NEW HETEROCYCLIC BIVALENT TIN AND GERMANIUM SPECIES (SCHIFF'S BASE)M(II) (M = Ge, Sn) AND RELATED METALLANETHIONES AND -SELONES

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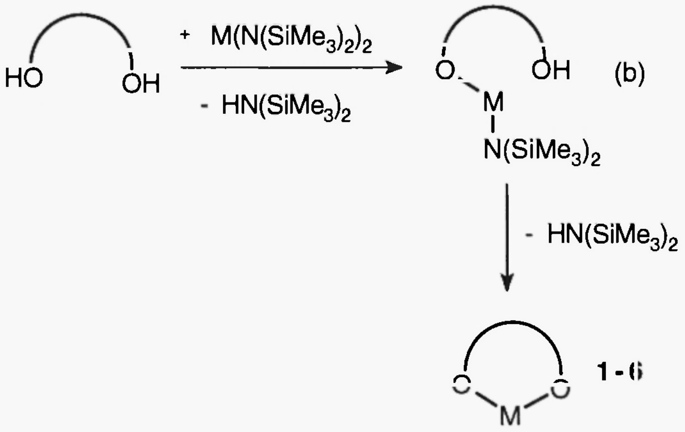
Abstract

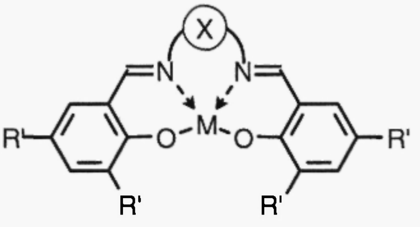
The syntheses of new stable bivalent homoleptic germanium and tin species L_2M (L_2 = (R,R)-(-)-N,N'-bis(3,5-di-*tert*-salicylidene)-1,2-cyclohexanediamine, M = Ge (**1**), M = Sn (**2**) ; L_2 = N,N'-bis(salicylidene) ethylenediamine, M = Ge (**3**), M = Sn (**4**) ; L_2 = N-methyl-2,2'-imino-bis(8-hydroxyquinoline), M = Ge (**5**), M = Sn (**6**) are described. New stable linear or cyclic organometallic compounds and metallanethiones and -selones $L_2M{=}E$ (E = S, Se) are obtained starting from **1**-**4**.

There has been remarkable progress over the last few years in the preparation of bivalent species of germanium and tin and of their transition metal complexes [1-5]. There are several known types of monomeric bivalent species [6], but there are relatively few reports of bivalent species stabilized by intramolecular coordination [6d, 7-10]. Therefore, following our studies on the $(ArO)_2M$ species [11] (Ar = 2,4,6-$[(CH_3)_2NCH_2]_3C_6H_2$; M = Ge, Sn, Pb) stabilized by dynamic intramolecular N...M...N coordination, we have investigated in this work the synthesis and spectroscopic analysis of new bivalent species L_2M using Schiff's base as ancillary ligands [L_2 = (R,R)-(-)-N,N'-bis(3,5-di-*tert*-salicylidene)-1,2-cyclohexanediamine, N,N'-bis(salicylidene)ethylenediamine, N-methyl-2,2'-imino-bis(8-hydroxyquin-oline)].

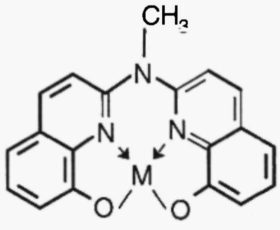
These new germylenes and stannylenes **1**-**6** have been readily obtained by cleavage reactions of the M-N bonds of the divalent $[(Me_3Si)_2N]_2M$ species with the corresponding Schiff's base diols in pentane (scheme 1).

Scheme 1





X = (R,R)-C_6H_{10} , R' = *t*Bu, M = Ge **1**
Sn **2**
X = CH_2CH_2 , R' = H , M = Ge **3**
Sn **4**



