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Synthesis of aluminum alkoxide and bis-alkoxide compounds containing bidentate pyrrolyl ligands

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Abstract

A series of aluminum alkoxide and bis-alkoxides compounds were synthesized and characterized. Reacting **1** with 1 and 2 equiv. of *t*-butanol in methylene chloride generates $[C_4H_3N(CH_2NMe_2)-2]_2Al(O-t-Bu)$ (**2**) and $[C_4H_3N(CH_2NMe_2)-2-H-C_4H_3N(CH_2NMe_2)-2]Al(O-t-Bu)_2$ (**3**) in 47% and 54% yield, respectively. The ^1H NMR spectrum of **2** exhibits two singlets for NMe_2 and CH_2N at δ 2.52 and 3.84, respectively, representing the symmetrical manner of molecular structure **2** in a solution. Compound **3** is not thermal stable in solution which decompose into substituted pyrrole ligand $C_4H_4N(CH_2NMe_2)-2$ and unknown aluminum alkoxides. Reacting **1** with 2 equiv. of triphenylsilanol in methylene chloride generates a tetra-coordinated aluminum "ate" compound $[C_4H_3N(CH_2NMe_2)-2-H-C_4H_3N(CH_2NMe_2)-2]Al(OSiPh_3)_2$ (**4**) in 49% yield. The ^1H NMR spectra of **4** at room temperature show a broad signal at δ 1.57 for NMe_2 fragments and the signals for CH_2N were not observed. VT ^1H NMR spectra of **4** show the NMe_2 fragments became two singlets (δ 1.27 and 2.12) and the CH_2N exhibited two doublets (δ 2.44 and 3.56) at 240 K. The fluxional energy barrier ($\Delta G^{\ddagger}$) is estimated at ca. 50 kJ/mol. The molecular structures of compounds **3** and **4** are determined by single-crystal X-ray diffractometer.
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1. Introduction

Highly reactive metal–hydrogen bonds play an important role in catalytic reactions [1]. Among these, aluminum hydrides are well known [2] and widely used due to their high reactivity and low cost. Reactions of aluminum hydrides with organic molecules to yield aluminum alkoxides compounds are very general methods in obtaining LAl(OR) compounds [3]. One of the applications for the LAl(OR) is used as a catalysts in the lactone and lactide ring-opening polymerization [4]. Further reactions of aluminum alkoxides with alcohol to generate an "ate" compounds are not seen very often [5]. Currently, we are interested in the chemistry of the bidentate, substituted pyrrolyl ligand $[C_4H_4N(CH_2NMe_2)-2]$ [6] as an auxiliary ligand in early transition metal [7] or group 13 metal com-

plexes [8]. Herein, we report the syntheses of aluminum alkoxides compounds bearing a bidentate substituted pyrrolyl ligand and their related "ate" compounds.

2. Experimental

2.1. General procedure

All the reactions were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or in glove box. Toluene and diethyl ether were dried over Na/benzophenone ketyl and distilled before use. CH_2Cl_2 was dried over P_2O_5 and distilled prior use. $[C_4H_4N(CH_2NMe_2)-2]$ and $[C_4H_3N(CH_2NMe_2)-2]_2AlH$ (**1**) were synthesized according to the published literature [6]. $CDCl_3$ was degassed by using freeze-and-thaw cycles and dried over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were collected on a Bruker AC300 instrument. Elemental analysis was performed on Heraeus CHN-OS Rapid.

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2.2. Synthesis of $Al[C_4H_3N(CH_2NMe_2)\text{-}2]_2(O^tBu)$ (2)

To a solution of **1** (0.30 g, 1.09 mmol) in 20 mL of methylene chloride was added *t*-butanol (0.013 mL, 1.09 mmol)/methylene chloride (10 mL) solution via cannula at 0 °C. The reaction was complete within 10 min and the volatiles were removed under vacuum to generate 0.18 g of sticky pale orange solid (47%). ^{1}H NMR (CDCl_3): δ 1.17 (s, 9H, OC*Me*_3), 2.52 (s, 12H, N*Me*_2), 3.84 (s, 4H, C*H*_2N), 6.06 (m, 2H, pyrrole C*H*), 6.19 (m, 2H, pyrrole C*H*), 6.88 (m, 2H, pyrrole C*H*). ^{13}C NMR (CDCl_3): δ 33.5 (q, $J_{CH} = 124$ Hz, OC*Me*_3), 46.1 (q, $J_{CH} = 137$ Hz, N*Me*_2), 59.4 (t, $J_{CH} = 138$ Hz, C*H*_2N), 68.7 (s, OC*Me*_3), 105.6 (d, $J_{CH} = 168$ Hz, pyrrole*C*H), 109.2 (d, $J_{CH} = 167$ Hz, pyrrole C*H*), 125.0 (d, $J_{CH} = 178$ Hz, pyrrole C*H*), 134.5 (s, pyrrole C_{ipso}).

