Journal of Organometallic Chemistry 696 (2011) 3673–3680

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and protonolysis of neutral aluminum dihydride compounds stabilized by tridentate-substituted pyrrolyl ligands: Synthesis, structural characterization and ring-opening polymerization of ε-caprolactone

Jr-Chiuan Chang[a], Ya-Chi Chen[a], Amitabha Datta[a], Chia-Her Lin[b], Ching-Sheng Hsiao[a], Jui-Hsien Huang[a,*]

[a] Department of Chemistry, National Changhua University of Education, 1 Jing-Der Rd, Changhua 50058, Taiwan
[b] Department of Chemistry, Chung-Yuan Christian University, Chun-Li 320, Taiwan

ARTICLE INFO

Article history:
Received 25 May 2011
Received in revised form
4 August 2011
Accepted 18 August 2011

Keywords:
Pyrrole
Aluminum
Ring-opening polymerization

ABSTRACT

A series of aluminum compounds containing tridentate pyrrolyl ligands were obtained from related aluminum dihydride compounds via protonolysis. Treatment of tetranuclear aluminum compound $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}Al_2H_5]_2$ (**1**) with two equivalents of $[C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}]$ in methylene chloride at 0 °C led to the formation of $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH_2$ (**2**). Similarly, when the deuterated aluminum compound **1D** was used, the corresponding aluminum compound $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlD_2$ (**2D**) could be isolated. The reaction of **2** with one or two equivalents of phenylethyne, triphenylmethanethiol, 2,6-diisopropylaniline, or triphenylsilanol generated mononuclear aluminum compounds $[[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlRR'$ (**3**, $R = -C{\equiv}CPh$, $R' = H$; **4**, $R = R' = -C{\equiv}CPh$; **5**, $R = -SCPh_3$, $R' = H$; **6**, $R = R' = -SCPh_3$; **7**, $R = -NH(2,6\text{-}{}^iPr_2Ph)$, $R' = H$; **8**, $R = R' = -NH(2,6\text{-}{}^iPr_2Ph)$; **9**, $R = -OSiPh_3$, $R' = H$; **10**, $R = R' = -OSiPh_3$). Related Al—D compounds of **3**, **5**, **7** and **9** were also synthesized and corresponding IR spectroscopic data well matched in comparison of the stretching frequencies of Al—H and Al—D. The molecular structures of **2D**, **4**, **5**, **5D**, **7**, and **10** have been determined by X-ray crystallography. Compounds **2**, **5**, and **7** initiated the ring-opening polymerization of ε-caprolactone and produced high-molecular weight of poly-ε-caprolactone.

1. Introduction

The ever-expanding vistas in metal hydride chemistry prompt continuing interest in organometallic chemistry. The corresponding derivatives are thought to be responsible for a plethora of organic transformations, catalytic cycles and olefin polymerization intermediates, or deactivation products [1–3]. Among the metal hydrides, aluminum hydrides such as $LiAlH_4$ have been used the most often in many different reactions because of their inexpensive cost compared with other metal hydrides. However, the solubility and control of reactivity are often major issues when using these aluminum hydrides [4,5]. Increasing the solubility of aluminum hydrides and controlling their reactivity often can be achieved by varying their environments.

Many aluminum hydrides that contain various organic ligands have been synthesized, and their reactivity has been studied [6–9]. The molecular structure of aluminum hydride compounds often shows a strong tendency to form dimeric, trimeric, or even polymeric structures. Structural characterized ligand-stabilized neutral monomeric aluminum dihydride compounds are relatively few [10–12]. In the past work, we employed bi- or tridentate, substituted pyrrolyl ligands $[C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}]$ [13,14] as auxiliary ligands with early transition metals [15–17] or group 13 metals [18,19] to form organometallic compounds, and we assessed their reactivity toward small organic molecules. Herein, we report a simple method for the synthesis of aluminum dihydride compounds containing tridentate-substituted pyrrolyl ligands and further explore their reactions with phenylethyne, triphenylmethanethiol, 2,6-diisopropylaniline, and triphenylsilanol. The reactions of aluminum dihydride compounds with phenylethyne produced novel neutral monomeric aluminum alkynyl compounds. Monomeric aluminum compounds with terminal alkynyl groups are relatively rare, and few of these compounds are characterized structurally [20–24]. In general the alkynyl groups of aluminum compounds can either coordinate to other metal centers [25–29] through the alkynyl π-electrons or aggregate to form a metal cluster [30,31]. In addition, some of the new compounds were evaluated as initiators of the ring-opening polymerization of ε-caprolactone.

---

* Corresponding author. Tel.: +886 7 5919465; fax: +886 7 5919348.
E-mail address: juihuang@cc.ncue.edu.tw (J.-H. Huang).

0022-328X/$ – see front matter
doi:10.1016/j.jorganchem.2011.08.021

2. Experimental section

2.1. Materials and physical measurements

Unless otherwise noted, all manipulations were performed under vacuum line using standard Schlenk techniques under an atmosphere of nitrogen or using glove box techniques. Diethyl ether and heptane were dried over Na/benzophenone ketyl and distilled before use. CH_2Cl_2 was dried over P_2O_5 and distilled prior use. $[C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}]$ [13,14], $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}Al_2H_5]_2$ (**1**) and $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH_2$ (**2**) [19] were synthesized according to published literature. $CDCl_3$ was degassed by using freeze-and-thaw cycles and dried over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 instrument. Elemental analysis was performed on Perkin–Elmer CHN-2400.

2.2. Synthesis of the complexes

2.2.1. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlD_2$ (**2D**)

2.2.1.1. *Method A.* To a stirred diethyl ether solution of **1D** (0.50 g, 1.02 mmol), 0.041 g (2.05 mmol) of D_2O was added at −78 °C via microsyringe. The solution was stirred at room temperature for another 12 h and filtered. The filtrate was vacuum dried and solid was recrystallized from diethyl ether to yield 0.23 g (54% yield) of product. ^1H NMR (C_6D_6): 6.27 (s, 2H, C_4H_2N), 3.31 (s, 4H, CH_2NMe_2), 2.17 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): 131.0 (s, C_{ipso}), 106.0 (d, $J_{CH} = 164$ Hz, CH), 60.9 (t, $J_{CH} = 137$ Hz, CH_2), 47.6 (q, $J_{CH} = 136$ Hz, CH_3). IR (KBr) for Al–D: 1261, 1307 cm^{-1}.

2.2.1.2. *Method B.* To a 10 mL stirred methylene chloride solution of **1D** (1.88 g, 3.85 mmol), 1.40 g (7.73 mmol) of $[C_4H_3N(CH_2NMe_2)_2\text{-}2,5]$ in 10 mL methylene chloride was added dropwise at 0 °C. The solution was stirred at room temperature for 12 h. Volatiles were removed under vacuum to generate 3.10 g of **2D** in 95% yield.