M = Ge **5**
Sn **6**

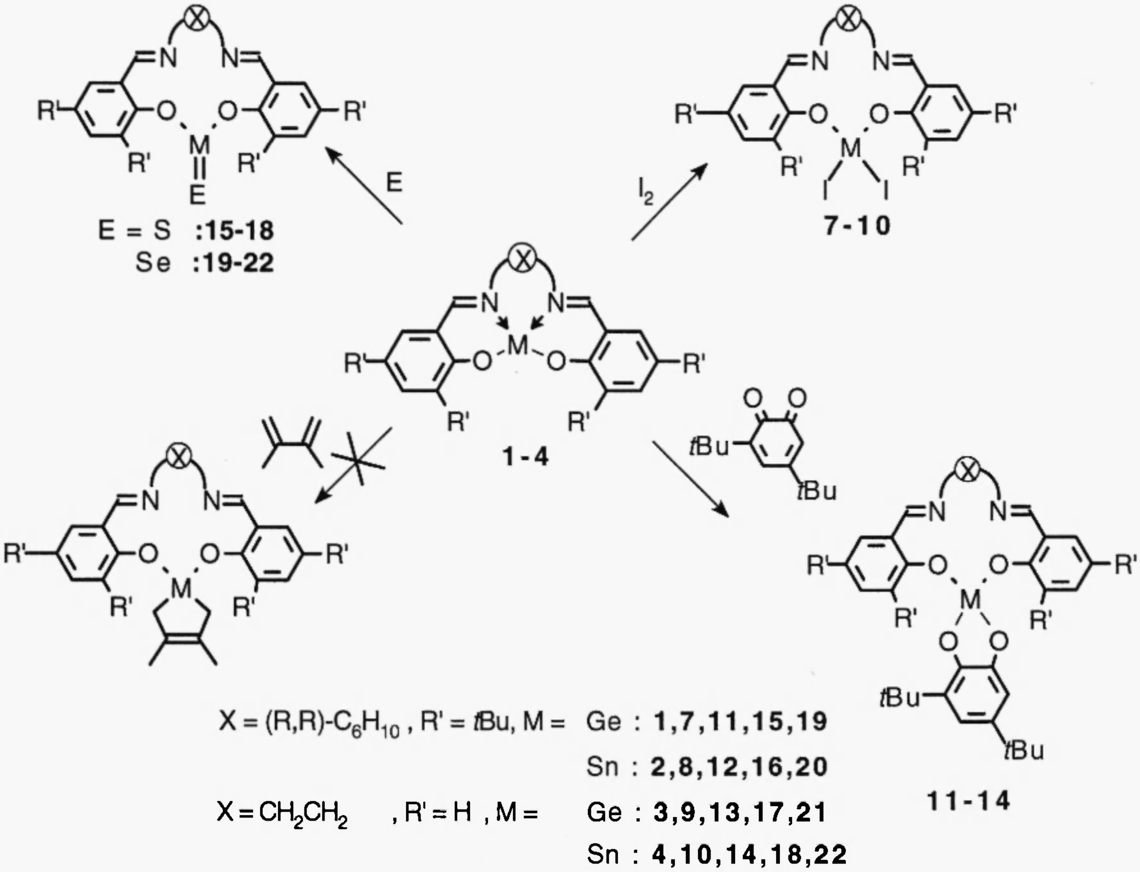
The synthesis reactions of the tin compounds **2,4,6** are nearly instantaneous and lead to new stannylenes in high yields. In contrast, in case of germanium, the synthesis reactions of **1,3,5** are complete only after six hours, and it was possible to characterize by ^{1}H NMR the intermediate heteroleptic germylenes (b) corresponding to only one Ge-N bond alcoholysis (scheme 1).

All these new germylenes and stannylenes (**1**-**6**) were isolated at room temperature as coloured solids . They are thermally stable in an inert atmosphere even at 100°C.
These bivalent species were characterized by EIMS, NMR, IR spectroscopies and elemental analysis.

All the bivalent species **1**-**4** show characteristic $\nu_{C=N}$ at 1610-1630 cm^{-1} and $\nu_{C\text{-}O}$ at 1025-1040 cm^{-1}. EIMS indicates a monomeric form for all these compounds.^{119}Sn NMR spectra of **2** and **4** are consistent with bivalent species stabilized by intramolecular N...Sn...N coordination.

