Reactivity of intramolecularly coordinated aluminum compounds to R_3EOH (E = Sn, Si). Remarkable migration of N,C,N and O,C,O pincer ligands

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Abstract

The reaction of organoaluminum compounds containing O,C,O or N,C,N chelating (so called pincer) ligands $[2,6-(YCH_2)_2C_6H_3]$-Al^iBu_2 (Y = MeO **1**, ^tBuO **2**, Me_2N **3**) with R_3SnOH (R = Ph or Me) gives tetraorganotin complexes $[2,6-(YCH_2)_2C_6H_3]SnR_3$ (Y = MeO, R = Ph **4**, Y = MeO, R = Me **5**; Y = ^tBuO, R = Ph **6**, Y = ^tBuO, R = Me **7**; Y = Me_2N, R = Ph **8**, Y = Me_2N, R = Me **9**) as the result of migration of O,C,O or N,C,N pincer ligands from aluminum to tin atom. Reaction of **1** and **2** with $(^nBu_3Sn)_2O$ proceeded in similar fashion resulting in **10** and **11** ($[2,6-(YCH_2)_2C_6H_3]Sn^nBu_3$, Y = MeO **10**; Y = ^tBuO **11**) in mixture with $^nBu_3Sn^iBu$. The reaction **1** and **3** with 2 equiv. of Ph_3SiOH followed another reaction path and ($[2,6-(YCH_2)_2C_6H_3]Al(OSiPh_3)_2$, Y = MeO **12**, Me_2N **13**) were observed as the products of alkane elimination. The organotin derivatives **4**–**11** were characterized by the help of elemental analysis, ESI-MS technique, ^1H, ^{13}C, ^{119}Sn NMR spectroscopy and in the case **6** and **8** by single crystal X-ray diffraction (XRD). Compounds **12** and **13** were identified using elemental analysis, ^1H, ^{13}C, ^{29}Si NMR and IR spectroscopy.
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1. Introduction

The reactivity of organoaluminum alkyls towards alcohols yielding organoaluminum alkoxides/aryloxides $R_{3-n}Al(OR'_3)_n$ has been extensively investigated, in reference to their wide use in organic synthesis [1]. The analogous organoaluminum silanoxanes $R_{3-n}Al(OSiR'_3)_n$ gain considerable attention due to their close relation to inorganic materials such as aluminosilicates and zeolites used as ion exchangers, catalyst or catalysts supports, and

molecular sieves [2]. However, work dealing with the reactions of the other group 14 metal hydroxides R_3EOH (E = Ge, Sn, Pb) with aluminum reagents are quite rare [3].

A significant difference was obtained in the reactivity of group 14 hydroxides to trimethyl aluminum. It was found that Me_3Al acts as alkylating agent in the reaction with Ph_3EOH (E = Sn, Pb) accompanying by MAO ($[MeAlO]_n$) elimination. In contrast, the reaction of Ph_3EOH (E = C, Si, Ge) did not produce MAO, rather the dimeric species $[Me_2Al(\mu\text{-}OER_3)]_2$ were formed via alkane elimination (Scheme 1). Obrey and Barron [3] suggested that this reaction pattern coincides with the basicity of these hydroxides.

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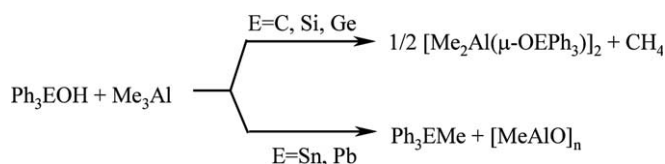
Scheme 1.

Nevertheless reaction of $(Ph_3Sn)_2O$ and Me_3Al led to dialkylaluminum stannoxides $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ and Ph_3SnMe [4]. The methylation of alcohol in reaction with Me_3Al can be also achieved under certain conditions (derivatives of stable carbocations, low temperature and presence of suitable Lewis acid catalysts) [3,5].

Only few reports concerning the reactivity of intramolecularly coordinated organoaluminum alkyls with heavier group 14 hydroxides (especially dealing with Si derivatives) were emerged [6]. To further explore this field, we have decided to prepare $[2,6\text{-}(YCH_2)_2C_6H_3]Al^iBu_2$ (Y, MeO (**1**), ^tBuO (**2**), Me_2N (**3**)) and to study their reactivity to R_3EOH (E = Sn, R = Me, or Ph; E = Si, R = Ph) with the aim to explore both possible reaction paths (alkylation versus alkane elimination, Scheme 1). The compounds **1–3** enable us to study the influence of donor atoms and spatial hindrance of the chelating ligands. The reactions of **1–3** to $(^nBu_3Sn)_2O$ are also included.

2. Experimental

2.1. General consideration

All manipulations were carried out under argon atmosphere using standard Schlenk technique. All solvents were dried by standard procedures and distilled prior to use.

^1H, ^{13}C, ^{27}Al, ^{29}Si, ^{119}Sn, $^1H–^{119}Sn$ HMBC NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers, using 5 mm tuneable broad-band probes. Appropriate chemical shifts in ^1H and ^{13}C NMR spectra were calibrated on the residual signals of the solvents $(C_6D_6$: $\delta(^1H) = 7.16$ ppm and $\delta(^{13}C) = 128.39$ ppm; C_7D_8: $\delta(^1H) = 2.09$ ppm and $\delta(^{13}C) = 20.40$ ppm). ^{27}Al NMR chemical shifts were related according to the external standard $[Al(H_2O)_6]^{+3}$ $\delta(^{27}Al) = 0.0$ ppm, ^{29}Si NMR spectra to the external Me_4Si $\delta(^{29}Si) = 0.0$ ppm and ^{119}Sn NMR spectra to the external Me_4Sn $\delta(^{119}Sn) = 0.0$ ppm. Positive-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1000 [7]. The electron ionization (EI) mass spectra were recorded on a quadrupole mass spectrometer MD 800 (Fisons, UK) with Particle Beam interface in the range m/z 50–800 and electron energy 70 eV. IR spectra were recorded in cyclohexane solution on Perkin Elmer 684 equipment.

2.1.1. X-ray structure determination

Colourless crystals were obtained by slow evaporation of saturated *n*-hexane solutions of **6** and **8**. The crystal of

compounds of **6** and **8** were mounted on glass fibre with epoxy cement and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 2, empirical absorption corrections [8] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97 [9]) and refined by a full matrix least squares procedure based on F^2 (SHELXL97 [10]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2 U_{eq}$(pivot atom), for the methyl moiety multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance.

2.2. Synthesis

The starting chemicals $^iBu_2AlCl$ (neat, 97%), $(^nBu_3\text{-}Sn)_2O$ (98%), Ph_3SiOH 98%, Me_3SnOH (97%) and Ph_3SnOH (97%) were obtained form commercial suppliers and used as delivered. The compounds 2,6-$(CH_3OCH_2)_2C_6H_3Br$ [11], 1,3-$[(CH_3)_2NCH_2]_2C_6H_4$ [12] and **2** [13] were prepared according to literature procedures.

