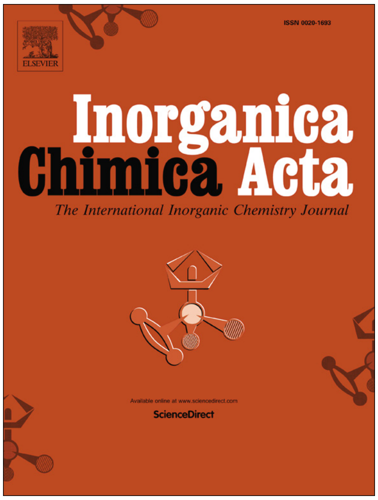

Research paper

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Synthesis and structural characterization of low-valent Group 14 metal complexes based on aminobisphenol ligands

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Abstract: Aminobisphenol supported germylenes (**1a-3a**), stannylenes (**1b-3b**) and plumbylenes (**1c-3c**) were synthesized by reaction of Lappert's tetrylenes, $[(Me_3Si)_2N]_2M$ (M = Ge, Sn, Pb), with corresponding aminobisphenols $R^1N(CH_2C_6H_2(OH)(t\text{-}Bu)R^2)_2$, **1-3** (**1**: R^1 = Et, R^2 = Me; **2**: R^1 = Et, R^2 = *t*-Bu; **3**: R^1 = CH_2(Py-2), R^2 = *t*-Bu). X-Ray diffraction analysis revealed different coordination mode for germylene **3a** and stannylene **3b** with additional nitrogen donor in the structure of the ligand. Germylene **1a** was converted to the rhenium complex **1aa** by the reaction with $Re(CO)_5Br$.

1. Introduction

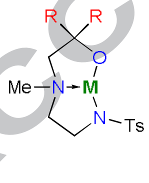
The isolation of the stable heavier carbene analogues, such as dialkyl and diamido substituted derivatives of germanium, tin and lead in the seventies of the last century [1], has led to significant increase of interest in these species and since then several reviews have appeared containing information on their synthesis and intriguing chemical properties [2].

At present it is generally accepted that most of these compounds are stable enough to be handled as "usual" molecular substances with application of appropriate techniques and have different stability depending on the structure of the ligands bound to metal atom. The low-valent metal centre may be stabilized by two possible ways. The first way is a thermodynamic (electron) stabilization including electron donation by oxygen or nitrogen containing groups (covalently or coordinatively bound to metal centre) into an empty p-orbital of the metal. The second way is a kinetic stabilization carried out by introduction of sterically demanding groups to the M atom.

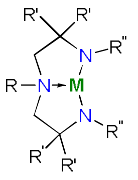
At the same time it is clear that excessive stabilization lowers reactivity. For example, as was recently shown for transition metal complexes with bulky carbene ligands, their catalytic activity is reduced in comparison with less sterically encumbered congeners [3]. It is therefore important to keep a balance between sufficient stability and a suitable reactivity.

The electronic structure of "heavy carbenes" allows them to possess dual reactivity. Thus, on the one side due to the electron deficiency their reactivity is enhanced so they may be used as precursors for synthesis of various organometallic compounds and intermediates *via* insertion into different σ-bonds and addition to π-bonds [4]. On the other side due to the lone electron pair, especial interest may arise from application of such derivatives as ligands in coordination chemistry. Recently several scientific groups successfully applied heavier carbene analogues as initiators in the ring-opening polymerization of lactide [5].

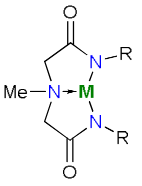
In order to gain more insight into structure and reactivity of 14 group heavier carbene analogues our group and Jurkschat group prepared several series of germylenes and stannylenes based on *N*,*N*,*O*-alkoxyamidoamine [6] (type **A**), *N*,*N*,*N*-diamidoamine [7] (types **B**, **C**) and *O*,*N*,*O*-ligands (substituted diethanolamine derivatives (types **D**, **E**) and di(hydroxyalkyl)pyridines (type **F**)) (Chart 1) which turned out to be monomeric or dimeric [8]. It should be noted that the third known type of stannylene structure (polymeric with bridging O atoms) has been established only in a single compound (type **G**) [8f].



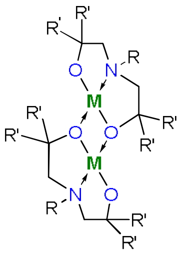
A
Zaitsev *et al.*



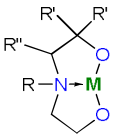
B
Huang *et al.*



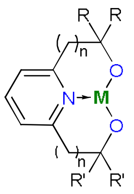
C
Jurkschat *et al.*



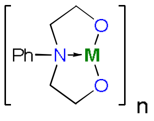
D
Jurkschat *et al.*
Huang *et al.*



E
Huang *et al.*



F
Huang *et al.*



G
Jurkschat *et al.*

M = Ge, Sn

Chart 1. The examples of germylenes and stannylenes based on *N*,*N*,*O*-, *N*,*N*,*N*- and *O*,*N*,*O*-ligands

It was found that in the case of monomeric derivatives insertion reactions cleanly proceed leading to the expected products with increased M atom oxidation state. In contrast, the reactions of dimeric derivatives often result in mixtures of unidentified compounds.

As a part of our program to prepare novel tetrylenes and investigate their structure and reactivity, we report herein the synthesis and structural characterization of germylenes **1a**-**3a**, stannylenes **1b**-**3b** and plumbylenes **1c**-**3c** based on aminobisphenol ligands of different types, **1**-**3**, without (**1**, **2**) or with pendant pyridine ring (**3**). In our opinion, such ligands may prove to be very convenient for stabilization of monomeric structures of the tetrylenes as they enable both steric protection by bulky *tert*-butyl groups and thermodynamic stabilization by additional transannular interaction with nitrogen atom of the ligands. In spite of this, aminobisphenols were not previously used as ligands for tetrylenes (except for a ligand with two aminobisphenol moieties bridged by an ethylene spacer which was used for preparation of complex with two tin centers [9]), while these compounds established themselves as suitable ones for preparation of plethora of metal complexes [10]. The structure of germylene **3a** and stannylene **3b** based on the same ligand **3** was studied by X-ray diffraction, and the different structural modes were found for Ge and Sn compounds. For preliminary investigation of reactivity of prepared compounds, complexation reaction of **1a** with $Re(CO)_5Br$ was performed what led to CO substitution in the Re coordination sphere and formation of novel complex **1aa** containing Ge-Re bond.