2.3. Synthesis of $Al[C_4H_3N(CH_2NMe_2)\text{-}2\text{-}H\text{-}C_4H_3N\text{-}(CH_2NMe_2)\text{-}2](O^tBu)_2$ (3)

To a solution of **1** (0.30 g, 1.09 mmol) in 20 mL of methylene chloride was added *t*-butanol (0.025 mL, 2.18 mmol)/methylene chloride (10 mL) solution via cannula at 0 °C. The reaction was complete within 10 min and the volatiles were removed under vacuum to generate white solid which was recrystallized from a toluene solution to yield 0.25 g of colorless crystals (54% yield). ^{1}H NMR (C_6D_6): δ 1.24 (s, 12H, N*Me*_2), 1.44 (s, 18H, OC*Me*_3), 1.48 (s, Al(OC*Me*_3)_3, decomposition impurity), 3.50 (s, 4H, C*H*_2N), 6.18 (m, 2H, pyrrole C*H*), 6.50 (m, 2H, pyrrole C*H*), 7.81 (m, 2H, pyrrole C*H*), 11.96 (s, 1H, N*H*N). ^{13}C NMR (C_6D_6): δ 33.9 (q, $J_{CH} = 124$ Hz, OC*Me*_3), 42.2 (q, $J_{CH} = 137$ Hz, N*Me*_2), 57.7 (t, $J_{CH} = 140$ Hz, C*H*_2N), 68.1 (s, OC*Me*_3), 109.1 (d, $J_{CH} = 160$ Hz, pyrrole C*H*), 111.4 (d, $J_{CH} = 171$ Hz, pyrrole C*H*), 128.2 (d, $J_{CH} = 158$ Hz, pyrrole C*H*), 129.5 (s, pyrrole C_{ipso}).

2.4. Synthesis of $Al[C_4H_3N(CH_2NMe_2)\text{-}2\text{-}H\text{-}C_4H_3N\text{-}(CH_2NMe_2)\text{-}2](OSiPh_3)_2$ (4)

To a solution of **1** (0.60 g, 2.18 mmol) in 20 mL of methylene chloride was added triphenylsilanol (1.24 g, 4.38 mmol)/methylene chloride (20 mL) solution via cannula at 0 °C. The reaction then was stirred at room temperature for 30 min and volatiles were removed under vacuum to yield a yellow solid. The solid was recrystallized from a methylene chloride solution to generate 0.44 g yellow crystals in 49% yield. ^{1}H NMR (CDCl_3): δ 1.27 (s, 6H, N*Me*_2), 2.12 (s, 6H, N*Me*_2), 2.44 (d, $^2J_{HH} = 13.8$ Hz, 2H, C*H_aH_b*N), 3.56 (d, $^2J_{HH} = 13.8$ Hz, 2H, CH_a H_bN), 6.06 (m, 2H, pyrrole C*H*), 6.11 (m, 2H, pyrrole C*H*), 7.13–7.38 (m, 32H, pyrrole C*H* + phenyl C*H*), 12.85 (s, 1H, N*H*N). ^{13}C NMR (CDCl3): δ 41.9 (q, $J_{CH} = 136$ Hz, N*Me*_2), 42.9 (q, $J_{CH} = 135$ Hz, N*Me*_2), 56.0 (t, $J_{CH} = 138$ Hz, C*H*_2N), 108.9 (d, $J_{CH} = 170$ Hz, pyrrole C*H*), 111.3 (d, $J_{CH} = 166$ Hz, pyrrole C*H*), 127.2 (d, $J_{CH} = 160$ Hz, phenyl C*H*), 128.2 (d, $J_{CH} = 181$ Hz, pyr-

