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Low coordinate germanium and tin compounds $(ArO)_2M{=}E$ and $(ArO)_2M{=}M'L_n$ $M = Ge, Sn$; $E = S, Se, -NSiMe_3$ $M' = Cr, W, Fe, Pt$ [Ar = 2,4,6-tris((dimethylamino)methyl)phenyl-]

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Abstract

The reactions of the divalent species $(ArO)_2M$ ($Ar = 2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2$; M = Ge, Sn) with either Me_3SiN_3, elemental S_8, Se or transition metal complexes $M'(CO)_{n+1}$ (M′ = Fe, $n = 4$; M′ = Cr, W; $n = 5$) $(Ph_3P)_2Pt\cdot C_2H_4$ have resulted in the isolation of either the new stable formal metallanimines $(ArO)_2M{=}N{-}SiMe_3$, germanethione, -selone $(ArO)_2Ge{=}E$ (E = S, Se) (the expected formations of the stannanethione and -selone were not observed), or the $(ArO)_2M{=}M'(CO)_n$, $(ArO)_2M{=}Pt(PPh_3)_2$ complexes, respectively. The direct oxidation of the $(ArO)_2M$ species with various oxidizing agents led to the formation of the corresponding metalloxanes $[(ArO)_2M{-}O{-}]_2$. All of the chalcogenido- and transition metal–metal 14 complexes have been physicochemically and chemically characterized. The reactions of the $(ArO)_2Ge{=}E$ (E = S, Se) compounds with 3,5-di-*tert*-butyl-1,2-benzoquinone produced, by extrusion of sulfur or selenium, the dioxametalloles corresponding to the formal addition of the divalent species $(ArO)_2M$ to the benzoquinone. A substitution reaction of chalcogen (S/Se) has been observed permitting to go from germaneselone to germanethione. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Metallanimine; Germanethione; Germaneselone; Transition metal complexes of M_{14} divalent species

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1. Introduction

The poor tendency of main group elements to give multiple bonds is perfectly illustrated by the behavior of the Group 14 elements [1–5]. Compounds with Si=Si bond, for example, are rare [6–8] and the first stable disilene was obtained only in 1981 [6]. However, numerous studies of metal 14 compounds involved in multiple bonds have appeared in the past 10 years and various stable derivatives of the types $>M{=}C<$, $>M{=}M<$ and $>M{=}E$ have been described (silicon [9–13]; germanium [13–17]; Group 14 elements [7,13,14,18]; Group 14 and 15 elements [19–21]). More uncommon are the structures $>M{=}E$ which could be stabilized; the chemistry of these species is mainly chemistry [15–17,22–29] of transient species and, in fact, we only know 14 stable species of the type metallanones, metallanethiones, -selones or -tellones [25,30–37] so far.

During the past few years several transition metal complexes have been used as catalysts in reactions of formation, or cleavage, of M–M bonds for the synthesis of precursors of new materials. Mechanisms involving intermediate [metallic divalent species–transition metal] complexes have been postulated to explain the role of the catalysts [38–42], thus renewing the researchers interest for metallic analogs of carbenic complexes of transition metals [43–64]; for reviews see ([47]a, [49]a, [49]b, [50,55], [61]a).

The species $>M{=}E$ and the complexes $>M{=}M'L_n$ can be obtained via different methods of synthesis.

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However, the direct reaction of divalent species >M with E or a transition metal appears to be the better method in both cases, provided the divalent species are stable or metastable under the experimental conditions.

In this context, we consider the stable divalent $(ArO)_2M$ [M = Ge **1**, M = Sn **2**] species whose syntheses and some aspects of their reactivity have been described [65] as precursors of type >M=E and $>M{=}M'L_n$ species. Some preliminary aspects of this work have been communicated earlier ([65]a)$(ArO)_2$ M=E; $(ArO)_2$ $M{=}M'L_n$ M = Ge, Sn; Ar = 2,4,6,-$[(CH_3)_2NCH_2]_3C_6H_2$ E = S, Se, $-NSiMe_3$; M′ = Fe, Cr, W; $L_n = (CO)_n(PPh_3)_2$.

2. Results and discussion

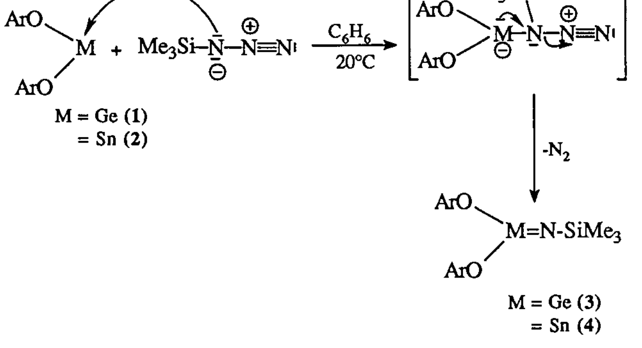
2.1. Metallanimines $(ArO)_2M{=}N{-}SiMe_3$

The germa- and stannanimines **3**, **4** have been obtained in excellent yields by the reaction of the divalent species $(ArO)_2M$ with trimethylsilylazide Me_3SiN_3. The nucleophilic attack of the azide on the divalent species probably leads to a dipolar intermediate which decomposes into nitrogen and germanimine (Scheme 1).

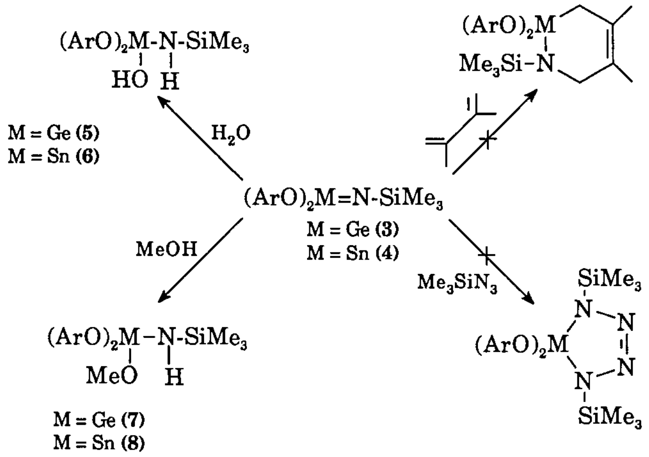
In these reactions, we could not detect any traces of tetraazene resulting from the 1-3 addition of the metallanimines to the trimethylsilylazide as has already been observed [16].

Cryoscopic mass determination showed that **3** and **4** are monomeric in benzene solution; they have been physicochemically characterized by ^1H-, ^{13}C-, ^{119}Sn-NMR, IR, and mass spectroscopy and chemically by reaction with protic reagents (Scheme 2).

For complexes **3** and **4**, the ^1H-NMR spectra at ambient temperature exhibit one broad singlet as signal for the four o-NMe_2 groups along with a singlet for the two corresponding p-NMe_2 groups. This suggests a structure for these metallanimines without intramolecular coordination between the dimethylamino side chains to the metal atom, or a non static nitrogen...metal 14 interaction, to account for the magnetic equivalence of the o-NMe_2 groups. We believe that the same N...M...N dynamic coordination phenomenon observed for the parent divalent species $(ArO)_2M$, [65] must be responsible for the equivalence of the o-NMe_2 groups. Thus these metallanimines probably have a molecular structure included between the limiting forms portrayed in Scheme 3, nevertheless we were not able to define the true nature of the interaction between the NMe_2 groups and the Group 14 atom since crystals suitable for X-ray structural analysis could not be obtained.



Scheme 1.



