Synthesis and Structure of Organoaluminum O,C,O Pincer Compounds

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ABSTRACT

The set of four organoaluminum compounds containing O,C,O chelating ligands [2, 6 - (ROCH₂)₂C₆H₃]AlCl₂; (R = Me (1); R = Et (2); R = *i*-Pr (3); R = *t*-Bu (4)), so called pincer ligands, have been prepared by the metathetical reaction of corresponding organolithium compounds with AlCl₃·Et₃N adduct, in moderate yields. Prepared compounds have been characterized by elemental analysis, multinuclear (¹H, ¹³C and ²⁷Al) NMR spectroscopy and cryoscopy measurements. The monomeric structure of studied compounds 1 – 4, containing a five-coordinated central aluminum atom, was obtained in diluted solutions of non-polar solvents (benzene, toluene), while the concentration of the samples resulted in monomer - dimer equilibrium based on ¹H, ²⁷Al NMR spectroscopy and cryoscopy. The XRD study of 4 revealed a monomeric structure, containing five-coordinated aluminum located in the centre of a *trans*-trigonal bipyramid.

Keywords: Aluminum, O,C,O chelating ligands, NMR spectroscopy,

1. INTRODUCTION

As early as 1955, Bähr and co-workers already reported on the first organoaluminum compounds showing intramolecular interaction Al - O in [EtO(CH₂)₄]AlEt₂ and Al - N in [Et₂N(CH₂)₃]AlEt₂, respectively /1/. Plenty of intramolecularly stabilized organoaluminum compounds have appeared since that time /2/ and some of them contain benzylic bi- or tridentate N - or P - donor ligands (Chart 1A) /3/. These intramolecularly stabilized group 13 halides have been often used as precursors for the synthesis of corresponding azides /4/, that constitute valuable candidates for CVD (chemical vapor deposition) of promising materials for microelectronic AlN, GaN and InN /5/. In contrast to the compounds stabilized by Al-N, derivatives showing Al - O interaction are very rare /1, 2/. Recently a bidentate benzylic ligand containing an oxygen donor atom (2 - CH₃OCH₂C₆H₄) has also been applied in intramolecular stabilization

of aluminum (Chart 1B). These compounds were used as active cocatalysts for Ziegler-Natta olefin polymerization /6/.

Chart 1

We have recently developed a new type of tridentate O,C,O - pincer ligands with increasing steric hindrance (2, 6 - (ROCH₂)₂C₆H₃, Chart 1C), that have been used in synthesis of some hypercoordinated organotin(IV) compounds /7/ and for stabilization of the corresponding organotin(IV) cations /8/. Here we report on synthesis of organoaluminum(III) compounds [2, 6 - (ROCH₂)₂C₆H₃]AlCl₂ (**1** – **4**, Scheme 1) and on structural studies both in solution (NMR spectroscopy) and in the solid state (XRD of **4**). These compounds enable us to observe the dependence of chemical behaviour of **1** – **4** on increasing ligand steric hindrance as well.

2. MATERIALS AND METHODS

2.1 General comments

All manipulations were carried out under argon atmosphere using the standard Schlenk technique. All solvents were dried by standard procedures and distilled prior to use. The synthesis of all starting O,C,O ligands (Chart 1C) and their lithiation was performed analogously to the literature /7/. ¹H, ¹³C and ²⁷Al NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers respectively, using 5 mm tuneable broad - band probes. Appropriate chemical shifts in ¹H and ¹³C NMR spectra were calibrated on the residual signals of the solvents (benzene-*d*₆: δ(¹H) = 7.16 ppm and δ(¹³C) = 128.39 ppm; toluene-*d*₈: δ(¹H) = 2.09 ppm and δ(¹³C) = 20.40 ppm). ²⁷Al NMR chemical shifts were related according to the external standard [Al(H₂O)₆]³⁺ δ(²⁷Al) = 0.0 ppm. Abbreviations used in ¹H NMR are: s = singlet; d = doublet; t = triplet; q = quartet; h = heptet.

