

行政院國家科學委員會專題研究計畫 期中進度報告

含雙陰離子吡咯與酮胺配位基之有機金屬錯合物的合成、鑑定、反應及應用(1/3)

計畫類別：個別型計畫

計畫編號：NSC93-2113-M-018-005-

執行期間：93年08月01日至94年07月31日

執行單位：國立彰化師範大學化學系暨研究所

計畫主持人：黃瑞賢

報告類型：精簡報告

報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫可公開查詢

中 華 民 國 94 年 4 月 14 日

含雙陰離子鋁咯與酮胺配位基之有機金屬錯合物的合成、鑑定、反應及應用(1/3)

計畫編號 93-2113-M-018-005-

國立彰化師範大學化學系暨研究所 黃瑞賢

(含出國報告)

Synthesis, reactivity, and structures of dialuminum complexes containing linked ketiminate ligands

Jui-Hsien Huang(黃瑞賢)

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

Taiwan 50058

Keyword: dialuminum, linked ketiminate, diboron, aluminum iodo

Abstract

Linked bis(ketimine) (**1**) can be prepared with the reaction of excess 2,4-pentandione and 4,4'-methylene-bis(2,6-diisopropylaniline) in methanol with small amount of formic acid as catalysts. The dialuminum alkyl complexes containing the linked bis(ketiminate) dianionic ligands, $[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2\text{-4})\text{AlR}_2]_2\text{CH}_2$ (**2**, **R=Me**; **3**, **R=Et**), were prepared by a reaction of 2 equiv AlR_3 with $[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{NH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2\text{-4})]_2\text{CH}_2$ in methylene chloride. Reactions of **2** with 2 and 4 equiv of I_2 gave corresponding aluminum iodo complexes **4** and **5**, respectively. Treatment of **5** with 2 equiv of AgBF_4 , however, gave a diboron complex, $[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2\text{-4})\text{BF}_2]_2\text{CH}_2$ (**6**) in 18 % isolated yield. All new complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and complexes **2**, **3**, and **6** are also confirmed by X-ray diffraction.

1. Introduction

Dinuclear transition metal complexes are rather common and may be useful for acting as catalysts [1-3] or metalloenzymes. [4-6] Among those, dinuclear metal complexes with bis-multidentate ligands, which contain two anionic ancillary ligands linked by a bridge, have been studied [7-14] because of their potential usage as two-center Lewis acid catalysts. Among that, group 13 dimetallic complexes containing bis-bidentate ligands have also been reported by Atwood et al. [15-16] The bis-bidentate ligands used in the dialuminum chemistry are mainly of the Salen classes bridged with backbones such as 1,4-butylene, 1,4-phenylene, and 1,2-cyclohexylene etc. The studies of the aluminum complexes with mono anionic bidentate ketiminate ligands have been reported. [17] Here we report the syntheses and characterization of dialuminum complexes containing linked bis(ketiminate) ligands and their related reactions.

2. Results and Discussion

2.1. *Synthesis and characterization*

Linked bis(ketimine) (**1**) can be prepared easily by modifying the published procedure [18] with the reaction of excess (> 2 equiv) 2,4-pentandione and 4,4'-methylene-bis(2,6-diisopropylaniline) in methanol with small amount of formic

acid as catalysts (scheme 1). The excess 2,4-pentandione can be removed under vacuum at elevated temperature to generate a pure bis(ketimine) ligand **1** in high yield. ^1H NMR spectrum of **1** reveals that the methylene protons between two phenyl rings appear at δ 3.97; while the methine proton of the ketiminate backbone appears at δ 5.18, which serve as an excellent indicator for evaluating the purity of the metal complexes.