role C*H*), 128.6 (d, $J_{CH} = 159$ Hz, phenyl C*H*), 128.9 (s, pyrrole C_{ipso}), 134.9 (d, $J_{CH} = 160$ Hz, phenyl C*H*), 138.5 (s, phenyl C_{ipso}). Anal. Calc. for C_50H_53AlN_4O_2Si_2: C, 72.78; H, 6.47; N, 6.79. Found: C, 72.98; H, 6.87; N, 6.52%.
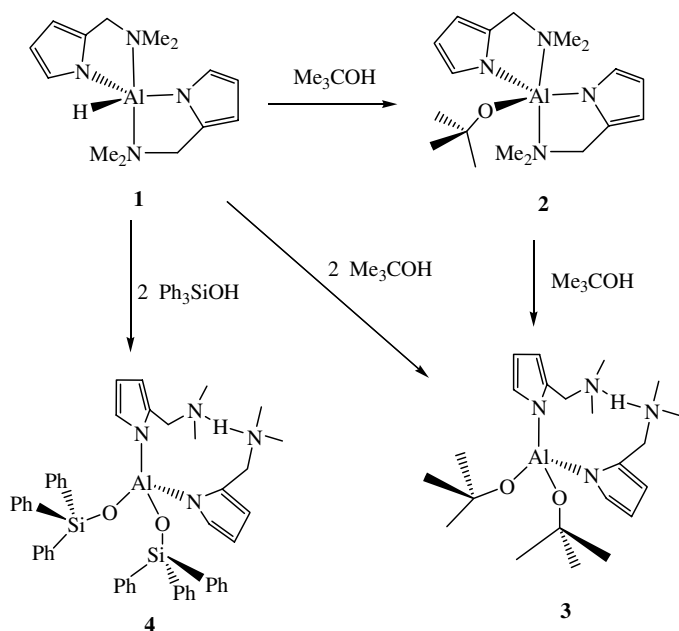
2.5. X-ray structure determination of compounds 3 and 4

The crystals were mounted on a glass fiber using epoxy resin and transferred to a goniostat. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation. Structural determinations were made using the SHELXTL package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are calculated. The crystal data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of compounds 2, 3, and 4

The synthesis of aluminum alkoxide and bis-alkoxides compounds from $[C_4H_3N(CH_2NMe_2)\text{-}2]_2AlH$ (**1**) is summarized in Scheme 1. Metal alkoxides are very common and some are often used as the polymerization catalysts for lactone and lactide. One way obtaining metal alkoxides is through the reactions of metal hydride with alcohols. Reacting **1** with 1 and 2 equiv. of *t*-butanol in methylene

Table 1
The summary of crystallographic data for compounds **3** and **4**

	3	4
Formula	C_22H_41AlN_4O_2	C_50H_52AlN_4O_2Si_2
Fw	420.57	824.12
Temperature (K)	150	150
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbcn$
a (Å)	14.1476(2)	19.8125(8)
b (Å)	11.68800(10)	11.6724(5)
c (Å)	16.2347(2)	19.2646(7)
β (°)	113.7290(10)	90
Volume (Å^3)/Z	2457.57(5), 4	4455.1(3), 4
D_{calc} (Mg/m^3)	1.137	1.229
Absorption coefficient (mm^{-1})	0.106	0.144
$F(000)$	920	1748
Crystal size (mm)	$0.56 \times 0.42 \times 0.35$	$0.22 \times 0.17 \times 0.06$
θ Range (°)	1.62–29.01	2.03–29.03
No. of reflections collected	30,623	60,919
No. of independent reflections (R_{int})	6454 (0.0240)	5926 (0.1167)
Maximum and minimum transmission	0.9639 and 0.9430	0.9914 and 0.9691
No. of data/restraints/parameters	6454/0/276	5926/170/324
Goodness-of-fit on F^2	1.058	1.066
Final R indices [$I > 2\sigma(I)$], R_1^a	$R_1 = 0.0447$	$R_1 = 0.0872$
wR_2^b	$wR_2 = 0.1275$	$wR_2 = 0.2323$
R indices (all data), R_1^a	$R_1 = 0.0572$	$R_1 = 0.1660$
wR_2^b	$wR_2 = 0.1359$	$wR_2 = 0.2539$
Largest difference in peak and hole (e Å^{-3})	0.739 and −0.431	0.361 and −0.365

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.
[b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Scheme 1.

chloride generates [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]$_2$Al(Ot-Bu) (**2**) and [C$_4$H$_3$N(CH$_2$NMe$_2$)-2-H-C$_4$H$_3$N(CH$_2$NMe$_2$)-2]Al(O-t-Bu)$_2$ (**3**) in 47% and 54% yield, respectively. The amount of t-butanol is very crucial for the reactions. Exact amount of t-butanol is needed for the reactions. While excess amount of t-butanol presenting in the reactions, **2** and **3** cannot be obtained cleanly and a small amount of aluminum tris(t-butoxide) can be seen in the products. Compound **2** is not thermal stable which gradually decomposes during the recrystallization procedure forming several aluminum compounds. The ^{1}H NMR spectrum of **2** exhibits two singlets for NMe$_2$ and CH$_2$N at δ 2.52 and 3.84, respectively, representing the symmetrical manner of molecular structure **2** in a solution. Compound **3** can also be obtained from the reaction of **2** with 1 equiv. of t-butanol. Compound **3** is not thermal stable in solution and ^{1}H NMR spectra in CDCl$_3$ shows it decomposed within 10 h to form the substituted pyrrole ligand C$_4$H$_4$N-(CH$_2$NMe$_2$)-2 and unknown aluminum alkoxides. The formation of **3** from **1** was accompanied by the elimination of 1 equiv. of hydrogen molecules and then a proton transformation. The reaction mechanism can be proved by monitoring the ^{1}H NMR spectra of [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]$_2$AlD (1-D) with t-butanol in CDCl$_3$ in a NMR tube. A triplet at δ 4.67 with J_{HD} = 43 Hz and a singlet at δ 11.96 representing the formation of HD and the proton transformation, respectively [9].