2. Experimental

2.1. General remarks

All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use: toluene and *n*-hexane were refluxed over Na and then distilled; THF and diethyl ether were stored over KOH, refluxed over Na/benzophenone and then distilled. Starting materials were synthesized according to the literature procedures: **2** [11], **3** [12], $[(Me_3Si)_2N]_2Ge$, $[(Me_3Si)_2N]_2Sn$, $[(Me_3Si)_2N]_2Pb$ [1b]. C_6D_6 (distilled over sodium) and $CDCl_3$ (distilled over CaH_2) are obtained from Deutero GmbH. ^1H (400.13 MHz), ^{13}C (100.6 MHz) and ^{119}Sn (149.2 MHz) NMR spectra were recorded on a Bruker Avance 400 or Agilent 400-MR spectrometers at room temperature (if otherwise stated). ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Elemental analyses were carried out in the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectrometry with ionization ESI-HRMS was performed at the Chemistry Department of Moscow State University. Samples were introduced into the high-resolution mass spectrometer Orbitrap Elite with electrospray ionization source via a syringe pump at a flow rate of 1-3 microliter per min.

2.2. Syntheses

2.2.1. Synthesis of ligands

*2.2.1.1. Synthesis of ligand **1***

In a flask 2-*tert*-butyl-4-methylphenol (3.97 g, 24.20 mmol), 36 % aqueous formaldehyde (1.62 ml, 19.40 mmol), 70 % aqueous $EtNH_2$ (0.78 ml, 12.10 mmol) and 10 ml of methanol were placed. Solution was refluxed for 23 h, and then all volatile materials were removed under reduced pressure. Orange oil obtained was dissolved in petroleum ether and left for slow evaporation of the solvent until crystals of compound **1** were formed. Crystals were thoroughly washed with *n*-hexane and dried in vacuo. Compound **1** was obtained as a white solid. It may be recrystallized from *n*-hexane for further purification. M.p. 109-110 °C.Yield 2.28 g (47%). ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.16$ (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 1.40 (s, 18H, $C(CH_3)_3$), 2.25 (s, 6H, CH_3-Ar), 2.63 (q, $J = 7.1$ Hz, 2H, CH_2CH_3), 3.65 (s, 4H, NCH_2Ar), 6.72-6.77 (m, 2H, Ar), 6.98-7.05 (m, 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.0$ (CH_2CH_3), 20.8 (CH_3-Ar), 29.6 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 47.0 (CH_2CH_3), 56.2 (NCH_2Ar), 122.4, 127.3, 128.1, 128.8, 136.8, 152.5 (Ar) ppm. Anal. Calcd. for $C_{26}H_{39}NO_2$ (397.5934): C, 78.54; H, 9.89; N, 3.52. Found: C, 78.53; H, 9.61; N, 3.79 %.

*2.2.1.2. Synthesis of ligand **2***

The synthesis had been carried out as reported in the literature [11]. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.1$ (CH_2CH_3), 29.7, 31.6 ($2C(CH_3)_3$), 34.2, 34.9 ($2C(CH_3)_3$), 47.2 (CH_2CH_3), 56.6 (NCH_2Ar), 121.6, 123.5, 125.0, 136.0, 141.5, 152.4 (Ar) ppm. Anal. Calcd. for $C_{32}H_{51}NO_2$ (481.7528): C, 79.78; H, 10.67; N, 2.91. Found: C, 79.62; H, 10.38; N, 3.02 %.

2.2.2. Synthesis of germylenes

*2.2.2.1. Synthesis of germylene **1a***

A solution of the ligand **1** (1.12 g, 2.82 mmol) in toluene (10 ml) was added to a stirred solution of $[(Me_3Si)_2N]_2Ge$ (1.11 g, 2.82 mmol) in toluene (5 ml). The solution gradually lost its intensive orange color and became almost colorless. After stirring overnight all volatile materials were removed under reduced pressure, *n*-hexane (5 ml) was added to the residue obtained and the solid formed was filtered off to give **1a** as a white solid. Yield 0.92 g (70%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 0.60 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.70 (s, 18H, $C(CH_3)_3$), 2.24 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 2.25 (s, 6H, CH_3-Ar), 2.95, 3.21 (2d, *J* = 12.4 Hz, each 2H, NCH_2Ar), 6.47, 7.29 (2d, *J* = 1.9 Hz, each 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, ppm): δ = 7.9 (CH_2CH_3), 21.1 (CH_3-Ar), 30.4 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 49.9 (CH_2CH_3), 53.4 (NCH_2Ar), 123.9, 127.7, 128.9, 129.0, 141.1, 154.6 (Ar) ppm. Anal. Calcd. for $C_{26}H_{37}NO_2Ge$ (468.2164): C, 66.70; H, 7.97; N, 2.99. Found: C, 66.46; H, 7.93; N, 3.03 %.

*2.2.2.2. Synthesis of germylene **2a***

Analogously to **1a** starting from **2** (0.80 g, 1.67 mmol) in toluene (10 ml) and $[(Me_3Si)_2N]_2Ge$ (0.66 g, 1.67 mmol) in toluene (5 ml). After addition of *n*-hexane (5 ml) and filtration **2a** was obtained as a white solid. Yield 0.39 g (42%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 0.6 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.38, 1.72 (2s, each 18H, $C(CH_3)_3$), 2.24 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 2.99, 3.25 (2d, *J* = 12.4 Hz, each 2H, NCH_2Ar), 6.75, 7.61 (2d, *J* = 2.3 Hz, each 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 8.0 (CH_2CH_3), 30.5, 32.0 ($C(CH_3)_3$), 34.4, 35.3 ($C(CH_3)_3$), 50.1 (CH_2CH_3), 54.0 (NCH_2Ar), 123.4, 125.0, 125.1, 140.5, 141.2, 154.5 (Ar) ppm. Anal. Calcd. for $C_{32}H_{49}NO_2Ge$ (552.3759): C, 69.58; H, 8.94; N, 2.54. Found: C, 69.64; H, 9.01; N, 2.48 %.