2.2.2. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH(C{\equiv}CPh)$ (**3**)

A 50 mL Schlenk flask was charged with **2** (0.30 g, 1.45 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and phenylethyne (0.15 g, 1.45 mmol) was added via syringe. The solution was stirred for 24 h at room temperature. The volatiles were removed under vacuum and the residual was washed with heptane. The resulting solid was recrystallized from methylene chloride to generate 0.138 g of colorless crystals (31% yield). ^1H NMR (C_6D_6): 7.51 (m, 2H, phenyl), 7.02 (m, 3H, phenyl), 6.24 (s, 2H, pyrrolyl), 3.22, 3.48 (dd, 4H, CH_2NMe_2), 2.19 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): 132.0, 131.6, 130.7, 128.0, 127.3, 124.9, 107.2, 104.2, 60.0, 47.6. IR (KBr) for C≡C: 2129 cm^{-1}.

Complex 3D: Same procedure as described for **3** excepting the starting material of **2D** was used.

2.2.3. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al(C{\equiv}CPh)_2$ (**4**)

Similar procedures were used as for **3**. **2** (0.87 g, 4.16 mmol) and phenylethyne (0.85 g, 8.33 mmol) were used for reaction. 1.06 g of colorless crystals of **4** were obtained (71% yield). ^1H NMR ($CDCl_3$): 7.45, 7.28 (10H, phenyl), 5.97 (2H, pyrrolyl), 3.73 (s, 4H, CH_2NMe_2), 2.73 (s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$): 131.6, 130.7, 128.0, 127.3, 124.9, 109.5, 107.2, 104.2, 60.0, 47.6. $C_{26}H_{28}AlN_3$ (409.49): calcd. C 76.26, H 6.89, N 10.26; found C 75.19, H 7.17, N 10.36. IR (KBr) for C≡C: 2355, 2322 cm^{-1}.

2.2.4. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH(SCPh_3)$ (**5**)

A 50 mL Schlenk flask was charged with **2** (0.50 g, 2.40 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and triphenylmethanethiol (0.70 g, 2.50 mmol) in 20 mL methylene chloride was added dropwise at 0 °C. The solution was stirred for 12 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from methylene chloride to generate 0.90 g of colorless crystals (78% yield). ^1H NMR (C_6D_6): 7.84–7.07 (m, 15H, phenyl), 6.16 (s, 2H, pyrrolyl), 3.52, 2.87 (dd, 4H, CH_2NMe_2), 1.89 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): 150.4, 131.0, 130.7, 128.3, 126.0, 105.5, 63.6, 59.0, 46.2.

Complex 5D: Same procedure as described for **5** excepting the starting material of **2D** was used. $C_{29}H_{33}DAlN_3S$ (484.65): cacld. C 71.87, H 7.28, N 8.67; found C 69.92, H 7.21, N 8.64.

2.2.5. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al(SCPh_3)_2$ (**6**)

A 50 mL Schlenk flask was charged with **2** (0.50 g, 2.40 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and triphenylmethanethiol (1.40 g, 2.50 mmol) in 20 mL methylene chloride was added dropwise at 0 °C. The solution was stirred for 12 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from methylene chloride to generate 1.30 g of colorless crystals (72% yield). ^1H NMR ($CDCl_3$): 7.50–7.08 (m, 30H, phenyl), 5.82 (s, 2H, pyrrolyl), 2.86 (s, 4H, CH_2NMe_2), 2.12 (s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$): 149.7, 133.7, 130.5, 128.0, 126.5, 108.3, 66.1, 59.8, 47.2.

2.2.6. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH[NH(2,6\text{-}{}^iPr_2Ph)]$ (**7**)

A 50 mL Schlenk flask was charged with **2** (0.50 g, 2.40 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and 2,6-diisoproylaniline (0.50 g, 2.50 mmol) in 20 mL methylene chloride was added dropwise at 0 °C. The solution was stirred for 7 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from a methylene chloride/diethyl ether mixed solution to generate 0.90 g of colorless crystals (97% yield). ^1H NMR (C_6D_6): 7.14–6.89 (m, 3H, phenyl), 6.21 (s, 2H, pyrrolyl), 3.39 (m, 2H, $CHMe_2$), 3.52, 3.14 (dd, 4H, CH_2NMe_2), 2.06 (s, 12H, NMe_2), 1.28, 1.25 (d, 12H, $CHMe_2$). ^{13}C NMR (C_6D_6): 147.8, 135.4, 131.5, 124.1, 117.7, 106.3, 60.2, 47.2, 29.3, 24.4.

Complex 7D: Same procedure as described for **7** excepting the starting material of **2D** was used.

2.2.7. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al[NH(2,6\text{-}{}^iPr_2Ph)]_2$ (**8**)

A 50 mL Schlenk flask was charged with **2** (0.50 g, 2.40 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and 2,6-diisopropylaniline (0.90 g, 5.10 mmol) in 20 mL methylene chloride was added dropwise. The solution was stirred for 7 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from methylene chloride to generate 1.10 g of colorless crystals (82% yield). ^1H NMR (C_6D_6): 7.10–6.96 (m, 6H, phenyl), 6.23 (s, 2H, pyrrolyl), 3.41 (m, 4H, $CHMe_2$), 3.39 (s, 4H, CH_2NMe_2), 2.89 (s, 2H, NH), 2.05 (s, 12H, NMe_2), 1.21, 1.18 (d, 24H, $CHMe_2$). ^{13}C NMR (C_6D_6): 146.4, 140.1, 133.2, 124.0, 120.9, 108.6, 60.9, 47.3, 29.2, 24.7.

2.2.8. $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH[OSiPh_3]$ (**9**)

A 50 mL Schlenk flask was charged with **2** (0.50 g, 2.40 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and triphenylsilanol (0.70 g, 2.50 mmol) in 20 mL methylene chloride was added dropwise at 0 °C. The solution was stirred for 12 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from a methylene chloride solution to generate 0.60 g of colorless crystals (51.9% yield). ^1H NMR (C_6D_6): 7.83 (m, 3H, phenyl), 7.21 (m, 12H, phenyl), 6.25 (s, 2H, pyrrolyl), 3.36, 3.11 (dd, 4H, CH_2NMe_2), 1.96 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): 140.1, 136.9, 136.4, 131.3, 130.2, 106.0, 60.4, 47.1.

Complex 9D: Same procedure as described for **9** excepting the starting material of **2D** was used.

2.2.9. *[$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}$]Al[$OSiPh_3$]$_2$] (**10**)*

A 50 mL Schlenk flask was charged with **2** (1.00 g, 4.80 mmol) in glove box under nitrogen atmosphere. The compound was dissolved in 20 mL methylene chloride and triphenylsilanol (2.70 g, 9.8 mmol) in 20 mL methylene chloride was added dropwise. The solution was stirred for 12 h at room temperature. The volatiles were removed under vacuum and the resulting solid was recrystallized from a methylene chloride solution to generate 3.50 g of colorless crystals (96% yield). ^1H NMR ($CDCl_3$): 7.61–7.31 (m, 30H, phenyl), 5.92 (s, 2H, pyrrolyl), 3.29 (s, 4H, $CHNMe_2$), 1.92 (s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$): 138.3, 135.3, 131.1, 129.2, 127.6, 104.2, 60.3, 47.4. $C_{46}H_{48}AlN_3O_2Si_2$ (758.05): calcd. C 72.88, H 6.38, N 5.54; found C 72.44, H 6.81, N 5.26.

