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O,*N*-Chelated germanium, tin and lead compounds containing 2-[*N*,*N*-(dimethylamino)methyl]phenolate as ligand

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ABSTRACT

Thirteen organotin(IV) and low valent complexes of group 14 (Ge, Sn, Pb) containing L^{NO} ligand(s) (where L^{NO} is 2-(*N*,*N*-dimethylaminomethyl)phenolate) were synthesized and its structure described by NMR techniques in solution and X-ray techniques in the solid state (for $L^{NO}_2SnPh_2$, $L^{NO}_2SnCl_2$, L^{NO}_2Ge and $L^{NO}SnCl$ which forms a dimer). Structures and properties of prepared species have been compared with previously published germanium and tin compounds containing $-OCH_2CH_2NMe_2$ as *O*,*N*- or L^{CN} (where L^{CN} is 2-(*N*,*N*-dimethylaminomethyl)phenyl) as *C*,*N*-chelating ligands. The solid state structures containing L^{NO} ligand(s) reveal much stronger intramolecular N → Sn coordination than complexes containing latter two ligands.

1. Introduction

A couple of decades after its discovery in ~1970, low valent group 14 metal and metalloid complexes received growing interest because of similar properties as the transition metal complexes mainly with respect to small molecule activation, as for example dihydrogen, ammonia, carbon dioxide and others [1]. The application of germanium and lead complexes in oxidative addition reactions is also studied in this class of compounds [2]. For the stabilization of metalloid or metal centre in oxidation state +II, a plethora of different ligand systems has been developed. These ligands can be divided to subclasses where bulky [3] or various *C*,*N*-, *N*,*C*,*N*-, *O*,*C*-, *O*,*C*,*O*-, *P*,*C*,*P*-chelating ligands are the most popular. For purposes of stabilization of organotin compounds, a *C*,*N*-chelating ligand (Fig. 1A), has been studied in our group [4]. Similarly, the hybrid *N*,*N*-chelating amino–amido ligand (Fig. 1B) was used by us for the preparation of low valent germanium, tin and lead compounds very recently [5]. The difference between mentioned two ligands is that the *N*,*N*-chelating one is able to make a six-membered diazametalla cycle, which is for desired stabilization surprisingly more efficient, instead of the five-membered one. Related papers on structure and reactivity of group 14 complexes using the 2-(*N*,*N*-dimethylamino)ethanol (Fig. 1C) as a ligand are reported by groups of Zemlyansky, Khrustalev and Nechaev [6]. The authors described tetrylenes, their reactivity towards oxidizing agents, low valent transition metal complexes, together with behaviour of complexes with metal in higher oxidation state and theoretical explanations and/or predictions. Unfortunately, there is lack of the ^{119}Sn NMR spectra determination of these compounds where only two particular values for $Sn(OCH_2CH_2NMe_2)_2$ ($\delta(^{119}Sn = -309.9$ ppm [6e]) and $[Ph(C_6F_5)Sn(OCH_2CH_2NMe_2)_2][H_2O\cdot B(C_6F_5)_3]$ ($\delta(^{119}Sn) = -395.6$ ppm [6d]) are reported.

It seems that the development of group 14 chemistry of *O*,*N*-chelating ligand (Fig. 1D, 2-(*N*,*N*-dimethylaminomethyl)phenolate, L^{NO}), is a logical step within this field of chemistry. The main difference between 2-(*N*,*N*-dimethylamino)ethanolate based and suggested ligand systems is the ring size (five- or six-membered), and the presence of the aromatic fragment within the L^{NO} ligand which will presumably lead to the differences in structure and reactivity of the target compounds. The L^{NO} ligand is mentioned for preparation of organotin(IV) compounds in a patent from 1965, but no physico-chemical data are available [7]. The same ligand and very similar bis-chelating ligands have been used for the preparation of alkali–metal complexes [8] and later applied for vanadium(IV) or molybdenum(VI) chemistry by van Koten [9] and Mösch-Zanetti [10]. It also attracted attention of Barrau [11] who prepared and studied the reactivity of potentially tris-chelating ligand in the class of group 14 metals.

This paper describes both synthesis and structural characterization of germanium(II), tin(II) and lead(II) complexes as well as

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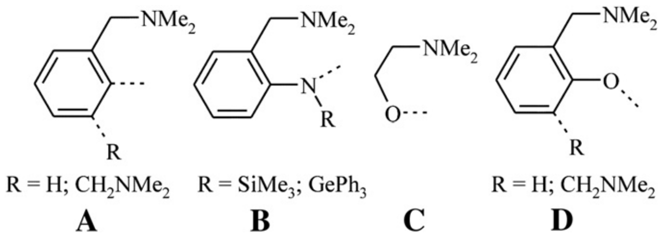


Fig. 1. Schematic drawings of common chelating ligands.

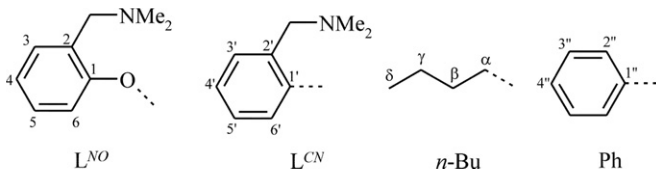


Fig. 2. General numbering of ligands and substituents used.

organotin(IV) compounds containing the L^{NO} ligand(s) or both L^{NO} and *C*,*N*-chelating (L^{CN}) ligands (Fig. 2).

2. Results and discussion

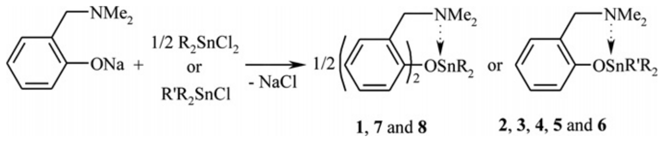
2.1. Synthesis

The target *O*,*N*-chelated group 14 metal complexes were prepared by two different synthetic strategies, (i) conversion of sodium salt L^{NO}Na with tri- and diorganotin(IV) chlorides (**1**–**8**; Scheme 1) and (ii) protonolytic reactions of the Lappert's type germylene, stannylenes and plumbylene with phenol L^{NO}H (for **9**–**13**; Scheme 2). Both pathways gave low to sufficient yields (20–80%) of desired compounds which are generally instable in the air. Surprisingly, compound **8** was also isolated from the reaction of homoleptic stannylene **10** with 1 M equivalent of (1,5-cyclooctadiene)palladium(II) dichloride. This reaction has been performed in order to prepare a heterobimetallic complex of Pd and Sn but the reduction of the palladium occurred essentially quantitatively (Scheme 3).

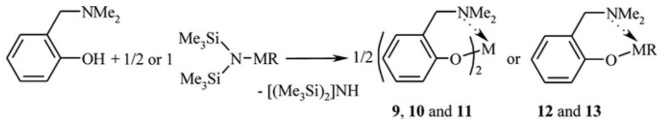
2.2. NMR studies in solution

2.2.1. General remarks

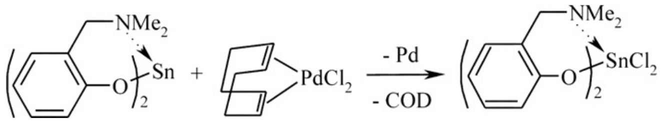
Except for compounds and **8**, **10** and **11** (Table 1), where the dynamic behaviour of the $CH_2N(CH_3)_2$ parts of molecules occurs because of the presence of two L^{NO} ligands, the rest of compounds reveal one set of narrow signals in ^{1}H, ^{13}C and ^{119}Sn NMR spectra. The labile geometry at the central metal atom in solution can affect the width of the resonances in the NMR spectra of **8**, **10** and **11**, too. Unfortunately, also very low solubility at decreased temperatures was observed for these compounds which thwarted the low-temperature NMR measurements. In the case of **7**, which is almost insoluble in common deuterated solvents, only ^{1}H NMR spectrum was recorded. For the rest of compounds, all possible NMR spectra parameters of usual nuclei (^{1}H, ^{13}C and ^{119}Sn) were determined. In general, the chemical shift values, integral intensities and multiplicity of each resonance in the ^{1}H NMR spectra of **1**–**13** correspond well to proposed composition with the respect to the number and nature of substituents bound to the central metal/metalloid atom.



Scheme 1. Preparation of compounds **1**–**8** (for **1** R = *n*-Bu; for **2** R′ = L^{CN}, R = *n*-Bu; for **3** R′ = Cl, R = *n*-Bu; for **4** R′ = R = Me; for **5** R′ = R = *n*-Bu; for **6** R′ = L^{CN}, R = Ph; for **7** R = Ph; and for **8** R = Cl).



Scheme 2. Preparation of compounds **9**–**13** (for **9** M = Ge; for **10** M = Sn; for **11** M = Pb; for **12** M = Sn, R = Cl; and for **13** M = Sn, R = $N(SiMe_3)_2$).



Scheme 3. Unexpected formation of **8** from **10**.