*2.2.2.3. Synthesis of germylene **3a***

Analogously to **1a** starting from **3** (0.87 g, 1.59 mmol) in toluene (10 ml) and $[(Me_3Si)_2N]_2Ge$ (0.63 g, 1.59 mmol) in toluene (5 ml). After staying overnight white precipitate was formed. The volume of solvent was reduced to approximately 3 ml, then *n*-hexane (4 ml) was added. After filtration **3a** was obtained as a white solid. Yield 0.85 g (87%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 1.34, 1.76 (2s, each 18H, $C(CH_3)_3$), 3.63, 3.82 (2d, *J* = 12.6 Hz, each 2H, NCH_2Ar), 3.68 (s, 2H, NCH_2Py) 6.45-6.55 (m, 2H, Py), 6.83-6.92 (m, 3H, Py and Ar), 7.62 (d, *J* = 2.5 Hz, 2H, Ar), 8.27-8.34 (m, 1H, Py) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 30.6, 31.9 ($C(CH_3)_3$), 34.3, 35.3

($C(CH_3)_3$), 54.5, 59.3 (NCH_2Ar and NCH_2Py), 122.9, 123.7, 125.0, 125.8, 125.9, 135.8, 140.4, 141.1, 149.6, 153.2, 155.0 (Py and Ar) ppm. Anal. Calcd. for $C_{36}H_{50}N_2O_2Ge$ (615.4344): C, 70.26; H, 8.19; N, 4.55. Found: C, 70.14; H, 7.87; N, 4.34 %.

2.2.3. Synthesis of stannylenes

*2.2.3.1. Synthesis of stannylene **1b***

Analogously to **1a** starting from **1** (0.65 g, 1.65 mmol) in toluene (10 ml) and $[(Me_3Si)_2N]_2Sn$ (0.73 g, 1.66 mmol) in toluene (5 ml). After evaporation of the solvent the residue was treated with *n*-hexane (4 ml) and solid was filtered to afford **1b** as a white solid. Yield 0.45 g (54%). ^1H NMR (400.13 MHz, C_6D_6): δ = 0.57 (t, J = 7.3 Hz, 3H, CH_2CH_3), 1.70 (s, 18H, $C(CH_3)_3$), 2.14 (q, J = 7.3 Hz, 2H, CH_2CH_3), 2.27 (s, 6H, CH_3-Ar), 3.00, 3.25 (2d, J = 12.6 Hz, each 2H, NCH_2Ar), 6.48, 7.31 (2d, J = 2.2 Hz, each 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, ppm): δ = 9.4 (CH_2CH_3), 21.0 (CH_3-Ar), 30.4 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 50.0 (CH_2CH_3), 54.7 (NCH_2Ar), 123.7, 126.2, 129.1, 129.8, 140.8, 156.8 (Ar) ppm. ^{119}Sn NMR (149.2 MHz, C_6D_6): δ = -420.4 (s) ppm. ESI-HRMS: Found: $[M+Na]^+$=538.1896, $[M_2+Na]^+$=1051.3598. Calculated: $[M+Na]^+$= 538.1743, $[M_2+Na]^+$= 1051.3882. Anal. Calcd. for $C_{26}H_{37}NO_2Sn$ (514.2864): C, 60.72; H, 7.25; N, 2.72. Found: C, 60.61; H, 7.32; N, 2.63 %.

*2.2.3.2. Synthesis of stannylene **2b***

Analogously to **1a** starting from **2** (0.77 g, 1.61 mmol) in toluene (15 ml) and $[(Me_3Si)_2N]_2Sn$ (0.71 g, 1.61 mmol) in toluene (5 ml). After filtration and washing with *n*-hexane (5 ml) **2b** was obtained as a white solid. Yield 0.61 g (64%). ^1H NMR (400.13 MHz, C_6D_6): δ = 0.56 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.39, 1.73 (2s, each 18H, $C(CH_3)_3$), 2.16 (q, J = 7.2 Hz, 2H, CH_2CH_3), 3.06, 3.30 (2d, J = 12.4 Hz, each 2H, NCH_2Ar), 6.75, 7.62 (2d, J= 2.5 Hz, each 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 9.4 (CH_2CH_3), 30.4, 32.0 ($C(CH_3)_3$), 34.3, 35.3 ($C(CH_3)_3$), 50.1 (CH_2CH_3), 55.3 (NCH_2Ar), 123.2, 125.1, 125.9, 139.7, 140.2, 156.7 (Ar) ppm. ^{119}Sn NMR (149.2 MHz, C_6D_6): δ = - 422.7 (s) ppm. Anal. Calcd. for $C_{32}H_{49}NO_2Sn$ (598.4459): C, 64.22; H, 8.25; N, 2.34. Found: C, 64.52; H, 8.24; N, 2.33 %.

*2.2.3.3. Synthesis of stannylene **3b***

At -20 ^{o}C toluene (20 ml) was added to the mixture of the ligand **3** (0.47 g, 0.86 mmol) and $[(Me_3Si)_2N]_2Sn$ (0.38 g, 0.87 mmol), then solution obtained was gradually warmed to room temperature and stirred overnight. After evaporation of the solvent the residue was treated with *n*-hexane (5 ml), filtered off and washed with *n*-hexane (5 ml) to afford **3b** as a white solid. Yield 0.38 g (67%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 1.36, 1.79 (2s, each 18H, $C(CH_3)_3$), 3.30, 3.54 (2d, *J* = 12.1 Hz, 4H, NCH_2Ar), 3.34 (s, 2H, NCH_2Py), 6.14 (d, *J* = 8.1 Hz, 1H, Py), 6.20-6.25 (m, 1H, Py), 6.62 (d, *J* = 2.5 Hz, 2H, Ar), 6.68-6.74 (m, 1H, Py), 7.51 (d, *J* = 2.5 Hz, 2H, Ar), 7.68 (d, *J* = 4.6 Hz, 1H, Py) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 30.6, 32.1 ($C(CH_3)_3$), 34.1, 35.4 ($C(CH_3)_3$), 59.5, 62.2 (NCH_2Ar and NCH_2Py), 122.1, 122.3, 123.4, 124.5, 125.4, 136.7, 137.9, 139.2, 146.9, 154.2, 158.5 (Py and Ar) ppm. ^{119}Sn NMR (149.2 MHz, C_6D_6): δ = -514.2 (s) ppm. ESI-HRMS: Found: $[M+H]^+$ = 663.2967. Calculated: $[M+H]^+$= 663.2957.