2.3. *Polymerization procedures and polymer characterization*

Polymerization of ε-caprolactone was carried out in a nitrogen filled Schlenk line. In a typical polymerization, monomer and initiator were dissolved in toluene in separate flasks. In general, the monomer was added to the initiator/toluene solution and the polymerizations are carried out at room temperature (28 °C) for a period of times or until they are solidified. The solutions are quenched with 0.5 mL of water and collected solids were washed with methanol. ^1H NMR spectroscopy and GPC (gel permeation chromatography) were used for characterization the conversions of monomers and molecular weights of PCL, respectively.

2.4. *Single crystal X-ray structure determination*

Colorless crystals of **4**, **5**, **5D**, and **10** suitable for X-ray structure determination were obtained from a saturated CH_2Cl_2 solution at −20 °C and data were collected at 150 K. Colorless crystals of **7** were obtained from a mixture of diethyl ether and methylene at −20 °C and data were collected at 298 K. Crystal data collection and refinement parameters are listed in Table 2. The crystal of **7** was sealed in glass capillaries and transferred to a goniostat. The crystals of **2D**, **4**, **5**, **5D**, and **10** were directly mounted on a glass fiber and transferred to a goniostat. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation. Intensity data were collected with a combination of ω and f scans. All data were corrected for Lorentz and polarization effects, and the program *SADABS* [65] was used for the absorption correction. Crystallographic computing was performed using SHELXTL [66,67] package of programs. On the basis of systematic absences and statistics of intensity distribution, the space group was determined for each complex. The structures were solved with Al and S atoms being disclosed first, followed by the atoms of O, N, and C located on successive difference Fourier maps. The H atoms were added in idealized positions and constrained to ride on their parent atoms. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the relevant crystallographic data and structure refinement parameters for **2D**, **4**, **5**, **7** and **10** are summarized in Table 1.

3. Results and discussion

3.1. *Synthesis and characterization of aluminum dihydride compound **2***

The synthesis of [$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}$]$AlH_2$ (2) is shown in Scheme 1. The reaction of tetranuclear aluminum compound [$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}Al_2H_5$]$_2$ (**1**) with two equivalents of H_2O in diethyl ether at −78 °C generated **2** in 54% yield [19]. However, the stoichiometric control of H_2O is crucial for the reaction. The use of an excess of H_2O resulted in the formation of [$C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}$] via hydrolysis. Alternatively, we found a simple method for the conversion of **1** to **2** by adding two equivalents of the tridentate ligand [$C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}$] to **1**, with a yield of 85%. The corresponding deuterated aluminum compound, [$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}$]$AlD_2$ (2D) was obtained upon reaction of deuterated aluminum compound **1D** with two equivalents of [$C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}$]. Solid-state IR spectra supported the existence of Al–H and Al–D. The Al–H stretching frequencies of **2** (1778 and 1797 cm^{-1}) disappeared when **2D** was used, and new Al–D stretching frequencies were observed at 1261 and 1307 cm^{-1}, which were calculated at 1257 and 1271 cm^{-1}. Compound **2** is relatively thermally stable which remains unchanged even at 100 °C for 4 days in C_6D_6. However, **2** is very moisture sensitive and releases free pyrrole ligand upon exposure to air.

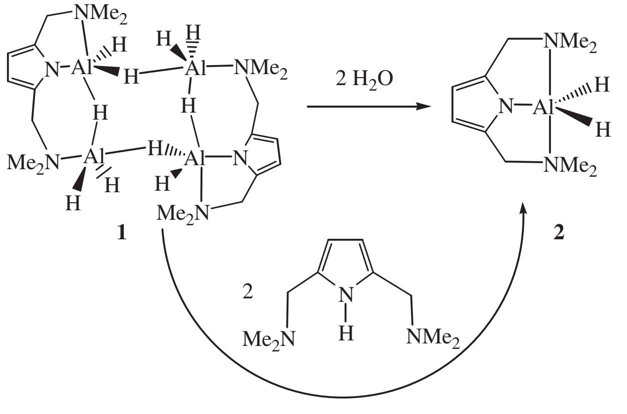
Table 1
IR stretching frequency of Al–H and Al–D for compounds **2**, **3**, **5**, **7** and **9**.

Compound	ν_{Al-H} (cm^{-1})	ν_{Al-D} (cm^{-1})	
		Calculation	Observed
2	1778/1797		
2D		1257/1271	1261/1307
3	1804		
3D		1298	NA[a]
5	1446		
5D		1022	985
7	1847		
7D		1329	NA
9	1812		
9D		1304	NA

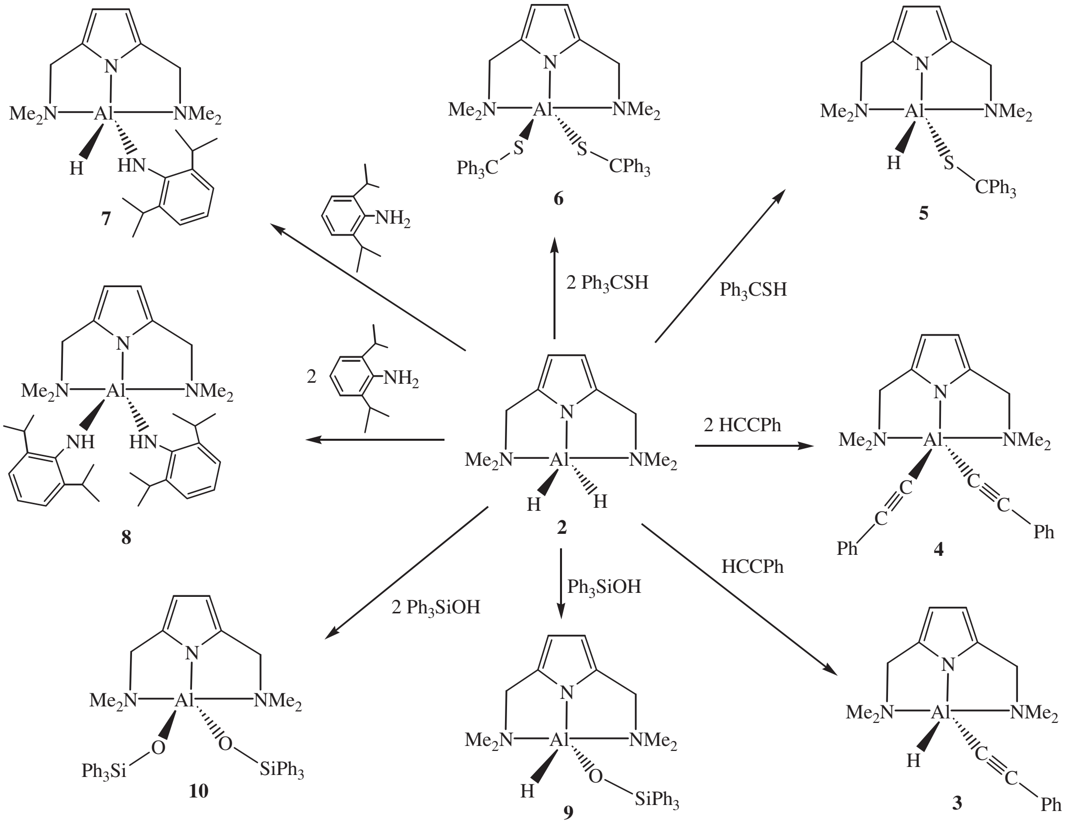
[a] NA: IR stretching frequency of Al–D is not available due to the overlapping with other absorption bands.