In the ^{1}H NMR spectra of compounds containing two L^{NO} ligands (*e.g.* **8**, **10** and **11**), broad resonances were observed for all functional groups from which especially the signals for methylene and methyl groups are close to decoalescence. There are two exceptions of this behaviour for $L^{NO}_2Sn(n\text{-}Bu)_2$ (**1**) and L^{NO}_2Ge (**9**) where well resolved spectra were obtained.

2.2.2. NMR studies on triorganotin(IV) compounds **2**, **4**, **5** and **6**

Surprisingly, in ^{119}Sn NMR spectra of triorganotin(IV) compounds **4** ($\delta(^{119}Sn) = 135.7$ ppm) and **5** ($\delta(^{119}Sn) = 105.2$ ppm) signals at very low field were detected. This is in strong contrast to ^{119}Sn chemical shift values reported for related *C*,*N*-chelated five-coordinated triorganotin(IV) compounds as for example $L^{CN}(n\text{-}Bu)_2SnCl$ and $L^{CN}Me_2SnCl$ ($\delta(^{119}Sn) \approx -50$ ppm) [12]. So, based on these findings, we assume that the six-membered azaoxastanna ring is not closed because of none or very limited intramolecular N → Sn interaction in **4** and **5**. This fact and the presumption of four-coordinated tin centre with pseudotetrahedral geometry in **4** and **5** (Table 1) is further supported by the close chemical shift values reported for starting chlorides Me_3SnCl and $(n\text{-}Bu)_3SnCl$ ($\delta(^{119}Sn) = 164$ and 141 ppm, respectively) in which the central tin

Table 1
Numbering and selected NMR spectra parameters of $L^{NO}R^1R^2R^3M$ and $L^{NO}R^1M$ types of compounds under investigation.

Cpd	R^1	R^2	R^3	M	$\delta(^{119}Sn)$ C_6D_6 [ppm]
1	L^{NO}	*n*-Bu	*n*-Bu	Sn	−201.0
2	L^{CN}	*n*-Bu	*n*-Bu	Sn	−86.9
3	*n*-Bu	*n*-Bu	Cl	Sn	−157.7[b]
4	Me	Me	Me	Sn	135.7
5	*n*-Bu	*n*-Bu	*n*-Bu	Sn	105.2
6	L^{CN}	Ph	Ph	Sn	−212.4
7	L^{NO}	Ph	Ph	Sn	[a]
8	L^{NO}	Cl	Cl	Sn	−575.9[b]
9	L^{NO}	–	–	Ge	–
10	L^{NO}	–	–	Sn	−528.0 −538.1[c]
11	L^{NO}	–	–	Pb	–
12	Cl	–	–	Sn	−379.5[b]
13	$N(SiMe_3)_2$	–	–	Sn	−53.4

[a] Insufficiently soluble for ^{119}Sn NMR investigation.
[b] Measured in THF-d_8.
[c] Measured in toluene-d_8 at −50 °C.

atom is obviously four-coordinated in the solution of a non-coordinating solvent [13].

Last two triorganotin(IV) compound of the series – $L^{NO}L^{CN}Sn(n\text{-}Bu)_2$ (**2**) and $L^{NO}L^{CN}SnPh_2$ (**6**) – contain two potentially chelating ligands. Nevertheless, according to the observed ^{119}Sn chemical shift values of −86.9 ppm (**2**) and −212.4 ppm (**6**), we suggest that only one of them acts as a chelating one while the second one exhibits a monodentate bonding fashion with respect to the tin atom. In addition, these values are in a parallel to the *C,N*-chelated di-*n*-butyl and diphenyltin(IV) compounds bearing a negative substituent (for example Cl (−51.7 and −177.1 ppm, respectively) [12,14], F (−77.1 and −198.6 ppm, respectively) [15] and O (−55.4 and −173.2 ppm) [16]) where the pentacoordinated tin atom was reported. Due to the reasons described above we assume the pentacoordination of the tin atom in both **2** and **6**.

2.2.3. NMR studies on diorganotin(IV) compounds **1**, **3** and **7**

From three synthesized diorganotin(IV) compounds, $L^{NO}{}_2SnPh_2$ (**7**) is sparingly soluble and moreover crystallizes rapidly in the magnetic field of the NMR machine, that is why only ^1H NMR spectrum of **7** is reported. The ^1H NMR spectrum of **7** displays resonances attributable to both two phenyl and two L^{NO} substituents at predictable positions.

The two remaining members of this group, $L^{NO}_2Sn(n\text{-}Bu)_2$ (**1**) and $L^{NO}(n\text{-}Bu)_2SnCl$ (**3**), reveal distinctly different $\delta(^{119}Sn)$ values of −201.1 (for **1**) and −157.7 ppm (for **3**). This indicates different coordination vicinity of the tin central atom in **1** and **3**, respectively. The coordination polyhedra of tin centre in **1** can be best described as di-capped distorted tetrahedron (*e.g.* [4 + 2] coordination) and a distorted trigonal bipyramid for **3**. This description is along with similar trend in $\delta(^{119}Sn)$ values reported earlier for compounds with comparable composition geometry $L^{CN}_2(n\text{-}Bu)SnCl$ ($\delta(^{119}Sn) = -118.1$ ppm, [4 + 2] coordination) and $L^{CN}(n\text{-}Bu)SnCl_2$ ($\delta(^{119}Sn) = -104.3$ ppm, pentacoordination of the tin atom) [12]. The only reported ^{119}Sn NMR chemical shift value for diorganotin(IV) compound containing a *N,O*-chelating ligand ($[Ph(C_6F_5)Sn(OCH_2CH_2NMe_2)_2][H_2O\cdot B(C_6F_5)_3]$ [6d]) is − 395.6 ppm, which is unfortunately incomparable to shifts found for **1** or **2** because of totally different structure of both compounds.

2.2.4. NMR studies on purely inorganic tin(IV) compound **8**

Prepared $L^{NO}_2SnCl_2$ (**8**) reveals different behaviour than $L^{CN}_2SnCl_2$ [17] in solution as detected by ^1H NMR spectroscopy. A broad signal with a saddle point was observed for the CH_2N groups while two distinct resonances for methyl groups ($\delta(^1H) = 2.94$ and 2.78 ppm, respectively) were observed in the ^1H NMR spectrum of **8**. Surprisingly, the methyl group resonances exhibit two different $^3J(^{119}Sn, {}^1H)$ values being 30 and 41 Hz, respectively, which is a unique observation among all compounds studied. In strong contrast to the ^1H NMR spectrum of **8**, an AX-spin pattern for CH_2 groups along with one broad resonance for methyls is observed in the ^1H NMR spectrum of $L^{CN}_2SnCl_2$. Nevertheless, we assume the pseudooctahedral vicinity of the tin atom in **8** with both oxygen and chlorine atoms being in mutual *cis* and both nitrogen atoms in *trans* arrangement. On the other hand, *C,C*-transoidal arrangement is reported for $L^{CN}_2SnCl_2$. These ^1H NMR behaviour dissimilarities are further reflected in the different ^{119}Sn NMR spectra of **8** and $L^{CN}_2SnCl_2$ with the $\delta(^{119}Sn)$ values at −575.9 ppm found for **8** and −254.2 ppm reported for $L^{CN}_2SnCl_2$, respectively. This discrepancy can be attributed to a cooperative effect of carbon atoms for more negative oxygen atoms exchange within the ligand's skeleton. The more efficient donation of the nitrogen atoms lone electron pairs to the tin centre and the use of THF-d_8 as a solvent can be considered as another explanation for such different ($\Delta\delta$ (^{119}Sn) ≈ 320 ppm) ^{119}Sn NMR chemical shift values of **8** and $L^{CN}_2SnCl_2$.

2.2.5. NMR studies on germanium(II), tin(II) and lead(II) compounds **9**–**13** bearing L^{NO} ligand(s)

For homoleptic divalent compounds of the L^{NO}_2M type (where M = Ge (**9**), Sn (**10**), Pb(**11**)) different ^1H NMR spectral patterns were found. Thus, for the complex of the smallest element – germanium (**9**) – well resolved spectra with narrow signals were found while broad resonances have been observed for remaining two complexes **10** and **11**. It could be explained by the fact that the germanium atom is probably not able efficiently accommodate available electron density. The ^{119}Sn NMR spectrum of **10** reveals very high upfield shift of −528.0 ppm when compared to the starting Lappert's stannylene ($\delta(^{119}Sn) = 770$ ppm) [18] and even to the only reported $\delta(^{119}Sn)$ for $Sn(OCH_2CH_2NMe_2)_2$ ($\delta(^{119}Sn) = -309.9$ ppm) [6e].