2.2 Synthesis of [2,6 - (CH₃OCH₂)₂C₆H₃]AlCl₂ (**1**).

Et₃N (0.95 g, 1.30 mL, 9.37 mmol) was added to the suspension of AlCl₃ (1.25 g, 9.37 mmol) in toluene (50 mL). To the resulting solution pre-cooled diethylether solution (-78°C, 30 mL) of [2,6-(CH₃OCH₂)₂C₆H₃]Li (1.62 g, 9.37 mmol) was added dropwise. The reaction mixture was stirred for 12 h at

room temperature, then insoluble material was filtered off and the filtrate was concentrated to 10 mL. Crystallization at -30°C afforded colourless crystals of **1**. Yield: 1.61 g (65 %). M.p.: $82 - 85^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{10}\text{H}_{13}\text{O}_2\text{AlCl}_2$ ($263.09\text{ g}\cdot\text{mol}^{-1}$): C, 45.65; H, 4.98; Cl, 26.95. Found: C, 45.49; H, 4.82; Cl, 26.88. Diluted solution – 0.3 M: Molecular weight determination: theor. $263.09\text{ g}\cdot\text{mol}^{-1}$; exp. $258.28\text{ g}\cdot\text{mol}^{-1}$. ^1H NMR (360 MHz, C_6D_6 , 300K): $\delta = 3.36$ (s, 6H, OCH_3), 4.01 (s, 4H, CH_2O), 7.10 (d, 2H, Ar-*H*3,5), 7.23 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6 , 300 K): $\delta = 58.4$ (2C, OCH_3), 75.2 (2C, CH_2O), 127.6 (2C, Ar-*C*3,5), 128.8 (1C, Ar-*C*4), 139.3 (2C, Ar-*C*2,6), Ar-*C*1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 104$, $\nu_{1/2} = 4.1\text{ kHz}$. High concentration – 1.5 M (NMR signals detected in addition to those obtained in diluted sample): ^1H NMR (360 MHz, C_6D_6 , 300 K): $\delta = 3.11$ (s, 6H, OCH_3), 4.26 (s, 4H, CH_2O), 6.64 – 7.23 (complex pattern, 6H, Ar-*H*). ^{27}Al -NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 110\text{ ppm}$, $\nu_{1/2} = 5.3\text{ kHz}$.

2.3 Synthesis of [2,6-($\text{CH}_3\text{CH}_2\text{OCH}_2$) $_2\text{C}_6\text{H}_3$]AlCl $_2$ (**2**).

Et_3N (0.72 g, 0.99 mL, 7.12 mmol) was added to the suspension of AlCl_3 (0.95 g, 7.12 mmol) in toluene (50 mL). To the resulting solution [2,6-($\text{CH}_3\text{CH}_2\text{OCH}_2$) $_2\text{C}_6\text{H}_3$]Li (1.42 g, 7.12 mmol) in hexane (30 mL) was added dropwise. The reaction mixture was stirred for 12 h at room temperature, then insoluble material was filtered off and the filtrate was concentrated to 10 mL. Crystallization at -30°C afforded colourless crystals of **2**. Yield: 1.24 g (60 %). M.p.: $81 - 83^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{12}\text{H}_{17}\text{O}_2\text{AlCl}_2$ ($291.15\text{ g}\cdot\text{mol}^{-1}$): C, 49.50; H, 5.89; Cl, 24.35. Found: C, 49.62; H, 5.91; Cl, 24.47. Diluted solution - 0.3 M: Molecular weight determination: theor. $291.15\text{ g}\cdot\text{mol}^{-1}$; exp. $287.1\text{ g}\cdot\text{mol}^{-1}$. ^1H NMR (360 MHz, C_6D_6 , 300K): $\delta = 1.06$ (t, 6H, CH_3), 3.34 (q, 4H, OCH_2), 4.34 (s, 4H, CH_2O), 7.18 (d, 2H, Ar-*H*3,5), 7.37 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6 , 300 K): $\delta = 15.4$ (2C, CH_3), 65.9 (2C, OCH_2), 72.7 (2C, CH_2O), 126.2 (2C, Ar-*C*3,5), 128.2 (1C, Ar-*C*4), 139.4 (2C, Ar-*C*2,6), Ar-*C*1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 102$, $\nu_{1/2} = 3.9\text{ kHz}$. High concentration - 1.5 M (NMR signals detected in addition to those obtained in diluted sample): ^1H NMR (360 MHz, C_6D_6 , 300 K): $\delta = 1.08$ (t, 6H, CH_3), 3.90 (q, 4H, OCH_2), 4.19 (s, 4H, CH_2O), 6.71 – 7.37 (complex pattern, 6H, Ar-*H*). ^{27}Al NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 108$, $\nu_{1/2} = 4.8\text{ kHz}$.