2.2.1. Preparation of $2,6\text{-}(MeOCH_2)_2C_6H_3Al^iBu_2$ (1)

An equimolar amount of ^nBuLi (1.6 M hexane solution, 4.84 ml, 7.75 mmol) was added to a solution of 2,6-$(MeOCH_2)_2C_6H_3Br$ (1.9 g, 7.75 mmol) in diethyl ether (30 ml) at -78 °C and resulting pale yellow solution was stirred for 2 h. Then it was added dropwise to the solution of $^iBu_2AlCl$ (1.37 g, 7.75 mmol) in hexane (30 ml) and was stirred for additional 12 h at room temperature. The insoluble material was filtered off and evaporating of the solvents in vacuo yielded **1** as an colourless oil, 1.88 g, 79%. Anal. Calc. for $C_{18}H_{31}AlO_2$: C, 70.56; H, 10.20. Found: C, 70.78; H, 10.43%. ^1H NMR (C_6D_6): -0.05 (4H, d, $CH_2\text{-}^iBu$), 0.84 (12H, d, $CH_3\text{-}^iBu$), 1.68 (2H, m, $CH\text{-}^iBu$), 2.96 (6H, s, CH_3O), 4.05 (4H, s, OCH_2), 6.56 (2H, d, Ar–$H3,5$), 6.98 (1H, t, Ar–$H4$). ^{13}C NMR (C_6D_6): 22.88 ($CH_2\text{-}^iBu$), 27.64 ($CH\text{-}^iBu$), 28.72 ($CH_3\text{-}^iBu$), 57.95 (CH_3O), 77.13 (OCH_2), 120.34 (Ar–$C3,5$), 127.28 (Ar–$C4$), 143.85 (Ar–$C2,6$), (Ar–$C1$) not found. ^{27}Al NMR (C_6D_6): 157.7 ($v_{1/2} = 7.4$ kHz).

2.2.2. Preparation of $2,6\text{-}(Me_2NCH_2)_2C_6H_3Al^iBu_2$ (3)

An equimolar amount of ^nBuLi (1.6 M hexane solution, 8.1 ml, 13 mmol) was added to a solution of 1,3-$(Me_2NCH_2)_2C_6H_4$ (2.5 g, 13 mmol) in hexane (20 ml) at room temperature and resulting pale yellow solution was stirred for 12 h. Then $^iBu_2AlCl$ (2.30 g, 13 mmol) in hexane (30 ml) was added dropwise and resulting white suspension was stirred for additional 12 h. The insoluble material was filtered off and evaporating of the solvents in vacuo yielded **3** as pale yellow oil, 3.24 g, 75%. Anal. Calc. for $C_{20}H_{37}AlN_2$: C, 72.24; H, 11.22. Found: C, 72.53; H,

11.43%. ^{1}H NMR (C_6D_6): 0.28 (4H, d, CH_2–^{i}Bu), 1.22 (12H, d, CH_3–^{i}Bu), 2.06 (2H, m, CH–^{i}Bu), 2.21 (12H, s, $(CH_3)_2$N), 3.42 (4H, s, NCH_2), 6.99 (2H, d, Ar–H3,5), 7.22 (1H, t, Ar–H4). ^{13}C NMR (C_6D_6): 21.62 (CH_2–^{i}Bu), 23.85 (CH–^{i}Bu), 29.37 (CH_3–^{i}Bu), 45.85 (($CH_3)_2$N), 67.80 (NCH_2), 124.24 (Ar–C3,5), 127.78 (Ar–C4), 146.64 (Ar–C2,6), (Ar–C1) not found. ^{27}Al NMR (C_6D_6): 156.3 ($v_{1/2}$ = 7.9 kHz).

2.3. Reactions of 1–3 with Ph$_3$SnOH

2.3.1. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$SnPh$_3$ (4)

Ph$_3$SnOH (0.48 g, 1.3 mmol) was added in one portion to a solution of **1** (0.4 g, 1.3 mmol) in hexane (50 ml) and resulting suspension was stirred for additional 24 h at room temperature. The reaction mixture was exposed to air for 12 h and the insoluble material was filtered off. Evaporating of the solvent yielded **4** as white crystals (in some cases recrystalization from hexane to remove traces of Ph$_3$SnOH or free ligand 1,3-(MeOCH$_2$)$_2$C$_6$H$_4$ was necessary) 0.31 g, 45%, m.p. 88–93 °C. Anal. Calc. for $C_{28}H_{28}O_2$Sn: C, 66.27; H, 5.48. Found: C, 66.12; H, 5.62%. MW = 516. MS: m/z 477, [M + K − C$_6$H$_6$]$^+$; m/z 461, [M + Na − C$_6$H$_6$]$^+$; m/z 439, 100% [M–C$_6$H$_5$]$^+$. ^{1}H NMR (C_6D_6): 2.58 (6H, s, CH_3O), 4.08 (4H, s, OCH_2), 7.13–7.58 (18H, complex pattern, SnPh$_3$, SnC$_6$H$_3$-ligand). ^{119}Sn NMR (C_6D_6): −162.5.

2.3.2. Preparation of 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$SnPh$_3$ (6)

Similar to procedure as for **4**: Ph$_3$SnOH (0.44 g, 1.2 mmol); **2** (0.47 g, 1.2 mmol) yielded white crystals of **6** 0.38 g, 53%, m.p. 155–157 °C. Anal. Calc. for $C_{34}H_{40}O_2$Sn: C, 68.13; H, 6.73. Found: C, 68.26; H, 6.90%. MW = 600. MS: m/z 639, [M + K]$^+$; m/z 623, 100% [M + Na]$^+$. ^{1}H NMR (C_6D_6): 0.85 (18H, s, (C$H_3)_3$CO), 4.38 (4H, s, OCH_2), 7.31–7.67 (18H, complex pattern, SnPh$_3$, SnC$_6$H$_3$-ligand). ^{119}Sn NMR (C_6D_6): −153.0.

2.3.3. Preparation of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnPh$_3$ (8)

Similar to procedure as for **4**: Ph$_3$SnOH (0.46 g, 1.26 mmol); **3** (0.42 g, 1.26 mmol), 48 h, yielded white crystals of **8** 0.28 g, 41%, m.p. 85–90 °C. Anal. Calc. for $C_{30}H_{34}N_2$Sn: C, 66.57; H, 6.33. Found: C, 66.36; H, 6.52%. MW = 542. MS: m/z 465, 100% [M − C$_6$H$_5$]$^+$. ^{1}H NMR (C_6D_6): 2.18 (12H, s, (C$H_3)_2$N), 3.30 (4H, s, NCH_2), 7.08–7.60 (18H, complex pattern, SnPh$_3$, SnC$_6$H$_3$-ligand). ^{119}Sn NMR (C_6D_6): −201.7.