Two novel heteroleptic stannylenes $L^{NO}SnCl$ (**12**) and $L^{NO}SnN(SiMe_3)_2$ (**13**) were prepared and characterized by ^1H and ^{119}Sn NMR spectroscopy. Both **12** and **13** reveal the dynamic behaviour with broad signals in ^1H NMR spectra. Moreover, two signals were found for both methylene ($\delta(^1H) = 3.83$ and 2.47 ppm, respectively) and methyl groups ($\delta(^1H) = 1.99$ and 1.56 ppm, respectively) in **13**. Different coordination polyhedra of both compounds is deduced from $\delta(^{119}Sn)$ values being −379.5 ppm for **12** and −53.4 ppm for **13**, respectively. This can be easily explained by presumably dimeric structure of **12** and a monomeric structure of **13** in the solution. Proposed dimeric structure of chloride complex **12** could be compared to the reported structure of oxo-bridged dimer $[Sn(OCH_2CH_2NMe_2)Cl]_2$ [19]. Similar dimeric structure has been found for analogous tin–amido complex $\{Sn(OCH_2CH_2NMe_2)[N(SiMe_3)_2]\}_2$, too [6c]. On the contrary, purely monomeric structure of the germanium analogue $Ge(OCH_2CH_2NMe_2)[N(SiMe_3)_2]$ has been reported in the same paper. According to this structure and the $\delta(^{119}Sn)$ comparison of **13** with chemical shifts values found for monomeric three-coordinated tin guanidinates [20], we propose the monomeric character of **13**, too.

2.3. Solid state studies

Four molecular structures of compounds **7**, **8**, **9** and **12** were determined by X-ray diffraction techniques. The common feature of first three structures as well as of structures reported in the literature containing two *O,N*-chelating ligands is the trans arrangement of the nitrogen donor atoms which are relatively strongly interacting with the metal centre.

The geometry of the tin centre in $L^{NO}_2SnPh_2$ (**7**, Fig. 3) can be best described as a distorted octahedron with all *trans* arrangement which have not been reported so far. Both nitrogen atoms are tightly connected to the tin centre (Sn1–N1 2.380(2) Å) clutching almost perfect straight angle (N1–Sn1–N1a = 179.98°). Similarly strong intramolecular connection N–Sn was found in the structure of monoorganotin(IV) compound $PhSn(OCH_2CH_2NMe_2)_2Cl$, where oxygen atoms of the ligand reveal mutual *cis* arrangement [21]. The angle between the pivotal carbon atom of the phenyl ring, oxygen and the tin atom is found to be 126.50(15)° which is more or less 20° more opened than is found in compounds bearing the $-OCH_2CH_2NMe_2$ ligand forming smaller rings [6,19,21,22].

Complex $L^{NO}_2SnCl_2$ (**8**, Fig. 4) has similar structural arrangement as $PhSn(OCH_2CH_2NMe_2)_2Cl$ [21] with only the phenyl ring substituted by chlorine atom. The intramolecular contact between Sn and N atoms is the strongest interaction (Sn1–N1 2.275(4); Sn1–N2 2.269(4) Å) ever found in the class of tin(IV) compounds chelated by an amino group. The direct comparison of **8** and $L^{CN}_2SnCl_2$ shows different arrangement of the tin coordination polyhedra in $L^{CN}_2SnCl_2$ with *cis*-arranged nitrogen atoms and much longer interatomic distances (Sn–N 2.618(3) and Sn–Cl 2.4390(3) Å). On the other hand, the Sn–Cl distance in $PhSn(OCH_2CH_2NMe_2)_2Cl$ is even longer (2.524 Å) and all O–Sn–O angles are close to the right angle.

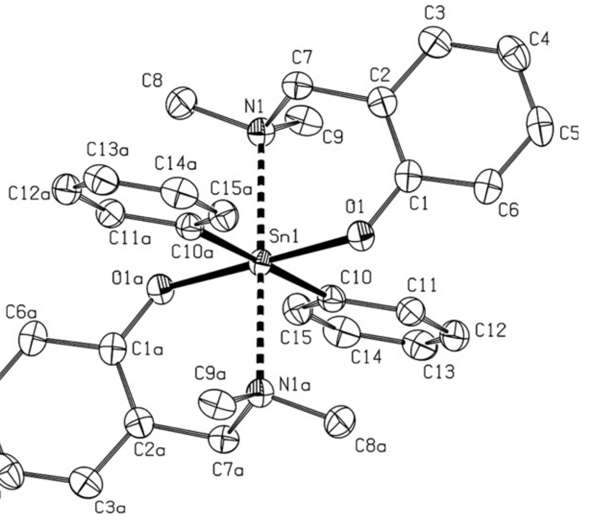


Fig. 3. Molecular structure of **7** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1—N1 2.380(2), Sn1—O1 2.111(2), Sn1—C10 2.171(3), O1—C1 1.338(4), C1—C2 1.408(4), C2—C7 1.506(4), N1—C8 1.479(3); N1—Sn1—N1a 179.98(8), O1—Sn1—O1a 179.98(9), C10—Sn1—C10a 180.00(7), O1—Sn1—N1 87.82(7), O1—Sn1—C10 90.55(9), Sn1—O1—C1 126.51(15), O1—C1—C2 122.8(2), C1—C2—C7 121.5(3), C2—C7—N1 113.9(2), C7—N1—Sn1 105.64(15), C1 O1 Sn1 126.50(15).

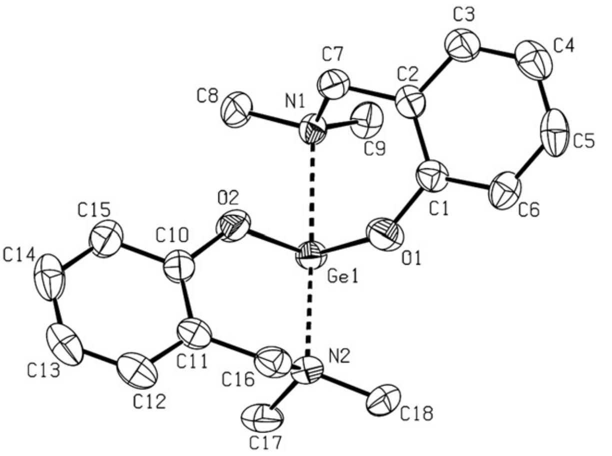


Fig. 5. Molecular structure of **9** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ge1—O1 1.857(3), Ge1—O2 1.857(3), Ge1—N1 2.306(3), Ge1—N2 2.328(3); O1—Ge1—O2 93.94(13); N1—Ge1—N2 165.28(11); C10—O2—Ge1 130.7(3); C1—O1—Ge1 131.5(3).

In divalent compounds **9** and **12**, the angle between the pivotal carbon atom of the phenyl ring, oxygen and the metalloid or metal atom is even bigger than in the tin(IV) compounds. On the other hand, the Ψ-trigonal bipyramidal structure, with nitrogen atoms in axial positions and oxygen atoms and the lone electron pair in the equatorial plane, of L_2^{NO}Ge (**9**, Fig. 5) is comparable to the structure of $Ge(OCH_2CH_2NMe_2)_2$ [6e] with only slightly different angles within the germanium primary coordination sphere. Also similarities between structure of **9** with $Sn(OCH_2CH_2NMe_2)_2$ [6e] are evident when taking different covalent radii of Ge and Sn atoms into the account.

The dimeric structure of L^{NO}SnCl (**12**, Fig. 6) formed by O—Sn contacts to dissymmetric non-planar four membered dioxadistanna ring was determined by crystallographic techniques. Similar type of structures of *O*,*N*-chelated compounds are reported for $\{Sn(OCH_2CH_2NMe_2)Cl\}_2$, $\{Sn(OCH_2CH_2NMe_2)F\}_2$ [6e] and $\{Sn(OCH_2CH_2NMe_2)N_3\}_2$ [22] but all these compounds are characteristic by planar central ring and the coordinated nitrogen atoms from ligands are located not far from this plane, too. On the other hand, the central ring in **12** reveals high degree of distortion with Sn2 and Sn4 atoms about 1 Å out for the plane defined by Sn1, O27 and O29, and Sn3, O19 and O20, respectively. Also the interatomic

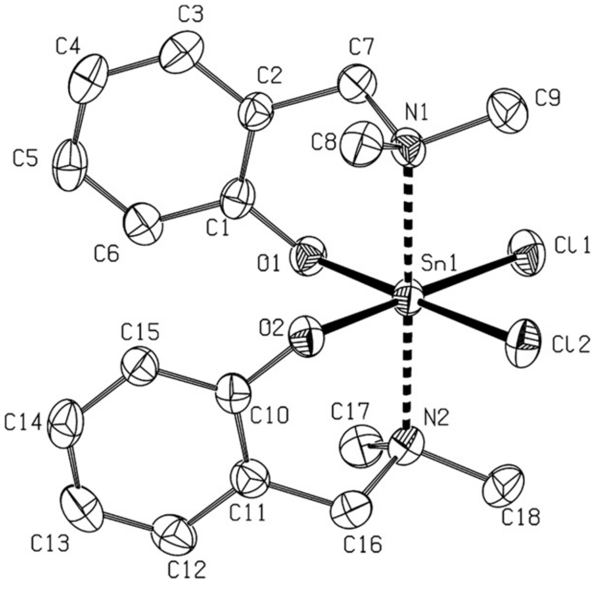


Fig. 4. Molecular structure of **8** (ORTEP view, 50% probability level). Hydrogen atoms and THF molecules are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1—O1 2.024(3), Sn1—O2 2.023(3), Sn1—Cl1 2.4101(13), Sn1—Cl2 2.4058(13), Sn1—N1 2.275(4), Sn1—N2 2.269(4), O1—C1 1.346(5); N1—Sn1—N2 178.95(13), N1—Sn1—Cl2 98.23(10), O1—Sn1—Cl2 177.62(9), O2—Sn1—Cl1 178.17(9), O2—Sn1—O1 90.63(9), C1—O1—Sn1 119.7(3), C10—O2—Sn1 120.9(3).