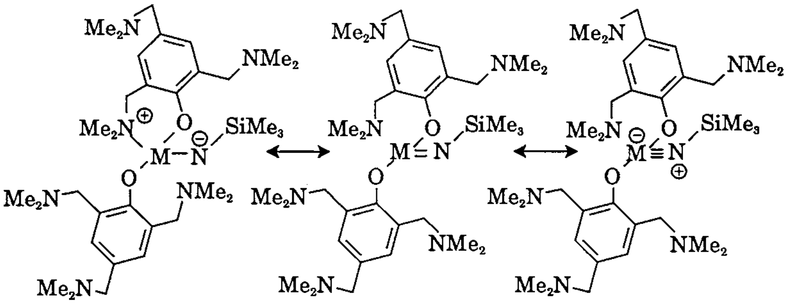
Scheme 2.

2.2. Metallanones, metallanethiones, -selones and -tellones

2.2.1. Metallanones

The direct oxidation of the divalent species $(ArO)_2M$ by pure oxygen, DMSO, or N-pyridine oxide leads to the corresponding metalloxanes **9** and **10** with various yields. Pure oxygen reacts at room temperature (r.t.) in a quasi-quantitative way with **1** and **2** leading to the cyclic oxides **9** and **10**, respectively, probably via transient metallanones $[(ArO)_2M{=}O]$. With DMSO and N-pyridine oxide, the reaction occurs only at high temperature leading to **9** and **10**, with low yield (Scheme 4).

It is noteworthy that the dihalogenated germylenes GeX_2 react exothermally with the same oxidation reagents [16]; the low reactivity of **1** and **2** towards DMSO and PhNO points to a loss of electrophilic character of the metal in the divalent species $(ArO)_2M$, this metal probably being engaged in intramolecular coordinations N...M...N with the o-dimethylamino side chains of the phenyl groups.



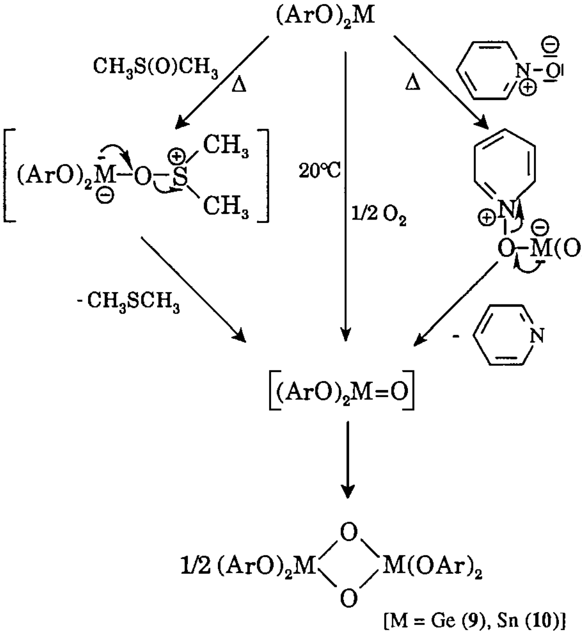
Scheme 3.

2.2.2. Metallanethiones

2.2.2.1. Case of germanium. Like oxygen, molecular sulfur reacts with germylene $(ArO)_2Ge$; the reaction is carried out in benzene at 80°C (Scheme 5). But in this case the species formed, **11**, is monomeric in benzene solution (cryoscopic mass determination), thermally stable and can be perfectly physicochemically and chemically characterized.

Complex **11** exhibits a moderate reactivity; the protic reagents such as water and methanol react in a nearly quantitative way with **11** leading to thiols **12** and **13**, respectively, but we could not observe any insertion reactions in various small strained heterocycles or any $[2+4]$ or $[2+2]$ cycloaddition with electron-poor or -rich dienes.

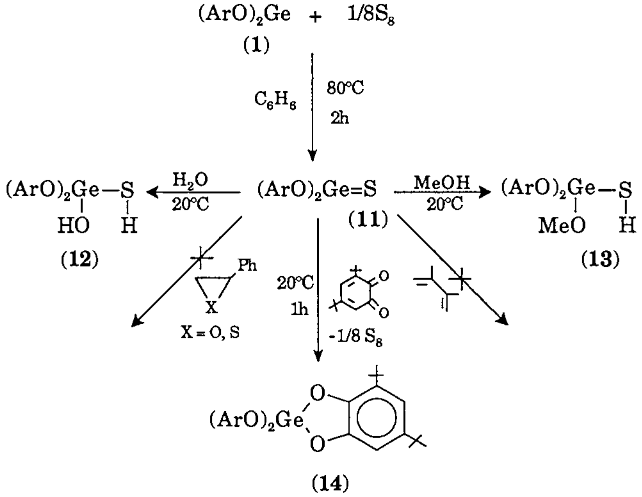
With the 3,5-di-*tert*-butyl-1,2-benzoquinone we observed an immediate reaction leading, (besides sulfur) to the single product dioxagermole **14** which is the formal adduct of the germylene $(ArO)_2Ge$ and the quinone (Scheme 5).



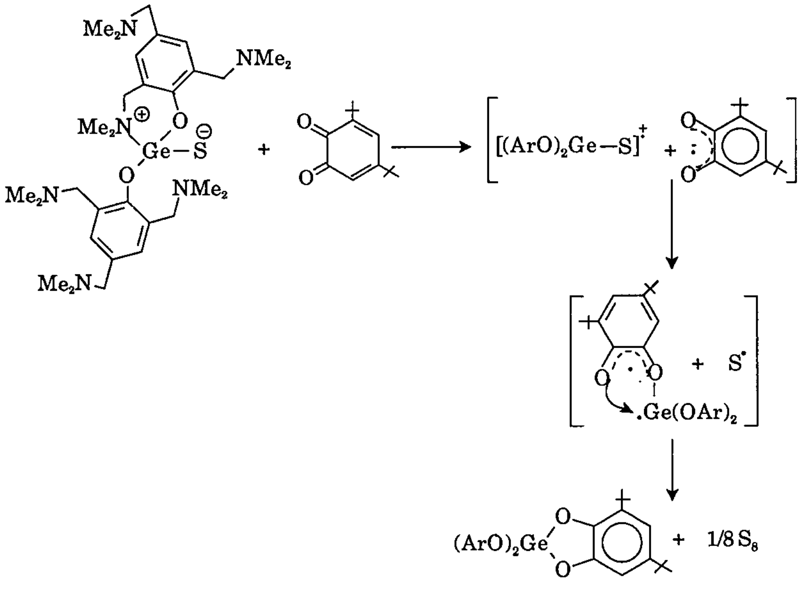
Scheme 4.

Complex **11** being inert towards isolated carbonyl groups like $Ph_2C{=}O$ and $(CH_3)_2C{=}O$, addition probably proceeds, like in the germylene case, through a one-electron transfer mechanism since a transitory *o*-semiquinonic radical structure has been characterized by ESR spectroscopy in this reaction (toluene, -40°C, $g = 2.0016$, $a^H = 2.9$ G). The germanium–sulfur bond of **11**, like various Ge–Y (Y = H, Cl, N) bonds [66–69] species, could act as electron-donor to the quinone and the mechanism summarized by Scheme 6 is therefore postulated to account for the formation of **14**.

Here again, the presence of (dimethylamino)methyl groups on the benzenic structure, giving to **11** a rather zwitterionic character, seem to be responsible for the loss of the characteristic aspects of the chemistry of (free transient or stabilized only by steric effect) germanethiones. Thus the stability and the reactivity which have been observed could be explained by a molecular structure of germanethione **11** included between the two mesomeric limiting forms **A** and **B** shown in Scheme 7. Such structures have been postulated for the silicon and tin series ([48]c, [54]b, [59]b). Only X-ray structural analysis of **11** could permit the identification of the correct nature of the germanium–sulfur bond in this compound, but we were unable to obtain crystals suitable for X-ray study.



Scheme 5.



Scheme 6.