2.4 Synthesis of {2,6-[(CH_3) $_2\text{CHOCH}_2$] $_2\text{C}_6\text{H}_3$ }AlCl $_2$ (**3**).

Procedure as for **2**: AlCl_3 (1.1 g, 8.25 mmol), {2,6-[(CH_3) $_2\text{CHOCH}_2$] $_2\text{C}_6\text{H}_3$ }Li (1.88 g, 8.25 mmol). Yield: 1.79 g (68 %). M.p. $85 - 87^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{14}\text{H}_{21}\text{O}_2\text{AlCl}_2$ ($319.20\text{ g}\cdot\text{mol}^{-1}$): C, 52.68; H, 6.63; Cl, 22.21. Found: C, 52.74; H, 6.75; Cl, 22.39. Diluted solution - 0.3 M: Molecular weight determination: theor. $319.20\text{ g}\cdot\text{mol}^{-1}$; exp. $312.5\text{ g}\cdot\text{mol}^{-1}$. ^1H NMR (360 MHz, C_6D_6 , 300K): $\delta = 1.10$ (d, 12H, CH_3), 3.52 (h, 2H, OCH), 4.41 (s, 4H, CH_2O), 7.18 (d, 2H, Ar-*H*3,5), 7.45 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6 , 300K): $\delta = 22.6$ (4C, CH_3), 70.5 (2C, CH_2O), 71.5 (2C, OCH), 126.9 (2C, Ar-*C*3,5), 128.8 (1C, Ar-*C*4), 140.2 (2C, Ar-*C*2,6), Ar-*C*1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 103$, $\nu_{1/2} = 4.1\text{ kHz}$. High concentration - 1.5 M (NMR signals detected in addition to those obtained in diluted sample): ^1H NMR (360 MHz, C_6D_6 , 300K): $\delta = 1.19$ (d, 12H, CH_3), 4.33 (s, 4H, CH_2O), 4.93 (h, 2H, OCH), 6.80 – 7.45 (complex pattern, 6H, Ar-*H*). ^{27}Al NMR (93.8 MHz, C_6D_6 , 300K): $\delta = 109$, $\nu_{1/2} = 4.9\text{ kHz}$.

2.5 Synthesis of {2,6-[(CH₃)₃COCH₂]₂C₆H₃}AlCl₂ (4).

Procedure as for 2: AlCl₃ (0.90 g, 6.74 mmol), {2,6-[(CH₃)₃COCH₂]₂C₆H₃}Li (1.79 g, 6.74 mmol). Yield: 1.36 g (58 %). M.p.: 88 - 90 °C. Anal. Calc. for C₁₆H₂₅O₂AlCl₂ (347.26 g mol⁻¹): C, 55.34; H, 7.26; Cl, 20.42. Found: C, 55.48; H, 7.35; Cl, 20.28%. Diluted solution - 0.3 M: Molecular weight determination: theor. 347.26 g.mol⁻¹; exp. 350.12 g.mol⁻¹. ¹H-NMR (360 MHz, C₆D₆, 300K): δ = 1.15 (s, 18H, CH₃), 4.28 (s, 4H, CH₂O), 7.25 (d, 2H, Ar-H3,5), 7.50 (t, 1H, Ar-H4). ¹³C NMR (90.6 MHz, C₆D₆, 300K): δ = 28.1 (6C, CH₃), 64.6 (2C, CH₂O), 73.4 (2C, OC), 126.5 (2C, Ar-C3,5), 128.4 (1C, Ar-C4), 140.9 (2C, Ar-C2,6), Ar-C1 not detected. ²⁷Al NMR (93.8 MHz, C₆D₆, 300K): δ = 104, ν_{1/2} = 3.8 kHz. High concentration - 1.5 M (NMR signals detected in addition to those obtained in diluted sample): ¹H NMR (360 MHz, C₆D₆, 300K): δ = 1.45 (s, 18H, CH₃), 4.55 (s, 4H, CH₂O), 6.80 – 7.50 (complex pattern, 6H, Ar-H). ²⁷Al NMR (93.8 MHz, C₆D₆, 300K): δ = 110, ν_{1/2} = 5.2 kHz.