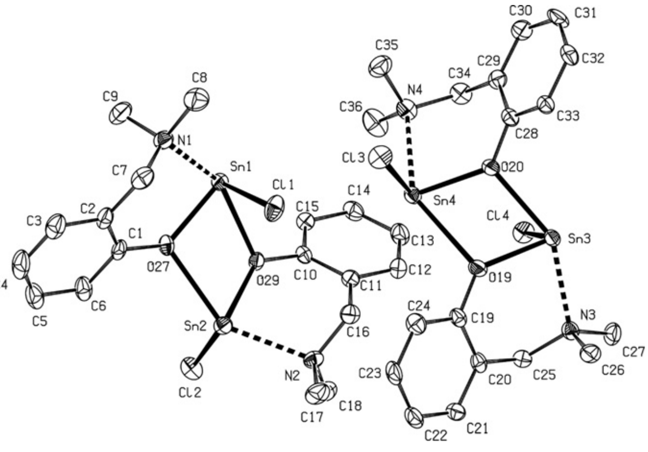


Fig. 6. Molecular structure of **12** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Both independent molecules are shown. Selected interatomic distances [Å] and angles [°]: Sn1—O27 2.109(3), Sn1—O29 2.366(3), Sn1—N1 2.407(4), Sn1—Cl1 2.4856(12), Sn2—O29 2.123(3), Sn2—N2 2.438(4), Sn2—Cl2 2.4784(12), Sn2—O27 2.480(3), Sn3—O19 2.090(3), Sn3—O20 2.363(3), Sn3—N3 2.426(4), Sn3—Cl4 2.4965(11), Sn4—O20 2.133(3), Sn4—N4 2.456(4), Sn4—Cl3 2.4681(12); O27—Sn1—O29 70.01(11), O27—Sn1—N1 81.99(12), O29—Sn1—N1 147.93(12), O27—Sn1—Cl1 91.83(9), O29—Sn1—Cl1 81.02(7), N1—Sn1—Cl1 84.67(10), C1—O27—Sn1 133.9(3), C1—O27—Sn2 116.7(3), Sn1—O27—Sn2 104.49(12), C10—O29—Sn2 132.6(3), C10—O29—Sn1 114.1(2), Sn2—O29—Sn1 108.05(12), O19—Sn3—O20 70.84(11), O19—Sn3—N3 82.31(12), O20—Sn3—N3 149.82(11), O19—Sn3—Cl4 90.78(9), O20—Sn3—Cl4 81.13(8), N3—Sn3—Cl4 85.83(9), O29—Sn2—N2 81.92(12), O29—Sn2—Cl2 91.92(8), N2—Sn2—Cl2 94.25(9), O29—Sn2—O27 67.55(10), N2—Sn2—O27 145.69(11), Cl2—Sn2—O27 101.77(8), O20—Sn4—N4 82.63(12), O20—Sn4—Cl3 89.37(9), N4—Sn4—Cl3 92.41(10).

distances within the tin polyhedra are elongated in **12** when related to other reported compounds, with the biggest difference in Sn4—O19 (2.600(3) Å) in comparison to 2.282 Å found for the longest Sn—O distance in $\{Sn(OCH_2CH_2NMe_2)F\}_2$ [6e]. In all previously reported compounds similarly as in **12**, the tin coordination geometry is square pyramidal with chlorine atom in the top and the rest of coordinated atoms as well as the lone electron pair in the basement of the pyramid.

3. Conclusion

In conclusion, thirteen new compounds of group 14 metalloid/metals containing *O,N*-chelating ligand(s) were prepared and structurally characterized. It seems, the intramolecular coordination between nitrogen and tin atoms, and thus the formation of the six-membered ring, is rather strong, and even stronger in the direct comparison to analogous compounds with five-membered rings with $OCH_2CH_2NMe_2$ as *O,N*- or L^{CN} as *C,N*-chelating ligands. Compounds bearing two L^{NO} ligands prefer mutual *trans* arrangement of the donor groups, the rest of the groups are arranged *trans* in diorganotin(IV) compounds or *cis* in the purely inorganic compound $L^{NO}_2SnCl_2$. In the cases of low valent complexes, monomeric bischelated germylene was observed while dimeric heteroleptic stannylene with bridging L^{NO} ligands and highly distorted was determined.

4. Experimental part

4.1. NMR spectroscopy

NMR spectra were recorded from solutions in benzene-d_6, toluene-d_8 or THF-d_8 on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5 mm probe) at frequencies for ^1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), and $^{119}Sn\{^1H\}$ (186.50 MHz) at 295 K. All deuterated solvents were degassed and stored over a potassium mirror under an argon atmosphere. Samples were obtained by dissolving approximately 40 mg (when possible) of each compound approximately in 0.5 mL of deuterated solvent. Values of ^1H chemical shifts were calibrated to internal standard – tetramethylsilane ($\delta(^1H) = 0.00$ ppm) or to residual signals of benzene ($\delta(^1H) = 7.16$ ppm), toluene ($\delta(^1H) = 2.09$ ppm) or THF ($\delta(^1H) = 1.73$ ppm), respectively. Values of ^{13}C chemical shifts were calibrated to signals of THF ($\delta(^{13}C) = 67.6$ ppm) or benzene ($\delta(^{13}C) = 128.4$ ppm). The ^{119}Sn chemical shift values are referred to external neat tetramethylstannane ($\delta(^{119}Sn) = 0.0$ ppm). Positive chemical shift values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. All ^{13}C NMR spectra were measured using standard proton-decoupled experiment and CH and CH_3 vs. C and CH_2 were differentiated by the help of APT method [23] and the rest of the signals was assigned according to the standard 2D measurements. Only mean values of $^3J(^1H, ^1H)$ of the observed dd resonances are given.

4.2. Crystallography

The X-ray data (Table 2) obtained from colourless crystals for all compounds were acquired at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and in the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [24]. The absorption was corrected by integration methods [25]. Structures were solved by direct methods (Sir92) [26] and refined by full matrix least-square based on F^2 (SHELXL97) [27]. Hydrogen atoms were mostly localized on a difference Fourier map, but in order to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C—H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively.

4.3. Synthesis

All syntheses were performed using standard Schlenk techniques under an inert argon atmosphere. Solvents and reactants were purchased from commercial sources and purified by standard procedures when necessary. Solvents were distilled over K/Na alloy, degassed and then stored over a K-mirror under an argon atmosphere. Single crystals suitable for XRD analyzes are obtained under argon from corresponding saturated solutions of products in toluene or hexane at −30 °C. Melting points were measured under a film of inert perfluoroalkylether and were uncorrected. ^1H and ^{13}C

Table 2
Selected crystallographic parameters of **7**, **8**·THF, **9**, and **12**.

Compound reference	**7**	**8**·THF	**9**	**12**
Chemical formula	$C_{30}H_{34}N_2O_2Sn$	$C_{18}H_{24}Cl_2N_2O_2Sn$, C_4H_8O	$C_{18}H_{24}GeN_2O_2$	$C_{18}H_{24}Cl_2N_2O_2Sn_2$
Formula mass	573.28	562.09	372.98	608.67
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	Cc	$P2_1/c$
a [Å]	10.0780(3)	9.5610(9)	13.2800(3)	14.7980(8)
b [Å]	9.1359(4)	13.0670(7)	16.0423(5)	9.4580(11)
c [Å]	16.1161(7)	19.4551(16)	8.6390(6)	31.752(3)
α [°]	90	90	90	90
β [°]	119.910(4)	90	98.102(3)	100.763(5)
γ [°]	90	90	90	90
Unit cell volume [Å^3]	1286.20(10)	2430.6(3)	1822.10(15)	4365.8(7)
Z	2	4	4	8
μ [mm^{-1}]	1.023	1.296	1.692	2.547
No. of reflections measured	12,518	17,143	11,125	27,143
No. of independent reflections[a]	2165	4646	3127	7476
R_{int}	0.0344	0.0436	0.0596	0.0442
Final R_1 values ($I > 2\sigma(I)$)[b]	0.0417	0.0480	0.0669	0.0362
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[b]	0.0522	0.0699	0.0710	0.0590
Goodness of fit on F^2 [c]	1.081	1.112	1.143	1.172

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$.
[b] Weighting scheme : $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$.
[c] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffr.} - N_{param.})]^{½}$.

