# Three coordinate divalent Group 14 element compounds with a β-diketiminate as supporting ligand $L^2MX$
## [$L^2$ = PhNC(Me)CHC(Me)NPh, X = Cl, I; M = Ge, Sn]

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## Abstract

The new heteroleptic divalent germanium and tin compounds $L^2MX$ [$L^2$ = PhNC(Me)CHC(Me)NPh. X = Cl; M = Ge (**1**), Sn (**2**). X = I; M = Ge (**3**), Sn (**4**)] have been synthesized and physicochemically and structurally (**2**) characterized. The halide ligand of all compounds can either be removed by reaction with $NaBPh_4$ leading to the cationic Ge(II) and Sn(II) species $L^2M^+$ or may be replaced by other groups after nucleophilic substitution giving $L^2MR$ compounds [R = $N(SiMe_3)_2$; M = Ge, Sn. M = Sn; R = $OSO_2CF_3$, $N_3$]. Reactions of **1** and **2** with elemental $S_8$, Se or transition metal complexes $M'(CO)_5 \cdot THF$ have resulted in the isolation of the new complexes $L^2(Cl)ME$ (E = S; M = Ge, Sn. E = Se, M = Ge) and $L^2(Cl)MM'(CO)_5$ (M' = Cr, W; M = Ge, Sn). © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* $M_{14}$ Divalent species; Diketiminato-ligands; Metallanethio- or selenoacid chloride; Transition metal complexes

## 1. Introduction

The study of divalent compounds of germanium and tin has received considerable attention over the past twenty years [1]. Generally these compounds are highly reactive and tend to oligomerise or polymerize. One can overcome this problem by judicious choice of the ligands on the metal center. Thus the use of sterically



X = Cl; M = Ge (**1**), Sn (**2**)
I;  Ge (**3**), Sn (**4**)
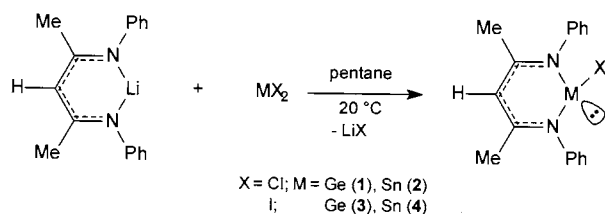
Scheme 1.

demanding ligands results in a kinetic stabilization of these species, while inter- and intramolecular coordination with Lewis base ligands gives thermodynamically stable monomeric compounds. In particular, different nitrogen containing ligands have been used to stabilize these compounds. A large number of homoleptic divalent germanium and tin species have been isolated by using these concepts but fewer examples of heteroleptic derivatives have been reported [2]. Noteworthy examples are the stabilization of neutral and cationic M(II) species by *N*-alkyl-2-(alkylamino)troponimate [3–5] and amidinate [2d,h,6,7]. We have recently described divalent germanium and tin compounds stabilized by amine substituted phenolate [8–10] or salen [11–14] ligands. Our interest has since turned to the synthesis of heteroleptic germanium(II) and tin(II) species supported by chelating β-diketiminato ligands. The study of these anions as ligands for various main group or transition metal chemistry has been explored [15–23]; they present steric and electronic properties which can be easily altered by varying the substituents on nitrogen. It is noteworthy that the divalent tin $L'^2SnX$

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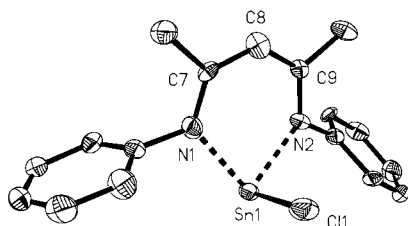
Fig. 1. Solid-state structure of $L_2SnCl$ (**2**).

Table 1
Selected bond lengths (Å) and angles (°) for **2**

| Bond distances | |
|---|---|
| Sn(1)–N(1) | 2.170(9) |
| Sn(1)–N(2) | 2.174(9) |
| Sn(1)–Cl(1) | 2.500(3) |
| N(1)–C(7) | 1.379(15) |
| N(2)–C(9) | 1.338(14) |
| C(7)–C(8) | 1.349(17) |
| C(8)–C(9) | 1.453(17) |
| Bond angles | |
| N(1)–Sn(1)–N(2) | 84.9(3) |
| N(1)–Sn(1)–Cl(1) | 90.6(3) |
| N(2)–Sn(1)–Cl(1) | 93.4(2) |
| C(7)–N(1)–Sn(1) | 125.7(7) |
| C(9)–N(2)–Sn(1) | 127.5(7) |
| C(8)–C(7)–N(1) | 125.5(11) |
| C(7)–C(8)–C(9) | 127.7(13) |
| N(2)–C(9)–C(8) | 123.9(11) |

structures $[L'^2 = Me_3SiNC(Ph)CHC(Ph)NSiMe_3$, $X = Br$; $L'^2 = Me_3SiNC(Ph)CHC(t\text{-}Bu)NH$, $X = Cl]$ have been evocated by Lappert in a short review concerning the work of his group on 1-aza-allyl- and β-diketiminato-metal complexes [23]. Herein we report the syntheses of the $L^2MX$ derivatives $[L^2 = PhNC(Me)CHC(Me)NPh$; $X = Cl$, $I$; $M = Ge$, $Sn]$ and some aspects of their reactivity. We particularly focused our attention on the functionalization of these compounds as well as their use as ligands for transition metal complexes.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopy

The reaction of one equivalent of $L^2Li$ with the divalent species $MX_2$ in toluene affords $L^2MX$ [X = Cl; M = Ge (**1**), Sn (**2**). X = I; M = Ge (**3**), Sn (**4**)] as orange solids in quantitative yields (Scheme 1). Surprisingly **1**–**4** failed to react with additional $L^2Li$ to give $(L^2)_2M$, since the same heteroleptic compounds were the only $M_{14}$ derivatives obtained, even when up to five equivalents of the lithium reagent were added to one equivalent of $MX_2$. All these compounds are air and moisture sensitive and give the halohydrate salts of the

diamine together with metal oxides as the hydrolysis products; they are particularly stable thermally, they can be subjected to temperatures as high as 150°C without decomposition or symmetrization. Compounds **1**–**4** are insoluble in aliphatic hydrocarbon solvents but soluble in aromatic or polar solvents and they could be conveniently purified by crystallization from toluene solutions.