2.4. Reactions of 1–3 with Me$_3$SnOH

2.4.1. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$SnMe$_3$ (5)

Me$_3$SnOH (0.32 g, 1.79 mmol) was added in one portion to a solution of **1** (0.55 g, 1.79 mmol) in hexane (50 ml) and resulting suspension was stirred for additional 24 h at room temperature. The reaction mixture was exposed to air for 12 h and the insoluble material was filtered off. Evaporat-

ing of the solvent yielded **5** as pale yellow oil (in some cases traces of free ligand 1,3-(MeOCH$_2$)$_2$C$_6$H$_4$ was removed under high vacuo) 0.33 g, 56%. Anal. Calc. for $C_{13}H_{22}O_2$Sn: C, 47.46; H, 6.74. Found: C, 47.51; H, 6.92%. MW = 330. MS: m/z 315, 100% [M − CH$_3$]$^+$. ^{1}H NMR (C_6D_6): 0.55 (9H, s, (C$H_3)_3$Sn, ^2J(^{119}Sn, ^{1}H) = 54 Hz), 3.10 (6H, s, CH_3O), 4.42 (4H, s, OCH_2), 7.23 (1H, t, Ar–H4), 7.36 (2H, d, Ar–H3,5). ^{13}C NMR (C_6D_6): −4.47 (($CH_3)_3$Sn, ^1J(^{119}Sn, ^{13}C) = 353 Hz), 57.29 (CH_3O), 76.66 (OCH_2, ^1J(^{119}Sn, ^{13}C) = 21.6 Hz), 126.73 (br, Ar–C3,5), 127.28 (br, Ar–C4), 142.31 (Ar–C1), 146.73 (Ar–C2,6, ^nJ(^{119}Sn, ^{13}C) = 28.0 Hz). ^{119}Sn NMR (C_6D_6): −50.5.

2.4.2. Preparation of 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$SnMe$_3$ (7)

Similar to procedure as for **5**: Me$_3$SnOH (0.2 g, 1.1 mmol); **2** (0.43 g, 1.1 mmol) yielded colourless oil **7** 0.24 g, 52%. Anal. Calc. for $C_{19}H_{34}O_2$Sn: C, 55.23; H, 8.29. Found: C, 55.62; H, 8.37%. MW = 414. MS: m/z 437, [M + Na]$^+$; m/z 453, 100% [M + K]$^+$; m/z 399, [M − CH$_3$]$^+$. ^{1}H NMR (C_6D_6): 0.47 (9H, s, (C$H_3)_3$Sn, ^2J(^{119}Sn, ^{1}H) = 54 Hz), 1.15 (18H, s, (C$H_3)_3$CO), 4.43 (4H, s, OCH_2), 7.24 (1H, t, Ar–H4), 7.43 (2H, d, Ar–H3,5). ^{13}C NMR (C_6D_6): −4.00 (($CH_3)_3$Sn, ^1J(^{119}Sn, ^{13}C) = 347 Hz), 28.12 (($CH_3)_3$CO), 67.10 (OCH_2, ^nJ(^{119}Sn, ^{13}C) = 29.6 Hz), 73.87 (($CH_3)_3C$O), 127.45 (Ar–C3,5, ^nJ(^{119}Sn, ^{13}C) = 41 Hz), 128.95 (Ar–C4, ^nJ(^{119}Sn, ^{13}C) = 9 Hz), 140.32 (Ar–C1, ^1J(^{119}Sn, ^{13}C) = 470 Hz), 147.96 (Ar–C2,6, ^nJ(^{119}Sn, ^{13}C) = 28.0 Hz). ^{119}Sn NMR (C_6D_6): −53.8.

2.4.3. Preparation of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnMe$_3$ (9)

Similar to procedure as for **5**: Me$_3$SnOH (0.31 g, 1.7 mmol); **3** (0.57 g, 1.7 mmol), 48 h, yielded colourless oil **9** 0.3 g, 49%. Anal. Calc. for $C_{15}H_{28}N_2$Sn: C, 50.74; H, 7.95. Found: C, 51.01; H, 8.05%. MW = 356. MS: m/z 341, 100% [M − CH$_3$]$^+$. ^{1}H NMR (C_6D_6): 0.37 (9H, s, (C$H_3)_3$Sn, ^2J(^{119}Sn, ^{1}H) = 53 Hz), 2.20 (12H, s, (C$H_3)_2$N), 3.60 (4H, s, NCH_2), 7.26 (3H, m, Ar–H3,4,5). ^{119}Sn NMR (C_6D_6): −85.9.

2.5. Reactions of 1 and 2 with (^{n}Bu$_3$Sn)$_2$O

2.5.1. Reaction of 1 with (^{n}Bu$_3$Sn)$_2$O

Solution of **1** (0.55 g, 1.79 mmol) in hexane (50 ml) was added to neat (^{n}Bu$_3$Sn)$_2$O (1.1 g, 1.79 mmol) and was stirred for additional 24 h at room temperature. The reaction mixture was exposed to air for 12 h and the insoluble material was filtered off. Evaporating of the solvent yielded mixture of ^{n}Bu$_3$Sn^{i}Bu and 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Sn^{n}Bu$_3$ (**10**). ^{1}H NMR (C_6D_6): 0.95–2.05 (complex pattern: ^{n}Bu$_3$-Sn^{i}Bu and **10**-Sn^{n}Bu$_3$), 3.17 (6H, s, CH_3O), 4.45 (4H, s, OCH_2), 7.20–7.25 (3H, m, Ar–H3,4,5). ^{119}Sn NMR (C_6D_6): −51.5 (**10**), −17.3 ^{n}Bu$_3$Sn^{i}Bu (ratio 1:1).

2.5.2. Reaction of 2 with (^{n}Bu$_3$Sn)$_2$O

Similar to procedure to 2.5.1: **2** (0.75 g, 1.91 mmol); (^{n}Bu$_3$Sn)$_2$O (1.14 g, 1.91 mmol) yielded mixture of

(^{n}Bu$_3$Sn)$_2$O, ^{n}Bu$_3$Sn^{i}Bu and 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sn^{n}Bu$_3$ (**11**). ^{1}H NMR (C$_6$D$_6$): 0.95–2.00 (complex pattern: (^{n}Bu$_3$Sn)$_2$O, ^{n}Bu$_3$Sn^{i}Bu and **11**-Sn^{n}Bu$_3$), 1.21 (18H, s, (C*H*$_3$)$_3$CO), 4.47 (4H, s, OC*H*$_2$), 7.25 (1H, m, Ar–*H*4), 7.50 (2H, d, Ar–*H*3,5). ^{119}Sn NMR (C$_6$D$_6$): −53.1 (**11**), −17.3 ^{n}Bu$_3$Sn^{i}Bu, 83.4 (^{n}Bu$_3$Sn)$_2$O (ratio 100:100:5).