Scheme 1 here

Treatment of **1** with two equiv of AlMe_3 and AlEt_3 in a methylene chloride solution generates the dialuminum complexes **2** and **3**, respectively, in high yield (Scheme 2). The reactions were proceeding along with the elimination of two equiv of methane or ethane. The complexes have been characterized by ^1H and ^{13}C NMR spectra, and X-ray structure determination. For both complexes **2** and **3**, ^1H NMR spectra exhibit one methine resonance and two methyl resonances for the isopropyl fragments, which is consistent with fast ring inversion and slow aryl rotation. [17] Moreover, the ^1H NMR spectra of the methine protons of the ketiminate backbones of **2** and **3** exhibit one singlet at δ 5.33 and 5.32, respectively. The AlMe_2 fragments of complex **2** appears as a singlet at δ -0.94 and the AlEt_2 of complex **3** exhibits one set triplet and multiplet at δ -0.22 and 0.84 for the CH_2 and CH_3 fragments. These data indicate symmetric structures for both complex **2** and **3**.

Scheme 2 here

Reactions of **2** with 2 and 4 equiv of iodine yield the expected aluminum methyl iodo complex **4** and aluminum diiodo complex **5**, respectively (Scheme 2). Complexes **4** and **5** have been characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The methine proton resonances of ketimate backbone for complexes **4** and **5** are shown as single resonance at δ 4.00 and 4.01, respectively. Complex **4** remains a C_2 symmetry through the bridged CH_2 fragment, however, the isopropyl groups of the phenyl rings exhibit asymmetrical geometry due to the unsymmetrical coordination geometry of the aluminum center. These phenomena can be seen from the ^{13}C NMR spectra showing more complicate phenyl and isopropyl resonances.

Attempts to remove the iodide of complex **5** to yield cationic aluminum center by adding AgBF_4 have resulted an unexpected di-borane complex **6** with 18 % isolated yield (Scheme 3). ^1H and ^{13}C NMR spectra proved the existence of the linked ketimate ligands and ^{11}B NMR spectrum also indicate the presence of boron in complex **6**. The ^{11}B NMR spectrum exhibits a triplet at δ 0.67 relative to the standard of $\text{BF}_3\cdot\text{OEt}_2$ showing the coupling of $J_{\text{BF}} = 15.4$ Hz.

Scheme 3 here

2.2. *Molecular structures of complexes 2, 3, and 6.*

A crystal structure determination of **2** confirms the bimetallic nature of the complex. The colorless crystals of **2** were obtained by cooling a saturated diethyl ether solution at $-20\text{ }^{\circ}\text{C}$. The molecular structure of **2** and selected bond distances and angles are shown in Figure 1 and Table 1, respectively. As expected, both the aluminum atoms in complex **2** are surrounded by two methyl groups and one bidentate ketiminate ligand forming a tetrahedral geometry. The biting angles of ketiminate ligands, $\text{N}(1)\text{-Al}(1)\text{-O}(1)$ (which is $94.58(17)^{\circ}$), is smaller than a regular tetrahedral bond angle of 109.28° . The backbone of ketiminate, $\text{O}(1)\text{-C}(3)\text{-C}(4)\text{-C}(5)\text{-N}(1)$, forms a plane and the aluminum atom is deviated from the plane at 0.5821 \AA . A large dihedral angle (98.5°) is observed between the phenyl ring and the ketiminate backbone plane, suggesting minimal steric interaction exists between the aluminum methyl groups and the phenyl rings in the solid state. In viewing half part of the molecular structure of **2**, it is similar to that of $(\text{OCMeCHCMeNAr})\text{AlMe}_2$. [17]

Figure 1 and Table 1 here

Crystals of **3** were obtained from a concentrated diethyl ether solution at $-20\text{ }^{\circ}\text{C}$. The molecular structure of **3** is shown in Figure 2 and selected bond distances and angles are listed in Table 1.

Figure 2 here

Crystals of **6** suitable for X-ray structure determination were directly obtained

from sublimation of solids. Due to the small molecule size, some of the high angle reflection data were omitted. The molecular structure of **6** is shown in Figure 3 and selected bond distances and angles are listed in Table 1. Complex **6** is consistent with a C_2 symmetry with two boron atoms located on the two ketiminate fragments. Each boron atom is surrounded by two fluorine atoms and one ketiminate fragments forming a tetrahedral geometry. The two B–F bond distances (ca. 1.36 Å) are similar to reported bidentate ligand chelated BF_2 complexes. [19-20] The ketiminate fragment chelates to the boron atom with an angle of 109.8(3), similar to the bond angles of tetrahedral geometry.