Cryoscopic mass determinations showed that **1**–**4** are monomeric in benzene solution. They were characterized by NMR, IR and mass spectroscopy. ^{1}H- and ^{13}C-NMR spectra display the expected set of ligand proton and carbon signals, these data indicate that the mirror symmetry of the $L^2$ ligand is maintained in these compounds. The chemical shifts of all the ^{13}C- and ^{1}H-NMR signals observed for **1**–**4** appear slightly downfield from the corresponding signals in the free $L^2$ ligand. The ^{119}Sn-NMR spectrum of **2** exhibits a broad resonance at $-281.18$ ppm indicating that tin in **2** is basically-three coordinate in solution.

### 2.2. Structural characterization of 2

Crystals of the tin derivative **2** were analysed by X-ray diffraction methods. The molecular structure of **2** appears in Fig. 1, while selected bond lengths and angles appear in Table 1. In **2** the $L^2$ ligand is σ-bound to the tin and the complex assumes a pyramidal geometry, the tin center being at the apex of a distorted trigonal pyramid (the tin atom is elevated by 1.32 Å from the $ClN_2$ plane). The planarity of the $L^2$ ligand is confirmed by the fact that the sum of the internal angles for the six-membered $L^2Sn$ ring is 715.2(8)°. The two C–C distances of 1.349(17) and 1.453(17) Å and the two C–N distances of 1.379(15) and 1.338(14) Å suggest significant delocalization within the π system of this ligand. The Sn–Cl distance of 2.500(3) Å and the Sn–N lengths of 2.170(9) and 2.174(9) Å are, respectively in the range of typical Sn–Cl and Sn–N distances in various three-coordinate Sn(II) systems [3,24,25]. The intraligand N–Sn–N angle of 84.9(3)° and the N–Sn–Cl angles of 90.6(3) and 93.4(2)° are typical for pyramidal tin(II) complexes; the tin(II) lone pair $^1\sigma^2$ is presumably located in a radially distributed s orbital [25].

### 2.3. Chemical reactivity

As divalent species, these compounds present a large potential for organometallic synthesis since five different reaction centers can be distinguished (Scheme 2). With these properties in mind, we studied the reactivity of these metal chloride derivatives, a summary of which is given in Scheme 3.

(i) Contrasting with free or kinetically stabilized divalent species [1] these coordinated analogues are, as expected, unreactive towards dienes and conjugated
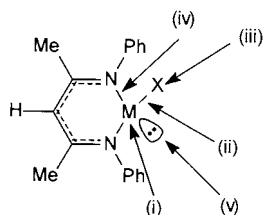
Scheme 2. Reactive centers present on L²MX compounds: (i) the low-valent tin atom, (ii) the heteropolar M–X bond, (iii) the halide ligand (Lewis-base properties), (iv) the M–N bond, (v) the lone pair.

carbonyl compounds. With 3,5-di-*tert*-butyl-1,2-benzo-quinone immediate heterocyclizations were observed at room temperature giving the cyclic derivatives **5** and **6**, respectively. A one-electron transfer mechanism as previously described for various divalent species [8,26–30] can explain these results. Note that **5** and **6** are thermally stable and even at 150°C no decomposition or symmetrization is observable.

We then considered oxidation of these compounds with elemental sulfur. Reactions of the L²MCl derivatives **1** and **2** with elemental sulfur in refluxing toluene