Reacting **1** with 2 equiv. of triphenylsilanol in methylene chloride generates a tetra-coordinated aluminum "ate" compound [C$_4$H$_3$N(CH$_2$NMe$_2$)-2-H- C$_4$H$_3$N(CH$_2$NMe$_2$)-2]Al(OSiPh$_3$)$_2$ (**4**) in 49% yield. Attempts to synthesize [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]$_2$Al(OSiPh$_3$) by reactions **1** with 1 equiv. of triphenylsilanol results the isolation of **4** and un-reacted **1**, which can further be converted to **4** by adding one more equivalent of triphenylsilanol. Compound **4**

is not thermal stable and decomposes within two days at room temperature in CDCl$_3$ to free substituted pyrrole ligands and other unknown products. The decomposition rate became very fast when the solution temperature rose to ca. 60 °C. No compound **4** was observed after 2 h. The ^{1}H NMR spectra of **4** at room temperature show a broad signal at δ 1.57 for NMe$_2$ fragments and the signals for CH$_2$N were not observed. Variable temperature ^{1}H NMR spectra (Fig. 1) show the NMe$_2$ fragments became two singlets (δ 1.27 and 2.12) and the CH$_2$N exhibited two doublets (δ 2.44 and 3.56) at 240 K. The fluxional energy barrier ($\Delta G^{\ddagger}$) is estimated at ca. 50 kJ/mol [10].

In order to prove that the acidic proton atom, which appears at δ 12.85, is trapped between the two NMe$_2$ groups, 2-D NOSEY NMR spectra were measured. A cross peak was observed between the acidic proton and the methyl groups of NMe$_2$ fragments indicating the short spacing ranges between the H$^+$ and Me protons (2D-NOSEY spectrum please see the Supporting information).

3.2. Molecular structure of 3 and 4

Crystals of **3** suitable for single-crystal X-ray diffraction are obtained from a toluene solution and crystals of **4** are obtained from a methylene chloride solution at −20 °C. The summary for data collections and selected bond
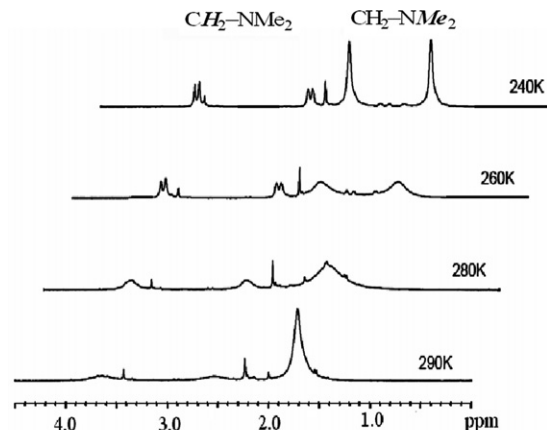

Fig. 1. The variable temperature ^{1}H NMR spectra of compound **4** in CDCl$_3$ using a 300 MHz NMR spectrometer.

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **3** and **4**

3			
Al(1)–O(1)	1.7186(10)	Al(1)–N(3)	1.8850(11)
Al(1)–O(2)	1.7194(10)	Al(1)–N(1)	1.8930(11)
O(1)–Al(1)–O(2)	120.96(5)	O(1)–Al(1)–N(3)	109.78(5)
O(2)–Al(1)–N(3)	104.01(5)	O(1)–Al(1)–N(1)	102.77(5)
O(2)–Al(1)–N(1)	111.21(5)	N(3)–Al(1)–N(1)	107.62(5)
4			
Al(2)–O(1)	1.710(3)	Al(2)–N(1BA)	1.910(3)
O(1)–Si(1)	1.598(3)		
O(1)–Al(2)–O(1A)	116.2(2)	N(1BA)–Al(2)–N(1B)	107.0(2)
O(1)–Al(2)–N(1BA)	113.95(19)		