2.6 X-ray structure determination

Colourless crystals of **4** suitable for X-ray structure analysis were obtained via crystallisation from diluted toluene solution at -30 °C. C₁₆H₂₅O₂AlCl₂, M = 347.24, orthorhombic, *Pbca*, *a* = 11.1050(1)Å, *b* = 16.1540(2)Å, *c* = 20.8340(2)Å, *V* = 3737.42(7)Å³, *Z* = 8, *D_x* = 1.234 Mg m⁻³. A colourless air-sensitive crystal of dimensions 0.5x0.45x0.35 mm was measured on a Nonius KappaCCD diffractometer by monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2)K. An absorption was neglected (μ = 0.396 mm⁻¹); a total of 55195 diffractions were measured in the range *h* = -13 to 13, *k* = -19 to 19, *l* = -24 to 24 (θ_{max} = 25.04°), from which 3291 were unique (R_{int} = 0.034) and 2966 observed according to the *I* > 2σ(*I*) criterion. Cell parameters were calculated from 3702 reflections (θ = 2.43-25.04°). The structure was solved by direct methods (SIR92, Altomare, 1994) and refined by full-matrix least squares based on *F*² (SHELXL97). The hydrogen atoms were fixed into idealised positions (riding model) and assigned temperature factors, either H_{iso}(H) = 1.2 U_{eq}(pivot atom) or H_{iso}(H) = 1.5 U_{eq}(pivot atom) for methyl moiety. Because of extensive disorder of *tert*-butyl moieties, their geometry was constrained during refinement. The refinement converged (Δ/σ_{max} = 0.005) to *R* = 0.1649 for observed reflections and *wR* = 0.5071, *GOF* = 4.960 for 185 parameters and all 19245 reflections. The quality of diffraction data did not allow to describe disorder satisfactorily, causing the large maxima on the final difference map (Δρ_{max} = 1.492, Δρ_{min} = -1.434 e.Å⁻³) in the vicinity of *tert*-butyl moieties together with their large displacement parameters.

3. RESULTS AND DISCUSSION

3.1 Synthesis of studied compounds

The first attempts to prepare compounds **1** - **4** via direct metathesis, using a toluene suspension of AlCl₃ and an appropriate organolithium salt (similar procedures have been applied for preparations of analogous compounds containing N,C,N ligands /3d-f/), afforded a mixture of decomposition products only. The similar decomposition of O,C,O ligand has recently been obtained for the reaction of [2, 6 - (ROCH₂)₂C₆H₃]Li with

SnCl_4 /7/. This decomposition is most probably the result of a coordination of strong Lewis acids (AlCl_3 or SnCl_4) to etheral oxygen atoms of O,C,O – chelating ligands prior to the desired metathesis reaction, and the propensity of aluminum halides to attack and cleave ethers is well known /9/. The above discussed conclusion is confirmed by the reaction of unsubstituted ligands [2, 6 - $(\text{ROCH}_2)_2\text{C}_6\text{H}_4$] with AlCl_3 , that resulted in a similar mixture of decomposition products. This suggestion led to the idea of moderating the reagent (AlCl_3) propensity to attack ligands by creating its base adduct with Et_3N . Another advantage of this procedure is the dissolution of AlCl_3 in toluene by forming $\text{AlCl}_3\text{NEt}_3$ adduct. The use of this complex for synthesis of **1 - 4** (Scheme 1), afforded the required compounds in moderate yields (about 60 %). No trace of Et_3N has been detected by ^1H NMR spectroscopy in the products after workup. The compounds **1 - 4** were characterized by elemental analysis, multinuclear NMR spectroscopy, XRD investigation (**4**) and cryoscopy in benzene.