led to the formation of green precipitates soluble only in polar solvents such as DMSO. Of the obtained novel species (formal metallanethioacid chlorides) L²(Cl)M=S [M = Ge **(7)**, Sn **(8)**], only the germanethioacid chloride **7** which is thermodynamically stable in solution could be fully physicochemically characterized. As in the divalent species ¹H- and ¹³C-NMR spectra indicate that the L² ligand is symmetric with respect to a mirror plane perpendicular to the 5-membered ring bisecting germanium and C(2). The I.C. and electronic impact mass spectra of **7** show the molecular ion peak indicating the particular stability of this compound. To our knowledge **7** is the first example of a stable metallanethioacid chloride. Unlike the germanethioacid chloride, the tin analogue **8** was unstable in solution; rapid loss of elemental sulfur in solution resulted in the recovery of **2**. This precluded ¹¹⁹Sn (¹¹⁹Sn-NMR spectrum consists of a singlet resonance at −281.18 ppm corresponding to the tin(II) compound **2**) and mass spectrocopic analyses; proton NMR resonances show a similar trend to those of **7**. This instability was also observed under thermolysis in the gas phase; since the
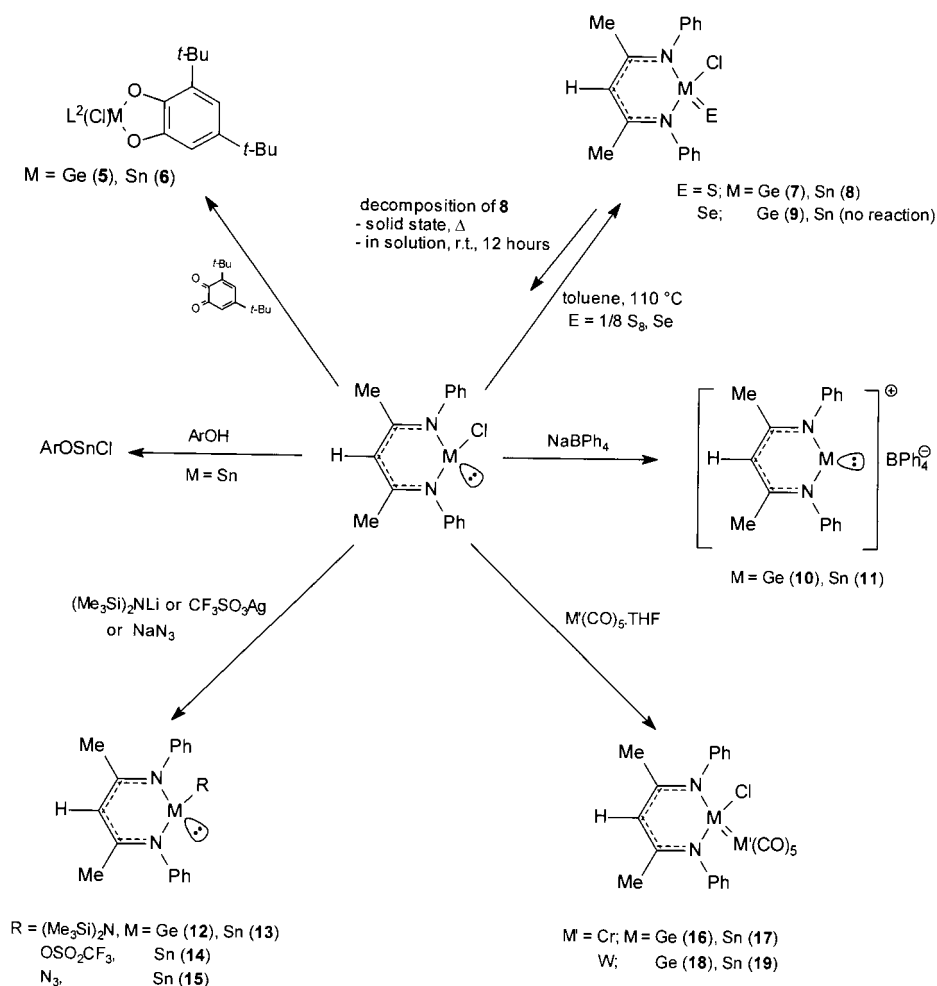


Scheme 3.

molecular peak of the stannylene **2** and not the stannanethioacid chloride **8** was observed in the electronic impact mass spectrum.

In the same experimental conditions black selenium reacted with $L^2GeCl$ to give the germaneselenoacid chloride $L^2(Cl)Ge=Se$ **(9)**. Like the germanethioacid chloride **7** this species is stable in solution, monomeric (cryoscopic mass determination) and was characterized by ^{1}H- and ^{13}C-NMR analysis and mass spectroscopy. Despite repeated attempts, we were unable to obtain crystals suitable for X-ray structural analysis. It is worth noting that no reaction between black selenium and $L^2SnCl$ **(2)** was observed under similar reaction conditions.

(ii) It has recently been reported that cationic Sn(II) and Ge(II) [5] species can be obtained by using $CpZrCl_3$ as a chloride extracting reagent [3,5]. We have used $NaBPh_4$ for our studies. In the case of germanium, we succeeded in isolating the derivative $[L^2Ge]^+[BPh_4]^-$ **(10)** by reaction of germylene **1** with $NaBPh_4$ in acetonitrile over two days at 82°C. Compound **10** was fully characterized by NMR spectroscopic, microanalytical and FAB mass spectroscopic methods. This reaction with formation of **10** contrasts markedly to that observed [5] when $Me_2ATIGeCl$ [$Me_2ATI = N$-methyl-2-(methylamino)troponiminate] was reacted with $NaBPh_4$, in this case a phenyl group transfer was observed resulting in the formation of the complex $Me_2ATIGePh·BPh_3$ rather than the formation of the corresponding salt. It is reasonable to assume that the stability of **10** towards phenyl group migration may be explained by the combination of the presence of a more bulky substituent on the germanium-bound nitrogen atoms and electronic properties of the $L^2$ system. Similarly, the reaction between $L^2SnCl$ and one equivalent of $NaBPh_4$ in acetonitrile during five days led to the formation of the salt $[L^2Sn]^+[BPh_4]^-$ **(11)** in quantitative yield; **11** was characterized by ^{1}H-, ^{13}C-, ^{119}Sn-NMR spectroscopy and FAB mass spectroscopy.

(iii) The Lewis base properties of these $L^2MX$ derivatives can easily be modified by replacing the halogen atom on the metal center by other groups. Thus we have achieved simple nucleophilic substitutions leading to the formation of the heteroleptic compounds $L^2MN(SiMe_3)_2$ [$M = Ge$ **(12)**, $Sn$ **(13)**], $L^2SnOSO_2CF_3$ **(14)** and $L^2SnN_3$ **(15)** by treatment of **1** or **2** with $(Me_3Si)_2NLi$, $AgOSO_2CF_3$ and $NaN_3$, respectively. Compounds **12–15** are stable under ordinary conditions. It is noteworthy that all attempts of reduction of **1** or **2** by reaction with slightly less than one equivalent of $C_8K$ or Na/Hg amalgam resulted only in obtention of the $M_{14}$ metal.