lengths and angles are listed in Table 1 and 2, respectively. Compound **3** contains a monoclinic crystal system with a space group of $P2_1/n$. The molecular structure of **3** is shown in Fig. 2. Compound **3** can be described as a distorted tetragonal with the angles of O(1)–Al(1)–O(2) and N(1)–Al(1)–N(3) at 120.96(5)° and 107.62(5)°, respectively. The aluminum atom contains two anionic butoxide ligands and two pyrrolyl anionic ligands forming an aluminum "ate" compound. The two NMe_2 fragments from the
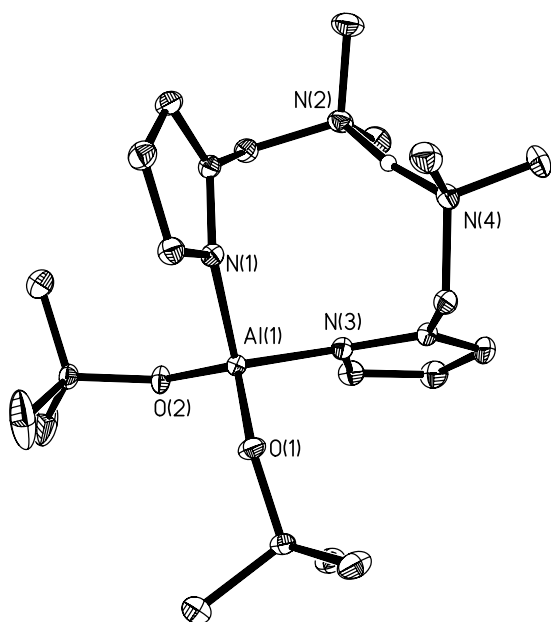

Fig. 2. The molecular structure of compound **3** showing the thermal ellipsoids in 50% probability. The hydrogen atoms were removed for clarity.
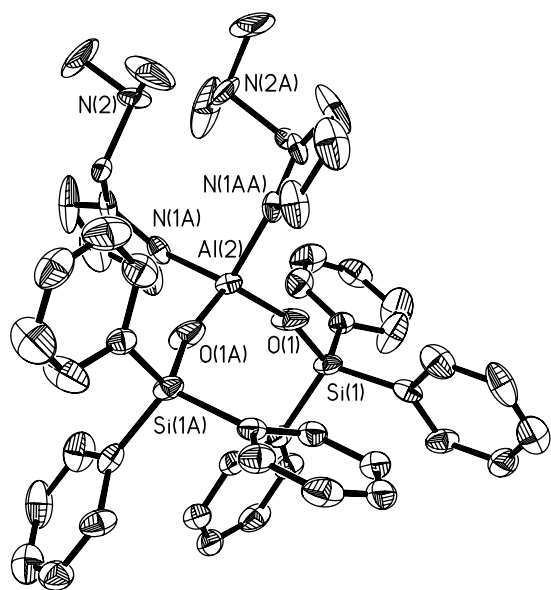

Fig. 3. The molecular structure of compound **4** showing the thermal ellipsoids in 30% probability. The hydrogen atoms were removed for clarity.

substituted pyrrolyl ligands act as proton sponge and a proton was trapped in the cage for the charge balance [11]. The bond angle of N(2)–H(4A)–N(4) is close to linearity (172°).

The molecular of **4** contains an orthorhombic crystal system and has a space system of *Pbcn*. The molecular structure of **4** contains a symmetry plane and the atoms of dimethylaminomethyl-pyrrolyl show disordered. The bond lengths and angles of **4** are very similar to those of **3** with the angles of O(1)–Al(2)–O(1A) and N(1B)–Al(2)–N(1BA) at 116.2(2)° and 107.0(2)°, respectively. The bond lengths of Al(2)–O(1) and Al(2)–N(1BA) are 1.710(3) Å and 1.910(3) Å, respectively. Due to the disordered of the pyrrolyl ligands, the proton atom between the two NMe_2 fragments cannot be obtained in a different map (see Fig. 3).

4. Conclusions

Reactions of aluminum hydride compound **1** with 1 equiv. of alcohols generated aluminum alkoxide compounds with the elimination of one equivalent of hydrogen molecules. The resulting aluminum alkoxides can further react with another equivalent of alcohol inducing a proton transformation from the alcohol to the NMe_2 groups and forming an aluminum dialkoxide "ate" compound. Further study of the deprotonation of various alcohols, amines, and alkynes with aluminum hydride compound **1** and succeeded proton transformation is currently under studied.

Acknowledgements

Appendix A. Supplementary material

CCDC 638980 and 638981 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.013.

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