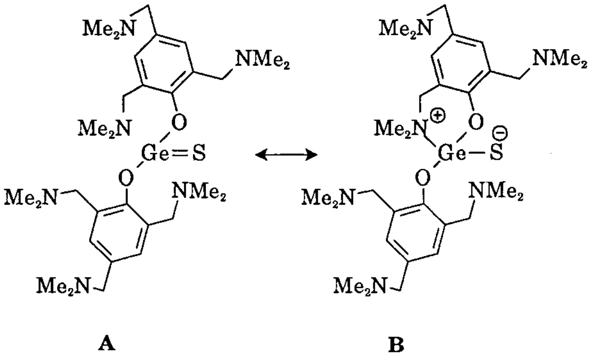
2.2.2.2. Case of tin. For the same experimental conditions as in the previous case, the reaction between the divalent tin species $(ArO)_2Sn$ and sulfur S_8 does not lead to the formation of the corresponding stannanethione since in the reaction of **2** with sulfur the starting materials were recovered with any transformation (Eq. 1).

$$(ArO)_2Sn + 1/8S_8 \xrightleftharpoons[80°C]{C_6H_6} (ArO)_2Sn{=}S \quad (1)$$

This, obviously, reveals the instability of the $(ArO)_2Sn{=}S$ species since the addition of sulfur to tin is not kinetically forbidden.

2.2.3. Metallaneselones

2.2.3.1. Case of germanium. The complex $(ArO)_2Ge$ and black selenium lead, at 80°C in benzene, to the germaneselone $(ArO)_2Ge{=}Se$ (Eq. 2). Like its sulfur homolog this species is stable, monomeric in benzene solution (cryoscopic mass determination), and was characterized by NMR (^1H-, ^{13}C-) and mass spectroscopy.



Scheme 7.

$$(ArO)_2Ge + Se \underset{80°C}{\overset{C_6H_6}{\rightarrow}} \underset{(15)}{(ArO)_2Ge = Se} \quad (2)$$

The analysis of mass spectroscopy obtained under electronic impact (70 eV) notably reveals the presence of two series of lines corresponding to the molecular $[M]^{+\bullet}$ ion and $[M-Se]^+$ ion. Since the fragmentation process of a molecule under electronic impact is correlated to its behavior under thermal effect, the presence of the signal $[M-Se]^+$ in the spectrogram of **15** as largely the most intense peak suggests the thermal instability of the germanium–selenium bond in this germaneselone (Eq. 3).

$$(ArO)_2Ge{=}Se \xrightarrow{\Delta} (ArO)_2Ge + Se \quad (3)$$

The chemical reactivity of this germaneselone is quite similar to the corresponding germanethione; we observed the same types of reactions with water, methanol and quinones (Scheme 8).

Thus a structure with a zwitterionic tendency could be attributed to the germaneselone as in the germanethione case (Scheme 9).

A substitution reaction of chalcogen could be observed from this germaneselone (Eq. 4). In fact, when we investigated the reaction of S_8 with germaneselone at 80°C in pure benzene, an exchange reaction between selenium–sulfur occurs, allowing the production from germaneselone of the germanethione probably via the divalent species $(ArO)_2Ge$.

$$\underset{(15)}{(ArO)_2Ge{=}Se} + 1/8\,S_8 \underset{\not\longleftarrow}{\xrightarrow{C_6H_6,\ 80°C,\ 2h}} \underset{(11)}{(ArO)_2Ge{=}S} + Se \quad (4)$$

This reaction is consistent with the respective mass spectra of the two $(ArO)_2Ge{=}X$ species. The relation between $[M]^{+\bullet}/[M-X]^{+}$ is more important for $(ArO)_2Ge{=}S$ than for $(ArO)_2Ge{=}Se$, which indicates that the energy of the Ge=Se bond is lower than the Ge=S bond.

2.2.3.2. Case of tin. Similar to sulfur, in the same experimental conditions, selenium is unreactive towards the divalent species $(ArO)_2Sn$, which again probably reveals the thermal instability of the species $(ArO)_2Sn{=}Se$ (Eq. 5).

$$(ArO)_2Sn + Se \underset{80°C}{\overset{C_6H_6}{\rightleftarrows}} (ArO)_2Sn{=}Se \quad (5)$$

2.3. Complexes $(ArO)_2M{=}M'L_n$ [$M = Ge, Sn$; $M'L_n = Fe(CO)_4, W(CO)_5, Cr(CO)_5, Pt(PPh_3)_2$]

Superior analogs of carbenes, the divalent derivatives $(ArO)_2M$ can be used as ligands in transition metal chemistry. The stability of carbene-transition metal complex is often explained by a σ, π synergetic effect, the σ-donor effect on the metal of the free pair of carbone being compensated by the π-donor effect of the occupied orbital of the metal on the p vacant orbital of the carbon atom. This concept is not easily applicable to $>M-M'L_n$ complexes, since the $>M$ divalent species are low p-π acceptors (no coordination of a divalent species carrying a Lewis base to a transition metal resulted in loss of the base complexing the divalent species).

Nevertheless, similar to all divalent organic derivatives of the heavier main Group 14 elements, the $(ArO)_2M$ divalent species are excellent σ-donors and thus have been used as ligands in transition metal complexes. With $(ArO)_2M$ species, various complexation reactions could be achieved with complexes of transition metals such as $Fe(CO)_4\cdot THF$, $W(CO)_5\cdot THF$, $Cr(CO)_5\cdot THF$ and $C_2H_4\cdot Pt(PPh_3)_2$ (Scheme 10). In all cases, after liberation of THF or ethylene, the reaction leads to the expected complexes **18–24**.

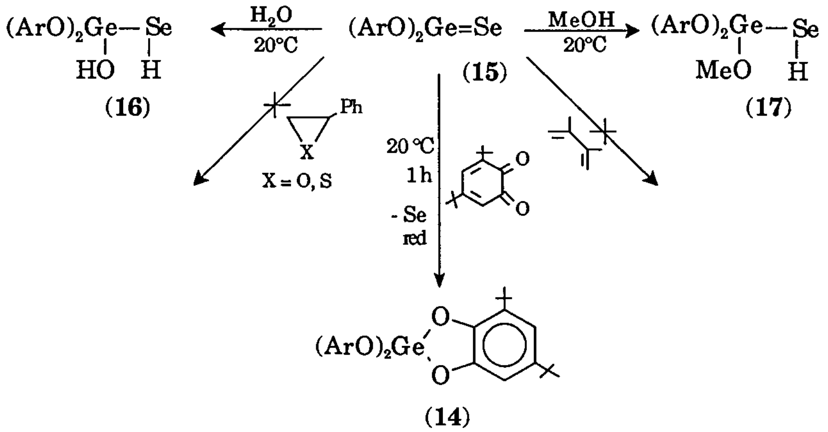
Complexes **18–25** are colored solids, soluble in aromatic solvents, insoluble in pentane, having a great sensitivity to oxygen and moisture. Cryoscopic mass determination showed that **18–23** are monomeric in C_6H_6; **18–25** have been characterized by NMR (^{1}H-, ^{13}C-, ^{31}P-, ^{119}Sn-), mass and IR spectroscopy (Table 1) but unfortunately it was also impossible in these cases to obtain, from various solvents at −20°C, crystals suitable for crystallography.

IR spectra for compounds **18** and **19** show the appearance of three carbonyl bands, with the usual intensity pattern for the $(^{t}BuS)_2SiFe(CO)_4\cdot HMPA$ ([49]c) species, which is characteristic of a C_{3v} local symmetry at iron with an axial coordination of the divalent species on the iron (Scheme 11).