(iv) The M–N bonds are very reactive toward reagents with some acidic character like phenols, alcohols, thiols and organic acids. Thus reaction in $CH_2Cl_2$ at room temperature of **2** with 2,4,6-tris(-dimethylaminomethyl)phenol results in the formation of the already known heteroleptic tin(II) compound $[2,4,6-(Me_2NCH_2)_3C_6H_2O](Cl)Sn$ [10] in high yield.

(v) As heavier analogues of carbenes the divalent derivatives $L^2MCl$ **1** and **2** can be used as ligands in transition metal chemistry [1d,12,13]. Thus reaction of $L^2MCl$ with $M'(CO)_5·THF$ ($M' = Cr$, W) results in the liberation of THF and the coordination of the divalent $M_{14}$ species to the transition metal giving the expected complexes $(L^2)(Cl)MM'(CO)_5$ [$M' = Cr$; $M = Ge$ **(16)**, Sn **(17)**. $M' = W$; $M = Ge$ **(18)**, Sn **(19)**] in quantitative yields. These compounds are colored solids, soluble in polar or aromatic solvents and insoluble in pentane. Cryoscopic mass determination showed that **16–19** are monomeric in benzene. Compounds **16–19** were characterized by IR, NMR and mass spectroscopy. The mass spectra of complexes **16–19** show the molecular ion $M^+$ peaks and a characteristic fragmentation pattern corresponding to loss of CO ligands from the transition metal center. From ^{1}H- and ^{13}C-NMR data it can be concluded that, as in the case of the parent divalent germanium and tin species, the $L^2$ ligand is symmetrically chelating, both phenyl and methyl groups being, respectively equivalent. The carbonyl region of the ^{13}C spectra show two peaks in the ratio of 4:1, which suggests a $C_{4v}$ symmetry about the transition metal. This structure is supported by the presence of three bands due to carbonyl stretching in the IR spectra. It is of interest to note that the $A'_1$ bands (involving the unique CO *trans* to the metal) for compounds **16–19** are 1976, 1984, 1979 and 1979 cm$^{-1}$, respectively. These values are consistent with a strong σ-donor weak π-acceptor character [12,13,31] of these divalent species.

## 3. Conclusions

New heteroleptic divalent germanium and tin species have been described. A particularly rich chemistry surrounds these species, which undergo a variety of transformations including oxidation and halide ion extraction. They give complexes with transition metals. The fact that the halogen atom can be replaced by simple nucleophilic substitution or removed suggests that one can easily modulate the electron density on the metal 14 atom, which in turn could tune the electron density on a transition metal center after complexation. These heteroleptic Ge(II) and Sn(II) compounds may yet find applications as ligands for catalytic processes.

## 4. Experimental

### 4.1. General

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents were employed throughout. All solvents were freshly distilled from $CaH_2$ or, where possible, from a Na–K alloy. $L^2H$, $L^2Li$, $GeCl_2 \cdot$dioxane, $W(CO)_5 \cdot$THF and $Cr(CO)_5 \cdot$THF were synthesized according to literature procedures. All other reagents were commercially available and used as received. $^1H$- and $^{13}C$-NMR spectra were recorded on a Brucker AC 200 MHz spectrometer (chemical shifts are reported in ppm ($\delta$) and are referenced with respect to residual solvent peaks). $^1H$- decoupled $^{19}F$-, $^{29}Si$- and $^{119}Sn$-NMR spectra were recorded on a bruker AC 400 MHz spectrometer (chemical shifts are reported in ppm ($\delta$) relative to external $CF_3C(O)OH$ or $Me_4Si$ or $Me_4Sn$, respectively as references). IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. 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. Melting points were obtained on a Leitz Biomed hot plate microscope apparatus and were uncorrected. Elemental analyses (C, H, N) were performed at the microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

### 4.2. $L^2GeCl$ (1)

A suspension of $L^2Li$ (0.40 g, 1.6 mmol) in pentane (20 ml) was added to a suspension of $GeCl_2 \cdot$dioxane (0.37 g, 1.6 mmol) in pentane (10 ml) at 0°C over 10 min. The reaction mixture was allowed warm to room temperature (r.t.) and left stirring for 2 days. After filtration, the product was extracted from the solid residue in toluene ($2 \times 30$ ml). 1 was isolated in the form of a yellow powder after evaporation of toluene in vacuo. Yield: 0.52 g, 91%. 1: m.p. 145–146°C. $^1H$-NMR (CDCl$_3$): 1.99 (s, 6H, CH$_3$), 5.40 (s, 1H, CH), 6.95–7.20 (m, 10H, C$_6$H$_5$). $^{13}C$-NMR (CDCl$_3$): 23.52 (CH$_3$), 101.50 (CH), 126.80 (m-aryl-C), 127.13 (p-aryl-C), 129.61 (o-aryl-C), 144.35 (C–N), 164.30 (C$_{quart}$). MS: $m/z = 358$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$ClGe: C, 57.13; H, 4.79; N, 7.84. Found: C, 56.61; H, 4.36; N, 7.79%.

### 4.3. $L^2SnCl$ (2)

According to the same procedure as above, the reaction of SnCl$_2$ (0.38 g, 2 mmol) with $L^2Li$ (0.51 g, 2 mmol) afforded 2. Yield: 0.62 g, 76%. 2: m.p. 93–95°C. $^{119}Sn$-NMR (CDCl$_3$): $-281.18$. $^1H$-NMR (CDCl$_3$): 1.96 (s, 6H, CH$_3$), 5.15 (s, 1H, CH), 7.00–7.40 (m, 10H, C$_6$H$_5$). $^{13}C$-NMR (CDCl$_3$): 23.96 (CH$_3$), 100.74 (CH), 125.97 (m-aryl-C), 126.13 (p-aryl-C), 129.68 (o-aryl-C), 146.01 (C–N), 165.09 (C$_{quart}$). MS: $m/z = 404$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$ClSn: C, 50.59; H, 4.24; N, 6.94. Found: C, 50.04; H, 3.88; N, 7.10%.