2.5.3. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Sn^{n}Bu$_3$ (10)

An equimolar amount of ^{n}BuLi (1.6 M hexane solution, 1.78 ml, 2.86 mmol) was added to a solution of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Br (0.7 g, 2.86 mmol) in diethyl ether (30 ml) at −78 °C and resulting pale yellow solution was stirred for 2 h. Then it was added dropwise to the solution of ^{n}Bu$_3$SnCl (0.93 g, 2.86 mmol) in hexane (30 ml) and was stirred for additional 12 h at room temperature. The insoluble material was filtered off and evaporating of the solvents in vacuo yielded **10** as pale yellow oil, 1.07 g, 82%. Anal. Calc. for C$_{22}$H$_{40}$O$_2$Sn: Found: C, 58.03; H, 8.91%. C, 58.04; H, 8.86. MW = 456. MS: *m/z* 399, 100% [M − Bu]$^+$. ^{1}H NMR (C$_6$D$_6$): 1.04 (9H, t, C*H*$_3$CH$_2$-CH$_2$CH$_2$–Sn), 1.29 (6H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$–Sn), 1.52 (6H, m, CH$_3$CH$_2$-C*H*$_2$CH$_2$–Sn), 1.72 (6H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$–Sn), 3.17 (6H, s, C*H*$_3$O), 4.45 (4H, s, OC*H*$_2$), 7.20–7.25 (3H, m, Ar–*H*3,4,5). ^{13}C NMR (C$_6$D$_6$): 13.22 (CH$_3$CH$_2$CH$_2$*C*H$_2$–Sn, ^1J(^{119}Sn, ^{13}C) = 344.4 Hz), 14.34 (*C*H$_3$CH$_2$CH$_2$CH$_2$–Sn), 28.43 (CH$_3$*C*H$_2$CH$_2$CH$_2$–Sn, ^3J(^{119}Sn, ^{13}C) = 66.6 Hz), 30.14 (CH$_3$CH$_2$*C*H$_2$CH$_2$–Sn, ^2J(^{119}Sn, ^{13}C) = 18.0 Hz), 57.57 (*C*H$_3$O), 77.25 (O*C*H$_2$, ^nJ(^{119}Sn, ^{13}C) = 20.8 Hz), 128.26 (Ar–*C*4, ^nJ(^{119}Sn, ^{13}C) = 10.0 Hz), 128.90 (Ar–*C*3,5, ^nJ(^{119}Sn, ^{13}C) = 36.0 Hz), 142.39 (Ar–*C*1, ^1J(^{119}Sn, ^{13}C) = 400.8 Hz), 146.74 (Ar–*C*2,6, ^nJ(^{119}Sn, ^{13}C) = 25.0 Hz). ^{119}Sn NMR (C$_6$D$_6$): −51.5.

2.5.4. Preparation of 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sn^{n}Bu$_3$ (11)

An equimolar amount of ^{n}BuLi (1.6 M hexane solution, 2.74 ml, 4.39 mmol) was added to a solution of 1,3-(^{t}BuOCH$_2$)$_2$C$_6$H$_4$ (1.1 g, 4.39 mol) hexane (30 ml) and resulting pale yellow solution was stirred for 2 h at room temperature. Then it was added dropwise to the solution of ^{n}Bu$_3$SnCl (1.43 g, 4.39 mmol) in hexane (30 ml) and was stirred for additional 12 h under reflux. The insoluble material was filtered off and evaporating of the solvents in vacuo yielded **11** as pale yellow oil, 2.03 g, 86%. Anal. Calc. for C$_{28}$H$_{52}$O$_2$Sn: C, 62.35; H, 9.72. MW = 540. Found: C, 62.47; H, 9.76%. MS: *m/z* 483, 100% [M − Bu]$^+$. ^{1}H NMR (C$_6$D$_6$): 0.92 (9H, m, C*H*$_3$CH$_2$CH$_2$CH$_2$–Sn), 1.18 (6H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$–Sn), 1.21 (18H, s, (C*H*$_3$)CO), 1.43 (6H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$–Sn), 1.62 (6H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$–Sn), 4.47 (4H, s, OC*H*$_2$), 7.25 (1H, t, Ar–*H*4), 7.50 (2H, d, Ar–*H*3,5). ^{13}C NMR (C$_6$D$_6$): 13.56 (CH$_3$CH$_2$CH$_2$*C*H$_2$–Sn, ^1J(^{119}Sn, ^{13}C) = 336.0 Hz), 14.37 (*C*H$_3$CH$_2$CH$_2$CH$_2$–Sn), 28.38 (CH$_3$*C*H$_2$CH$_2$CH$_2$–Sn, ^3J(^{119}Sn,

^{13}C) = 64.0 Hz), 28.43 ((*C*H$_3$)$_3$CO), 30.16 (CH$_3$CH$_2$CH$_2$-C*H*$_2$–Sn, ^2J(^{119}Sn, ^{13}C) = 18.0 Hz), 67.26 (O*C*H$_2$, ^1J(^{119}Sn, ^{13}C) = 27.0 Hz), 73.92 ((CH$_3$)$_3$*C*O), 127.29 (Ar–*C*3,5, ^nJ(^{119}Sn, ^{13}C) = 37.0 Hz), 128.97 (Ar–*C*4, ^nJ(^{119}Sn, ^{13}C) = 10.0 Hz), 139.26 (Ar–*C*1, ^1J(^{119}Sn, ^{13}C) = 405.0 Hz), 147.77 (Ar–*C*2,6, ^nJ(^{119}Sn, ^{13}C) = 26.4 Hz). ^{119}Sn NMR (C$_6$D$_6$): −53.1.

2.6. Reactions of 1 and 3 with Ph$_3$SiOH

2.6.1. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Al(OSiPh$_3$)$_2$ (12)

The two equivalents of Ph$_3$SiOH (1.26 g, 4.57 mmol) was added in one portion to a solution of **1** (0.7 g, 2.28 mmol) in toluene (50 ml) and resulting pale yellow solution was stirred for additional 12 h at room temperature. The reaction mixture was evaporated and the residue was extracted with hexane (2 × 20 ml). Evaporating of the solvent yielded **12** as pale yellow powder 1.1 g, 65%, m.p. 160 °C dec. Anal. Calc. for C$_{46}$H$_{43}$AlO$_4$Si$_2$C, 74.36; H, 5.83. Found: C, 74.45; H, 5.92%. ^{1}H NMR (C$_6$D$_6$): 3.11 (6H, s, C*H*$_3$O), 4.20 (4H, s, OC*H*$_2$), 7.08–7.17 (21H, complex pattern, OSiPh$_3$–*H*3,4,5, AlC$_6$*H*$_3$-ligand), 7.68–7.75 (12H, m, SiPh$_3$–*H*2,6). ^{13}C NMR (C$_6$D$_6$): 58.18 (*C*H$_3$O), 74.98 (O*C*H$_2$), 127.69 (ligand-Ar–*C*3,5), 129.06 (ligand-Ar–*C*4), 139.56 (ligand-Ar–*C*2,6), (ligand-Ar–*C*1) not found, 128.33, 129.71, 136.08, 138.8 (OSiPh$_3$). ^{29}Si NMR (C$_6$D$_6$): −31.4. IR (cyclohexane, cm^{-1}): 514(s), 1067 (s), 1115 (s).