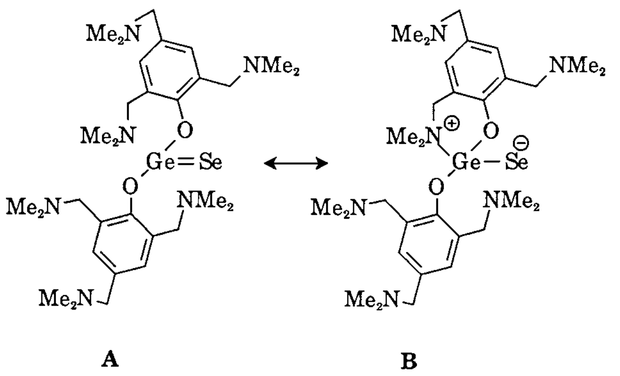
For complexes **20–23**, the existence of three bands in the IR spectra and of two ^{13}C-NMR peaks for the CO groups are compatible with molecular models with a C_{4v} symmetry (Scheme 12).

The mass spectra of complexes **18–23** exhibit peaks corresponding to molecular ions $M^{+\bullet}$ (weak intensity) and to the characteristic fragmentations of such structures (loss of carbonyl groups and of substituents on the Ge and Sn atoms, in particular).

In all cases, we notice the equivalence of the four o-NMe_2 groups in ^{1}H-NMR under an ambient temper-



Scheme 8.



Scheme 9.

ature. Thus, the observation of a single sharp methyl resonance for the *o*-NMe$_2$ groups is characteristic of a 'flip-flop' N...M...N dynamic coodination mode, similar to the one observed for the precursors (ArO)$_2$M [65].

The monomeric structure of **24** has been confirmed by ^{31}P-NMR, since no coupling $^3J_{(Pt-P)}$ characteristic of a dimeric structure has been observed. Thus **24** is likely to have a planar triangular structure of three groups around the platinum metal (Scheme 13).

All these complexes, with strongly polar metal 14-transition metal bonds, appear as precursors with high potential in organometallic synthesis. They can either behave like precursors of divalent species or can lead to the expected reactions for compounds with Group 14 metal-transition metal bonds, particularly towards oxygen, CO$_2$, CS$_2$ and unsaturated systems for instance; these reactions and silicon grafting reactions are now under investigation.

3. Experimental section

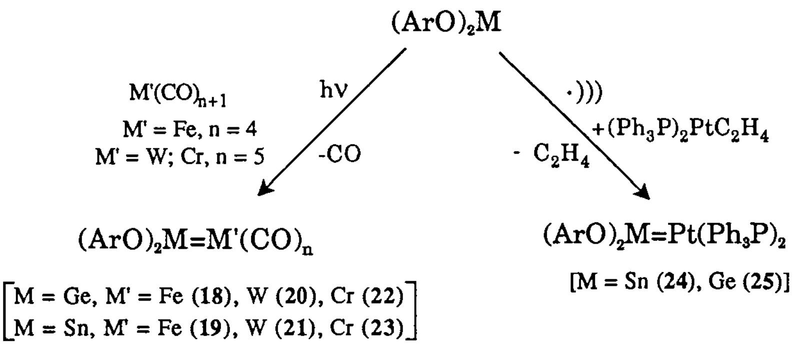
3.1. General procedures

All reactions and manipulations were carried out under an argon or nitrogen atmosphere with the use of standard Schlenk and high-vacuum line techniques. All solvents were dried by distillation from Na/K alloy and deoxygenated by standard methods. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are given in ppm (δ) relative to Me$_4$Si), ^{13}C- spectra on a AC-200 MHz spectrometer; the multiplicity of the ^{13}C-NMR signals was determined by the APT technique and quoted as (+) for CH$_3$ or CH, (−) for CH$_2$ and (C$_{quat}$) for quaternary carbon atoms. ^{31}P-NMR spectra were measured on a Bruker AC-200 MHz (spectrometer frequency 81.015 MHz). The ^{31}P chemical shifts are externally referenced to 85% H$_3$PO$_4$. ^{119}Sn{^{1}H}-NMR spectra were recorded on a Bruker AC-200 or 400 MHz (spectrometer frequency 74.63 or 149.21 MHz, chemical shifts are reported in ppm (δ) relative to external Me$_4$Sn as reference). Mass spectra were recorded on a Nermag R10-10H or a Hewlett Packard 5989 instrument operating, in the electron impact mode at 70 and 30 eV and samples were contained in glass capillaries under argon, or in the chemical ionization mode (CH$_4$). IR spectra were obtained on a Perkin-Elmer 1600 FT-IR. Irradiations were carried out at 25°C by using a low-pressure mercury immersion lamp in a quartz tube. Reactions under ultrasonic wave were carried out at 47 MHz using a Bransonic B 2200E apparatus. Melting points were taken on a hot-plate microscope apparatus Leitz Biomed. Elemental analyses (C, H, N) were performed at the Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

3.2. Germanimine (ArO)$_2$Ge=N–SiMe$_3$ (3)

A solution of trimethylsilylazide (0.03 g, 0.26 mmol) in 10 ml of benzene was added dropwise to a solution of (ArO)$_2$Ge (0.16 g, 0.26 mmol) in 15 ml of benzene. Nitrogen evolved immediately and the solution turned to yellow. The mixture was stirred at r.t. for 20 h and dried in vacuo giving a yellow residue which was extracted with 20 ml of pentane. After cooling to −20°C complex **3** was filtered off as yellow crystals and dried in vacuo (0.12 g, 70%).

Complex **3**: m.p. 144–145°C. ^{1}H-NMR (C$_6$D$_6$): 0.24



Scheme 10.

Table 1
Spectroscopic data for compounds **18**–**23**

	NMR (C_6D_6; δ ppm)							
	Ge	**(18)**	**(20)**	**(22)**	Sn	**(19)**	**(21)**	**(23)**
^{1}H								
p-NMe_2		2.07	2.07	2.06		2.18	2.04	2.05
o-NMe_2		2.19	2.19	2.19		2.24	2.18	2.19
p-CH_2N		3.36	3.36	3.34		3.26	3.35	3.34
o-CH_2N		3.54	3.53	3.51		3.49	3.51	3.50
C_6H_2		7.15	7.23	7.22		7.24	7.22	7.21
^{13}C								
p-NMe_2		44.96	44.79	44.71		45.09	44.72	44.87
o-NMe_2		45.49	45.39	45.36		45.72	45.32	45.38
p-CH_2N		60.33	60.28	60.19		60.23	60.28	60.29
o-CH_2N		64.46	64.02	63.95		64.06	63.97	64.10
C_6H_2		127.07	127.07	126.92		127.65	127.60	127.48
		128.61	128.60	128.33		128.66	128.29	128.08
		129.37	129.37	129.05		130.39	130.57	130.15
		157.42	157.04	157.18		157.91	157.65	157.96
CO		211.30	197.15	218.40		216.93	213.77	219.39
		214.62	200.05	221.14		218.76	215.53	223.56
^{119}Sn								
		−225.9	−391.2	−213.29				
IR (C_6H_6, ν_{CO} cm^{-1})								
	1984	1981	2092			2001	1974	2087
	1968	1948	1954			1946	1933	1935
	1887	1867	1914			1893	1859	1889

(s, 9H, SiMe), 2.06 (s, 24H, NMe), 2.13 (s, 12H, NMe), 3.29 (s, 4H, CH_2), 3.38 (s, 8H, CH_2), 7.27 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 2.83 (+), 44.92 (+), 45.47 (+), 60.81 (−), 64.61 (−), 125.71 (C_{quat}), 127.30 (+), 131.68 (C_{quat}), 160.8 (C_{quat}). MS: $m/z = 644$ $[M{-}3Me]^+$. IR (C_6H_6, cm^{-1}): $\nu_{Ge=N} = 1090$. Anal. Found: C, 57.42; H, 8.74; N, 14.08. $C_{33}H_{61}N_7O_2SiGe$. Calc.: C, 57.59; H, 8.87; N, 14.25.