3.2. *Deprotonation of small organic molecules with aluminum dihydride compound **2***

The reactions of **2** with small organic molecules such as phenylethyne, triphenylmethanethiol, 2,6-diisopropylaniline, and triphenylsilanol are summarized in Scheme 2. The aluminum dihydride compound **2** acted as a proton-abstracting reagent that removed the acidic proton from organic molecules to yield dihydrogen molecules. The reaction of **2** with one or two equivalents of phenylethyne in methylene chloride at room temperature produced compounds [$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}$]$AlH(C{\equiv}CPh)$ (**3**) and [$C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}$]$Al(C{\equiv}CPh)_2$ (**4**), respectively, with



Scheme 1.



Scheme 2.

the elimination of hydrogen. Compound **3** can also be obtained from the reaction of **2** and **4** in toluene through ligand redistribution. Compound **4** was thermally stable and remained intact in $CDCl_3$ at 70 °C for 2 days. Related Al–D compounds of **3**, **5**, and **7** were synthesized by similar methods.

The ^{1}H and ^{13}C NMR spectra of **3D** are the same as those of **3** in C_6D_6. The ^{1}H NMR spectrum of **3** reveals a C_s-symmetric geometry, as evidenced by an AB pattern (δ 3.22 and 3.48) for the methylene protons of the substituted pyrrolyl ligands. In contrast, the ^{1}H NMR spectrum of compound **4** indicates a symmetrical coordination of the substituted pyrrolyl ligand, as evidence by the singlet (δ 3.73) observed for the methylene protons of the ligand. Moreover, the ^{13}C NMR spectra revealed the existence of the alkynyl groups of **3** and **4**. Two distinct singlets were observed at δ 107.2 and 130.7 for the resonances of the ethynyl carbons of **4**.

The reaction of **2** with one or two equivalents of triphenylmethanethiol in methylene chloride at room temperature afforded compounds $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH(SCPh_3)$ (**5**) and $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al(SCPh_3)_2$ (**6**) in 78% and 72% yield, respectively, with the elimination of hydrogen. Again, the distinct signals of methylene protons of CH_2NMe_2 were used to establish the purity of compounds **5** and **6**. The ^{1}H NMR spectrum of compound **5** revealed an AB pattern with two doublets at δ 3.52 and 2.87, and the spectrum of **6** showed one singlet at δ 2.86 for the methylene protons. The most characteristic feature of the ^{13}C NMR spectra for **5** and **6** was the resonance of the tertiary carbon atom of CPh_3 at δ 63.6 and 66.1, respectively.

The aluminum amide or aluminum siloxide compounds **7**–**10** were obtained under similar conditions as for compounds **5** and **6** (Scheme 2). Treatment of **2** with one or two equivalents of 2,6-diisopropylainiline or triphenylsilanol in a methylene chloride solution at room temperature led to the rapid evolution of hydrogen, and the compounds $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH[NH(2,6\text{-}^iPr_2Ph)]$ (**7**), $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al[NH(2,6\text{-}^iPr_2Ph)]_2$ (**8**), $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]AlH[OSiPh_3]$ (**9**), and $[C_4H_2N\{2,5\text{-}(CH_2NMe_2)_2\}]Al[OSiPh_3]_2$ (**10**) were isolated in good yield. Compounds **7**, **8**, **9**, and **10** were also characterized by ^{1}H and ^{13}C NMR spectroscopy, which showed similar resonance patterns as those described for the previous compounds. Heating **7** in toluene at 80 °C for 5 days resulted in ligand redistribution, and compounds **2** and **8** were observed. Compound **9** was an air- and moisture-sensitive solid that decomposed during the recrystallization to unidentified compounds, along with the formation of hexaphenyldisiloxane [32].

The hydride resonances of compounds **2**, **3**, **5**, **7**, and **9** in C_6D_6 were not observed with a 200 MHz spectrometer, even at −40 °C. However, solid-state IR spectra supported the existence of Al–H (terminal), as evidenced by the absorptions of ν_{Al-H} at ~1850–1800 cm^{-1}, which were not observed for the corresponding Al–D compounds. Table 1 compares the Al–H and corresponding Al–D stretching frequencies.

3.3. Molecular structures of compounds **2D**, **4**, **5**, **5D**, **7**, and **10**

Summaries of the crystallographic data and selected bond lengths and angles are presented in Table 2 and 3, respectively. The molecular structure of **2D** is shown in Fig. 1. The structure of **2D** is an isostructure of that of **2** [19]. Single crystal X-ray structures that include Al–D bond lengths are rare in the literature [19,33,34]. The bond lengths of the Al(1)–D(1) and Al(1)–D(2) are at 1.48(2) Å and 1.62(2) Å.

The crystal structure of **4** revealed a monomeric, five-coordinated aluminum center surrounded by a tridentate pyrrolyl ligand and two phenylethynyl groups where the two

Table 2
The summaries of crystallographic data for compounds **2D**, **4**, **5**, **7**, and **10**.

