $CH_2$); 3.52 (s, 8H, $CH_2$); 7.19 (s, 4H, $C_6H_2$). $^{119}$Sn NMR ($C_6D_6$) $\delta$ (ppm): −138. $^{13}$C NMR ($C_6D_6$) $\delta$ (ppm): 3.13 ($SiMe_3$); 46.59 ($NMe_2$); 47.29 ($NMe_2$); 61.46 ($CH_2$); 66.11 ($CH_2$); 127.55, 128.74, 130.48, 161.41 (aromatics). Mass spectrum: $m/z = 735$ ($M^+$). **10**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 2.14 (s, 24H, $NMe_2$); 2.46 (s, 12H, $NMe_2$); 3.28 (s, 4H, $CH_2$); 3.58 (s, 8H, $CH_2$); 7.20 (s, 4H, $C_6H_2$). $^{119}$Sn NMR ($C_6D_6$) $\delta$ (ppm): −225.98, $J_{SnFe} = 1338$ Hz. $^{13}$C NMR ($C_6D_6$) $\delta$ (ppm): 43.24 ($NMe_2$); 45.45 ($NMe_2$); 60.22 ($CH_2$); 64.06 ($CH_2$); 127.6, 130.37, 157.91 (aromatics); 216.88, 218.75 (CO). IR (KBr) $\nu$ ($cm^{-1}$): 1471.9, 1605.4, 1946.2, 2000.1. **11**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 2.20 (s, 24H, $NMe_2$); 2.27 (s, 12H, $NMe_2$); 2.69 (s, 3H, NMe); 3.45 (s, 8H, $CH_2$); 3.66 (s, 4H, $CH_2$); 7.20 (s, 4H, $C_6H_2$). $^{119}$Sn NMR ($C_6D_6$) $\delta$ (ppm): −448. $^{13}$C NMR ($C_6D_6$) $\delta$ (ppm): 21.10 (NMe); 44.95 ($NMe_2$); 45.50 ($NMe_2$); 60.46 ($CH_2$); 64.52 ($CH_2$); 127.27, 128.49, 130.19, 158.1 (aromatics). **12**: $^1$H NMR ($C_6D_6$) $\delta$ (ppm): 2.11 (s, 24H, $NMe_2$); 2.20 (s, 12H, $NMe_2$); 3.37 (s, 4H, $CH_2$); 3.58 (s, 8H, $CH_2$); 6.80–7.20 (m, 14H, $C_6H_2$ and $C_6H_5$). Mass spectrum: $m/z = 812$ ($M^+$). $^{13}$C NMR ($C_6D_6$) $\delta$ (ppm): 44.54 ($NMe_2$); 45.18 ($NMe_2$); 60.20 ($CH_2$); 64.20 ($CH_2$); 127.49, 132.14, 188.70 (aromatics); 212.3 (C=C).



Scheme 1.

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