2.2.4. *Synthesis of plumbylenes*

2.2.4.1. *Synthesis of plumbylene **1c***

A solution of **1** (0.33 g, 0.85 mmol) in toluene (10 ml) was added to a stirred solution of $[(Me_3Si)_2N]_2Pb$ (0.45 g, 0.85 mmol) in toluene (5 ml). After stirring overnight the precipitate formed was filtered off, washed with toluene (2 ml) and dried in vacuo to give **1c** as a white solid. Yield 0.39 g (78%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 0.5 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.73 (s, 18H, $C(CH_3)_3$), 2.23 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 2.35 (s, 6H, CH_3-Ar), 3.37, 3.51 (2d, *J* = 11.6 Hz, each 2H, NCH_2Ar), 6.56 (m, 2H, Ar), 7.40 (m, 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 10.3 (CH_2CH_3), 21.0 (CH_3-Ar), 30.7 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 48.9 (CH_2CH_3), 54.7 (NCH_2Ar), 124.6, 125.2, 128.9, 130.2, 141.4, 158.8 (Ar) ppm. Anal. Calcd. for $C_{26}H_{37}NO_2Pb$ (602.7764): C, 51.81; H, 6.19; N, 2.32. Found: C, 51.99; H, 6.19; N, 2.21 %.

2.2.4.2. *Synthesis of plumbylene **2c***

Analogously to **1c** starting from **2** (0.43 g, 0.90 mmol) in toluene (10 ml) and $[(Me_3Si)_2N]_2Pb$ (0.48 g, 0.90 mmol) in toluene (5 ml). After filtration and washing with *n*-hexane (5 ml) **2c** was obtained as white solid. Yield 0.48 g (79%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 0.49 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 1.40 (s, 18H, $C(CH_3)_3$), 1.75 (s, 18H, $C(CH_3)_3$), 2.29 (q, *J* = 7.0 Hz, 2H, CH_2CH_3), 3.44, 3.57 (2d, *J* = 11.4 Hz, each 2H, NCH_2Ar), 6.78-6.86 (m, 2H, Ar), 7.67-7.74 (m, 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 10.4 (CH_2CH_3), 30.7, 32.2 ($C(CH_3)_3$), 34.1, 35.4 ($C(CH_3)_3$), 49.0 (CH_2CH_3), 55.3 (NCH_2Ar), 124.1, 124.8, 126.3, 138.7, 140.7, 158.8 (Ar) ppm. Anal. Calcd. for $C_{32}H_{49}NO_2Pb$ (686.9359): C, 55.95; H, 7.19; N, 2.04. Found: C, 55.71; H, 7.19; N, 1.97 %.

2.2.4.3. Synthesis of plumbylene ***3c***

Analogously to **1c** starting from the ligand **3** (0.54 g, 1.00 mmol) in toluene (10 ml) and $[(Me_3Si)_2N]_2Pb$ (0.53 g, 1.00 mmol) in toluene (5 ml). After filtration and washing with *n*-hexane (5 ml) **3c** was obtained as a white solid. Yield 0.54 g (74%). ^1H NMR (400.13 MHz, C_6D_6): δ = 1.41, 1.81 (2s, each 18H, $C(CH_3)_3$), 3.57, 3.80 (2d, J = 11.7 Hz, each 2H, NCH_2Ar), 3.57 (s, 2H, NCH_2Py), 6.27 (d, J = 7.8 Hz, 1H, Py), 6.29-6.34 (m, 1H, Py), 6.74-6.80 (m, 1H, Py), 6.84 (d, J = 2.4 Hz, 2H, Ar), 7.58 (d, J = 4.7 Hz, 1H, Py), 7.66 (d, J = 2.4 Hz, 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 30.8, 32.3 ($C(CH_3)_3$), 34.0, 35.4 ($C(CH_3)_3$), 59.1 (br, CH_2Py), 61.9 (NCH_2Ar), 122.2, 124.0, 123.9, 124.5, 126.1, 137.0, 140.0, 147.3, 156.4, 160.3 (Ar and Py) ppm. Signal of one aromatic carbon was not found. Anal. Calc. for $C_{36}H_{50}N_2O_2Pb$ (749.9933): C, 57.65; H, 6.72; N, 3.74. Found: C, 57.87; H, 6.91; N, 3.58 %.

2.2.5. Reaction of ***1a*** *with $Re(CO)_5Br$. Synthesis of rhenium complex* ***1aa***

Solid $Re(CO)_5Br$ (0.096 g, 2.350 mmol) was added to **1a** (0.110 g, 2.350 mmol) in toluene (10 ml) in one portion and after stirring for 30 h at 70˚C (periodically evacuating the flask to remove CO) the amount of solvent was reduced to 2 ml, *n*-hexane (5 ml) was added to the residue and the precipitate formed was filtered off to give **1aa** as a white solid. Yield 0.09 g (45%). ^1H NMR (400.13 MHz, C_6D_6, 40˚C): δ = 0.50 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.58 (s, 18H, $C(CH_3)_3$), 2.14 (s, 6H, CH_3-Ar), 3.49 (q, J = 7.0 Hz, 2H, CH_2CH_3), 3.44-3.53, 3.68-3.92 (2m, each 2H, NCH_2Ar), 6.17-6.24, 7.15-7.21 (2m, each 2H, Ar) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 68˚C): δ = 5.3 (CH_2CH_3), 20.8 (CH_3-Ar), 30.8 ($C(CH_3)_3$), 35.3 ($C(CH_3)_3$), 48.8 (CH_2CH_3), 54.0 (NCH_2Ar), 119.3, 128.9, 129.4, 129.8, 140.1, 152.5 (Ar), 184.1 (CO), 185.1 (2CO), 190.2 (CO) ppm. Anal. Calc. for $C_{30}H_{37}BrGeNO_6Re$ (846.3678): C, 42.57; H, 4.41; N, 1.65. Found: C, 40.14; H, 4.33; N, 1.48 %. Found value for carbon is lower than calculated one due to possible formation of rhenium carbide during analysis.

2.3. X-ray diffraction studies

Intensity data for **3a**, **3b** and **1aa** were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.71073$ Å) using ω-scan mode. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [13]. All H atoms were placed in calculated positions and refined using a riding model. Details of X-ray diffraction experiments are given in Table 1.