Scheme 1: Synthesis of studied compounds

3.2 Solution NMR spectroscopy

^1H and ^{13}C NMR spectra of compounds **1 - 4** in diluted benzene- d_6 or toluene- d_8 solutions (0.3 M) afforded only one set of sharp signals for all protons at 300K. This resonance pattern in ^1H NMR spectra was preserved during the whole studied temperature range 350 - 180K in toluene- d_8 . The ^{27}Al NMR chemical shifts for **1 - 4** fit the region typical for five-coordinated aluminum atoms /10/ in organoaluminum compounds (the value of $\delta(^{27}\text{Al})$ [ppm] is 104 for **1**, 102 for **2**, 103 for **3**, 104 for **4**), and are similar to those found in the structurally resembling five-coordinated complex $\{2,6-[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2]_2\text{C}_6\text{H}_3\}\text{AlCl}_2$ /3f/. These findings indicate five-coordinated central aluminum atoms (based on the values of $\delta(^{27}\text{Al})$) and the equivalence of both CH_2OR groups of the ligand (one set of signals in ^1H and ^{13}C NMR spectra during the whole studied temperature range). It can be deduced that both oxygen donor atoms of O,C,O – chelating ligands are coordinated to central aluminum atom in mutually *trans* positions (on the contrary to *cis* positions of both oxygen atoms in corresponding organotin compounds /7/, where AX spin system has been observed for CH_2OR groups) through two Al - O intramolecular interactions, resulting in *trans* trigonal bipyramidal geometry in **1 - 4**. This strong coordination of both oxygen atoms to the central metal (Fig. 2A) is retained in the whole studied temperature range (350 – 180K) - ^1H NMR spectroscopy in diluted toluene- d_8 solutions.

This conclusion indicates analogous structure of **1** – **4**, regardless of increasing spatial hindrance of the ligands.

However, more concentrated toluene- d_8 or benzene- d_6 solutions (1.5 M) of studied compounds **1** – **4** revealed a second set of signals in addition to the previous one (suggested monomeric structures of **1** – **4** in 0.3 M solutions) in ^1H NMR at 300K (Fig. 1a illustrates the example of the appropriate ^1H NMR spectrum of **2**). New single resonance was observed in the ^{27}Al NMR spectra of **1** – **4** at this concentration (1.5 M) as well. The values of $\delta(^{27}\text{Al})$ of new signals varied between 108 – 111 ppm, again proving the five - coordinated central aluminum atoms /10/. The ^1H NMR spectra of **1** – **4** are concentration dependent, the new resonances observed in concentrated solutions lost their intensities during dilution of the samples and they disappeared at concentration around 0.3 M resulting to ^1H NMR spectra consistent with those of monomeric structures of **1** – **4** (Figs. 1b and 1c illustrates this process on ^1H NMR spectra of **2**). The whole process is reversible and the concentration of the sample led again to the mixture of two species. The ^1H NMR study of 1.5 M toluene- d_8 solutions of **1** – **4** at various temperatures (350 – 180K) revealed the broadening of new CH_2O group signals (originated from concentration dependent set) below 190K, while the CH_2O signals observed both in diluted and concentrated solutions of **1** – **4** remained unchanged even at 180K.

The ratios between both species at 1.5 M concentrations (Fig. 1a) of **1** – **4** determined by ^1H NMR spectroscopy at 300K do not change significantly over the whole studied temperature range (180 – 350K).

These NMR parameters (the values of $\delta(^{27}\text{Al})$ falling to five coordinated aluminum region and the broadening of new CH_2O signals below 190K indicating a dynamic process in **1** – **4**) and well-known inclination of organoaluminum halides to form dimers (even higher adducts) via halide bridges /11/, suggest possible monomer - dimer equilibrium (see Fig. 2). We suppose, that the dimer structures of **1** – **4** (bearing central Al_2Cl_2 core, and O,C,O chelating ligands with fluxional behaviour) are similar to that found in the solid state for analogous C,N - chelated compound (monomeric in solution /3b/) $2\text{-}[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\text{AlCl}_2$ /12/. It is interesting, that the other paper reported on the monomeric structure of same compound in solid state /3d/. The existence of monomer - dimer equilibrium in solution and monomeric structure in the solid state has been observed in intramolecularly stabilized $(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{Al}(\text{CH}_3)_2$ compounds as well /13/.

Fig. 1: Aliphatic region of ^1H NMR spectra for compound **2** – concentration dependence; 300 K; benzene- d_6 : (a) 1.5 M solution of **2**; (b) 0.7 M solution of **2**; (c) 0.3 M solution of **2**; * overlap of two triplets.