	2D	**4**	**5**	**7**	**10**
Empirical formula	$C_{10}H_{18}AlD_2N_3$	$C_{26}H_{28}AlN_3$	$C_{29}H_{34}AlN_3S$	$C_{22}H_{37}AlN_4$	$C_{46}H_{48}AlN_3O_2Si_2$
Formula weight	211.28	409.49	483.63	384.54	758.03
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	Cc	C2/c
a, Å	6.3011(8)	9.9646(7)	9.1023(7)	9.1950(15)	27.4978(15)
b, Å	24.801(3)	8.7484(6)	33.388(3)	30.076(5)	11.7057(7)
c, Å	8.5998(11)	26.7661(18)	9.4926(7)	8.6300(14)	25.9438(14)
β,°	107.778(3)	91.195(2)	117.133(1)	98.010(4)	96.294(1)
Volume, $Å^3$/Z	1279.7(3)/4	2329.7(3)/4	2567.4(3)/4	2363.3(7)/4	8300.5(8)/8
D_{calcd}, Mg/m^3	1.097	1.168	1.251	1.081	1.213
μ (mm^{-1})	0.130	0.104	0.183	0.099	0.148
F(000)	456	872	1032	840	3216
Cryst size (mm)	0.45 × 0.42 × 0.32	0.30 × 0.28 × 0.20	0.24 × 0.22 × 0.20	0.35 × 0.30 × 0.28	0.34 × 0.28 × 0.22
θ(min), *θ*(max)	1.64–27.56°	2.05–27.51°	2.44–27.53°	2.34–26.37°	1.49–27.52°
Reflns collected	8037	14,339	16,289	6909	26,003
Ind reflns	2909 ($R_{int} = 0.0457$)	5309 ($R_{int} = 0.0293$)	5872 ($R_{int} = 0.0506$)	3291 ($R_{int} = 0.1052$)	9457 ($R_{int} = 0.0461$)
Max. and min. transmn.	0.9486 and 0.4553	0.9486 and 0.7304	0.9486 and 0.8404	0.9486 and 0.2440	0.9682 and 0.9515
Data/restraints/params	2909/0/189	5309/0/275	5872/0/315	3291/2/248	9457/0/491
Goodness-of-fit on F^2	0.779	0.924	0.711	0.690	0.907
R [$I > 2\sigma(I)$]	R1 = 0.0389 wR2 = 0.0944	R1 = 0.0404 wR2 = 0.10091	R1 = 0.039 wR2 = 0.0759	R1 = 0.0410 wR2 = 0.0835	R1 = 0.0403 wR2 = 0.0921
R (all data)	R1 = 0.0893 wR2 = 0.1273	R1 = 0.0639 wR2 = 0.1089	R1 = 0.0879 wR2 = 0.0885	R1 = 0.1006 wR2 = 0.0946	R1 = 0.0772 wR2 = 0.1192
Largest diff. peak and hole (e $Å^3$)	0.186 and −0.123	0.314 and −0.209	0.275 and −0.260	0.144 and −0.175	0.385 and −0.285

dimethylamino nitrogen atoms occupying the axial positions (Fig. 2). The bond angle of N(2)–Al(1)–N(3) is 154.35(5)°. Further, the coordinated phenylethynyl groups (–C≡CPh) exhibited relatively short carbon–carbon triple bond lengths for the C(11)–C(12) and C(19)–C(20) at 1.201(2) Å and 1.181(2) Å, respectively. The Al–C≡C bond angles of **4** are linear with the bond angles of Al(1)–C(11)–C(12) and Al(1)–C(19)–C(20) at 175.42(13) and 177.13(14)°, respectively. The short C≡C triple bond lengths and linearity of Al–C≡C angles indicate the terminal alkynyl fragments bind to aluminum atom in a σ bonding mode and no bridging character was observed. The bonding modes and structures of alkynyl aluminum compounds have been reviewed by Zheng and Roesky [35] where the reactive aluminum hydride replaces the CH-acidic alkynes forming alkynyl aluminum compounds.

Compounds **5** and **5D** are isostructural and only the molecular structure of **5** is shown in Fig. 3. The geometry of **5** can be described as a distorted trigonal bipyramidal structure with the two dimethylamino nitrogen atoms occupying axial positions. The bond

Table 3
Selected bond lengths (Å) and angles (°) of compounds **2D**, **4**, **5**, **7**, and **10**.

2D					
Al(1)–N(1)	1.844(2)	Al(1)–N(2)	2.211(2)	Al(1)–N(3)	2.271(2)
Al(1)–D(1)	1.48(2)	Al(1)–D(2)	1.62(2)		
N(2)–Al(1)–N(3)	155.48(7)	N(1)–Al(1)–N(2)	77.82(7)	N(1)–Al(1)–N(3)	77.66(7)
4					
Al(1)–N(1)	1.836(1)	Al(1)–N(2)	2.278(1)	Al(1)–N(3)	2.201(1)
Al(1)–C(11)	1.942(2)	Al(1)–C(19)	1.967(2)		
N(2)–Al(1)–N(3)	154.35(5)	N(1)–Al(1)–N(2)	76.25(5)	N(1)–Al(1)–N(3)	78.10(5)
Al(1)–C(11)–C(12)	175.42(13)	Al(1)–C(19)–C(20)	177.13(1)		
5					
Al(1)–H(1)	1.53(2)	Al(1)–S(1)	2.2716(8)	Al(1)–N(1)	1.8371(17)
Al(1)–N(2)	2.2596(17)	Al(1)–N(3)	2.2866(17)		
N(2)–Al(1)–N(3)	153.39(6)	N(1)–Al(1)–N(2)	76.96(7)	N(1)–Al(1)–N(3)	76.87(6)
Al(1)–S(1)–C(11)	119.61(6)	S(1)–Al(1)–H(1)	124.5(7)	N(1)–Al(1)–S(1)	111.93(6)
N(1)–Al(1)–H(1)	123.6(7)				
7					
Al(1)–H(1)	1.55(3)	Al(1)–N(4)	1.821(3)	Al(1)–N(1)	2.261(4)
Al(1)–N(2)	2.274(3)	Al(1)–N(3)	1.833(4)		
N(2)–Al(1)–N(3)	77.40(15)	N(1)–Al(1)–N(2)	153.81(14)	N(1)–Al(1)–N(3)	76.86(16)
Al(1)–N(4)–C(11)	146.0(3)	N(4)–Al(1)–H(1)	123.27(99)	N(3)–Al(1)–N(41)	113.22(16)
N(3)–Al(1)–H(1)	124(1)				
10					
Al(1)–O(1)	1.7231(15)	Al(1)–O(2)	1.7091(16)	Al(1)–N(1)	1.839(2)
Al(1)–N(2)	2.231(2)	Al(1)–N(3)	2.300(2)	O(1)–Si(1)	1.5994(15)
O(2)–Si(2)	1.6005(16)				
N(2)–Al(1)–N(3)	152.73(8)	N(1)–Al(1)–N(2)	77.04(8)	N(1)–Al(1)–N(3)	76.14(8)
Al(1)–O(1)–Si(1)	160.30(11)	Al(1)–O(2)–Si(2)	169.93(11)	N(1)–Al(1)–O(2)	127.61(9)
N(1)–Al(1)–O(1)	120.17(9)	O(1)–Al(1)–O(2)	112.22(8)		

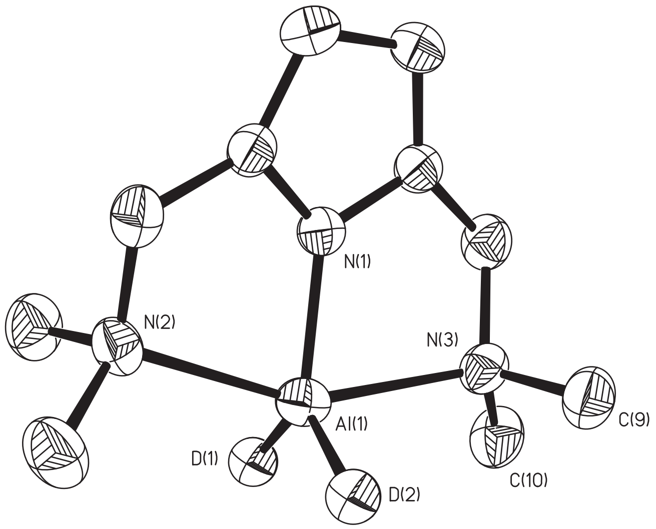


Fig. 1. The molecular structure of **2D**. Ellipsoids are dawn at the 50% probability level and hydrogen atoms are omitted for clarity.

angle of N(2)–Al(1)–N(3) is 153.39(6)°. There are numbers of terminal t-butylthiolate aluminum compounds reported in the literature [36–38]; however, no terminal bulky triphenylmethanethiolate aluminum compound was seen before. The bond angle of Al(1)–S(1)–C(11) (119.61(6)°) is larger than a normal angle of sp^3 hybridization and normal Al-thiolate bond angles presumably due to the steric effect of the large triphenylmethyl group.