X-ray diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS.

The crystallographic data for **3a**, **3b** and **1aa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC numbers 1508528-1508530. This information may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. The crystallographic data for compounds **3a**, **3b** and **1aa**.

	3a	3b	1aa
empirical formula	$C_{36}H_{50}GeN_2O_2$	$C_{36}H_{50}N_2O_2Sn$	$C_{30}H_{37}BrGeNO_6Re$
M_w	615.37	661.47	846.31
temperature (K)	173(2)	180(2)	150(2)
size (mm)	0.40 x 0.25 x 0.20	0.40 x 0.17 x 0.08	0.25 x 0.20 x 0.20
cryst. system	triclinic	monoclinic	monoclinic
space group	P-1	$P2_1$/c	$P2_1$/c
a (Å)	11.4695(16)	11.8693(9)	13.9716(8)
b (Å)	12.7942(18)	10.2384(7)	12.5033(7)
c (Å)	13.971(3)	28.385(2)	18.4706(10)
α (deg)	99.213(3)	90	90
β (deg)	110.588(3)	93.147(1)	99.700(1)
γ(deg)	112.117(2)	90	90
V (Å^3)	1673.8(5)	3444.2(4)	3180.5(3)
Z	2	4	4
ρ_{cald}(g*cm^{-3})	1.221	1.276	1.767
abs coeff. (mm^{-1})	0.947	0.773	6.045
F(000)	656	1384	1656
θ range (deg)	2.15 – 27.00	2.18 – 27.00	2.20 – 28.00
collected rflns.	16212	30231	32386
unique rflns., R_{int}	7302, 0.0319	7493, 0.0370	7688, 0.0339
data/restraints/params.	7302 / 0 / 382	7493 / 0 / 382	7688 / 0 / 370
Goof on F^2	1.052	1.029	1.041

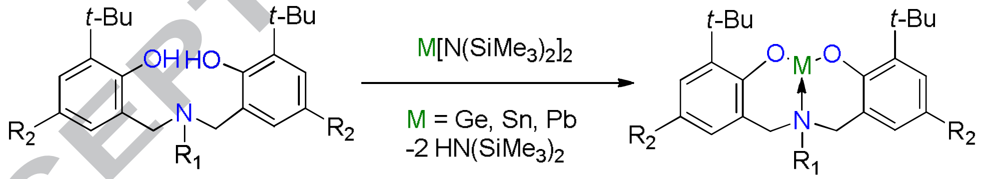
final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0366$, $wR_2 = 0.0830$	$R_1 = 0.0265$, $wR_2 = 0.0606$	$R_1 = 0.0226$, $wR_2 = 0.0534$
R indices (all data)	$R_1 = 0.0449$, $wR_2 = 0.0863$	$R_1 = 0.0338$, $wR_2 = 0.0641$	$R_1 = 0.0288$, $wR_2 = 0.0554$
largest diff. peak/hole (e/Å^3)	0.489 / -0.377	0.452 / -0.297	0.970 / -0.480

3. Results and discussion

3.1. Synthesis of tetrylenes

Ligands **1**-**3** were obtained according to the previously reported general procedure by Mannich condensation of corresponding phenol, formalin and amine in methanol at reflux. Ligand **1** is a novel compound. It was isolated as a white powder in 47% yield.

Among others [8h,i] the most suitable method for synthesis of $M(OR)_2$ is a reaction of alkoxydesamination of $[(Me_3Si)_2N]_2M$ with appropriate alcohols [8a, 14]. This reaction was earlier successfully applied for the preparation of various closely related germylenes and stannylenes based on aminodialcohols (see Chart 1). Corresponding germylenes **1a**-**3a**, stannylenes **1b**-**3b** and plumbylenes **1c**-**3c** were prepared in moderate yields by treating ligands with amides in toluene at room temperature (Scheme 1). Such procedure is easy to perform and the by-products formed in the course of the reaction may be easily removed under reduced pressure.



1 - 3

1, R_1 = Et, R_2 = Me
2, R_1 = Et, R_2 = *t*-Bu
3, R_1 = CH_2(Py-2), R_2 = *t*-Bu

1a-1c, **2a-2c**, **3a-3c**

1a, R_1 = Et, R_2 = Me, M = Ge, 70%
2a, R_1 = Et, R_2 = *t*-Bu, M = Ge, 42%
3a, R_1 = CH_2(Py-2), R_2 = *t*-Bu, M = Ge, 87%
1b, R_1 = Et, R_2 = Me, M = Sn, 54%
2b, R_1 = Et, R_2 = *t*-Bu, M = Sn, 64%
3b, R_1 = CH_2(Py-2), R_2 = *t*-Bu, M= Sn, 67%
1c, R_1 = Et, R_2 = Me, M = Pb, 78%
2c, R_1 = Et, R_2 = t-Bu, M = Pb, 79%
3c, R_1 = CH_2(Py-2), R_2 = *t*-Bu, M = Pb, 74%

Scheme 1. Synthesis of tetrylenes **1a-c**, **2a-c** and **3a-c**

Germylenes **1-3a**, stannylenes **1**-**3b** and plumbylenes **2c**, **3c** are soluble in toluene, C_6D_6 and only sparingly soluble in *n*-hexane, while plumbylene **1c** is poorly soluble in toluene and even in THF.

3.2. Structure and reactivity of tetrylenes

^{1}H and ^{13}C NMR spectra confirm the suggested structure of the compounds. There is one set of signals in the ^{1}H NMR spectra for all compounds in solution, which implies the equivalence of both C*H*$_2$ArO groups in the tetrylene. Methylene protons NC*H*$_2$Ar become diastereotopic and split into two doublets suggesting strong transannular interaction between nitrogen atom of (-CH$_2$)NR^1 group and the metal atom. Methylene protons NC*H*$_2$Py in tetrylenes **3a-3c** appear as a singlet and are not diastereotopic. It seems that strong coordination $M \leftarrow N_{Py}$ is not observed in solution or there are fast dynamic processes (in NMR time scale) in solution where this bond forms and breaks. This observation is in correlation with X-ray diffraction data (see below) according to which there is no contact between Ge and N_{Py} atoms in **3a** and the $Sn \leftarrow N_{Py}$ bond in **3b** is a weak one.