2.6.2. Preparation of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Al(OSiPh$_3$)$_2$ (13)

Similar to procedure as for **13**: Ph$_3$SiOH (0.67 g, 2.4 mmol); **3** (0.4 g, 1.2 mmol) yielded crystals **13** 0.61 g, 67%, m.p. 190 °C dec. Anal. Calc. for C$_{48}$H$_{49}$AlN$_2$O$_2$Si$_2$: C, 74.96; H, 6.42. Found: C, 75.01; H, 6.53%. ^{1}H NMR (C$_6$D$_6$): 1.83 (12H, s, (C*H*$_3$)$_2$N), 3.04 (4H, s, NC*H*$_2$), 7.07–7.16 (21H, complex pattern, SiPh$_3$–*H*3,4,5, AlC$_6$*H*$_3$-ligand), 7.80–7.86 (12H, m, SiPh$_3$–*H*2,6). ^{13}C NMR (C$_6$D$_6$): 45.27 ((*C*H$_3$)$_2$N), 64.30 (N*C*H$_2$), 123.64 (ligand-Ar–*C*3,5), 129.78 (ligand-Ar–*C*4), 146.66 (ligand-Ar–*C*2,6), (ligand-Ar–*C*1) not found, 128.44, 129.27, 136.4, 140.6 (OSiPh$_3$). ^{29}Si NMR (C$_6$D$_6$): −34.0. IR (cyclohexane, cm^{-1}): 514(s), 1063 (s), 1109 (s).

3. Results and discussion

### 3.1. Synthesis of organoaluminum derivatives 1–3

The compounds **1** and **3** were prepared via reaction of ^{i}Bu$_2$AlCl with equimolar amount of corresponding organo-lithium derivatives of chelating ligands in good yields (79% for **1** and 75% for **3**, Scheme 2). The values of ^{27}Al NMR chemical shifts (157.7 ppm for **1** and 156.3 ppm for **3**) suggest four-coordinated central aluminum atom [14]. The

only one set of signals detected in ^{1}H and ^{13}C NMR spectra (equivalence of YCH$_2$ groups, Y = O or N at 300 K), indicates well-known fluxional process [15] – dissociation/association of both ligands' arms at 300 K resulting in coordination number four for central aluminum atom. Compounds **1** and **3** are readily soluble in aliphatic (aromatic) hydrocarbons, as well as in etheral solvents, are moisture and air sensitive. Compound **2** was prepared and characterized according to literature [13].

3.2. Reactions of 1–3 with R$_3$SnOH (R = Me or Ph)

The reaction of **1** with one equivalent of Ph$_3$SnOH led to the expected migration of organic group to the tin atom (Scheme 3). Since the O,C,O ligand is bound more tightly to aluminum through both C$_{ipso}$–Al bond and O–Al interaction than ^{i}Bu group, the formation of Ph$_3$Sn^{i}Bu as a product of tin alkylation was assumed. However 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$SnPh$_3$ (**4**) was isolated as the only tin containing product (yield 45%), identified by the help of ^{1}H and ^{119}Sn NMR parameters consistent with literature (Scheme 3) [16]. IBAO ([^{i}BuAlO]$_n$) is presumed as a by-product in regard to reactivity of Me$_3$Al in similar reactions [3].

The inspection of ^{119}Sn NMR spectra of the crude product revealed only signal of $\delta(^{119}$Sn) = −162.5 ppm corresponding to **4** [16] and minor signal (less than 5% main peak intensity) of unreacted Ph$_3$SnOH $\delta(^{119}$Sn) = −86.0 ppm [17]. No other compounds containing tin atom were detected. It means, that this reaction proceed through unusual selective migration of Y,C,Y chelating ligand between two main group metals, from aluminum to tin atom (reaction of organolithium reagents with metallic halides is not taken into consideration). Several similar reactions
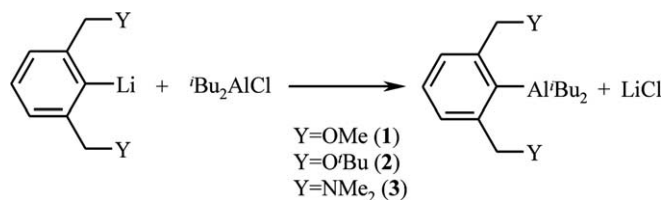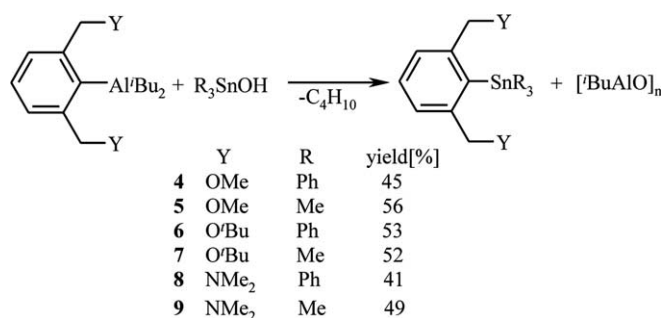
Table 1
Selected ^{1}H and ^{119}Sn NMR parameters of **4**–**11** in C$_6$D$_6$ at 300 K

Compound	$\delta(^1$H, YCH$_2$)	$\delta(^{119}$Sn)
4	4.08	−162.5
5	4.42	−50.5
6	4.38	−153
7	4.43	−53.8
8	3.30	−201.7
9	3.60	−85.9
10	4.45	−51.5
11	4.47	−53.1

accompanied by migration of N,C,N chelating ligand (2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3^-$) were discovered by van Koten, but these examples were restricted for migration between two transition metals, where the 2,6-(Me$_2$NCH$_2$)$_2$-C$_6$H$_3$AuPPh$_3$ acted as arylating agent for other metals such as Ni, Pd, Pt, Fe, etc. [18], or for reaction of organotin or organosilicon precursors yielding organopalladium derivatives [19].

The investigation of this reaction was further extended on several combinations of aluminum chelates **1**–**3** (containing O,C,O or N,C,N ligand) with both Ph$_3$SnOH and Me$_3$SnOH. All reactions lead to the tetraorganotin derivatives of the corresponding Y,C,Y chelating ligands **4**–**9** in moderate yields (Scheme 3, Table 1). The reactivity of **3** was lower in comparison to **1**, **2** and longer reaction time was necessary. Compounds **4**, **6**, **8** and **9** were identified by elemental analysis, ESI-MS spectra, ^{1}H and ^{119}Sn NMR data that are in good agreement with literature [16,19,20]. Compounds **5** and **7** represent novel derivatives of O,C,O chelating ligands and were characterized by elemental analysis, ^{1}H, ^{13}C,^{119}Sn NMR spectroscopy and ESI-MS.