The structure of **7**, which is similar to that of **5**, is shown in Fig. 4. The bond length of Al–N(4) (1.821(3) Å) and bond angle of Al(1)–N(4)–C(11) (146.0(3)°) are in the normal range of aluminum 2,6-diisopropylphenylanilide [39–45]. Moreover, the bond angle of Al(1)–N(4)–C(11) is even larger than that of Al(1)–S(1)–C(11) in **5**, probably because of the bulky 2,6-diisopropylphenyl group pushing the aryl ring away from the aluminum atom.

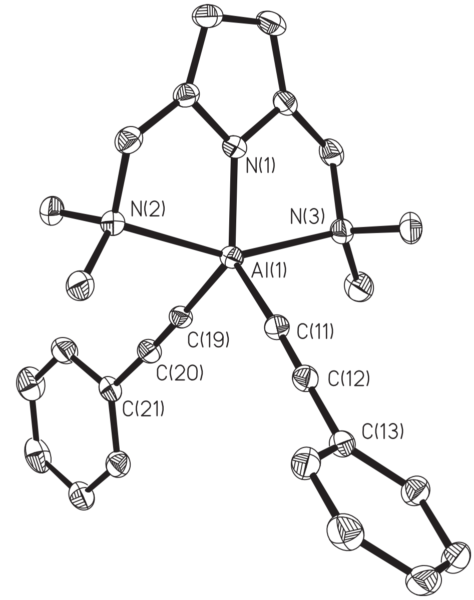


Fig. 2. The molecular structure of **4**. Ellipsoids are dawn at the 50% probability level and hydrogen atoms are omitted for clarity.

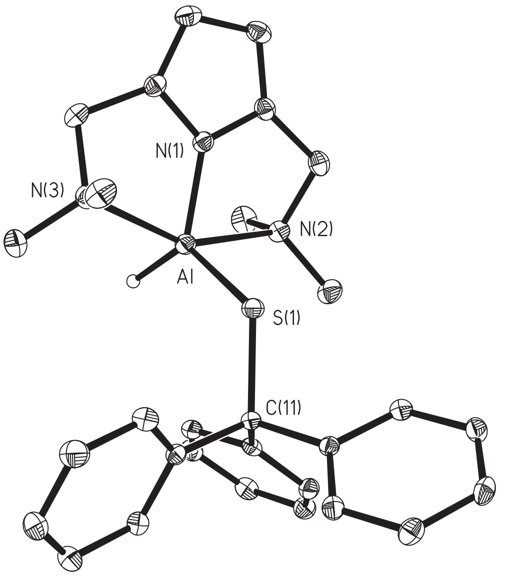


Fig. 3. The molecular structure of **5**. Ellipsoids are dawn at the 50% probability level. Excepting the hydride atom, all hydrogen atoms are omitted for clarity.

In compound **10** (Fig. 5), the geometry around the aluminum atom is similar to that of **4** showing a distorted trigonal bipyramidal. The bond angles of Al(1)–O(1)–Si(1) and Al(1)–O(2)–Si(2) (160.30(11)° and 169.93(11)°) are larger than normal sp^3 hybridization. The short Al–O (1.7231(15) Å and 1.7091(16) Å) bond lengths and doubly bonded O–Si (1.6005(16) Å and 1.5994(15) Å) likely explain the large angle of Al–O–Si. However, the bond lengths of Al–O and O–Si and related Al–O–Si bond angles do not show any correlation indicating the steric hindrance dominates the Al–O–Si bond angles. A comparison of the bond angles of Al–O–Si and the bond lengths of Al–O and Si–O for compound **10** with those of reported structures is shown in Table 4 [46–49].

3.4. Initiation of ring-opening polymerization of ε-caprolactone by aluminum compounds

Ring-opening polymerizations (ROP) of ε-caprolactone initiated by metal compounds has been studied [50–52]. ROP initiated by aluminum alkoxides is well known [53–61]; however, ROP

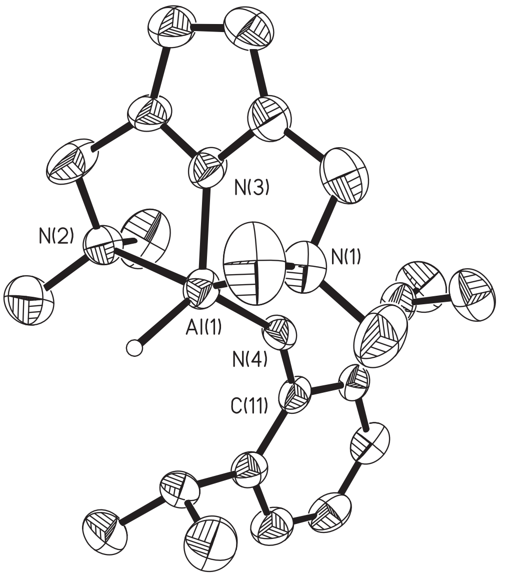


Fig. 4. The molecular structure of **7**. Ellipsoids are dawn at the 30% probability level. Excepting the hydride atom, all hydrogen atoms are omitted for clarity.

Table 4
A comparison of the bond angles of Al–O–Si and bond lengths of Al–O and Si–O for compound **10** with that of reported structures.

Compound	Bond angle(s) (°)	Bond length(s) (Å)	Ref
	Al–O–Si	Al–O/Si–O	
10	160.30(11) 169.93(11)	1.7231(15)/1.5994(15) 1.7091(16)/1.6005(16)	This work
Salen (^{t}Bu)AlOSiPh$_3$	157.9(14)	1.719(14)/1.608(13)	16a
Salpen (^{t}Bu)AlOSiPh$_3$	166.3(2)	1.726(2)/1.597(2)	16a
Salophen (^{t}Bu)AlOSiPh$_3$	166.8(6)	1.702(9)/1.603(9)	16a
AlMe(OSiPh$_3$)$_2$(THF)	149.8(2) 165.5(3)	1.715(4)/1.596(4) 1.699(3)/1.596(4)	16b
Al(OSiPh$_3$)$_2$[C(SiMe$_3$)$_3$](thf)	163.71(18) 170.42(18)	1.726(3)/1.616(3) 1.726(3)/1.616(3)	16c
L[Al(OSiPh$_3$)$_2$	163.13(3)	1.710(3)/1.598(3)	16d

Salen (^{t}Bu) = N,N′-ethylenebis(3, 5-di-tert-butylsalicylideneimine).
Salpen (^{t}Bu) = N,N′-propylenebis(3, 5-di-tert-butylsalicylideneimine).
Salophen (^{t}Bu) = N,N′-phenylenebis(3, 5-di-tert-butylsalicylideneimine).
L = $C_4H_3N(2\text{-}CH_2NMe_2)\text{-}H\text{-}C_4H_3N(2\text{-}CH_2NMe_2)$.

initiated by metal hydrides and amides is less studied [62,63]. We previously reported the ROP of ε-caprolactone using the aluminum compounds as initiators [64]. Similarly, here we applied the resulting aluminum compounds as initiators for the ROP of ε-caprolactone. The results are reported in Table 5.