As stated above, one of the most important questions in structural chemistry of tetrylenes is a clarification of the structural mode, i.e. the establishment of the monomeric or dimeric structure. The data obtained from ^{1}H and ^{13}C spectra stands for either the existence of tetrylenes as monomer species or the presence of fast (in NMR time scale) equilibrium between monomeric and dimeric structures. According to X-ray diffraction data for **3a** we can conclude that all studied germylenes (**1a**, **2a** and **3a**) are monomeric in solution because **3a** is monomeric even in the solid state without any $Ge \leftarrow N_{Py}$ contact.

^{119}Sn NMR spectroscopy is a powerful tool for determination of tin coordination number. The data of ^{119}Sn NMR spectra obtained for **1b**-**3b** are the following: chemical shifts of the ^{119}Sn resonance in stannylenes **1b**, **2b** and **3b** (C_6D_6 solution) are -420.4, -422.7 and -514.3 ppm, respectively, what correlates well with tetracoordinated tin atom in these compounds. These data are in agreement with those previously found for dimeric stannylenes with NO$_3$-environment of Sn atom (~ -450 ppm [8a]) and stannylenes with N_2O_2 environment (~ -530 ppm) [15]. The chemical shift value of the ^{119}Sn resonance in dimeric $\{[(t\text{-BuO-}\mu)(Ph_3SiO)]Sn\}_2$ (–225.79 ppm (C_6D_6) [16]) with tricoordinated Sn atom with O$_3$-environment is downfield shifted in comparison with those for **1b**-**3b**. We further studied the ^{119}Sn NMR spectra for **1b** in DMSO-d6 and in pyridine-d5. Chemical shift of the ^{119}Sn NMR resonance in stannylene **1b** in DMSO-d6 solution is -490.8 ppm, in pyridine-d5 solution is -482.4 ppm, respectively. One can suppose, that in the system stannylene : donor solvent complexes of $R_2Sn\leftarrow$Base may exist in fast equilibrium with dimeric $[R_2Sn]_2$ with the same coordination number of tin as well as with monomeric species R_2Sn (coordination number of tin = 3). This supposition explains observed chemical shift values in **1b** characteristic for tetracoordinated tin and one set of signals for two symmetrical parts of the ligand framework. The same situation is observed in **2b**. With regard to compound **3b** we assume on the basis of chemical shift for complex **1b**←Py-d5 that compound **3b** exists in solution most likely as monomer and coordination number 4 arises from additional intramolecular coordination with pyridine. One more proof for monomeric structure of **3b** in solution and the existence of monomer-dimer equilibrium in stannylenes **1b** and **2b** is data obtained from mass-spectrometry ESI HRMS (acetonitrile solution). In ESI spectra both monomer ([**1b**+Na]: 538.1896) and dimer ([$\mathbf{1b_2}$+Na]:1051.3882) were detected. For **3b** no dimer was detected. As far as plumbylenes are concerned we assume that they also exist in equilibrium.

To further investigate structure of the tetrylenes obtained in the solid state we performed single crystal X-ray diffraction analysis. Crystals of compound **3a** suitable for diffraction studies were obtained from *n*-hexane/toluene solution. In **3a** (Figure 1) germanium atom has a distorted tetrahedral geometry where the electron lone pair of Ge occupies one coordination place. The values of the O–Ge–O and N–Ge–O angles (~ 90 - 97º) exhibit the significant s-character of this pair. It should be noted, that coordination number of Ge atom is three, and possible intramolecular bond between nitrogen atom of the pyridine ring and germanium atom is not observed in this compound. It turned out that germanium center in **3a** is non-attractive for the second Ge←N (i.e. with pyridine pendant group) bond formation due to the presence of lone pair of electrons. For the germanium atom in **3a** the “octet rule” is followed so the Ge←N bond is a classical donor-acceptor interaction. The geometrical characteristics of **3a** are close to those found earlier in the related monomeric structures: $[2,6\text{-}C_5H_3N(CH_2CPh_2O)_2]Ge$ (*d*(Ge–O) 1.827(1), 1.881(1), *d*(Ge–N) 2.110(1) Å) [8a], $MeN(CH_2CPh_2O)((R,S)\text{-}CHMeCHPhO)Ge$ (*d*(Ge–O) 1.833(3), 1.855(3), *d*(Ge–N) 2.113(3) Å) [8b]. It should be noted that the *d*(Ge–O) in **3a** are close to the distances found in monomeric dialkoxygermane ($Ge[OC(t\text{-}Bu)_3]_2$ (1.83(1) Å)) where the coordination number of Ge atom is 2 [17]. Thus, aminobisphenol ligands are bulky enough to stabilize monomeric structure of germylene. At the same time it should be noted that nowadays there are no known structures of chelated phenol stabilized germylenes. The structure of $(MesO)_2Ge(Me_2NCH_2CH_2NMe_2)$ [18] is a single compound related to ones obtained in the course of this work.

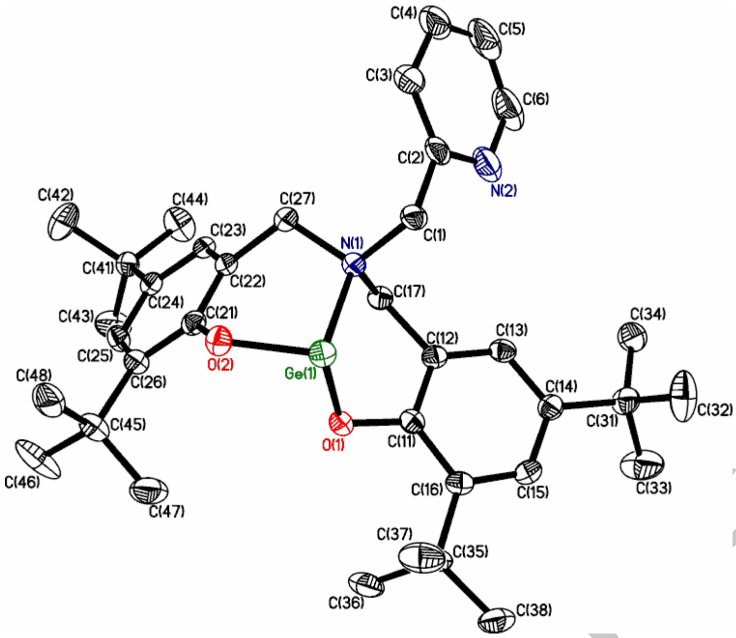


Figure 1. Molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-O(2) 1.8516(13), Ge(1)-O(1) 1.8607(13), Ge(1)-N(1) 2.1614(15); O(2)-Ge(1)-O(1) 97.61(6), O(2)-Ge(1)-N(1) 93.29(6), O(1)-Ge(1)-N(1) 90.47(6).