### 4.4. $L^2GeI$ (3)

Using the same experimental procedure as for the synthesis of 1, the reaction of GeI$_2$ (1.30 g, 4 mmol) with $L^2Li$ (1.02 g, 4 mmol) gave 3. Yield: 1.20 g, 67%. 3: m.p. (dec.) 158–159°C. $^1H$-NMR (CDCl$_3$): 1.53 (s, 6H, CH$_3$), 5.20 (s, 1H, CH), 6.90–7.29 (m, 10H, C$_6$H$_5$). $^{13}C$-NMR (CDCl$_3$): 23.30 (CH$_3$), 103.29 (CH), 126.12 (m-aryl-C), 127.32 (p-aryl-C), 129.54 (o-aryl-C), 143.55 (C–N), 165.94 (C$_{quart}$). MS: $m/z = 450$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$IGe: C, 45.85; H, 3.81; N, 6.24. Found: C, 46.05; H, 3.95; N, 6.15%.

### 4.5. $L^2SnI$ (4)

Using the same experimental procedure as for the synthesis of 1, the reaction of SnI$_2$ (1.49 g, 4 mmol) with $L^2Li$ (1.02 g, 4 mmol) gave $L^2SnI$. Yield: 1.20 g, 67%. 4: m.p. (dec.) 117–118°C. $^{119}Sn$-NMR (CDCl$_3$): $-172.02$. $^1H$-NMR (CDCl$_3$): 1.96 (s, 6H, CH$_3$), 5.27 (s, 1H, CH), 6.90–7.39 (m, 10H, C$_6$H$_5$). $^{13}C$-NMR (CDCl$_3$): 23.94 (CH$_3$), 102.82 (CH), 125.50 (m-aryl-C), 126.32 (p-aryl-C), 129.60 (o-aryl-C), 145.67 (C–N), 165.20 (C$_{quart}$). MS: $m/z = 496$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$ISn: C, 41.25; H, 3.46; N, 5.65. Found: C, 41.95; H, 3.71; N, 5.42%.

### 4.6. Reaction of 1 with 3,5-di-tert-butyl-1,2-benzoquinone

A solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.09 g, 0.4 mmol) in toluene (10 ml) was added to 1 (0.14 g, 0.4 mmol) in toluene (15 ml). After 4 h reacting at r.t., the mixture was concentrated and the solid residue extracted with pentane. Compound 5 was obtained in the form of a green powder after evaporation of pentane in vacuo. Yield: 0.20 g, 86%. 5: m.p. (dec.) 162–164°C. $^1H$-NMR (C$_6$D$_6$): 1.29 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.41 (s, 6H, CH$_3$), 4.80 (s, 1H, CH), 7.80–7.20 (m, 12H, Ar). $^{13}C$-NMR (C$_6$D$_6$): 24.17 (CH$_3$), 30.03 (*t*-Bu), 32.09 (*t*-Bu), 34.39 (C-quart), 34.48 (C-quart), 98.81 (CH), 107.16 (o-aryl-C), 112.29 (m-aryl-C), 127.58 (m-aryl-C), 128.06 (p-aryl-C), 129.63 (o-aryl-C), 144.80 (C–N), 156.91 (p-aryl-quinone), 169.10 (C$_{quart}$). MS: $m/z = 578$ [M]$^+$. Anal. Calc. for C$_{31}$H$_{37}$N$_2$O$_2$ClGe: C, 64.45; H, 6.45; N, 4.84. Found: C, 63.88; H, 6.09; N, 5.19%.

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

Using the same procedure as for the above reaction, compound **2** (0.16 g, 0.4 mmol) was added to 3,5-di-*tert*-butyl-1,2-benzoquinone (0.09 g, 0.4 mmol) and compound **6** was obtained. Yield: 0.21 g, 84%. **6**: m.p. (dec.) 128–129°C. $^{119}$Sn-NMR (C$_6$D$_6$): − 567.85. $^1$H-NMR (C$_6$D$_6$): 1.27 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu), 1.54 (s, 6H, CH$_3$), 4.75 (s, 1H, CH), 7.70–7.20 (m, 12H, C$_6$H$_5$, C$_6$H$_2$). $^{13}$C-NMR (C$_6$D$_6$): 24.33 (CH$_3$), 30.08 (*t*-Bu), 32.11 (*t*-Bu), 34.41 (C$_{quart}$), 34.52 (C$_{quart}$), 99.10 (CH), 108.26 (*o*-aryl), 112.53 (*m*-aryl), 124.72 (*m*-aryl), 126.19 (*p*-aryl), 128.32 (*o*-aryl), 145.92 (C–N), 157.21 (*p*-aryl), 169.36 (C$_{quart}$). MS $m/z = 624$ [M]$^+$. Anal. Calc. for C$_{31}$H$_{37}$N$_2$O$_2$ClSn: C, 59.68; H, 5.97; N, 4.49. Found: C, 60.32; H, 6.11; N, 4.23%.