Compounds **9** and **10** were inactive in the ROP of ε-caprolactone. In contrast, compounds **2**, **5**, and **7** showed activity in the polymerization of ε-caprolactone to form poly-ε-caprolactone (PCL). The aluminum hydrides of compound **2** initiated the ROP of ε-caprolactone to yield poly-ε-caprolactone (PCL); however, the polydispersity index (PDI, M_w/M_n) values of PCL initiated by **2** were relatively broad ranging from 1.24 to 1.41, probably because of the side reactions or multiple reacting sites (Al–H or Al–N). Similarly, the PDI values of PCL initiated by **5** and **7** were in the range of 1.12–1.39. Steric effect can be considered as the main reason for the differing activities of these compounds toward ε-caprolactone. Short Al–O bond lengths (**10**, 1.7201(13) Å) prevents the monomer from coordinating to the aluminum center and blocks the polymerization, whereas the longer Al–N and Al–S bond lengths (**7**, 1.821(3) Å and **5D**, 2.2746(16) Å) allow the polymerization to proceed.

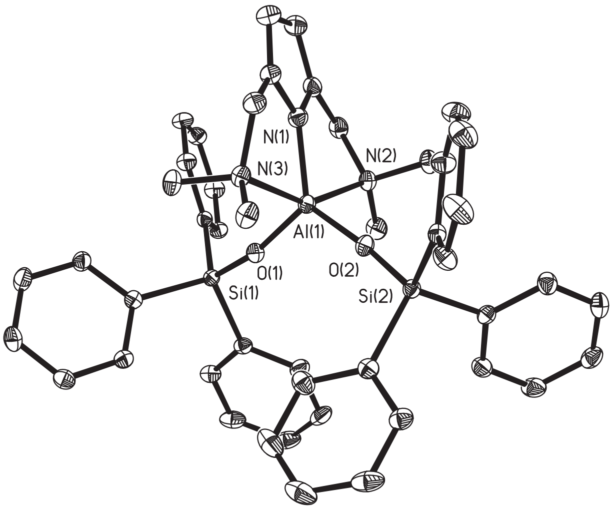


Fig. 5. The molecular structure of **10**. Ellipsoids are dawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 5
Ring-opening polymerization of ε-caprolactone initiate by aluminum compounds.

Compound	[M]/[I]	Time	Toluene (mL)	Mn	PDI	Yield
2	50	30[a] m	10	7800	1.24	95.1
2	100	30[a] m	20	10,700	1.41	94.5
2	150	20[a] m	20	12,000	1.33	89.4
5	50	24 h	20	8200	1.27	88.9
5	100	24 h	20	11,200	1.26	74.6
5	150	3.5[a] h	20	14,700	1.28	76.4
5	200	2.5[a] h	20	16,200	1.39	80.3
7	50	24 h	20	7600	1.12	33.3
7	100	24 h	20	12,200	1.37	91.0
7	150	3[a] h	20	15,000	1.27	79.9
7	200	2.5[a] h	20	17,300	1.27	87.1

[M]/[I]: the ratio of monomer to initiator in toluene.
[a] Solidified.

4. Conclusion

A simple method was developed to synthesize the reactive aluminum dihydride compound **2**. Compound **2** is a good starting material for the preparation of corresponding amide, alkoxide, and siloxide compounds. The structure of compound **4** represents a novel neutral monomeric dialkynyl aluminum compound, which was stabilized by tridentate-substituted pyrrolyl ligands. The aluminum dialkynyl compound may be useful as an alkynyl transfer reagent in organic synthesis. Further, the dialkynyl groups of **4** act as two π-donating groups, which can react with other transition metals to form a heterobimetallic compound [22,23]. Some of the compounds were catalytically active in the ring-opening polymerization of ε-caprolactone. Steric effect is proposed as the main variable that affected the rate of the polymerization.

Acknowledgments

We thank the National Science Council of Taiwan for the financial support, the National Computing Center for High Performance for databank searching, and the National Changhua University of Education for the X-ray structure analyses.

Appendix. Supplementary material

CCDC 813665, 813666, 813667, 813668, 813669 and 813664 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry, vol. 1, Pergamon, Oxford, U.K., 1982, (Chapter 6).
[2] D.S. Moore, S.D. Robinson, Chem. Soc. Rev. 12 (1983) 415.
[3] J.P. McCue, Coord. Chem. Rev. 10 (1973) 265.
[4] V. Gevorgyan, E. Lukevics, J. Chem. Soc., Chem. Commun. (1985) 1234.
[5] E.C. Ashby, J.R. Sanders, P. Claudy, R.D. Schwartz, Inorg. Chem. 12 (1973) 2860.
[6] R.J. Wehmschulte, P.P. Power, Polyhedron 19 (2000) 1649.
[7] M.G. Gardiner, C.L. Raston, Coord. Chem. Rev. 166 (1997) 1.
[8] M. Ephritikhine, Chem. Rev. 97 (1997) 2193.
[9] C.L. Raston, J. Organomet. Chem. 475 (1994) 15.
[10] L. Contreras, A.H. Cowley, F.P. Gabbaï, R.A. Jones, C.J. Carrano, M.R. Bond, J. Organomet. Chem. 489 (1995) C1–C3.
[11] S. Bensiek, M. Bangel, B. Neumann, H.-G. Stammler, P. Jutzi, Organometallics 19 (2000) 1292.
[12] C. Jones, G.A. Koutsantonis, C.L. Raston, Polyhedron 12 (1993) 1829.
[13] W. Herz, K. Dittmer, S.J. Cristol, J. Am. Chem. Soc. 69 (1947) 1698.
[14] I.T. Kim, R.L. Elsenbaumer, Tetrahedron Lett. 39 (1998) 1087.
[15] J.-H. Huang, P.-C. Kuo, G.-H. Lee, S.-M. Peng, J. Chin. Chem. Soc. 47 (2000) 1191.