3.3. Reaction of **3** with H_2O

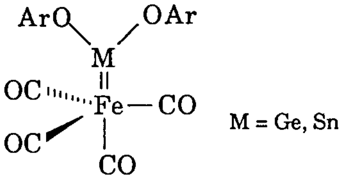
H_2O (0.002 g, 0.14 mmol) was added to a stirred solution of **3** (0.1 g, 0.14 mmol) in 20 ml of benzene. The volatile material was removed in vacuo affording a white solid. Crystallization from pentane (ca. 20 ml) yielded **5** as a white crystals (0.09 g, 90%).

Complex **5**: m.p. 134–135°C. ^{1}H-NMR (C_6D_6): 0.3 (s, 9H, SiMe), 2.12 (s, 12H, NMe), 2.18 (s, 24H, NMe), 3.33 (s, 4H, CH_2), 3.41 (s, 8H, CH_2), 7.26 (s, 4H, C_6H_2). MS: $m/z = 662$ $[M{-}3Me]^+$. IR (C_6H_6, cm^{-1}): ν_{OH}, ν_{NH} = 3330–3438. Anal. Found: C, 56.08; H, 8.86; N, 13.76. $C_{33}H_{63}N_7OSiGe$. Calc.: C, 56.12; H, 8.92; N, 13.88.

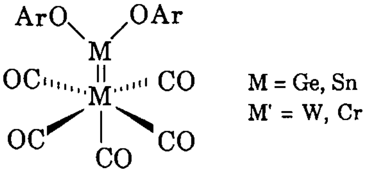
3.4. Reaction of **3** with methanol

To a solution of **3** (0.1 g, 0.14 mmol) in 5 ml of benzene was added an excess of MeOH (0.009 g, 0.28 mmol)). Progressively, the color of the mixture changed. The solvent was removed in vacuo. Crystallization from pentane (ca. 10 ml) afforded **7** (0.08 g, 87%).

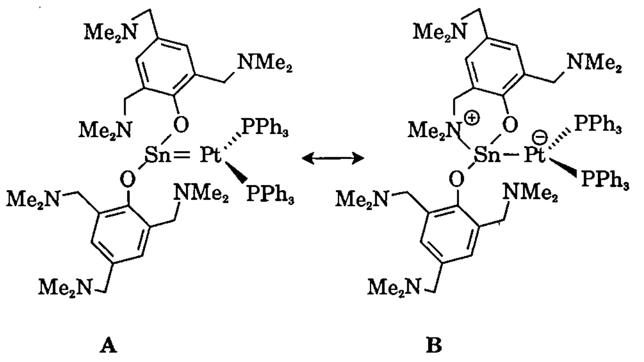
Complex **7**: m.p. 127–128°C. ^{1}H-NMR (C_6D_6): 0.28 (s, 9H, SiMe), 2.14 (s, 12H, NMe), 2.19 (s, 24H, NMe), 3.34 (s, 4H, CH_2), 3.42 (s, 8H, CH_2), 3.69 (s, 3H, OMe), 7.26 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 2.79 (+), 44.67 (+), 45.28 (+), 53.90 (+), 59.90 (−), 64.61 (−), 125.65 (C_{quat}), 127.12 (+), 131.48 (C_{quat}), 159.70



Scheme 11.



Scheme 12.



Scheme 13.

(C_{quat}). MS: $m/z = 721$ $[M]^{+\bullet}$. IR (C_6H_6, cm^{-1}): $\nu_{NH} = 3325$. Anal. Found: C, 56.49; H, 8.92; N, 13.43. $C_{34}H_{65}N_7O_3SiGe$. Calc.: C, 56.69; H, 9.03; N, 13.62.

*3.5. Stannanimine $(ArO)_2Sn{=}N{-}SiMe_3$ (**4**)*

A solution of trimethylsilylazide (0.05 g, 0.46 mmol) in 10 ml of benzene was added dropwise to a solution of $(ArO)_2Sn$ (0.2 g, 0.46 mmol) in 20 ml of benzene. Nitrogen evolved immediately and the solution turned to yellow. The mixture was stirred for a further 20 h at r.t. The solvent was removed in vacuo, affording a yellow–orange powder which was dissolved in pentane (ca. 25 ml). After cooling to −20°C **4** was filtered off and dried in vacuo (0.21 g, 65%).

Complex **4**: m.p. 150–151°C. $^{119}Sn\{^1H\}$-NMR (C_6D_6): −138.3. ^1H-NMR (C_6D_6): 0.25 (s, 9H, SiMe), 2.08 (s, 24H, NMe), 2.19 (s, 12H, NMe), 3.36 (s, 4H, CH_2), 3.52 (s, 8H, CH_2), 7.19 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 3.13 (+), 46.59 (+), 47.29 (+), 61.46 (−), 66.11 (−), 127.55 (C_{quat}), 129.96 (+), 139.55 (C_{quat}), 160. 41 (C_{quat}). MS: $m/z = 735$ $[M]^{+\bullet}$. IR (C_6H_6, cm^{-1}): $\nu_{Sn{=}N} = 1100$. Anal. Found: C, 53.79; H, 8.12; N, 13.15. $C_{33}H_{61}N_7O_2SiSn$. Calc.: C, 53.97; H, 8.31; N, 13.35.

*3.6. Reaction of **4** with H_2O*

The procedure for complex **5** was followed with complex **4** (0.15 g, 0.2 mmol) and H_2O (0.0037 g, 0.2 mmol) to give **6** (0.13 g, 92%).

Complex **6**: m.p. 143–144°C. $^{119}Sn\{^1H\}$-NMR (C_6D_6): −485.4. ^1H-NMR (C_6D_6): 0.28 (s, 9H, SiMe), 2.14 (s, 24H, NMe), 2.21 (s, 12H, NMe), 3.38 (s, 4H, CH_2), 3.54 (s, 8H, CH_2), 7.22 (s, 4H, C_6H_2). MS: $m/z = 753$ $[M-3Me]^+$. IR (C_6H_6, cm^{-1}): ν_{OH}, $\nu_{NH} = 3330–3442$. Anal. Found: C, 52.58; H, 8.26; N, 12.89. $C_{33}H_{63}N_7O_3SiSn$. Calc.: C, 52.68; H, 8.38; N, 13.04.

*3.7. Reaction of **4** with methanol*

To a solution of **4** (0.08 g, 0.12 mmol) in 10 ml of benzene was added an excess of MeOH (0.008 g, 0.25 mmol). The volatiles were removed in vacuo. Crystallization from pentane (ca.10 ml) and filtration gave **8** (0.08 g, 85%).

Complex **8**: m.p. 137–138°C. $^{119}Sn\{^1H\}$ (C_6D_6): −182.6. ^1H-NMR (C_6D_6): 0.31 (s, 9H, SiMe), 2.14 (s, 24H, NMe), 2.20 (s, 12H, NMe), 3.39 (s, 4H, CH_2), 3.41 (s, 8H, CH_2), 3.55 (s, 3H, OMe), 7.24 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 2.91 (+), 45.65 (+), 46.98 (+), 51.05 (+), 60.26 (−), 65.85 (−), 127.55 (C_{quat}), 129.82 (+), 131.48 (C_{quat}), 160.20 (C_{quat}). MS: $m/z = 767$ $[M]^{+\bullet}$. IR (C_6H_6, cm^{-1}): $\nu_{NH} = 3332$. Anal. Found: C, 53.12; H, 8.36; N, 12.65. $C_{34}H_{65}N_7O_3SiSn$. Calc.: C, 53.28; H, 8.48; N, 12.79.

*3.8. Oxidation reaction of **1** and **2***

3.8.1. Reaction with oxygen

Dry oxygen was bubbled through a solution of **1** (0.3 g, 0.5 mmol), or **2** (0.323 g, 0.5 mmol), in 15 ml of benzene for 2 h. The solvent was evaporated in vacuo affording **9**, or **10**, which were purified by crystallization from pentane (ca. 5 ml). Complex **9** (0.29 g, 94%); **10** (0.31 g, 94%).