### 4.8. $L^2(Cl)Ge = S$ (7)

A solution of **1** (0.29 g, 0.81 mmol) in toluene (10 ml) was added to a suspension of sulfur (0.026 g, 0.81 mmol) in toluene (5 ml). The reaction mixture was heated at 110°C during 3 h during which time the reaction mixture became red. After evaporation of the solvent, the residue was washed with pentane and the product **7** was obtained in the form of a green powder. Yield 0.23 g, 80%. **7**: m.p. 172–173°C. $^1$H-NMR (DMSO-d$_6$): 2.01 (s, 6H, CH$_3$), 5.79 (s, 1H, CH), 7.20–7.50 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (DMSO-d$_6$): 23.56 (CH$_3$), 99.51 (CH), 127.43 (*m*-aryl-C), 128.28 (*p*-aryl-C), 129.29 (*o*-aryl-C), 149.49 (C–N), 169.74 (C$_{quart}$). MS: $m/z = 390$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$ClSGe: C, 52.43; H, 4.39; N, 7.19. Found: C, 52.98; H, 4.68; N, 6.86%.

### 4.9. $L^2(Cl)Sn = S$ (8)

Using the same experimental procedure as for the synthesis of **7**, the reaction of **2** (0.20 g, 0.49 mmol) with elemental sulfur (0.016 g, 0.5 mmol) gave **8**. Yield: 0.95 g, 46%. **8**: m.p. (dec.) 201–202°C. $^{119}$Sn-NMR (DMSO-d$_6$): − 228. $^1$H-NMR (DMSO-d$_6$): 1.97 (s, 6H, CH$_3$), 5.55 (s, 1H, CH), 6.80–7.32 (m, 10H, C$_6$H$_5$). MS: $m/z = 404$[M − S]$^+$.

### 4.10. $L^2(Cl)Ge=Se$ (9)

Using the same experimental procedure as for the synthesis of **7**, the reaction of **1** (0.25 g, 0.69 mmol) with elemental selenium (0.54 g, 0.69 mmol) gave **9** as a green solid. **9**: m.p. 198–199°C. $^1$H-NMR (DMSO-d$_6$): 2.00 (s, 6H, CH$_3$), 5.80 (s, 1H, CH), 7.20–7.54 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (DMSO-d$_6$): 23.59 (CH$_3$), 89.79 (CH), 127.52 (*m*-aryl-C), 128.26 (*p*-aryl-C), 129.24 (*o*-aryl-C), 149.65 (C–N), 169.18 (C$_{quart}$). MS: $m/z = 436$ [M]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_2$ClGeSe: C, 46.79; H, 3.92; N, 6.42. Found: C, 46.12; H, 3.48; N, 6.81%.

### 4.11. $[L^2Ge]^+[BPh_4]^-$ (10)

A solution of **1** (0.28 g, 0.77 mmol) in acetonitrile (10 ml) was added to NaBPh$_4$ (0.26 g, 0.77 mmol) in acetonitrile (10 ml). The reaction mixture was left for 2 days at 82°C. After cooling to r.t. the mixture was filtered and the solvent removed in vacuo. Yield 0.41 g, 82%. **10**: $^1$H-NMR (CDCl$_3$): 1.97 (s, 6H, CH$_3$), 5.39 (s, 1H, CH), 6.82–7.55 (m, 30H, C$_6$H$_5$). MS FAB > 0: $m/z = 323$ [M]$^+$, FAB < 0: $m/z = 319$ [M]$^-$. $^{13}$C-NMR (CDCl$_3$): 24.3 (CH$_3$), 96.1 (CH), 122.07 (*m*-aryl-C), 125.97 (*p*-aryl-C), 127.99 (*o*-aryl-C), 128.39 (*m*-aryl), 134.77 (*p*-aryl), 136.18 (*o*-aryl), 147.36 (C–N), 155.33 (C$_{quart}$), 166.62 (C$_{quart}$). MS: FAB > 0 $m/z = 323$ [L$^2$Ge]$^+$, FAB < 0 $m/z = 319$ [Ph$_4$B]$^-$. Anal. Calc. for C$_{41}$H$_{37}$N$_2$GeB: C, 76.80; H, 5.81; N, 4.36. Found: C, 76,02; H, 5.12; N, 3.78%.

### 4.12. $[L^2Sn]^+[BPh_4]^-$ (11)

Using the same experimental procedure as for the synthesis of **10**, the reaction of **2** (0.2 g, 0.5 mmol) with NaBPh$_4$ (0.172 g, 0.5 mmol) gave **11**. Yield: 0.23 g, 67%. **11**: $^{119}$Sn-NMR: − 26.02. $^1$H-NMR (CDCl$_3$): 1.68 (s, 6H, CH$_3$), 4.83 (s, 1H, CH), 6.86–7.47 (m, 30H, Ar). $^{13}$C-NMR (CDCl$_3$): 23.86 (CH$_3$), 98.48 (CH), 123.13 (*m*-aryl-C), 126.18 (*p*-aryl-C), 128.55 (*o*-aryl-C), 129.63 (*p*-aryl), 136.28 (*o*-aryl), 145.89 (C–N), 153.12 (C$_{quart}$), 164.25 (C$_{quart}$). MS FAB > 0 = 369 [L$^2$Sn]$^+$, FAB < 0 = 319 [Ph$_4$B]$^-$. Anal. Calc. for C$_{41}$H$_{37}$N$_2$SnB: C, 71.63; H, 5.42; N, 4.07. Found: C, 70.98; H, 5.03; N, 3.72%.