Furthermore products **6** and **8** were characterized by XRD study, crystal data, selected structural parameters are given in Tables 2, 3 and both structures are depicted in Figs. 1, 2. The crystal structure of **6** can be described as distorted tetrahedron, both oxygen atoms are situated out of the tin coordination sphere with both Sn1–O1 4.779(2) and Sn1–O2 4.538(2) bond distances significantly longer than the sum of van der Waals radii of tin and oxygen atoms 3.7 Å.

In contrast to **6** in the crystal structure of **8** both ligands' arms are coordinated to central tin atom through very week Sn–N interactions, bond distances Sn1–N1 3.0793(18) and Sn1–N2 3.1653(19) are both slightly shorter than the sum of van der Waals' radii of tin and nitrogen atoms 3.7 Å. Both donor atoms are mutually situated in *cis* fashion with the angle N1–Sn1–N2 113.27(5) and the resulting tin atom polyhedron can be described as bicapped tetrahedron. Similar geometry on the tin atom was found in [2,3,5,6-(Me$_2$NCH$_2$)$_4$C$_6$]-1,4-(SnMe$_3$)$_2$ [19].

The conceivable explanation for the selective migration of O,C,O or N,C,N ligands in these reactions may be derived from the transition state proposed by Barron et al. for the reaction of trimethylaluminum with group 14 hydroxides (Fig. 3A) [3]. The first step is believed to be

Scheme 2.

	Y	R	yield[%]
4	OMe	Ph	45
5	OMe	Me	56
6	O^{t}Bu	Ph	53
7	O^{t}Bu	Me	52
8	NMe$_2$	Ph	41
9	NMe$_2$	Me	49

Scheme 3.

Table 2
Crystal data and structure refinement of **6** and **8**

	6	**8**
Empirical formula	$C_{34}H_{40}O_2Sn$	$C_{30}H_{34}N_2Sn$
Color	Colourless	Colourless
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a (Å)	19.9450(1)	9.3240(2)
b (Å)	9.5970(2)	16.6200(3)
c (Å)	31.1680(3)	17.5250(3)
β (°)		104.3680(10)
Z	8	4
μ (mm^{-1})	0.884	0.991
D_x (Mg m^{-3})	1.335	1.367
Crystal size (mm)	$0.25 \times 0.17 \times 0.1$	$0.35 \times 0.3 \times 0.27$
Crystal shape	Bar	Prism
θ Range (°)	1–27.5	1–27.5
T_{min}, T_{max}	0.871, 0.916[a]	0.760, 0.821[a]
Number of reflections measured	83,228	37,748
Number of unique reflections, R_{int}	6826, 0.074	6024, 0.041
Number of observed reflections, [$I > 2\sigma(I)$]	4795	5192
Number of parameters	340	302
S[b] all data	1.034	1.040
Final R[a] indices [$I>2\sigma(I)$]	0.034	0.026
wR_2[a] indices (all data)	0.085	0.063
w_1/w_2[c]	0.0420/1.9339	0.0275/1.8549
$\Delta\rho$, max., min. (e Å^{-3})	1.166, −0.674	0.867, −0.620

[a] Correction by SORTAV program.
[b] Definitions: $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.
[c] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$, $R_{int} = \sum |F_o^2 - F_o^2(mean)|/\sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

Table 3
Selected bond distances (Å) and bonding angles (°) of **6** and **8**

Compound 6	
Sn1–O1	4.779(2)
Sn1–O2	4.538(2)
Sn1–C11	2.165(2)
Sn1–C21	2.156(2)
Sn–C31	2.149(2)
Sn1–C41	2.148(2)
C11–Sn1–C21	118.63(9)
C11–Sn1–C31	107.98(9)
C11–Sn1–C41	109.73(9)
C21–Sn1–C31	105.94(9)
C21–Sn1–C41	105.35(9)
C31–Sn1–C41	108.87(9)
Compound 8	
Sn1–N1	3.079(2)
Sn1–N2	3.165(2)
Sn1–C11	2.172(2)
Sn1–C21	2.162(2)
Sn–C31	2.165(2)
Sn1–C41	2.142(2)
C11–Sn1–C21	107.98(7)
C11–Sn1–C31	108.65(8)
C11–Sn1–C41	121.55(7)
C21–Sn1–C31	95.51(7)
C21–Sn1–C41	110.06(7)
C31–Sn1–C41	109.94(7)
N1–Sn1–N2	113.27(5)

coordination of hydroxides to aluminum resulting in the higher acidity of OH group and partial positive charge on the central E atom. Tin and lead hydroxides then undergo alkylation accompanied by MAO elimination, on the other hand more acidic carbon, silicon and germanium analogues reveal [Me$_2$Al(μ-OER$_3$)]$_2$ via methane evolution. If this process is accepted, then there are a few reasons, that could lead to the preferential migration of chelating ligands. The coordination of R$_3$SnOH to **1–3** should result in the partial positive charge on the tin atom along with saturation of electron deficient at aluminum by hydroxide oxygen and
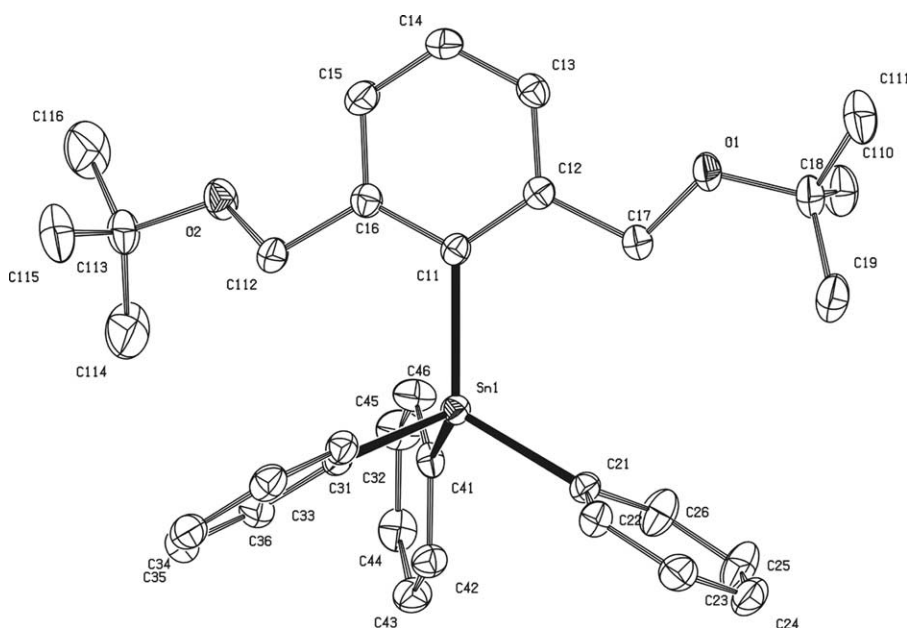