Single crystals of stannylene **3b** suitable for X-ray diffraction analysis (Figure 2) were grown from concentrated *n*-hexane solution**.** In contrast to found for the related **3a** tin atom in **3b** possesses the [3+1] coordination mode due to the formation of two transannular Sn←N interactions: strong bond with amine N atom and weak interaction with pyridine N atom. Thus, tin atom in **3b** is more attractive than Ge atom in closely related **3a** for formation of additional week interaction between pyridine nitrogen atom and tin atom due to both larger radii and more electropositive character of Sn than Ge. The coordination polyhedron of the Sn atom in **3b** represents a distorted tetragonal pyramid with two oxygen atoms, nitrogen atom N(2) and a lone pair in the base of the pyramid and nitrogen atom N(1) in its vertex.

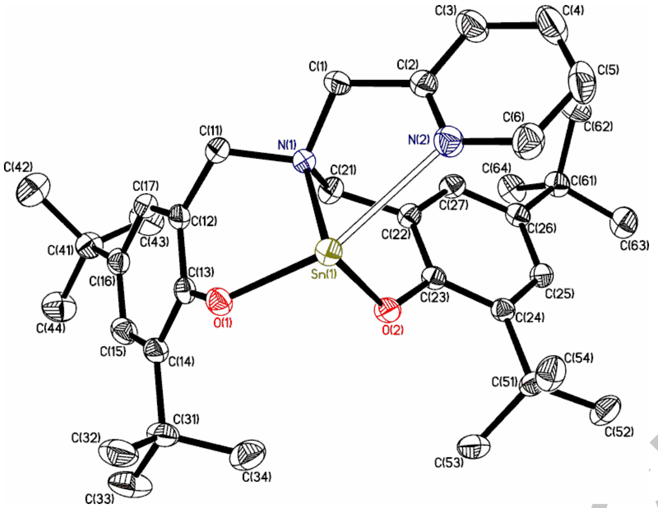
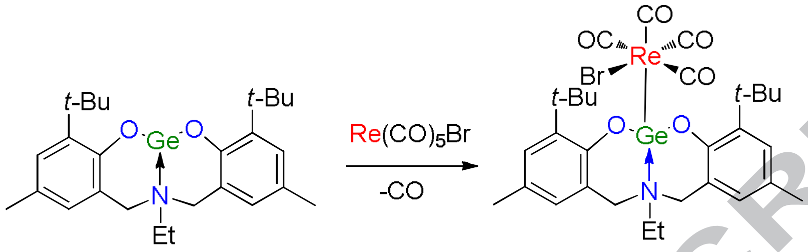


Figure 2. Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)-O(2) 2.0415(13), Sn(1)-O(1) 2.1136(13), Sn(1)-N(1) 2.3192(15), Sn(1)-N(2) 2.7059(17); O(2)-Sn(1)-O(1) 91.85(5), O(2)-Sn(1)-N(1) 85.62(5), O(1)-Sn(1)-N(1) 84.38(5), O(2)-Sn(1)-N(2) 85.25(5), O(1)-Sn(1)-N(2) 152.49(5), N(1)-Sn(1)-N(2) 68.13(5).

The Sn–O and Sn–N bond lengths in **3b** are comparable with the same in dimeric $[Me_2NCH_2CH_2OSnN_3]_2$ (dimeric due to an additional O→Sn bond formation) which possesses close related O_2N_2 coordination environment for the tin atom (except for two coordination N→Sn bonds in **3b** and one O→Sn bond and one N→Sn bond in azide) [19]. The values for azide are Sn–O 2.125(4), O→Sn 2.225(4), N→Sn 2.505(5), N–Sn 2.220(5) Å. One should note the presence of a very strong transannular interaction between amine N atom and tin atom in **3b**; furthermore under comparison two these structures (azide and **3b**) it is possible to state that the donor properties of the pendant Py group are sufficient to stabilize monomeric structure, especially taking into account the smaller donor ability of phenolic oxygens in comparison with alkylalkoxy groups. In general the structures such as **3b** are very rare and this one is close to published earlier $[(Py)Sn]_2(CH_2N(CH_2C_6H_2(O)(t\text{-}Bu)_2)_2$ [9]. It should also be noted that in closely related stannylene $[Me_2NCH_2CH_2N(CH_2CMe_2O)_2Sn]_2$ [8i] the coordination number of the tin atom is also 4, but additional bond appears from dimerization of stannylene through O atom. Thus, one can conclude, that steric hindrance and ligand structure (phenolic groups, pendant Py group) in **3b** are sufficient to prevent dimerization.

In order to investigate the ability of the tetrylenes synthesized to act as a ligand in transition metal complexes the reaction of **1a** with $Re(CO)_5Br$ was performed (Scheme 2). The complex **1aa** was obtained in moderate yield. ^{1}H, ^{13}C NMR spectra in C_6D_6 were registered at 68˚C (due to reduced solubility of the complex) and it may be concluded that the overall structure has a *cis*-arrangement of germylene and bromine ligands (3 signals for CO groups), what corresponds to the XRD data.