Complex **9**: m.p. 214–215°C. ^1H-NMR (C_6D_6): 2.06 (s, 24H, NMe), 2.18 (s, 12H, NMe), 3.33 (s, 8H, CH_2), 3.52 (s, 4H, CH_2), 7.21 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 45.22 (+), 45.59 (+), 60.16 (−), 64.01 (−), 127.95 (C_{quat}), 129.17 (+), 131.87 (C_{quat}), 158.52 (C_{quat}). MS: $m/z = 1190$ $[M-NMe_2]^+$. IR (C_6H_6, cm^{-1}): $\nu_{Ge-O} = 842$. Anal. Found: C, 58.22; H, 8.36; N, 13.49. $C_{60}H_{104}N_{12}O_6Ge_2$. Calc.: C, 58.38; H, 8.43; N, 13.62.

Complex **10**: m.p. 228–229°C. $^{119}Sn\{^1H\}$-NMR (C_6D_6): −148.7. ^1H-NMR (C_6D_6): 2.07 (s, 24H, NMe), 2.19 (s, 12H, NMe), 2.35 (s, 8H, CH_2), 3.53 (s, 4H, CH_2), 7.22 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 45.42 (+), 45.67 (+), 60.21 (−), 64.06 (−), 128.09 (C_{quat}), 129.29 (+), 132.57 (C_{quat}), 157.91 (C_{quat}). MS: $m/z = 1282$ $[M-NMe_2]^+$. IR (C_6H_6, cm^{-1}): $\nu_{Sn-O} = 870$. Anal. Found: C, 54.16; H, 7.68; N, 12.49. $C_{60}H_{104}N_{12}O_6Sn_2$. Calc.: C, 54.32; H, 7.84; N, 12.67.

3.8.2. Reaction with dimethylsulfoxide

A solution of **1** (0.4 g, 0.66 mmol), or **2** (0.43 g, 0.66 mmol), in 20 ml of benzene was treated with (0.55 g, 1.9 mmol) of dimethylsulfoxide. The mixture was refluxed for 2 h. The volatiles were removed in vacuo and the crude product was crystallized from pentane (ca. 20 ml). **9** (0.34 g, 79%); **10** (0.35 g, 80%).

3.8.3. Reaction with pyridine N-oxide

A mixture of **1** (0.4 g, 0.66 mmol), or **2** (0.43 g, 0.66 mmol), and pyridine *N*-oxide (0.06 g, 0.66 mmol) in 20 ml of benzene was refluxed for 2 h. The volatile was removed in vacuo. The crude product was crystallized from pentane (ca. 20 ml). **9** (0.35 g, 85%); **10** (0.35 g, 80%).

3.9. Reaction of **1** with sulfur

A solution of **1** (0.81 g, 1.34 mmol) in 20 ml of benzene was added to a stirred suspension of sulfur (0.04 g, 1.34 mmol) in 10 ml of benzene. The mixture was refluxed for 3 h. Concentration in vacuo afforded the crude product which was recrystallized from toluene/pentane (1/1, 20 ml) at −30°C. Filtration gave **11** (0.47 g, 55%).

Complex **11**: m.p. 120 − 121°C. ^{1}H-NMR (C_6D_6): 2.13 (s, 24H, NMe), 2.18 (s, 12H, NMe), 3.35 (s, 4H, CH_2), 3.55 (s, 8H, CH_2), 7.22 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.87 (+), 45.42 (+), 60.34 (−), 64.45 (−), 127.57 (C_{quat}), 129.36 (+), 130.07 (C_{quat}), 150.8 (C_{quat}). MS: $m/z = 634$ $[M]^{+\bullet}$. Anal. Found: C, 56.75; H, 8.04; N, 13.09. $C_{30}H_{52}N_6O_2SGe$. Calc.: C, 56.91; H, 8.22; N, 13.28.

3.10. Reaction of **11** with H_2O

To a solution of **11** (0.09 g, 0.14 mmol) in 10 ml of benzene was added (0.002 g, 0.1 mmol) of water. Immediately, the color of the reaction mixture changed. The solvent was removed in vacuo. Crystallization from pentane (ca. 10 ml) afforded **12** as orange crystals (0.08 g, 98%).

Complex **12**: m.p. 104–105°C. ^{1}H-NMR (C_6D_6): 2.07 (s, 24H, NMe), 2.12 (s, 12H, NMe), 3.32 (s, 4H, CH_2), 3.49 (s, 8H, CH_2), 7.19 (s, 4H, C_6H_2). MS: $m/z = 635$ $[M–OH]^+$. IR (C_6H_6, cm^{-1}): $\nu_{OH,\ SH} = 3274$; 2650. Anal. Found: C, 55.17; H, 8.21; N, 12.76. $C_{30}H_{54}N_6O_3SGe$. Calc.: C, 55.33; H, 8.30; N, 12.91.

3.11. Reaction of **11** with methanol

A solution of methanol (0.012 g, 0.38 mmol) in 5 ml of benzene was added dropwise to a solution of **11** (0.13 g, 0.2 mmol) in 10 ml of benzene. The reaction mixture was stirred for a further 30 min and the volatile removed in vacuo. Crystallization from pentane (ca. 10 ml) and filtration gave **13** (0.11 g, 81%).

Complex **13**: m.p. 98–100°C. ^{1}H-NMR (C_6D_6): 2.05 (s, 24H, NMe), 2.19 (s, 12H, NMe), 3.02 (s, 3H, OMe), 3.36 (s, 4H, CH_2), 3.52 (s, 8H, CH_2), 7.16 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.43 (+), 45.31 (+), 51.54 (+), 60.26 (−), 64.32 (−), 127.46 (C_{quat}), 129.28 (+), 130.11 (C_{quat}), 150.05 (C_{quat}). MS: $m/z = 635$ $[M–OMe]^+$. IR (C_6H_6, cm^{-1}): $\nu_{SH} = 2650$. Anal. Found: C, 55.81; H, 8.36; N, 12.91. $C_{31}H_{56}N_6O_3SGe$. Calc.: C, 55.97; H, 8.43; N, 12.64.

3.12. Reaction of **11** with 3,5-di-*tert*-butyl-1,2-quinone

A solution of **11** (0.36 g, 0.56 mmol) in 20 ml of benzene was added to a solution of 3,5-di-*tert*-butyl-1,2-quinone (0.12 g, 0.56 mmol) in 15 ml of benzene. The reaction mixture was stirred for 1 h at r.t. After filtration of the formed sulfur 30 ml of pentane was added; filtration and dried in vacuo afforded the complex **14** (0.41 g, 90%).

Complex **14**: m.p. 133–135°C. ^{1}H-NMR (C_6D_6): 1.34 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu) 1.90 (s, 3H, NMe), 2.07 (s, 3H, NMe), 2.18 (s, 12H, NMe), 2.76 (s, 6H, NMe), 2.23 (s, 6H, NMe), 2.60 (s, 3H, NMe), 2.71 (s, 3H, NMe), 3.13 and 3.61 (AB system, 2H, $J_{AB} = 12$ Hz), 3.94 (s, 4H, CH_2), 3.51 (s, 2H, CH_2), 3.54 (s, 2H, CH_2), 4.03 and 4.65 (AB system, 2H, $J_{AB} = 12$ Hz), 6.81 and 7.58 (dd, 4H, C_6H_2), 6.9 (d, 1H, $J_{HH} = 2.4$ Hz), 7.23 (d, 1H, $J_{HH} = 2.4$ Hz). ^{13}C-NMR (C_6D_6): 30.10 (+), 32.32 (+), 34.59 (C_{quat}), 35.18 (C_{quat}), 44.01 (+), 47.09 (+), 59.06 (−), 64.05 (−), 109.6 (+), 111.9 (+), 127.73 (C_{quat}), 132.1 (+), 132.5 (C_{quat}), 139.0 (C_{quat}), 146.9 (C_{quat}), 151.2 (C_{quat}), 159.01 (C_{quat}), 159.1 (C_{quat}). MS: $m/z = 822$ $[M]^{+\bullet}$. Anal. Found: C, 64.22; H, 8.71; N, 10.12. $C_{44}H_{72}O_4N_6Ge$. Calc.: C, 64.34; H, 8.77; N, 10.23.