Selected analytical and spectroscopic data: 2: bright yellow powder. Yield: 80%. m.p. 230-232°C (dec.). ^{1}H NMR (C_6D_6) δ (ppm): 1.41 (s, 9H, *t*Bu), 1.43 (s, 9H, *t*Bu), 1.85 (s, 9H, *t*Bu), 1.87 (s, 9H, *t*Bu), 1.20-2.05 (m, 8H, CH_2), 2.90-2.98 (m, 2H, CH), 6.96 (m, 2H, arom), 7.75 (m, 2H, arom), 7.90 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ (ppm): 30.31, 30.43, 31.79, 31.85, 63.43, 66.17, 117.00, 117.50, 136.90, 142.76, 162, 164, 160.56 (CH=N), 167.20 (CH=N). ^{119}Sn{^{1}H} NMR (C_6D_6) δ (ppm): -524.5. Mass spectrum: m/z = 664 (M$^+$). Correct elemental analysis. **3:** pale yellow powder. Yield: 82%. m.p. 170-180°C (dec.). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.60-4.18 (m, 4H, CH_2), 6.50-7.40 (m, 8H, arom), 8.10 (s, 2H, CH=N).). ^{13}C NMR ($CDCl_3$) δ: (ppm): 54.91, 117.19, 122.83, 134.79, 135.35, 164.20 (CH=N), 168.94 (CH=N). Mass spectrum: m/z = 340 (M$^+$). Correct elemental analysis. **4:** bright yellow powder. Yield: 83%. m.p. 255-260°C (dec.). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.58-4.07 (m, 4H, CH_2), 6.51-7.37 (m, 8H, arom), 8.11 (s, 2H, CH=N). ^{13}C NMR ($CDCl_3$) δ: (ppm): 55.59, 116.22, 124.10, 133.80, 134.92, 166.99 (CH=N). ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ (ppm): - 554.7. Mass spectrum: m/z = 386 (M$^+$). Correct elemental analysis.

Scheme 2



All these L_2M bivalent species exhibit high potential in organometallic chemistry, but they neither react with electron-poor or -rich 1,3-dienes nor with oxadienes. The loss of this characteristic aspect of the chemistry of free germylenes [1, 3] points out an N···M intramolecular coordination. By insertion reactions in selected σ bonds or addition reactions to various diketones and quinones, L_2M compounds can lead to new linear or cyclic organometallic compounds (scheme 2). They can act also as precursors of various stable $>M_{14}=E$ (E = S, Se) doubly bonded M_{14} derivatives (scheme 2) and $>M_{14}=M'L_n$ ($M'L_n$ = $Fe(CO)_4$, $Cr(CO)_5$) complexes. It is noteworthy that relatively rare are the structures $>M_{14}=E_{16}$ which could be stabilized [6d, 8, 11-19].

Selected analytical and spectroscopic data: 12: bright orange powder. Yield: 70% m.p. 220°C (dec.).^1H NMR (C_6D_6) δ (ppm): 1.26 (s, 9H, *t*Bu), 1.33 (s, 9H, tBu), 1.39 (s, 9H, *t*Bu), 1.53 (s, 9H, *t*Bu), 1.58 (s, 9H, *t*Bu), 1.96 (s, 9H, *t*Bu) 1.20-2.05 (m, 8H, CH_2), 2.94 (m, 2H, CH), 6.86 (m, 1H, CH arom), 7.01 (m, 1H, CH arom), 7.08 (m, 1H, CH arom), 7.14 (m, 1H, CH arom), 7.67 (m, 1H, CH arom), 7.83 (m, 1H, CH arom), 7.88 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ (ppm): 29.78, 29,91, 30.64, 31.57, 31.61, 32.25, 22.88, 27.29 , 34.44, 35.24, 61.76, 66.67, 109.92, 111.34, 129.66, 130.97, 131.56, 118.16, 119.32, 133.98, 139.78, 139.96, 143.06, 143.16, 146.88, 150.49, 165.39, 165.80, 166.35 (CH=N), 169.63 (CH=N). $^{119}Sn\{^1H\}$ NMR (C_6D_6) δ (ppm): - 568.2. Mass spectrum: m/z = 884 (M^+). Correct elemental analysis. **13**: orange powder. ^1H NMR ($CDCl_3$) δ (ppm): 1.14 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu), 3.75-3.91 (m, 2H, CH_2), 4.32-4.43 (m, 2H, CH_2), 6.55-7.44 (m, 10H, CH arom), 8.15 (s, 2H, CH=N). ^{13}C NMR ($CDCl_3$) δ (ppm): 29.87, 31.90, 51.66, 54.92, 107.62, 112.11, 118.16, 118.90, 120.46, 122.25, 122.72, 131.91, 133.73, 136.00, 136.81, 165.93 (CH=N), 169.46 (CH=N). Correct elemental analysis. **16:** ^1H NMR (C_6D_6) δ (ppm): 1.21 (s, 9H, *t*Bu), 1.23 (s, 9H, *t*Bu), 1.80-2.85 (m, 8H, CH_2), 2.91-2.97 (m, 2H, CH), 6.88 (m, 2H, arom), 7.77 (m, 2H, arom), 7.91 (s, 2H, CH=N). ^{13}C NMR (C_6D_6) δ (ppm): 24.47, 24.71, 29.77, 30.69, 31.20, 33.18, 34.13, 34.20. 59.53, 72.13, 118.51, 126.54, 126.98, 129.56, 136.79, 140.41, 158.74, 166.61 (CH=N). $^{119}Sn\{^1H\}$ NMR (C_6D_6) δ (ppm): - 878.9. Correct elemental analysis.