1aa, 45%

Scheme 2. Synthesis of rhenium complex **1aa**

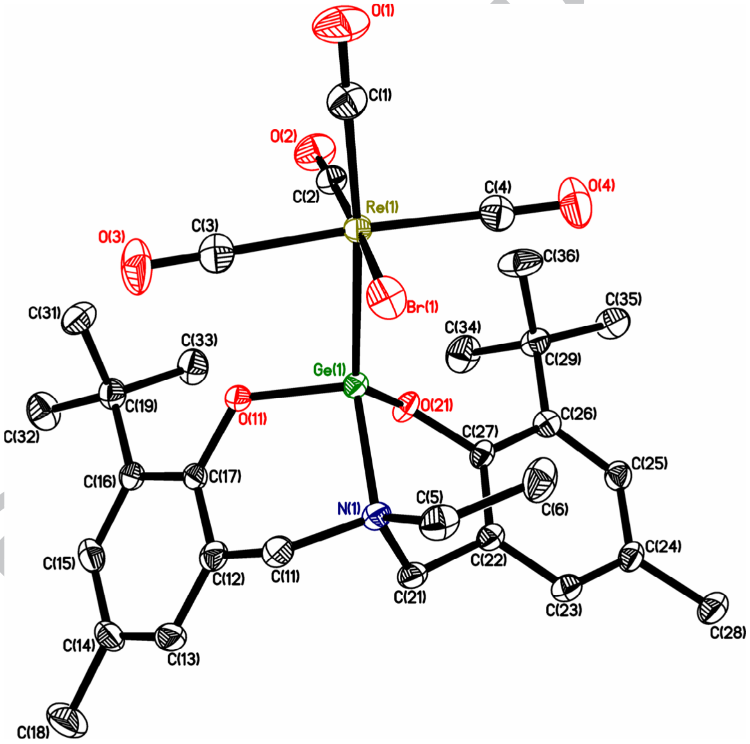


Figure 3. Molecular structure of **1aa**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re(1)-C(2) 1.925(3), Re(1)-C(1) 1.965(3), Re(1)-C(4) 1.995(3), Re(1)-C(3) 2.019(3), Re(1)-Ge(1) 2.5446(3), Re(1)-Br(1) 2.6376(3), Ge(1)-O(11) 1.8012(17), Ge(1)-O(21) 1.8074(18), Ge(1)-N(1) 2.031(2); C(2)-Re(1)-C(1) 93.59(12), C(2)-Re(1)-C(4) 92.18(12), C(4)-Re(1)-C(3) 176.27(12), C(2)-Re(1)-Ge(1) 85.89(8), C(1)-Re(1)-Ge(1) 174.95(9), C(4)-Re(1)-Ge(1) 93.19(8), C(3)-Re(1)-Br(1) 86.06(9), Ge(1)-Re(1)-Br(1)

96.638(10), O(11)-Ge(1)-O(21) 99.33(8), O(11)-Ge(1)-N(1) 97.85(8), O(11)-Ge(1)-Re(1) 103.49(6), O(21)-Ge(1)-Re(1) 126.84(6), N(1)-Ge(1)-Re(1) 127.46(6).

The structure of **1aa** was studied with X-ray diffraction analysis. Despite the fact that coordination chemistry of heavier carbene analogues has experienced an exponential growth in the past few years, the examples of such complexes of 7 Group metals (Mn, Re) are very rare [20]. To the best of our knowledge complex **1aa** is the third structurally characterized derivative of germanium(II) where germylene is a ligand in rhenium complex after two chlorogermylidene complexes $Cl(L)(PMe_3)_3Re{=}Ge(Cl)C_6H_3$-2,6-$Trip_2$ (L = CO, MeNC) [20b].

The molecular structure of **1aa** is shown in Figure 3. According to X-ray diffraction data, coordination polyhedron of Re atom in **1aa** is a distorted octahedron, where germylene ligand and bromine atom are in *cis*-positions relative to each other. The same *cis*-ligand arrangement in metal coordination sphere was detected in closely related manganese complex [MnBr{Ge-(*i*-Pr_2bzam)Bu-*t*}$(CO)_4$] (where *i*-Pr_2bzam = *N*,*N′*-bis(isopropyl)benzamidinate) [20a]. The Re–Ge distance in **1aa** (2.5446(3) Å) is noticeably longer than the same distance in $Cl(L)(PMe_3)_3Re{=}Ge(Cl)C_6H_3$-2,6-$Trip_2$ (2.3422(4) Å, 2.3253(4) Å) cited above [20b]. The Re–Br and Re–C bond distances in **1aa** are close to the same bond distances in parent $Re(CO)_5Br$ (Re–Br 2.619(2) Å, Re–C 1.889(5) (*trans* to Br), 1.975(5), 1.991(6) Å) [21].

The coordination environment of the Ge atom in **1aa** is formed by two covalent bonded oxygen atoms and one dative bonded nitrogen atom and may be regarded as a trigonal pyramid with a lone pair in one vertex. The Ge–O and Ge–N bond distances in **1aa** are noticeably shorter than those in the related **3a** (free germylene) due to donation of lone electron pair from Ge atom to vacant orbital of Re atom.

4. Conclusions

So, we investigated a new class of heavier carbene analogues (germylenes, stannylenes and plumbylenes) that were successfully stabilized by aminobisphenols. According to the X-ray diffraction analysis germylenes and stannylenes with pendant nitrogen donor differ in coordination mode. The nature of the ligand (phenolic *vs.* alkylalkoxy groups) and pendant donor group (pyridinyl *vs.* alkylamino) strongly effects on tetrylene structure determining the aggregation degree (monomeric or dimeric). Reaction of germylene **1a** with $Re(CO)_5Br$ gave complex **1aa** with Re-Ge bond.

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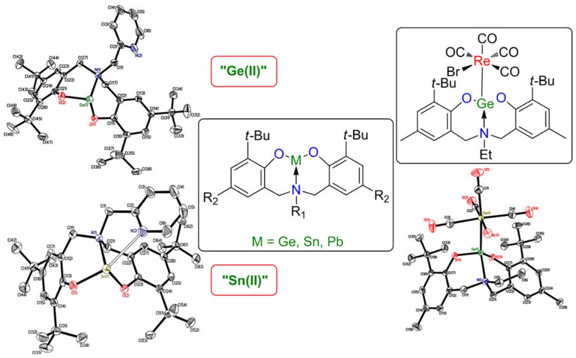

Graphical abstract

Graphical Abstract (text part)

Aminobisphenol supported germylenes, stannylenes and plumbylenes were prepared starting from the reaction of corresponding Lappert's tetrylene with aminobisphenols. XRD analysis revealed different coordination mode for germylene and stannylene with additional nitrogen donor in the structure of the ligand. Germylene was converted to the rhenium complex in reaction with $Re(CO)_5Br$ featuring Re←:Ge dative bond.

- Heavier carbene analogues based on aminobisphenols were successfully synthesized
- Different coordination mode for Ge, Sn tetrylenes with additional N donor was found
- Reaction of germylene with $Re(CO)_5Br$ gives complex with Re–Ge bond