### 4.13. $L^2GeN(SiMe_3)_2$ (12)

A solution of LiN(SiMe$_3$)$_2$ (0.084 g, 0.50 mmol) in ether (10 ml) was added to a solution of **1** (0.18 g, 0.50 mmol) in ether (10 ml) at r.t. The reaction mixture was left stirring overnight. After filtration, the solvent was removed in vacuo and the product **12** was washed with pentane. Yield: 0.19 g, 78%. **12**: m.p. 142–143°C. $^{29}$Si-NMR (C$_6$D$_6$): 2.30. $^1$H-NMR (C$_6$D$_6$): 0.26 (s, 18H, SiMe$_3$), 1.56 (s, 6H, CH$_3$), 4.67 (s, 1H, CH), 6.90–7.20 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (C$_6$D$_6$): 5.81 (SiMe$_3$), 23.20 (CH$_3$), 98.49 (CH), 126.18 (*m*-aryl-C), 126.97 (*p*-aryl-C), 129.32 (*o*-aryl-C), 145.82 (C–N), 163.77 (C$_{quart}$). MS: $m/z = 483$ [M − N$_3$]$^+$. Anal. Calc. for C$_{23}$H$_{35}$N$_3$Ge: C, 57.14; H, 7.24; N, 8.69. Found: C, 56.68; H, 6.89; N, 9.03%.

### 4.14. $L^2SnN(SiMe_3)_2$ (13)

Following the same experimental procedure as for the synthesis of **12**, the reaction of LiN(SiMe$_3$)$_2$ (0.082 g, 0.49 mmol) with **2** (0.2 g, 0.49 mmol) gave **13**. Yield: 0.22 g, 84%. **13**: m.p. 96–97°C. $^{119}$Sn-NMR (C$_6$D$_6$): −151.79. $^{29}$Si-NMR (C$_6$D$_6$): 2.35. $^1$H-NMR (C$_6$D$_6$): 0.30 (s, 18H, SiMe$_3$), 1.67 (s, 6H, CH$_3$), 4.75 (s, 1H, CH), 6.90–7.20 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (C$_6$D$_6$): 6.46 (SiMe$_3$), 23.93 (CH$_3$), 98.38 (CH), 125.71 (*m*-aryl-C), 126.08 (*p*-aryl-C), 129.50 (*o*-aryl-C), 146.96 (C–N), 164.41 (C$_{quart}$). MS: $m/z = 529$ [M]$^+$. Anal. Calc. for C$_{23}$H$_{35}$N$_3$Si$_2$Sn: C, 52.17; H, 6.61; N, 7.39. Found: C, 51.54; H, 6.10; N, 8.52%.

### 4.15. $L^2SnOSO_2CF_3$ (14)

A solution of **2** (0.2 g, 0.5 mmol) in toluene (10 ml) was added to a suspension of AgOSO$_2$CF$_3$ (0.13 g, 0.5 mmol) in toluene cooled at −30°C; the reaction mixture was warmed to r.t. and stirred for 24 h. The resulting precipitateous solution was filtered and the solid was washed with toluene until colorless washings were obtained. After concentration of the toluene solution, **14** was precipitated as a very slightly yellow powder by adding pentane, collected by filtration and dried in vacuo. Yield: 0.2 g, 78%. **14**: m.p. 220–230°C. $^{119}$Sn-NMR (CDCl$_3$): −397.92. $^{19}$F-NMR (CDCl$_3$): −2.38. $^1$H-NMR (CDCl$_3$): 1.99 (s, 6H, CH$_3$), 5.32 (s, 1H, CH), 7.18–7.30 (m, 10H, C$_6$H$_5$). MS: $m/z = 518$ [M]$^+$. Anal. Calc. for C$_{18}$H$_{17}$N$_2$O$_3$F$_3$SSn: C, 41.80; H, 3.31; N, 5.41. Found: C, 41.62; H, 2.98; N, 5.04%.

### 4.16. $L^2SnN_3$ (15)

A solution of **2** (0.2 g, 0.5 mmol) in THF (10 ml) was added to a suspension of NaN$_3$ (0.03 g, 0.5 mmol) in THF (5 ml) cooled at −30 °C; the reaction mixture was warmed to r.t. and stirred for 48 h. Removal of solvent in vacuo, addition of toluene and filtration, concentration of the toluene solution and drying in vacuo yielded **15** as a slightly yellow powder. Yield: 0.18 g, 90%. **15**: $^{119}$Sn-NMR (CDCl$_3$): −156.18. $^1$H-NMR (CDCl$_3$): 2.01 (s, 6H, CH$_3$), 4.95 (s, 1H, CH), 7.16–7.32 (m, 10H, C$_6$H$_5$). MS: $m/z = 369$ [M − N$_3$]$^+$. Anal. Calc. for C$_{17}$H$_{17}$N$_5$Sn: C, 49.79; H, 4.17; N, 17.07. Found: C, 49.51; H, 3.85; N, 16.81%.

### 4.17. $L^2(Cl)GeCr(CO)_5$ (16)

A solution of **1** (0.1 g, 0.27 mmol) in THF (10 ml) was added dropwise to a solution of Cr(CO)$_5$·THF (0.07 g, 0.27 mmol) in THF (30 ml). After 2 h stirring at r.t. the solution was concentrated and the solid residue washed with pentane (20 ml). The complex **16** was isolated in the form of a yellow solid. Yield: 0.14 g,

94%. **16**: m.p. (dec.) 184–186°C. $^1$H-NMR (DMSO-d$_6$): 2.05 (s, 6H, CH$_3$), 5.54 (s, 1H, CH), 7.50–7.60 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (DMSO-d$_6$): 23.10 (CH$_3$), 113.82 (CH), 124.96 (*m*-aryl-C), 127.22 (*p*-aryl-C), 129.32 (*o*-aryl-C), 146.63 (C-N), 168.23 (C$_{quart}$), 185.61 (CO), 199.82 (CO). IR (Nujol, KBr, cm$^{-1}$): $\nu_{CO}$: 1931, 1976, 2056. MS: $m/z = 550$ [M]$^+$. Anal. Calc. for C$_{22}$H$_{17}$N$_2$O$_5$GeClCr: C, 48.00; H, 3.09; N, 5.09. Found: C, 47.42; H, 2.77; N, 5.81%.