[16] J.-H. Huang, L.-S. Chi, F.-M. Huang, P.-C. Kuo, C.-C. Zhou, G.-H. Lee, S.-M. Peng, J. Chin. Chem. Soc. 47 (2000) 895.
[17] J.-H. Huang, L.-S. Chi, R.-C. Yu, G.J. Jiang, W.T. Yang, G.-H. Lee, S.-M. Peng, Organometallics 20 (2001) 5788.
[18] J.-H. Huang, H.-J. Chen, J.-C. Chang, C.-C. Zhou, G.-H. Lee, S.-M. Peng, Organometallics 20 (2001) 2647.
[19] J.-C. Chang, C.-H. Hung, J.-H. Huang, Organometallics 20 (2001) 4445.
[20] W. Zheng, N.C. Mösch-Zanetti, H.W. Roesky, M. Hewitt, F. Cimpoesu, T.R. Schneider, A. Stasch, J. Prust, Angew. Chem. Int. Ed. 39 (2000) 3099.
[21] M. Schiefer, N.D. Reddy, H.-J. Ahn, A. Stasch, H.W. Roesky, A.C. Schlicker, H.-G. Schmidt, M. Noltemeyer, D. Vidovic, Inorg. Chem. 42 (2003) 4970.
[22] H. Zhu, R.B. Oswald, H. Fan, H.W. Roesky, Q. Ma, Z. Yang, H.-G. Schmidt, M. Noltemeyer, K. Starke, N.S. Hosmane, J. Am. Chem. Soc. 128 (2006) 5100.
[23] J. Zhao, H. Song, C. Cui, Organometallics 26 (2007) 1947.
[24] H. Zhu, J. Chai, H. Fan, H.W. Roesky, C. He, V. Jancik, H.-G. Schmidt, M. Noltemeyer, W.A. Merrill, P.P. Power, Angew. Chem. Int. Ed. 44 (2005) 5090.
[25] G.D. Stucky, A.M. McPherson, W.E. Rhine, J.J. Eisch, J.L. Considine, J. Am. Chem. Soc. 96 (1974) 1941.
[26] M.J. Albright, W.M. Butler, T.J. Anderson, M.D. Glick, J.P. Oliver, J. Am. Chem. Soc. 98 (1976) 3995.
[27] M. Albrecht, G. Erker, M. Nolte, C. Krüger, J. Organomet. Chem. 427 (1992) C21.
[28] G. Erker, M. Albrecht, C. Krüeger, M. Nolte, S. Werner, Organometallics 12 (1993) 4979.
[29] M. Schiefer, H. Hatop, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Organometallics 21 (2002) 1300.
[30] N.D. Reddy, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 41 (2002) 2374.
[31] W. Uhl, F. Breher, J. Grunenberg, A. Lützen, W. Saak, Organometallics 19 (2000) 4536.
[32] The hexaphenyldisiloxane is characterized by ^{1}H NMR spectroscopy and X-ray single crystal diffractometry.
[33] A.V. Khvostov, B.M. Bulychev, V.K. Belsky, A.I. Sizov, J. Organomet. Chem. 568 (1998) 113.
[34] Y.K. Gun'ko, B.M. Bulychev, V.K. Belsky, G.L. Soloveichik, J. Organomet. Chem. 440 (1992) 47.
[35] W. Zheng, H.W. Roesky, J. Chem. Soc., Dalton Trans. (2003) 2787.
[36] S. Daniel, D.M. Hoffman, Inorg. Chem. 41 (2002) 3843.
[37] W.-Y. Chen, C. Eaborn, I.B. Gorrell, P.B. Htichcock, J.D. Smith, J. Chem. Soc., Dalton Trans. (2000) 2313.
[38] J. Knizek, H. Nöth, A. Schlegel, Eur. J. Inorg. Chem. (2001) 181.
[39] K.M. Waggoner, K. Ruhlandt-Senge, R.J. Wehmschulte, X. He, M.M. Olmstead, P.P. Power, Inorg. Chem. 32 (1993) 2557.
[40] X.-W. Li, J. Su, G.H. Robinson, Chem. Commun. (1998) 1281.
[41] T. Bauer, S. Schulz, H. Hupfer, M. Nieger, Organometallics 21 (2002) 2931.
[42] D. Rutherford, D.A. Atwood, J. Am. Chem. Soc. 118 (1996) 11535.
[43] M.L. Montero, H. Wessl, H.W. Roesky, M. Teichert, I. Usón, Angew. Chem. Int. Ed. 36 (1997) 629.
[44] M.A. Beswick, N. Choi, C.N. Harmer, M. McPartlin, M.E.G. Mosquera, P.R. Raithby, M. Tombul, D.S. Wright, Chem. Commun. (1998) 1383.
[45] H. Zhu, Z. Yang, J. Magull, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Organometallics 24 (2005) 6420.
[46] D.A. Atwood, M.S. Hill, J.A. Jegier, D. Rutherford, Organometallics 16 (1997) 2659.
[47] S.J. Obrey, S.G. Bott, A.R. Barron, Organometallics 20 (2001) 5119.
[48] A.G. Avent, C. Eaborn, I.B. Gorrell, P.B. Hitchcock, J.D. Smith, J. Chem. Soc., Dalton Trans. (2002) 3971.
[49] C.-Y. Lin, H.M. Lee, J.H. Huang, J. Organomet. Chem. 692 (2007) 3718.
[50] Ph. Lecomte, F. Stassin, R. Jerome, Macromol. Sym. 215 (2004) 325.
[51] S. Agarwal, C. Mast, K. Dehnicke, A. Greiner, Macromol. Rapid Commun. 21 (2000) 195.
[52] W.M. Stevels, P.J. Dijkstra, J. Feijen, Trends Polym. Sci. 5 (1997) 300.
[53] S. Gong, H. Ma, Dalton Trans. (2008) 3345.
[54] A. Kowalski, J. Libiszowski, K. Majerska, A. Duda, S. Penczek, Polymer 48 (2007) 3952.
[55] S. Dagorne, F. Le Bideau, R. Welter, S. Bellemin-Laponnaz, A. Maisse-Francois, Chem. Eur. J. 13 (2007) 3202.
[56] T. Muraki, K. Fujita, A. Oishi, Y. Taguchi, Polym. J. 37 (2005) 847.
[57] J. Lewinski, P. Horeglad, K. Wojcik, I. Justyniak, Organometallics 24 (2005) 4588.
[58] L.M. Alcazar-Roman, B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, Dalton Trans. (2003) 3082.
[59] T.-C. Liao, Y.-L. Huang, B.-H. Huang, C.-C. Lin, Macromol. Chem. Phys. 204 (2003) 885.
[60] T.-L. Yu, C.-H. Huang, L.-F. Yang, B.-T. Ko, C.-C. Lin, J. Chin. Chem. Soc. 47 (2000) 1185.
[61] P. Dubois, I. Barakat, R. Jerome, P. Teyssie, Macromolecules 26 (1993) 4407.
[62] K.-C. Hsieh, W.-Y. Lee, L.-F. Hsueh, H.M. Lee, J.-H. Huang, Eur. J. Inorg. Chem. (2006) 2306.
[63] P.W. Roesky, M.T. Gamer, M. Puchner, A. Greiner, Chem. Eur. J. 8 (2002) 5265.
[64] R.-C. Yu, C.-H. Hung, J.-H. Huang, H.-Y. Lee, J.-T. Chen, Inorg. Chem. 41 (2002) 6450.
[65] Bruker, SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
[66] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112.
[67] Bruker, SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA, 2010.