Fig. 1. ORTEP drawing (50% probability atomic displacement ellipsoids) of 2,6-(*t*BuOCH$_2$)$_2$C$_6$H$_3$SnPh$_3$ (**6**). Hydrogen atoms have been omitted for clarity.
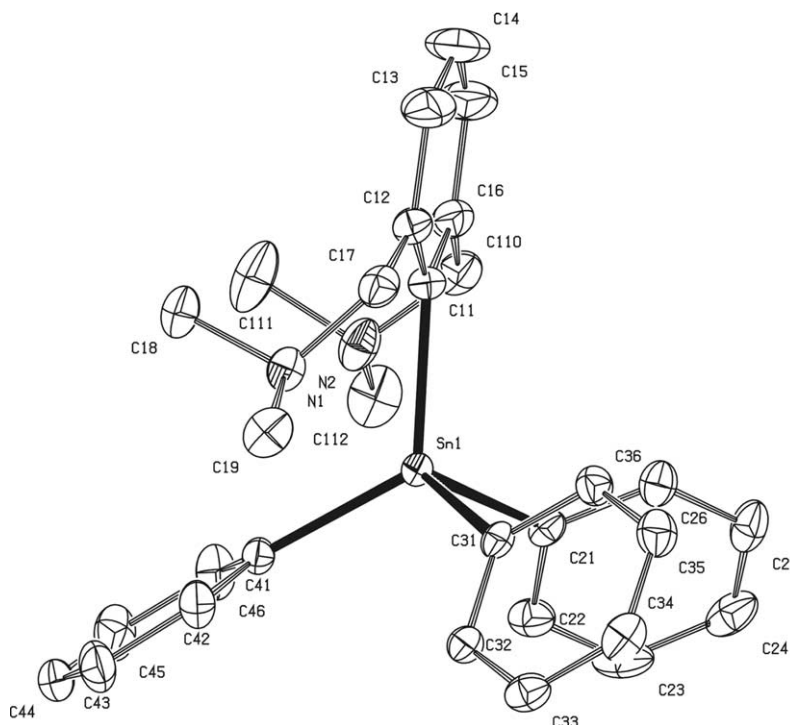
Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of 2,6-$(Me_2NCH_2)_2C_6H_3SnPh_3$ (**8**). Hydrogen atoms have been omitted for clarity.
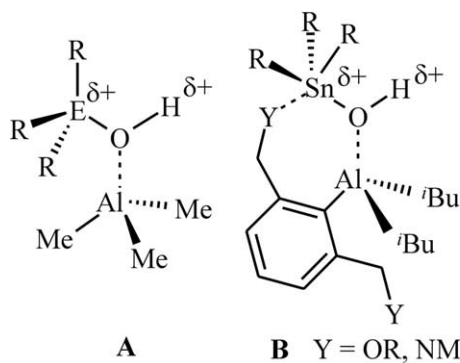

Fig. 3. Proposed intermediate for the reaction of **1–3** with R_3SnOH.

rising of steric repulsion of bulky groups in the vicinity of aluminum (Fig. 3B). In this situation the pendant arms of ligand may coordinate tin atom leading to more favourable environment for migration of ligand in comparison to the ^{i}Bu groups. Also the capability of both N,C,N and O,C,O ligands coordinate organotin cations was well established [21].

Reactions of **1–3** with two equivalents of R_3SnOH (R=Ph or Me) resulted in the same products (**4–9**) in the mixture with the unreacted R_3SnOH approximately in 1:1 ratio only (based on ^{119}Sn NMR spectroscopy).

### 3.3. Reactions of 1–3 with ($^nBu_3Sn)_2O$

The reaction of organoaluminum alkyls **1** and **2** with ($^nBu_3Sn)_2O$ was believed to result in the formation of stan-

noxanes containing Al–O–Sn bond, similarly to the published reaction of Me_3Al with $(Ph_3Sn)_2O$ [4]. The ^1H and ^{13}C NMR spectra revealed only one type of compound containing O,C,O pincer ligand in the reaction mixtures, however the presence of $^nJ(^{119}Sn, ^{13}C(OCH_2))$ coupling (20.8 Hz for the reaction of **1** and 27.0 Hz for **2**) indicates, that the transmetallation proceed rather than formation of Al–O–Sn bond via isobutane elimination (Scheme 4). Also the stability of these compounds to air and moisture clearly pointed to absence of desired organoaluminum stannoxanes. The ^{119}Sn NMR spectrum for the reaction of **1** with ($^nBu_3Sn)_2O$ revealed two signals at −17.4 and −51.5 ppm (1:1 ratio). The first one $\delta(^{119}Sn) = -17.4$ ppm was established to $^nBu_3Sn^iBu$. This ^{119}Sn chemical shift approximates values found for analogous compounds $^nBu_3Sn^iBu$ (−7.9 ppm) [22] and $^nBu_4Sn$ (−12 ppm) [23]. The ^1H–^{119}Sn HMBC experiment showed cross peaks of this ^{119}Sn signal with protons from butyl region only (Fig. 4). Furthermore closer check of this spectrum revealed cross peak between this tin signal and the complex pattern at around 2 ppm (Fig. 4A) most probably belonging to CH–^iBu proton. The second ^{119}Sn NMR signal at $\delta(^{119}Sn) = -51.5$ ppm was assigned to 2,6-$(MeOCH_2)_2$-$C_6H_3Sn^nBu_3$ (**10**), hence interaction of this tin signal to CH_3O, OCH_2 groups and aromatic protons were detected in ^1H–^{119}Sn HMBC spectrum (Fig. 4). Also the presence of peak $m/z = 399$ ([M − Bu]$^+$) in ESI/MS spectrum established the identity of **10**.