### 4.18. $L^2(Cl)SnCr(CO)_5$ (17)

Using the same experimental procedure as for the synthesis of **16** reaction of **2** (0.2 g, 0.5 mmol) with Cr(CO)$_5$·THF (0.11 g, 0.5 mmol) gave **17**. Yield: 0.26 g, 87%. **17**: m.p. (dec.) 139–140°C. $^{119}$Sn-NMR (THF–C$_6$D$_6$): 141.68. $^1$H-NMR (DMSO-d$_6$): 2.03 (s, 6H, CH$_3$), 5.32 (s, 1H, CH), 7.0–7.50 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (DMSO-d$_6$): 23.46 (CH$_3$), 105.18 (CH), 128.21 (*m*-aryl-C), 129.46 (*p*-aryl-C), 130.45 (*o*-aryl-C), 144.25 (C–N), 168.30 (C$_{quart}$), 189.92 (CO), 211.10 (CO). IR (Nujol, KBr, cm$^{-1}$): $\nu_{CO}$: 1929, 1984, 2057. MS: $m/z = 596$ [M]$^+$. Anal. Calc. for C$_{22}$H$_{17}$N$_2$O$_5$SnClCr: C, 44.29; H, 2.85; N, 4.69. Found: C, 43.78; H, 2.10; N, 5.34%.

### 4.19. $L^2(Cl)GeW(CO)_5$ (18)

Using the same experimental procedure as for the synthesis of **16**, the reaction of **1** (0.2 g, 0.57 mmol) with W(CO)$_5$·THF (0.22 g, 0.57 mmol) gave **18**. Yield: 0.34 g, 90%. **18**: m.p. 139–140°C. $^1$H-NMR (DMSO-d$_6$): 2.05 (s, 6H, CH$_3$), 5.61 (s, 1H, CH), 6.80–7.40 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (DMSO): 21.91 (CH$_3$), 118.86 (CH), 124.96 (*m*-aryl-C), 127.25 (*p*-aryl-C), 129.31 (*o*-aryl-C), 146.56 (C–N), 168.20 (C-quart-aryl), 191.16 (CO), 196.55 (CO). IR (Nujol, KBr, cm$^{-1}$): $\nu_{CO}$ 1901, 1979, 2067. MS $m/z = 682$ [M]$^+$. Anal. Calc. for C$_{22}$H$_{17}$N$_2$O$_5$GeClW: C, 38.70; H, 2.49; N, 4.10. Found: C, 38.12; H, 1.98; N, 4.85%.

### 4.20. $L^2(Cl)SnW(CO)_5$ (19)

Following the same experimental procedure as for the synthesis of **16**, the reaction of **2** (0.20 g, 0.5 mmol) with W(CO)$_5$·THF (0.19 g, 0.5 mmol) gave **19**. Yield: 0.25 g, 68%. **18**: m.p. 143–144°C. $^{119}$Sn-NMR (THF–CDCl$_3$): −84.33. $^1$H-NMR (C$_6$D$_6$): 1.50 (s, 6H, CH$_3$), 4.83 (s, 1H, CH), 6.80–7.10 (m, 10H, C$_6$H$_5$). $^{13}$C-NMR (C6D6): 23.97 (CH3), 101.03 (CH), 128.35 (*m*-aryl-C), 129.39 (*p*-aryl-C), 130.38 (*o*-aryl-C), 144.21 (C–N) 168.27 (C-quart-aryl), 195.62 (CO), 213.05 (CO). IR (Nujol, NaCl, cm$^{-1}$): $\nu_{CO}$: 1934, 1978, 2069. MS: $m/z = 728$ [M]$^+$. Anal. Calc. for C$_{22}$H$_{17}$N$_2$O$_5$SnClW: C, 30.21; H, 2.33; N, 3.84. Found: C, 29.57; H, 1.82; N, 4.36%.

## 4.21. Crystal data for **2**

$C_{17}H_{17}ClN_2Sn$, $M_r = 403.47$, monoclinic, $C2/c$, $a = 29.477(2)$, $b = 8.6530(6)$, $c = 14.6554(10)$ Å, $\beta = 112.065(1)°$, $V = 3464.3(4)$ Å$^3$, $Z = 8$, $\rho_{calc}$ 1.547 Mg m$^{-3}$ $F(000) = 1600$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, $\mu$ (Mo–K$_\alpha$) = 1.624 mm$^{-1}$, crystal size $0.4 \times 0.5 \times 0.8$ mm, $5.21 = \Theta = 23.25°$, 12957 reflections (5321 independent) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. At the beginning of the refinement, we were blocked at $R_1 = 0.2$ and the Difference Fourier gave a high rest electron density peak, which gave no chemical sense. By using the program package GEMINI [32], we found two orientation matrices [$A1 = 0.01414$ $-0.10611$ $0.00493$, $-0.00767$ $0.00020$ $-0.07252$, $0.03287$ $0.04569$ $0.01175$ and $A2 = 0.01407$ $0.10624$ $0.01652$, $-0.00733$ $-0.00090$ $0.06130$, $0.03300$ $-0.04552$ $0.03735$] corresponding to a non-meroheral twin formed by rotation of 180° around the reciprocal vector 100 (for more information about twinned systems have a look at [33,34]). The reflection intensities for each twin component were integrated. The structure was solved by direct methods (SHELXS-97) [35] and 199 parameters were refined using the least-squares method on $F^2$ [36]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Largest electron density residue: 0.971 e Å$^{-3}$, $R_1$ (for $F > 2\sigma(F)$) = 0.0663 and $wR_2 = 0.1743$ (all data) with $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$.

## 5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151 236. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc. cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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