3.13. Reaction of **1** with selenium

A solution of **1** (0.97 g 1.6 mmol) in 20 ml of benzene was added to a stirred suspension of selenium (0.12 g, 1.6 mmol) in 10 ml of benzene. The mixture was refluxed for 3 h and the solvent removed by evaporation under reduced pressure. The resulting solid product, **15**, was purified by crystallization from toluene/pentane (1/1, 20 ml) at −30°C. Yield: 0.65 g, 60%.

Complex **15**: m.p. 135–136°C. ^{1}H-NMR (C_6D_6): 2.11 (s, 24 H, NMe), 2.14 (s, 12 H, NMe), 3.32 (s, 4H, CH_2), 3,54 (s, 8H, CH_2), 7,27 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.92 (+), 45.68 (+), 60.66 (−), 64.71 (−), 127.83 (C_{quat}), 129.45 (+), 130.34 (C_{quat}), 151.12 (C_{quat}). MS: $m/z = 680$ $[M]^{+\bullet}$. Anal. Found: C, 52.75; H, 7.52; N, 12.26. $C_{30}H_{52}N_6O_2SeGe$. Calc.: C, 52.97; H, 7.65; N, 12.36.

3.14. Reaction of **15** with H_2O

H_2O (0.002 g, 0.14 mmol) was added to a solution of **15** (0.1 g, 0.14 mmol) in 10 ml of benzene. Immediately, the mixture reaction turned color. The solvent was evaporated in vacuo, the residue was extracted with pentane (ca. 10 ml) and cooled (−30°C) to give **16** as yellow crystals (0.11 g, 94%).

Complex **16**: m.p. 123–124°C. ^{1}H-NMR (C_6D_6): 2.04 (s, 24 H, NMe), 2.11 (s, 12 H, NMe), 3.31 (s, 4H, CH_2), 3,48 (s, 8H, CH_2), 7,18 (s, 4H, C_6H_2). MS: $m/z = 681$ $[M–OH]^+$. IR (C_6H_6, cm^{-1}): $\nu_{OH,\ SeH} = 3330$; 2570. Anal. Found: C, 51.44; H, 7.67; N, 11.91. $C_{30}H_{54}N_6O_3GeSe$. Calc.: C, 51.61; H, 7.74; N, 12.04.

3.15. Reaction of **15** with methanol

A solution of MeOH (0.009 g, 0.28 mmol) in 5 ml of benzene was added to a solution of **15** (0.1 g, 0.14 mmol) in 10 ml of benzene. The solution was stirred for 30 min. The volatile materials were removed under reduced pressure, and the residue was crystallized in pentane (ca. 10 ml). Filtration and dried in vacuo afforded **17** (0.9 g, 90%).

Complex **17**: m.p. 112–113°C. ^{1}H-NMR (C_6D_6): 2.04 (s, 24H, NMe) 2.17 (s, 12H, NMe), 3.01 (s, 3H, OMe), 3,34 (s, 4H, CH_2), 3.49 (s, 8H, CH_2), 7.17 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.47 (+), 45.49 (+), 51.50 (+), 60.31 (−), 64.43 (−), 127.47 (C_{quat}), 129.33 (+), 130.17 (C_{quat}), 150.12 (C_{quat}). MS: $m/z = 681$ $[M-OMe]^+$. IR (C_6H_6, cm^{-1}): $\nu_{SeH} = 2570$. Anal. Found: C, 52.12; H, 7.80; N, 11.67. $C_{31}H_{56}N_6O_3GeSe$. Calc.: C, 52.28; H, 7.80; N, 11.67.

3.16. *Reaction of **15** with 3,5-di-tert-butyl-1,2-quinone*

Complex **15** (0.30 g, 0.44 mmol) in benzene (20 ml) was added to 3,5-di-*tert*-butyl-1,2-quinone (0.10 g, 0.44 mmol) in benzene (10 ml). The mixture was stirred at r.t. for 1 h. A red precipitate of selenium appeared which was eliminated by filtration. Addition of 50 ml of pentane to the filtrate, filtration and dried in vacuo gave **14** as yellow crystals (0.33 g, 92%).

3.17. *Reaction of **15** with sulfur*

Complex **15** (0.58 g, 0.96 mmol) in benzene (25 ml) was added to a suspension of sulfur (0.07 g, 0.96 mmol) in benzene (10 ml). The mixture was refluxed for 3 h. A black precipitate of selenium appeared. Filtration and evaporation of the filtrate provided a yellow powder. Crystallization from pentane/toluene (1/1, 50 ml) at −30°C afforded **11** as a yellow powder (0.54 g, 90%).

3.18. *$(ArO)_2Ge{=}Fe(CO)_4$ (**18**)*

A solution of $Fe(CO)_5$ (0.08 g, 0.42 mmol) in 80 ml of THF was irradiated for 1.5 h. CO was eliminated by bubbling of nitrogen in the reaction mixture during 15 min, then $(ArO)_2Ge$ (0.27 g, 0.42 mmol) in THF (20 ml) was added. The solution turned dark maroon. After stirring at r.t. for 1 h the volatile materials were removed under reduced pressure. The residual solid was recrystallized from pentane (ca. 80 ml). Filtration gave **18** (0.25 g, 79%).

Complex **18**: m.p. 105–107°C. ^{1}H-NMR (C_6D_6): 2.07 (s, 12H, NMe), 2.19 (s, 24H, NMe), 3,36 (s, 4H, CH_2), 3.54 (s, 8H, CH_2), 7.15 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.96 (+), 45.49 (+), 60.33 (−), 64.46 (−), 127.07 (C_{quat}), 128.60 (+), 129.37 (C_{quat}), 157.42 (C–O), 211.30 (C=O), 214.60 (C=O). MS: $m/z = 686$ $[M-3CO]^+$. IR (C_6H_6, cm^{-1}): $\nu_{C=O} = 1984$, 1968, 1887. Anal. Found: C, 53.02; H, 6.61; N, 10.89. $C_{34}H_{52}N_6O_6FeGe$. Calc.: C, 53.09; H, 6.76; N, 10.93.

3.19. *$(ArO)_2Sn{=}Fe(CO)_4$ (**19**)*

Using the same operating conditions as in the preceding preparation, **19** was obtained from $(ArO)_2Sn$ (0.27 g, 0.42 mmol) and $Fe(CO)_5$ (0.08 g, 0.42 mmol). Yield: 0.29 g, 85%.

Complex **19**: m.p. 110–112°C. ^{119}Sn{^{1}H}-NMR (C_6D_6): −225.9 ($^1J_{SnFe} = 1338$ Hz). ^{1}H-NMR (C_6D_6): 2.18 (s, 12H, NMe), 2.24 (s, 24H, NMe), 3,26 (s, 4H, CH_2), 3.49 (s, 8H, CH_2), 7.24 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 45.09 (+), 45.72 (+), 60.23 (−), 64.06 (−), 127.65 (C_{quat}), 128.66 (+), 130.39 (C_{quat}), 157.91 (C_{quat}), 157.91 (C–O), 216.93 (C=O), 218.76 (C=O). MS: $m/z = 732$ $[M-3CO]^+$. IR (C_6H_6, cm^{-1}): $\nu_{C=O} =$ 2001, 1946, 1893. Anal. Found: C, 50.02; H, 6.26; N, 10.26. $C_{34}H_{52}N_6O_6FeSn$. Calc.: C, 50.09; H, 6.38; N, 10.31.

