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

Che-Yu Lin, Hon Man Lee, Jui-Hsien Huang *

Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan

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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 $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Al(O\text{-}t\text{-}Bu)$ (**2**) and $[C_4H_3N(CH_2NMe_2)\text{-}2\text{-}H\text{-}C_4H_3N(CH_2NMe_2)\text{-}2]Al(O\text{-}t\text{-}Bu)_2$ (**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 $C_4H_4N(CH_2NMe_2)\text{-}2$ and unknown aluminum alkoxides. Reacting **1** with 2 equiv. of triphenylsilanol in methylene chloride generates a tetra-coordinated aluminum "ate" compound $[C_4H_3N(CH_2NMe_2)\text{-}2\text{-}H\text{-}C_4H_3N(CH_2NMe_2)\text{-}2]Al(OSiPh_3)_2$ (**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.

Keywords: Aluminum; Alkoxides; Pyrrolyl

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 $[C_4H_4N(CH_2NMe_2)\text{-}2]$ [6] as an auxiliary ligand in early transition metal [7] or group 13 metal complexes [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. $[C_4H_4N(CH_2NMe_2)\text{-}2]$ and $[C_4H_3N(CH_2NMe_2)\text{-}2]_2AlH$ (**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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* Corresponding author. Tel.: +886 4 7232105; fax: +886 4 7211190.
E-mail address: juihuang@cc.ncue.edu.tw (J.-H. Huang).

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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, OCMe_3), 2.52 (s, 12H, NMe_2), 3.84 (s, 4H, CH_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, OCMe_3), 46.1 (q, $J_{CH} = 137$ Hz, NMe_2), 59.4 (t, $J_{CH} = 138$ Hz, CH_2N), 68.7 (s, O*C*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, NMe_2), 1.44 (s, 18H, OCMe_3), 1.48 (s, Al$(OCMe_3)_3$, decomposition impurity), 3.50 (s, 4H, CH_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, OCMe_3), 42.2 (q, $J_{CH} = 137$ Hz, NMe_2), 57.7 (t, $J_{CH} = 140$ Hz, CH_2N), 68.1 (s, O*C*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, NMe_2), 2.12 (s, 6H, NMe_2), 2.44 (d, $^{2}J_{HH} = 13.8$ Hz, 2H, CH_aH_bN), 3.56 (d, $^{2}J_{HH} = 13.8$ Hz, 2H, CH$_a$ $_{Hb}$N), 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, NMe_2), 42.9 (q, $J_{CH} = 135$ Hz, NMe_2), 56.0 (t, $J_{CH} = 138$ Hz, CH_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, pyrrole *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 $C_{50}H_{53}AlN_4O_2Si_2$: C, 72.78; H, 6.47; N, 6.79. Found: C, 72.98; H, 6.87; N, 6.52%.

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

	3	**4**
Formula	$C_{22}H_{41}AlN_4O_2$	$C_{50}H_{52}AlN_4O_2Si_2$
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 × 0.42 × 0.35	0.22 × 0.17 × 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] $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

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