NMR spectra of starting 2-[(dimethylamino)methyl]phenol were determined in deuterated chloroform. Preparation of starting compounds containing L^{CN} ligand [12], L^{NO}Na [8], and $[(Me_3Si)_2N]_2M$ [2] is published elsewhere, the rest of the compounds of sufficient purity was obtained from commercial sources (Sigma–Aldrich).

4.3.1. General method for preparation of tin(IV) and phenolates

To a solution (suspension) of appropriate starting organotin(IV) chloride in toluene (**4**, **5**, **7**), benzene (**2**) or THF (**1**, **3**, **6** and **8**) at room temperature, corresponding equivalent(s) of starting sodium 2-(*N,N*-dimethylaminomethyl)phenolate was added. Reaction mixtures were stirred overnight and filtered. Afterwards all volatiles from obtained filtrates were evaporated in *vacuo* giving desired products of sufficient purity. Products were washed with hexanes when necessary.

*4.3.1.1. Preparation of $L^{NO}_2Sn(n\text{-}Bu)_2$ (**1**).* 0.725 g of $(n\text{-}Bu)_2SnCl_2$ (2.39 mmol) and 0.826 g of L^{NO}Na (4.78 mmol) was mixed in 40 ml of tetrahydrofuran. 0.974 g (76%) of yellow oily **1** was obtained. ^{1}H NMR (C_6D_6, 295 K, ppm): 7.11 (m, 6H, H(3, 5, 6)); 6.73 (dd, 2H, H(4), ^{3}J = 7.2 Hz); 3.38 (s, 4H, CH_2N); 2.07 (s, 6H, $N(CH_3)_2$); 1.72 (br, 4H, H(α)); 1.35 (br, 4H, H(β)); 1.28 (m, 4H, H(γ)); 0.83 (t, 6H, H(δ), ^{3}J = 7.3 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm): 162.5 (C(1), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 131.1 (C(3)); 129.6 (C(5)); 126.0 (br, C(2)); 121.0 (C(4)); 118.0 (C(6), $^{3}J(^{119}Sn, ^{13}C)$ = 56 Hz); 62.4 (CH_2N); 46.4 ($N(CH_3)_2$); 28.2 (C(β), $^{2}J(^{119}Sn, ^{13}C)$ = 30 Hz); 27.6 (C(γ), $^{3}J(^{119}Sn, ^{13}C)$ = 64 Hz); 21.8 (br, C(α), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 14.2 (C(δ)). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −201.0. Elemental analysis (%): found: C, 57.7; H, 7.9; N, 5.0 Calcd (%) for $C_{26}H_{42}N_2O_2Sn$ (533.33): C 58.56; H 7.94; N 5.25.

*4.3.1.2. Preparation of $L^{NO}L^{CN}Sn(n\text{-}Bu)_2$ (**2**).* 0.272 g of L^{NO}Na (1.57 mmol) and 0.632 g of $L^{CN}Bu_2SnCl$ (1.57 mmol) was mixed in 30 ml of benzene. 0.520 g (64%) of pale yellow oily **2** was obtained. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.38 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6'))$ = 6.9 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 56 Hz); 7.64 (d, 1H, H(6), $^{3}J(^{1}H(5), ^{1}H(6))$ = 7.2 Hz); 7.16–7.11 (m, 3H, H(4′, 5′, 6)); 6.91 (d, 1H, H(3′), $^{3}J(^{1}H(3'), ^{1}H(4'))$ = 6.5 Hz); 6.85 (dd, 2H, H(4, 5), ^{3}J = 7.0 Hz); 3.84 (s, 2H, CH_2N (L^{NO})); 3.04 (s, 2H, CH_2N (L^{CN})); 2.38 (s, 6H, $N(CH_3)_2$ (L^{NO})); 1.74 (s, 6H, $N(CH_3)_2$ (L^{CN})); 1.72 (m, 4H, H(β)); 1.35 (m, 4H, H(γ)); 1.23 (t, 4H, H(α), ^{3}J = 7.6 Hz, $^{2}J(^{119}Sn, ^{1}H)$ = 59 Hz); 0.87 (t, 6H, H(δ), ^{3}J = 7.4 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm): 163.3 (C(1), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 143.5 (C(2′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 142.6 (C(1′), $^{1}J(^{119}Sn, ^{13}C)$ was not observed); 138.9 (br, C(6′)); 131.0 (C(3)); 129.7 (C(2), $^{3}J(^{119}Sn, ^{13}C)$ was not observed); 129.3 (C(5)); 128.7 (C(4′)); 127.9 (C(5′), $^{3}J(^{119}Sn, ^{13}C)$ was not observed); 127.3 (C(3′)); 119.0 (C(4)); 116.8 (C(6), $^{3}J(^{119}Sn, ^{13}C)$ was not observed); 65.7 (CH_2N (L^{CN}), $^{n}J(^{119}Sn, ^{13}C)$ = 25 Hz); 59.5 (CH_2N (L^{NO})); 46.2 ($N(CH_3)_2$ (L^{CN})); 45.2 ($N(CH_3)_2$ (L^{NO})); 28.6 (C(β), $^{2}J(^{119}Sn, ^{13}C)$ = 29 Hz); 27.5 (C(γ), $^{3}J(^{119}Sn, ^{13}C)$ = 79 Hz); 16.0 (C(α), $^{1}J(^{119}Sn, ^{13}C)$ = 479 Hz); 14.0 (C(δ)). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −86.9. Elemental analysis (%): found: C, 60.2; H, 8.1; N, 5.2. Calcd (%) for $C_{26}H_{42}N_2OSn$ (517.33): C 60.36; H 8.18; N 5.41.

*4.3.1.3. Preparation of $L^{NO}(n\text{-}Bu)_2SnCl$ (**3**).* 1.146 g of L^{NO}Na (6.61 mmol) and 2.010 g of $(n\text{-}Bu)_2SnCl_2$ (6.61 mmol) was mixed in 30 ml of tetrahydrofuran. 2.404 g (68%) of pale yellow oily **3** was obtained. ^{1}H NMR (THF-d_8, 295 K, ppm): 7.13 (dd, 1H, H(5), ^{3}J = 7.5 Hz); 6.99 (dd, 1H, H(3), ^{3}J = 7.5 Hz); 6.71 (d, 1H, H(6), $^{3}J(^{1}H(5), ^{1}H(6))$ = 8.0 Hz); 6.60 (dd, 1H, H(4), ^{3}J = 7.4 Hz); 3.80 (s, 2H, CH_2N); 2.65 (s, 6H, $N(CH_3)_2$); 1.78 (m, 4H, H(β)); 1.57 (t, 4H, H(α), ^{3}J = 7.5 Hz, $^{2}J(^{119}Sn, ^{1}H)$ = 80 Hz); 1.36 (m, 4H, H(γ)); 0.91 (t, 6H, H(δ), ^{3}J = 7.5 Hz). ^{13}C NMR (THF-d_8, 295 K, ppm): 163.9 (C(1), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 131.2 (C(3)); 131.1 (C(5)); 123.6 (C(2), $^{3}J(^{119}Sn, ^{13}C)$ was not observed); 120.9 (C(4)); 117.8 (C(6)); 64.9 (CH_2N); 46.9 ($N(CH_3)_2$); 33.0 (br, C(α), $^{1}J(^{119}Sn, ^{13}C)$ = could not be read); 27.7 (C(β), $^{2}J(^{119}Sn, ^{13}C)$ = 28 Hz); 25.8 (C(γ), $^{3}J(^{119}Sn, ^{13}C)$ = 101 Hz); 12.5 (C(δ)). ^{119}Sn NMR (THF-d_8, 295 K, ppm) δ: −157.7. Elemental analysis (%): found: C, 49.0; H, 7.4; N, 3.3. Calcd (%) for $C_{17}H_{30}ClNOSn$ (418.58): C 48.78; H 7.22; N 3.35.

*4.3.1.4. Preparation of $L^{NO}SnMe_3$ (**4**).* 0.869 g of L^{NO}Na (5.02 mmol) and 1.000 g (5.02 mmol) of Me_3SnCl was mixed in 30 ml of toluene. After the workup of the reaction mixture, the crude product was washed with hexane to give 0.667 g (42%) of white crystalline **4**. ^{1}H NMR (C_6D_6, 295 K, ppm): 7.48 (d, 1H, H(3), ^{3}J (^{1}H(4), ^{1}H(3)) = 8.7 Hz); 7.22 (m, 1H, H(5)); 6.94 (dd, 1H, H(4), ^{3}J = 9.1 Hz); 6.78 (d, 1H, H(6), ^{3}J (^{1}H(5), ^{1}H(6)) = 9.7 Hz); 3.61 (s, 2H, CH_2N); 2.22 (s, 6H, $N(CH_3)_2$); 0.26 (s, 9H, $Sn(CH_3)_3$, $^{2}J(^{119}Sn, ^{1}H)$ = 57 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm): 161.7 (C(1), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 131.8 (C(3)); 129.0 (C(5)); 123.9 (C(2)); 120.1 (C(4)); 119.2 (C(6)); 60.0 (CH_2N); 46.2 ($N(CH_3)_2$); −2.9 ($Sn(CH_3)_3$, $^{1}J(^{119}Sn, ^{13}C)$ = 392 Hz). ^{119}Sn NMR (C_6D_6, 295 K, ppm) δ: 135.7. Elemental analysis (%): found: C, 45.9; H, 6.7; N, 4.5. Calcd (%) for $C_{12}H_{21}NOSn$ (314.00): C 45.90; H 6.74; N 4.46.