Similarly the reaction of **2** with ($^nBu_3Sn)_2O$ gave mixture of $^nBu_3Sn^iBu$ ($\delta(^{119}Sn) = -17.4$ ppm) and 2,6-$(^tBuOCH_2)_2$-
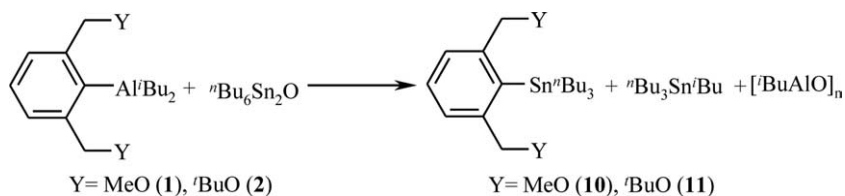
Scheme 4.
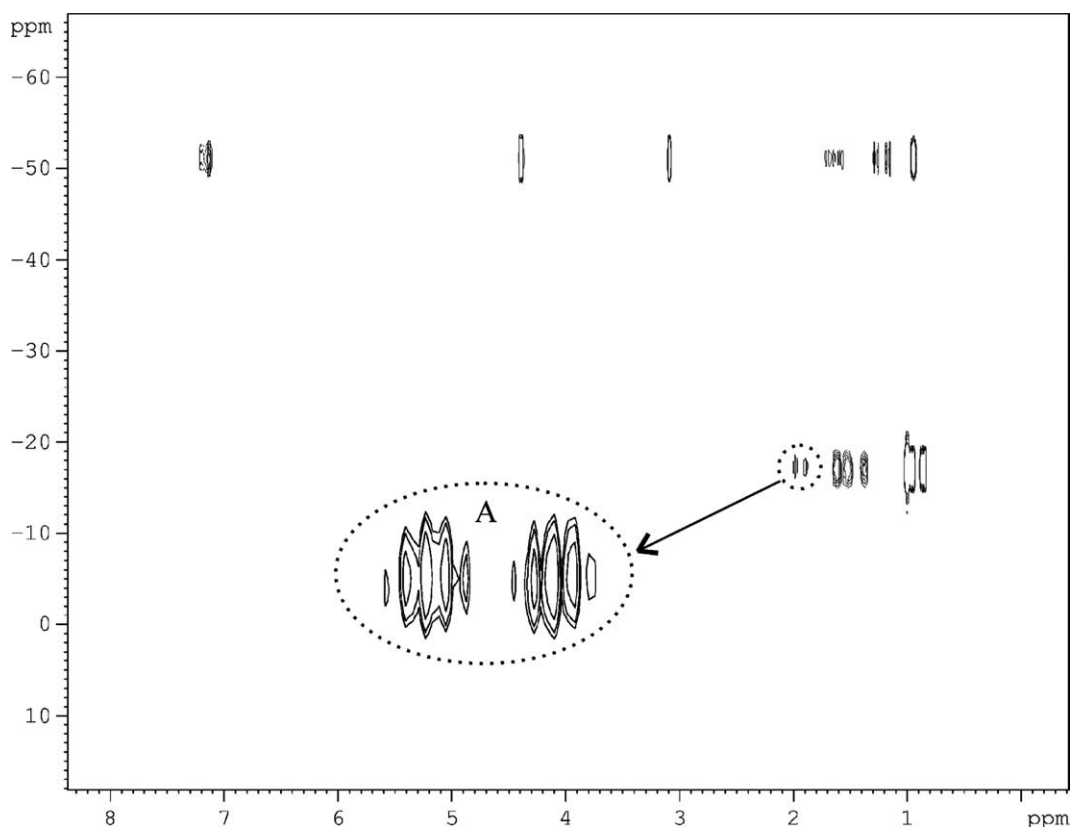
Fig. 4. ^1H–^{119}Sn HMBC spectrum of the reaction mixture for reaction of **1** with $(^nBu_3Sn)_2O$.

$C_6H_3Sn^nBu_3$ (**11**) ($\delta(^{119}Sn) = -53.1$ ppm) in 1:1 ratio. Furthermore traces of starting $(^nBu_3Sn)_2O$ (δ ($^{119}Sn) = 83.4$ ppm [24]) were detected (less than 5% based on ^{119}Sn NMR spectroscopy, and ^1H–^{119}Sn HMBC spectrum). To prove the identity of **10** and **11**, these derivatives were prepared by conventional method (reaction of organolithium derivatives of both chelating ligands with $^nBu_3SnCl$, Table 1). All experimental data coincide with those found for both compounds obtained by the reaction of **1** and **2** with $(^nBu_3Sn)_2O$.

The reaction of **3** with $(^nBu_3Sn)_2O$ in hexane after 24 h resulted in even more strange mixture of products (eight signals in ^{119}Sn NMR spectrum) and no attempts to characterize reaction products were performed. The presence of $2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn^nBu_3$ can be confirmed, because the signal $\delta(^{119}Sn) = -71.8$ ppm published earlier for this compound was clearly detected in ^{119}Sn NMR spectrum [25].

3.4. Reactions of 1–3 with Ph₃SiOH

The reaction of **1** and **3** with two equivalents of Ph_3SiOH in toluene followed supposed reaction path (alkane elimination, Scheme 5) and led to $[2,6\text{-}(YCH_2)_2\text{-}C_6H_3]Al(OSiPh_3)_2$ (Y = MeO (**12**), Me_2N (**13**)). Compounds **12** and **13** bearing two triphenylsiloxane groups were characterized by elemental analysis, ^1H, ^{13}C, ^{29}Si NMR and IR spectroscopy. The ^1H NMR measurement
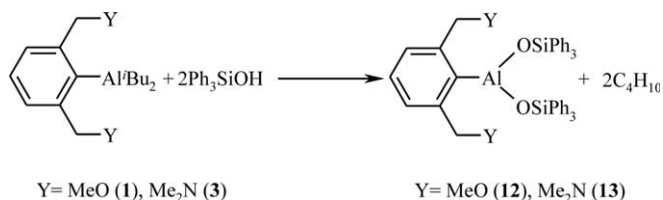
Scheme 5.

revealed sharp singlets for both YCH_2 (Y = N, or O), CH_3O for **12** and $(CH_3)_2N$ for **13** groups, respectively. The ^1H NMR signals of $OSiPh_3$ substituents are well separated – *ortho-H* observed as multiplet at 7.71 ppm and *meta*, *para-H* at 7.12 ppm for **12** (7.83 and 7.12 ppm for **13**), the difference between these signals in free Ph_3SiOH is only 0.46 ppm in C_6D_6 and also the integral intensity is in accordance with proposed structure. Variable temperature ^1H NMR spectroscopy (range 300–190 K) revealed no decoalescence and proved the symmetrical rigid coordination of both ligands arms to central aluminum resulting most probably in *trans*-trigonalbipyramidal environment around central aluminum atom in solution. Moreover ^{29}Si NMR chemical shifts $\delta(^{29}Si) = -31.4$ ppm for **12** and $\delta(^{29}Si) = -34.0$ ppm for **13** approximate those found in other compounds bearing Al–O–SiPh$_3$ linkages [6d,26]. The presence of **12** and **13** was proved by IR spectroscopy in cyclohexane solution as well, where bands of 1115, 1067 cm^{-1} for **12** and 1109, 1063 cm^{-1} for **13** are in the region for Al–O–Si bond vibrations [27,6d]. The bands of 514 cm^{-1} detected both for **12** and **13** correspond to SiPh$_3$ group [27,6d]. Unfortunately all attempts to obtain single crystals for X-ray diffraction were unsuccessful.

No reaction was detected by ^1H NMR spectroscopy between **2** and Ph_3SiOH in toluene after 24 h at room temperature, heating of this reaction mixture for 2 days (or even 6 days) to 70 °C resulted only in slow decomposition of **2** to the starting ligand 1,3-($^tBuOCH_2)_2C_6H_4$ and completely insoluble deep brown precipitate.

4. Conclusions

The interesting transmetallation of O,C,O or N,C,N pincer ligands was observed in the reactions between intramolecularly coordinated organoaluminum alkyls **1**–**3** with R_3SnOH. Organoaluminum derivatives containing O,C,O chelating ligands react in similar fashion with ($^nBu_3Sn)_2O$ as well, however the tetraorganotin products **10** and **11** could be obtained only in mixture with $^nBu_3Sn^iBu$. On the contrary the reactions of **1** and **3** with two equivalents of Ph_3SiOH reveal aluminosiloxanes containing two Al–O–Si linkages via isobutane elimination.

5. Supplementary data

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278848 and 278849 for **6** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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