References

[1] J. Barrau, J. Escudie and J. Satge, *Chem Rev.*, **90** (1990) 283.
[2] M. F. Lappert and R.S. Rowe, *Coord. Chem. Rev.*, **100** (1990) 267.
[3] P. W. Neumann, *Chem. Rev.*, **91** (1991) 311.
[4] P. Jutzi, Adv. *Organomet. Chem.*, **26** (1986) 217.
[5] K. M. Baines and W. G. Stibbs, *Adv. Organomet. Chem.*, **39** (1996) 275.
[6] For recent structurally characterized compounds see for example: Ge: (a) M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto and H. Sakurai, *Organometallics*, **15** (1996) 3767. (b) P. Jutzi, H. Schmidt, B. Neumann and H. G. Stammler, *Organometallics*, **15** (1996) 741. (c) R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, **16** (1997) 1920. (d) G. Ossig, A. Melier, C. Brönneke, O. Muller, M. Schäfer and R. Herbst-Irmer, *Organometallics*, **16** (1997) 2116. Sn: (c). (e) M. Saito, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, **115** (1993) 2065. (f) M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. Von Schnering and H. Marsmann, *Angew. Chem, Int. Ed. Engl.*, **33** (1994) 1846. (g) K. W. Klinkhammer and W. Schwartz, *Angew. Chem, Int. Ed. Engl.*, **34** (1995) 1334.
[7] M. Veith and R. Lisowsky, *Angew. Chem* ,**100** (1988) 1124, *Int. Ed. Engl.*, **27** (1988) 1087.
[8] M. C. Kuchta and G. Parkin, *J. Chem. Soc, Chem. Commun.*, (1994) 1351.
[9] D. A. Atwood, V. O. Atwood, A. K. Cowley, J. L. Atwood and E. Roman, *Inorg. Chem.*, **31** (1992) 3871.
[10] H. V. R. Dias and Z.Wang, *J. Am. Chem. Soc.*, **119** (1997) 4650.
[11] J. Barrau, G. Rima and T. El Amraoui, *Inorg. Chim. Acta*, **241** (1996) 9 and *Organometallics* (1998) in press.
[12] M. Veith, S. Becker and V. Huch, *Angew. Chem, Int. Ed. Engl.*, **28** (1989) 1237.
[13] M. Veith, S. Becker and V. Huch, *Angew. Chem, Int. Ed. Engl.*, **29** (1990) 216.
[14] N. Tokitoh, T. Matsumoto, K. Manmaru and R. Okazaki, *J. Am. Chem. Soc.*, **115** (1993) 8855.
[15] N. Tokitoh, T. Matsumoto and R. Okazaki, *Chem. Lett.*, (1995) 1087.
[16] N. Tokitoh, Y. Matsuhashi, K. Shibata, T. Matsumoto, H. Suzuki, M. Saito, K. Manmaru and R. Okazaki, *Main Group Met. Chem.*, **17** (1994) 55.
[17] M. Veith and A. Detemple, *Phosphorus, Sulfur and Silicon*, **65** (1992) 17.
[18] R. Okazaki, *Phosphorus, Sulfur and Silicon*, **95-96** (1994) 21.
[19] N. Tokitoh, T. Matsumoto and R. Okazaki, *J. Am. Chem. Soc.*, **119** (1997) 2337.

Received: November 4, 1997 - Accepted: November 6, 1997 - Accepted in revised camera-ready format: November 7, 1997