*4.3.1.5. Preparation of $L^{NO}Sn(n\text{-}Bu)_3$ (**5**).* 1.146 g of L^{NO}Na (6.61 mmol) and 2.153 g (6.61 mmol) of $(n\text{-}Bu)_3SnCl$ was mixed in 40 ml of toluene overnight. Resulting suspension was filtered and the filtrate was evaporated to dryness *in vacuo*. 1.44 g (49%) of pale yellow oily **5** was obtained. ^{1}H NMR (C_6D_6, 295 K, ppm): 7.37 (d, 1H, H(3), ^{3}J (^{1}H(4), ^{1}H(3)) = 7.4 Hz); 7.07 (dd, 1H, H(5), ^{3}J = 7.7 Hz); 6.78 (dd, 1H, H(4), ^{3}J = 7.5 Hz); 6.64 (d, 1H, H(6), ^{3}J(^{1}H(5), ^{1}H(6) = 7.9 Hz)); 3.52 (s, 2H, CH_2N); 2.20 (s, 6H, $N(CH_3)_2$); 1.56 (m, 6H, H(β)); 1.25 (m, 6H, H(γ)); 1.12 (t, 6H, H(α), ^{3}J = 6.1 Hz, $^{2}J(^{119}Sn, ^{1}H)$ = 51 Hz); 0.85 (t, 9H, H(δ), ^{3}J = 6.2 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm)δ: 161.9 (C(1), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 131.5 (C(3)); 130.3 (C(2)); 128.4 (C(5)); 119.5 (C(4)); 118.8 (C(6)); 59.7 (CH_2N); 46.5 ($N(CH_3)_2$); 28.6 (C(β), $^{2}J(^{119}Sn, ^{13}C)$ = 21 Hz); 27.8 (C(γ), $^{3}J(^{119}Sn, ^{13}C)$ = 61 Hz); 16.6 (C(α), $^{1}J(^{119}Sn, ^{13}C)$ = 350 Hz); 14.3 (C(δ)). ^{119}Sn NMR (C_6D_6, 295 K, ppm): 105.2. Elemental analysis (%): found: C, 57.5; H, 9.1; N, 3.2. Calcd (%) for $C_{21}H_{39}NOSn$ (440.25): C 57.29; H 8.93; N 3.18.

*4.3.1.6. Preparation of $L^{NO}L^{CN}SnPh_2$ (**6**).* 0.431 g of L^{NO}Na (2.49 mmol) and 1.102 g (2.49 mmol) of $L^{CN}Ph_2SnCl$ was mixed in 50 ml of THF. The mixture was heated to reflux for 2 h. Obtained suspension was filtered and the resulting filtrate was evaporated to dryness *in vacuo*. The residue was washed with hexane, and the product was extracted with benzene. Evaporation of benzene extract *in vacuo* gave 0.507 g (36%) of white crystalline **6**. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.92 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6'))$ = 7.0 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 61 Hz); 7.75 (d, 4H, H(2″), $^{3}J(^{1}H(3''), ^{1}H(2''))$ = 7.8 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 57 Hz); 7.43–7.38 (m, 2H, H(3, 5′)); 7.27 (m, 1H, H(4′)); 7.17 (m, 6H, H(3″, 4″)); 7.00 (d, 1H, H(3′), ^{3}J = 9.0 Hz); 6.88 (dd, 1H, H(5), ^{3}J = 9.1 Hz); 6.72 (d, 1H, H(6), $^{3}J(^{1}H(5), ^{1}H(6))$ = 9.0 Hz); 6.66 (dd, 1H, H(4), ^{3}J = 7.6 Hz); 3.73 (s, 2H, CH_2N (L^{NO})); 3.08 (s, 2H, CH_2N (L^{CN})); 2.30 (s, 6H, $N(CH_3)_2$ (L^{NO})); 1.43 (s, 6H, $N(CH_3)_2$ (L^{CN})). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −212.4. Elemental analysis (%): found: C, 64.9; H, 6.3; N, 4.9. Calcd (%) for $C_{30}H_{34}N_2OSn$ (557.31): C 64.66; H 6.15; N 5.03.

*4.3.1.7. Preparation of $L^{NO}_2SnPh_2$ (**7**).* 1.212 g of L^{NO}Na (7.00 mmol) and 1.203 (3.50 mmol) of Ph_2SnCl_2 was mixed together in 50 ml of toluene. Obtained suspension was filtered and the filtrate was evaporated to dryness *in vacuo*. White crystalline **7** was obtained. Single crystals of **7** were obtained from its toluene solution after the addition of hexane within few days at ambient temperature. M.p. 255–256 °C. ^{1}H NMR (THF-d_8, 295 K, ppm): 7.48 (d, 4H, H(2″), $^{3}J(^{1}H(3''), ^{1}H(2''))$ = 7.8 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 54 Hz); 7.32 (br, 2H, H(3));

7.30 (dd, 2H, H(5), $^3J = 2.0$ Hz); 7.27 (m, 4H, H(3″)); 6.93 (d, 2H, H(6), $^3J(^1H(5), ^1H(6)) = 7.6$ Hz); 6.67 (br, 2H, H(4)); 3.57 (s, 4H, CH_2N); 2.26 (s, 12H, $N(CH_3)_2$). Elemental analysis (%): found: C, 63.1; H, 6.2; N, 4.7 Calcd (%) for $C_{30}H_{34}N_2O_2Sn$ (573.31): C 62.85; H 5.98; N 4.89.

*4.3.1.8. Preparation of $L_2^{NO}SnCl_2$ (**8**).* 0.376 g of (COD)$PdCl_2$ (1.32 mmol) and 0.553 g of SnL_2^{NO} (1.32 mmol, (**10**), see below) was mixed in 30 ml of THF. Obtained suspension was filtered and the filtrate was evaporated under *vacuo* to dryness and washed with hexane. White powder was obtained. Single crystals of **8** were isolated from its saturated THF solution which was stored in a freezing box for several days. M.p. 152 °C (dec.). ^1H NMR (THF-d_8, 295 K, ppm): 7.04 (m, 4H, H(3, 5)); 6.68 (dd, 2H, (H(4)), $^3J = 7.8$ Hz); 6.38 (br d, 2H, H(6), $^3J(^1H(5), ^1H(6)) = 7.8$ Hz); 4.11 and 4.06 (broad with a saddle point, 4H, CH_2N); 2.94 (s, 6H, anisochronous $N(CH_3)_2$, $^3J(^{119}Sn, ^1H) = 30$ Hz); 2.78 (s, 6H, anisochronous $N(CH_3)_2$, $^3J(^{119}Sn, ^1H) = 41$ Hz). ^{13}C NMR (THF-d_8, 295 K, ppm): 162.5 (C(1), $^2J(^{119}Sn, ^{13}C)$ was not observed); 130.8 (C(3)); 130.6 (C(5)); 123.7 (C(2)); 121.4 (C(4)); 118.9 (C(6)); 64.2 (CH_2N); 48.0 (anisochronous $N(CH_3)_2$); 47.9 (anisochronous $N(CH_3)_2$). ^{119}Sn NMR (THF-d_8, 295 K, ppm): −575.9. Elemental analysis (%): found: C, 44.1; H, 4.8; N, 5.8. Calcd (%) for $C_{18}H_{24}Cl_2N_2O_2Sn$ (490.01): C 44.12; H 4.94; N 5.72.

4.3.2. General method for the preparation of homoleptic germanium(II), tin(II) and lead(II) phenolates

To a solution of bis[bis(trimethylsilyl)amino]metal(II) or metalloid(II) in toluene at room temperature, two equivalents of starting 2-[*N*,*N*-dimethyl(aminomethyl)]phenol were added. Reaction mixtures were stirred, until change of colour from yellow to colourless was observed. The solutions were then filtered, toluene and formed hexamethyldisilazane were evaporated *in vacuo*. Residues were washed with petroleum ether giving desired products of sufficient purity in relatively low to moderate yields.