3.20. *$(ArO)_2Ge{=}W(CO)_5$ (**20**)*

Using the same operating conditions as in the preceding preparation, **20** was obtained from $(ArO)_2Ge$ (0.20 g, 0.34 mmol) and $W(CO)_6$ (0.12 g, 0.34 mmol). Yield: 0.25 g, 82%.

Complex **20**: m.p. 193–195°C. ^{1}H-NMR (C_6D_6): 2.07 (s, 12H, NMe), 2.19 (s, 24H, NMe), 3.36 (s, 4H, CH_2), 3.53 (s, 8H, CH_2), 7.23 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.79 (+), 45.39 (+), 60.28 (−), 64.02 (−), 127.07 (C_{quat}), 128.60 (+), 129.37 (C_{quat}), 157.04 (C–O), 197.15 (C=O), 200.05 (C=O). MS: $m/z = 896$ $[M-CO]^{+\bullet}$. IR (C_6H_6, cm^{-1}): $\nu_{C=O} = 1981$, 1948, 1867. Anal. Found: C, 45.32; H, 5.56; N, 8.87. $C_{35}H_{52}N_6O_7WGe$. Calc.: C, 45.43; H, 5.62; N, 9.08.

3.21. *$(ArO)_2Sn{=}W(CO)_5$ (**21**)*

In a similar way the reaction of $(ArO)_2Sn$ (0.22 g, 0.34 mmol) with $W(CO)_6$ (0.12 g, 0.34 mmol) afforded **21** (0.28 g, 87%).

Complex **21**: m.p. 206–208°C. ^{119}Sn{^{1}H}-NMR (C_6D_6): −391.2 ($^1J_{Snw} = 1010$ Hz). ^{1}H-NMR (C_6D_6): 2.04 (s, 12H, NMe), 2.18 (s, 24H, NMe), 3,35 (s, 4H, CH_2), 3.51 (s, 8H, CH_2), 7.22 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.72 (+), 45.32 (+), 60.28 (−), 63.97 (−), 127.60 (C_{quat}), 128.29 (+), 130.57 (C_{quat}), 157.65 (C–O), 213.77 (C=O), 215.53 (C=O). MS: $m/z = 942$ $[M-CO]^+$. IR (C_6H_6, cm^{-1}): $\nu_{C=O} = 1974$, 1933, 1859. Anal. Found: C, 43.18; H, 5.16; N, 8.49. $C_{35}H_{52}N_6O_7WSn$. Calc.: C, 43.27; H, 5.36; N, 8.65.

3.22. *$(ArO)_2Ge{=}Cr(CO)_5$ (**22**)*

Using the same operating conditions as in the preceding preparation, **22** was obtained from $(ArO)_2Ge$ (0.28 g, 0.48 mmol) and $Cr(CO)_6$ (0.10 g, 0.48 mmol). Yield: 0.25 g, 82%.

Complex **22**: m.p. 138 − 140°C. ^{1}H-NMR (C_6D_6): 2.06 (s, 12H, NMe), 2.18 (s, 24H, NMe), 3.34 (s, 4H, CH_2), 3.51 (s, 8H, CH_2), 7.22 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.71 (+), 45.36 (+), 60.18 (−), 63.95 (−), 126.92 (C_{quat}), 128.33 (+), 129.05 (C_{quat}), 157.18 (C–O), 218.40 (C=O), 221.10 (C=O). MS: $m/z = 766$ [M–CO]$^{+\bullet}$. IR (C_6H_6, cm^{-1}): $\nu_{C=O} = 2092$, 1954, 1914. Anal. Found: C, 52.71; H, 6.43; N, 10.38. $C_{35}H_{52}N_6O_7CrGe$. Calc.: C, 52.99; H, 6.56; N, 10.59.

*3.23. (ArO)$_2$Sn=Cr(CO)$_5$ (**23**)*

In a similar way the reaction of (ArO)$_2$Sn (0.31 g, 0.48 mmol) with W(CO)$_6$ (0.10 g, 0.48 mmol), afforded **23** (0.35 g, 88%). ^{119}Sn{^{1}H}-NMR (C_6D_6): −213.3. ^{1}H-NMR (C_6D_6): 2. 05 (s, 12H, NMe), 2.19 (s, 24H, NMe), 3.34 (s, 4H, CH_2), 3.50 (s, 8H, CH_2), 7.21 (s, 4H, C_6H_2). ^{13}C-NMR (C_6D_6): 44.87 (+), 45.38 (+), 60.29 (−), 64.10 (−), 127.48 (C_{quat}), 128.08 (+), 130.15 (C_{quat}), 157.96 (C–O), 218.39 (C=O), 223.56 (C=O). MS: $m/z = 812$ [M–CO]$^{+\bullet}$. IR (C_6H_6, cm $-^{1}$): $\nu_{C=O} = 2087$, 1935, 1889. Anal. Found: C, 49.97; H, 6.02; N, 9.88. $C_{35}H_{52}N_6O_7CrSn$. Calc.: C, 50.07; H, 6.20; N, 10.01.

*3.24. (ArO)$_2$Sn=Pt(PPh$_3$)$_2$ (**24**)*

A sample of bis(triphenylphosphine)(ethylene)platine (0.13 g, 0.18 mmol) in 10 ml of benzene was added to a solution of (ArO)$_2$Sn (0.12 g, 0.18 mmol) in 10 ml of benzene at r.t. The mixture reaction was ultra-sonicated for 4 h, the solution turned a brick-red color. Volatiles were evaporated under reduced pressure, and the residue was recrystallized from toluene/diethyl ether (1/1, 20 ml) at −20°C. Filtration gave **24** as orange crystals (0.22 g, 90%).

Complex **24**: m.p. 237–239°C. ^{119}Sn{^{1}H}-NMR (C_6D_6): −8.39 ($^1J_{SnPt} = 17901$ Hz). $^2J_{SnP} = 3224$ Hz. ^{31}P {^{1}H}-NMR (C_6D_6): 5.22, $^1J_{PPt} = 3211$ Hz, $^2J_{PSn} = 3224$ Hz. ^{1}H-NMR (C_6D_6): 2.06 (s, 12H, NMe), 2.18 (s, 24 H, NMe), 3.36 (s, 4H, CH_2), 3.52 (s, 8H, CH_2), 7.18 (s, 4H, C_6H_2), 7.29–8.12 (m, 30H, C_6H_5). ^{13}C-NMR (C_6D_6): 44.86 (+), 45.40 (+), 60.34 (−), 64.47 (−), 127.60 (C_{quat}), 128.57 (+), 129.24 (C_{quat}), 134.25 (C_{quat}), 152.77 (C–O). MS: $m/z = 1367$ [M + 1]$^{+\bullet}$. Anal. Found: C, 57.77; H, 5.84; N, 5.94. $C_{66}H_{82}N_6O_2P_2SnPt$. Calc.: C, 57.93; H, 5.99; N, 6.14.

*3.25. (ArO)$_2$Ge=Pt(PPh$_3$)$_2$ (**25**)*

An extremely air-sensitive yellow solid, was obtained in 45% yield, under conditions described above for **24**, from (ArO)$_2$Ge (0.11 g, 0.18 mmol) and (Ph$_3$P)$_2$Pt·C$_2$H$_4$ (0.13 g, 0.18 mmol). Analysis by ^{31}P-NMR and mass spectroscopy of this crude material showed that it was a mixture of **25** [^{31}P-NMR (C_6D_6; δ ppm): 8.72, $J_{PPt} = 3400$ Hz; MS: $m/z = 1321$ [M + 1]$^{+\bullet}$ and of a compound whose nature is still obscure (^{31}P-NMR (C_6D_6; d ppm): 53.27, $J_{PPt} = 4800$ Hz)]. All attempts of separation of these products by recrystallization from various solvents (toluene/diethyl ether/pentane) at −20°C failed.

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