These conclusions are in good agreement with results revealed by cryoscopy measurement. The determined molecular weights establish monomeric structure of **1** - **4** in 0.3 M benzene solutions (see Experimental section), contrarily to nearly 90 % monomer – 10 % dimer equilibrium detected in more concentrated (0.5 M) benzene solutions, where the molecular weights are 288.24 g.mol $^{-1}$ for **1** ; 317.23 g.mol $^{-1}$ for **2**; 346.50 g.mol $^{-1}$ **3**; 378.83 g.mol $^{-1}$ **4** (theoretical molecular weights of the corresponding monomers are 263.09 g.mol $^{-1}$ for **1**, 291.15 g.mol $^{-1}$ for **2**, 319.20 g.mol $^{-1}$ for **3** and 347.26 g.mol $^{-1}$ for **4**). These findings coincide with ^1H NMR spectroscopy, where the ratios between monomer and dimer (comparison of integral intensities of signals appropriate to CH_2O groups) are approximately 90% monomer/10% dimer in 0.5 M benzene- d_6 solutions and 67%/33% in 1.5 M samples.

Fig. 2: Proposed monomer – dimer equilibrium in high concentrated solutions; **A** monomeric structure, **B** proposed dimer.

3.3 Solid - state structure of 4

Unfortunately, all single crystals were very mechanically labile, if handled outside the mother liquor, they rapidly decompose to polycrystalline material or thin plates. All other attempts to obtain single crystals by changing experimental conditions (solvent system, temperature, concentration) failed.

In spite of these problems, the solid-state structure of **4** was determined by X-ray techniques, however *t*-Bu groups on ligand's skeleton are disordered. The coordination vicinity of aluminum was not influenced by this defect and the main structural parameters can be derived from this structure (Fig. 3).

Fig. 3: ORTEP drawing of **4** showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity and only one position of disordered *t*-Bu groups is displayed. Selected bond lengths(Å) and angles(°): Al1 – O1 2.166(5); Al1 – O2 2.338(4); O1 – Al1 – O2 156.31(17).

The five-coordinated aluminum atom is located in the center of a distorted *trans* - trigonal bipyramid, where both oxygen donor atoms O(1) and O(2) adopt pseudo axial positions (while in corresponding organotin compounds both oxygen atoms were bound in mutually *cis* positions [7]), and both chlorines Cl(1) and Cl(2) together with carbon C(1) form the equatorial plane. The sum of angles in the Cl(1) – Cl(2) – C(1) girdle almost accurately attains the ideal value for equatorial plane by 359.87(17). The notable deviation from ideal environment is the magnitude of angle O(1) – Al(1) – O(2) 156.31(17)°, but this defect is constrained by rigidity of the pincer ligand. The same type of deviation from ideal trigonal bipyramidal shape was observed for structurally similar compound {2,6-[(CH₃CH₂)₂NCH₂]₂C₆H₃}AlCl₂, where the angle N – Al – N (158.19(10)°) was determined [3f]. One of the Al-O distances Al(1) – O(1) 2.166(5)Å is considerably shorter than the second one Al(1) – O(2) 2.338(4)Å, but both approximate the covalent bond distance for Al – O bond 1.92Å [14a] and are considerably shorter than the sum of van der Waals radii of Al and O 3.52Å [14b], thus confirming the existence of a strong intramolecular interaction between both oxygen donor atoms and the central aluminum atom. The Al(1) – O(1) bond distance is comparable to those found in other intramolecularly coordinated compounds [2 - CH₃OC₆H₄CH₂]₂AlCH₃ 2.1523(17); [2 - CH₃OC₆H₄CH₂]₂AlCl

2.0700(11); [8 - CH₃OC₁₀H₆]₂AlCH₃ 2.135(3) and [8-CH₃CH₂OC₁₀H₆]₂AlCl 2.120(4) /6/.

4. CONCLUSIONS

Metathetical reaction using AlCl₃·Et₃N has been applied for preparation of the studied compounds. Analogous behaviour has been observed for studied compounds **1** - **4** in solution, in spite of increasing steric hindrance of the O,C,O pincer ligand. Monomeric structures of **1** - **4** (similar to that detected for **4** in the solid state) have been confirmed in diluted solutions mainly by multinuclear spectroscopy and cryoscopy in benzene. However, a concentration-dependent equilibrium (monomer/dimer) has been established in high concentrated solutions for **1** - **4**.

SUPPORTING INFORMATION

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 232261. 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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