*4.3.2.1. Preparation of $L_2^{NO}Ge$ (**9**).* 0.459 g of $[(Me_3Si)_2N]_2Ge$ (1.16 mmol) and 0.351 g of $L^{NO}H$ (2.32 mmol) were mixed in 30 ml of toluene. After the workup, 0.186 g (44%) of white crystalline **9** was obtained. Single crystals of **9** were isolated from its saturated toluene solution which was stored in a freezing box for several days. M.p. 124–125 °C. ^1H NMR (toluene-d_8, 295 K, ppm): 7.19 (dd, 2H, H(5) $^3J = 7.3$ Hz); 6.89 (d, 2H, H(3), $^3J(^1H(4), ^1H(3)) = 7.9$ Hz); 6.83 (d, 2H, H(6), $^3J(^1H(5), ^1H(6)) = 6.8$ Hz); 6.74 (dd, 2H, H(4), $^3J = 7.2$ Hz); 3.90 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) = 12.1$ Hz); 2.87 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) = 12.1$ Hz); 2.00 (s, 12H, $N(CH_3)_2$). ^{13}C NMR (toluene-d_8, 295 K, ppm): 160.2 (C(1)); 130.8 (C(3)); 130.0 (C(5)); 126.0 (C(2)); 121.4 (C(4)); 118.5 (C(6)); 60.5 (CH_2N); 44.0 ($N(CH_3)_2$). Elemental analysis (%): found: C, 57.5; H, 6.8; N, 7.6. Calcd (%) for $C_{18}H_{24}N_2O_2Ge$ (373.00): C 57.91; H 6.48; N 7.51.

*4.3.2.2. Preparation of $L_2^{NO}Sn$ (**10**).* 1.441 g of $[(Me_3Si)_2N]_2Sn$ (3.28 mmol) and 0.991 g of $L^{NO}H$ (6.56 mmol) were mixed in 30 ml of toluene. After the workup, 0.288 g (21%) of white powder was obtained. ^1H NMR (C_6D_6, 295 K, ppm): 7.31 (dd, 2H, H(5), $^3J = 7.7$ Hz); 7.05 (d, 2H, H(3), $^3J(^1H(4), ^1H(3)) = 8.0$ Hz); 6.90 (d, 2H, H(6), $^3J(^1H(5), ^1H(6)) = 6.6$ Hz); 6.79 (dd, 2H, H(4), $^3J = 7.3$ Hz); 4.15 (extremely broad, 2H, anisochronous CH_2N); 2.85 (extremely broad, 2H, anisochronous CH_2N); 1.92 (extremely broad, 12H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6, 295 K, ppm): 162.0 (C(1), $^2J(^{119}Sn, ^{13}C)$ was not observed); 131.3 (C(3)); 130.2 (C(5)); 125.1 (C(2)); 121.2 (C(4)); 117.3 (C(6)); 60.8 (CH_2N); 45.3 ($N(CH_3)_2$). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −528.0. ^1H NMR (toluene-d_8, 220 K, ppm): 7.35 (br, 2H, H(5)); 7.04 (br, 2H, H(3)); 6.87 (br, 2H, H(6)); 6.83 (br, 2H, H(4)); 4.27 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) = 10.4$ Hz); 2.56 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) = 10.4$ Hz); 2.23 (s, 6H, anisochronous $N(CH_3)_2$); 2.50 (s, 6H, anisochronous $N(CH_3)_2$). ^{119}Sn NMR (toluene-d_8, 220 K, ppm): −538.1. Elemental analysis (%): found: C, 51.8; H, 5.8; N, 6.4 Calcd (%) for $C_{18}H_{24}N_2O_2Sn$ (419.09): C 51.59; H 5.77; N 6.68.

*4.3.2.3. Preparation of $L_2^{NO}Pb$ (**11**).* 0.627 g of $[(Me_3Si)_2N]_2Pb$ (1.19 mmol) and 0.360 g (2.38 mmol) of $L^{NO}H$ were mixed in 30 ml of toluene. After the workup and re-crystallization from toluene 0.144 g (24%) of white powder was obtained. ^1H NMR (THF-d_8, 295 K, ppm): 7.08 (dd, 2H, H(5), $^3J = 9.3$ Hz); 6.92 (d, 2H, H(3), $^3J(^1H(4), ^1H(3)) = 8.8$ Hz); 6.72 (broad, 2H, H(4)); 6.49 (br, 2H, H(6)); 3.55 (broad, 4H, CH_2N); 2.20 (broad, 12H, $N(CH_3)_2$). ^{13}C NMR (THF-d_8, 295 K, ppm): 164.3 (br, C(1)); 130.4 (br, C(3, 5)); 125.1 (br, C(2)); 120.6 (br, C(4)); 115.3 br, (C(6)); 61.5 (CH_2N); 44.0 ($N(CH_3)_2$). Elemental analysis (%): found: C, 42.6; H, 4.8; N, 5.5. Calcd (%) for $C_{18}H_{24}N_2O_2Pb$ (507.59): C 42.59; H 4.77; N 5.52.

4.3.3. Preparation of heteroleptic tin(II) phenolates

To a solution of [bis(trimethylsilyl)amino]tin(II) chloride (or bis [bis(trimethylsilyl)amino]tin(II)) in toluene at room temperature, one equivalent of starting 2-[*N*,*N*-dimethyl(aminomethyl)]phenol was added. Reaction mixture was stirred until the reaction mixture became colourless. The solution was then filtered, toluene and hexamethyldisilazane were evaporated *in vacuo*. The residue was washed with petroleum ether to give pure product in sufficient yields.

*4.3.3.1. Preparation of $[L^{NO}SnCl]_2$ (**12**).* 1.450 g (4.61 mmol) of [bis(trimethylsilyl)amino]tin(II) chloride and 0.697 g (4.61 mmol) of $L^{NO}H$ was stirred in 50 ml of toluene. 0.490 g (35%) of white crystalline **12** was obtained. Single crystals of **12** were isolated from its saturated toluene solution which was kept in a freezing box for several days. M.p. 165–170 °C. ^1H NMR (THF-d_8, 295 K, ppm): 7.14 (dd, 1H, H(5), $^3J = 7.2$ Hz); 7.02 (d, 1H, H(3), $^3J(^1H(4), ^1H(3)) = 6.8$ Hz); 6.77 (d, 1H, H(6), $^3J(^1H(5), ^1H(6)) = 8.0$ Hz); 6.69 (br, 1H, H(4)); 3.88 (s, 2H, CH_2N); 2.52 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (THF-d_8, 295 K, ppm): 159.6 (C(1), $^2J(^{119}Sn, ^{13}C)$ could not be read); 128.7 (C(3)); 127.9 (C(5)); 124.0 (C(2)); 121.7 (C(4)); 117.7 (C(6)); 61.4 (CH_2N); 43.1 ($N(CH_3)_2$). ^{119}Sn NMR (THF-d_8, 295 K, ppm): −379.5. Elemental analysis (%): found: C, 35.6; H, 4.1; N, 4.4. Calcd (%) for monomeric $C_9H_{12}ClNOSn$ (304.36): C 35.52; H 3.97; N 4.60.

*4.3.3.2. Preparation of $L^{NO}SnN(SiMe_3)_2$ (**13**).* 0.793 g (1.80 mmol) of bis[bis(trimethylsilyl)amino]tin(II) and 0.273 g (1.80 mmol) of $L^{NO}H$ was mixed in 30 ml of toluene. After the workup, 0.179 g (23%) of white powder was obtained. ^1H NMR (C_6D_6, 295 K, ppm): 7.23 (dd, 1H, H(5), $^3J = 7.5$ Hz); 7.11 (d, 1H, H(3), $^3J(^1H(4), ^1H(3))) = 8.0$ Hz); 6.76–6.70 (m, 2H, (H4, 6)); 3.83 (broad, 1H, anisochronous CH_2N); 2.47 (broad, 1H, anisochronous CH_2N); 1.99 (broad, 3H, anisochronous NCH_3); 1.56 (broad, 3H, anisochronous NCH_3); 0.38 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (C_6D_6, 295 K, ppm): 162.6 (C(1), $^2J(^{119}Sn, ^{13}C)$ was not observed); 131.4 (C(3)); 128.7 (C(5)); 124.9 (C(2)); 122.7 (C(4)); 118.3 (C(6)); 61.6 (CH_2N); 45.9 (br, anisochronous NCH_3); 44.6 (br, anisochronous NCH_3); 6.9 ($Si(CH_3)_3$). ^{119}Sn NMR C_6D_6, 295 K, ppm): −53.4. Elemental analysis (%): found: C, 42.2; H, 7.3; N, 6.1. Calcd (%) for $C_{15}H_{30}N_2OSi_2Sn$ (429.29): C 41.97; H 7.04; N 6.53.

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Appendix A. Supplementary material

CCDC 921159–921162 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) , in: Z. Rappoport (Ed.), The Chemistry of Organic Germanium, Tin and Lead Compounds, vol. 1 and 2, Wiley VCH, Weinheim, 2003;
(b) A.G. Davies, in: Organotin Chemistry, Wiley VCH, Weinheim, 1997 & 2004;
(c) M.F. Lappert, A.V. Protchenko, P.P. Power, A. Seeber, Metal Amide Chemistry, Wiley, John Wiley and Sons, Ltd, Chichester, UK, 2009. (Chapter 9);
(d) D.H. Harris, M.F. Lappert, J. Chem. Soc. Chem. Commun. (1974) 895–896;
(e) P.J. Davidson, D.H. Harris, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1976) 2268–2274;
(f) Y. Peng, J.D. Guo, B.D. Ellis, Z.L. Zhu, J.C. Fettinger, S. Nagase, P.P. Power, J. Am. Chem. Soc. 131 (2009) 16272–16282;
(g) Y. Peng, B.D. Ellis, S. Wang, J.C. Fettinger, P.P. Power, Science 325 (2009) 1668–1670;
(h) P.P. Power, Science 463 (2010) 171–177.

[2] (a) J.D. Cotton, P.J. Davidson, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1976) 2275–2286;
(b) M.J.S. Gynane, M.F. Lappert, S.J. Miles, P.P. Power, J. Chem. Soc. Chem. Commun. (1976) 256–257;
(c) M.J.S. Gynane, M.F. Lappert, S.J. Miles, P.P. Power, J. Chem. Soc. Chem. Commun. (1978) 192–193;
(d) M.F. Lappert, M.C. Misra, M. Onyszchuk, R.S. Rowe, P.P. Power, M.J. Slade, J. Organomet. Chem. 330 (1987) 31–46;
(e) I. Gűmrűkçű, A. Hudson, M.F. Lappert, M.J. Slade, P.P. Power, J. Chem. Soc. Chem. Commun. (1980) 776–777;
(f) K.A. Miller, J.M. Bartolin, R.M. O'Neil, R.D. Sweeder, T.M. Owens, M.M. Kampf, M.M. Banaszak Holl, N.J. Wells, J. Am. Chem. Soc. 125 (2003) 8986–8987;
(g) A. Kavara, T.T. Boron, Z.S. Ahsan, M.M. Banaszak Holl, Organometallics 29 (2010) 5033–5039;
(h) J.M. Bartolin, A. Kavara, J.W. Kampf, M.M. Banaszak Holl, Organometallics 25 (2006) 4738–4740.

[3] For example: E. Rivard, P.P. Power Inorg. Chem. 46 (2007) 10047–10064;
(a) R. Okazaki, M. Unno, N. Inamoto, Chem. Lett. (1987) 2293–2295;
(b) R. Okazaki, M. Unno, N. Inamoto, G. Yamamoto, Chem. Lett. (1989) 493–495;
(c) M. Saito, N. Tokitoh, R. Okazaki, Organometallics 15 (1996) 4531–4536;
(d) R.S. Simons, L. Pu, M.M. Olmstead, P.P. Power, Organometallics 16 (1997) 1920–1925.

[4] (a) Z. Padělková, M.S. Nechaev, Z. Černošek, J. Brus, A. Růžička, Organometallics 27 (2008) 5303–5308;
(b) Z. Padělková, H. Vaňkátová, I. Císařová, M.S. Nechaev, T.A. Zevaco, O. Walter, A. Růžička, Organometallics 28 (2009) 2629–2632;
(c) Z. Padělková, I. Císařová, M.S. Nechaev, A. Růžička, J. Organomet. Chem. 694 (2009) 2871–2874;
(d) Z. Padělková, M.S. Nechaev, A. Lyčka, J. Holubová, T.A. Zevaco, A. Růžička, Eur. J. Inorg. Chem. (2009) 2058–2061;
(e) Z. Padělková, I. Císařová, K. Fejfarová, J. Holubová, A. Růžička, J. Holeček, Collect. Czech. Chem. Commun. 72 (2007) 629–636;
(f) J. Bareš, P. Richard, P. Meunier, N. Pirio, Z. Padělková, Z. Černošek, I. Císařová, A. Růžička, Organometallics 28 (2009) 3105–3108.

[5] H. Vaňkátová, L. Broeckaert, F. De Proft, R. Olejník, J. Turek, Z. Padělková, A. Růžička, Inorg. Chem. 50 (2011) 9454–9464.

[6] For example: (a) M.S. Nechaev, J. Mol. Struct. Theochem. 862 (2008) 49–52;
(b) V.N. Khrustalev, M.Yu. Antipin, N.N. Zemlyansky, I.V. Borisova, Y.A. Ustynyuk, V.V. Lunin, J. Barrau, R.J. Ghassoub, Organomet. Chem. 689 (2004) 478–483;
(c) V.N. Khrustalev, I.A. Portnyagin, N.N. Zemlyansky, I.V. Borisova, M.S. .Nechaev, Y.A. Ustynyuk, M.Yu. Antipin, V.V. Lunin, J. Organomet. Chem. 690 (2005) 1172–1177;
(d) M.S. Nechaev, M.S. Chernov, I.A. Portnyagin, V.N. Khrustalev, R.R. Aysin, V.V. Lunin, J. Organomet. Chem. 695 (2010) 365–369;
(e) N.N. Zemlyansky, I.V. Borisova, M.G. Kuznetsova, V.N. Khrustalev, M.S. Nechaev, V.V. Lunin, J. Barrau, R. Ghassoub, Organometallics 22 (2003) 1675–1681.

[7] R.F. Merten, P.-E. Frohberger, F. Steinfatt, Bayer AG, US3210245 (A), 1965.

[8] P.A. van der Schaaf, J.T.B.H. Jastrzebski, M.P. Hogerheide, W.J.J. Smeets, A.L. Spek, J. Boersma, G. van Koten, Inorg. Chem. 32 (1993) 4111–4118.

[9] H. Hagen, A. Barbon, E.E. van Faasen, B.T.G. Lutz, J. Boersma, A.L. Spek, G. van Koten, Inorg. Chem. 38 (1999) 4079–4086.

[10] M.E. Judmaier, A. Wallner, G.N. Stipicic, K. Kirchner, J. Baumgartner, F. Belaj, N.C. Mösch-Zaneti, Inorg. Chem. 48 (2009) 10211–10221.

[11] J. Barrau, G. Rima, T. El-Amraoui, J. Organomet. Chem. 561 (1998) 167–174.

[12] (a) A. Růžička, V. Pejchal, J. Holeček, A. Lyčka, K. Jacob, Collect. Czech. Chem. Commun. 63 (1998) 977–989;
(b) A. Růžička, unpublished results.

[13] (a) B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 16 (1985) 73–186;
(b) B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 38 (1999) 203–264.

[14] A. Růžička, R. Jambor, J. Brus, I. Císařová, J. Holeček, Inorg. Chim. Acta 323 (2001) 163–170.

[15] J. Bareš, P. Novák, M. Nádvorník, R. Jambor, T. Lébl, I. Císařová, A. Růžička, J. Holeček, Organometallics 23 (2004) 2967–2971.

[16] Z. Padělková, T. Weidlich, L. Kolářová, A. Eisner, I. Císařová, T.A. Zevaco, A. Růžička, J. Organomet. Chem. 692 (2007) 5633–5645.

[17] (a) P. Novák, Z. Padělková, L. Kolářová, I. Císařová, A. Růžička, J. Holeček, Appl. Organomet. Chem. 19 (2005) 1101–1108;
(b) P. Novák, J. Brus, I. Císařová, A. Růžička, J. Holeček, J. Fluorine Chem. 126 (2005) 1531–1538.

[18] L. Broeckaert, J. Turek, R. Olejník, A. Růžička, M. Biesemans, P. Geerlings, R. Willem, F. De Proft, Organometallics, in press.

[19] V.N. Khrustalev, N.N. Zemlyansky, I.V. Borisova, M.G. Kuznetsova, E.B. Krut'ko, M.Yu. Antipin, Izv. Akad. Nauk SSSR, Ser. Khim. (Russ. Chem. Bull.) (2007) 259–263.

[20] T. Chlupatý, Z. Padělková, F. DeProft, R. Willem, A. Růžička, Organometallics 31 (2012) 2203–2211.

[21] I.A. Portnyagin, M.S. Nechaev, V.N. Khrustalev, N.N. Zemlyansky, I.V. Borisova, M.Yu. Antipin, Yu. A. Ustynyuk, V.V. Lunin, Eur. J. Inorg. Chem. (2006) 4271–4277.

[22] V.N. Khrustalev, I.A. Portnyagin, N.N. Zemlyansky, I.V. Borisova, Y.A. Ustynyuk, M.Yu. Antipin, J. Organomet. Chem. 690 (2005) 1056–1062.

[23] S. Patt, J.N. Shoolery, J. Magn. Reson. 46 (1982) 535–539.

[24] Z. Otwinowski, W. Minor, Meth. Enzymol. 276 (1997) 307–326.

[25] P. Coppens, in: F.R. Ahmed (Ed.), Crystallographic Computing, Munksgaard, Copenhagen, 1970, pp. 255–270.

[26] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.

[27] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, 1997. p. 1.