Figure 3 here

3. Conclusions

In conclusion, the synthesis of a linked bis(ketimine) ligand is described. Reactions of the bis(ketimine) with $AlMe_3$ yield a new type of dialuminum alkyl complex **2**, which can be converted to corresponding aluminum iodo complexes by adding various amount of I_2 . A diboron compound, $[OC(Me)CHC(Me)N(2,6-{}^iPr_2C_6H_2-4)BF_2]_2CH_2$ (**6**), can be obtained from the reaction of **2** with 2 equiv of $AgBF_4$ via metal exchange. A further study of aluminum hydride complexes containing this bis(ketiminate) ligands is currently undergoing.

4. Experimental Section

4.1. General Procedures.

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5 . All solvents were distilled and stored in solvent reservoirs which contained 4Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of CDCl_3 (δ 7.24, 77.0) and C_6D_6 (δ 7.15, 128.0). ^{11}B NMR spectra were recorded on a Bruker Avance 300 M Hz spectrometer with $\text{BF}_3\cdot\text{OEt}_2$ as reference at δ 0 ppm. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU.

4.2. Synthesis of $[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{NH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2\text{-}4)]_2\text{CH}_2$ (1)

Excess 2, 4-pentanedione (6.0 g, 60.0 mmol) and 4,4'-methylenebis-(2,6-diisopropylaniline) (10 g, 27.3 mmol) were placed in a flask and dissolved in 50 mL methanol. Small amount of formic acid was added as

catalyst. The mixture was stirred at room temperature for 12 h and volatiles were removed under vacuum to generate 14.4 g pale yellow solids in 99.4% yield. ^1H NMR (CDCl_3): δ 1.07 (d, 12H, CHMe_2), 1.14 (d, 12H, CHMe_2), 1.62 (s, 6H, CMe), 2.09 (s, 6H, CMe), 2.95 (m, 4H, CHMe_2), 3.97 (s, 2H, CH_2), 5.18 (s, 2H, CMeCHCMe), 6.93 (s, 4H, Ph), 11.92 (s, br, 2H, NH). ^{13}C NMR (CDCl_3): δ 19.1 (q, $J_{\text{CH}} = 128$ Hz, CH_3), 22.6 (q, $J_{\text{CH}} = 126$ Hz, CH_3), 24.4 (q, $J_{\text{CH}} = 127$ Hz, CH_3), 28.3 (d, $J_{\text{CH}} = 128$ Hz, CHMe_2), 28.6 (q, $J_{\text{CH}} = 126$ Hz, CH_3), 41.5 (t, $J_{\text{CH}} = 127$ Hz, CH_2), 95.6 (d, $J_{\text{CH}} = 161$ Hz, CMeCHCMe), 124.0 (d, $J_{\text{CH}} = 155$ Hz, phenyl CH), 131.2 (s, phenyl C_{ipso}), 140.5 (s, phenyl C_{ipso}), 145.9 (s, phenyl C_{ipso}), 164.2 (s, CN), 195.8 (s, CO). Anal. Calcd. for $\text{C}_{35}\text{H}_{50}\text{N}_2\text{O}_2$: C, 79.20; H, 9.49; N, 5.28. Found: C, 79.07; H, 9.91; N, 5.22.

4.3. Synthesis of $[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_2\text{-}4)\text{AlMe}_2]_2\text{CH}_2$ (**2**)

A solution of trimethylaluminum (2M in toluene, 18.87 mL, 37.74 mmol) was added dropwise at 0 °C to a stirred solution of **1** (10.0 g, 18.87 mmol) in methylene chloride (70 mL). The resulting solution was stirred at room temperature for 5 h. Volatiles were removed under vacuum to generate 12.0 g of yellow solids in 98 % yield. Colorless crystals of **2**, which are suitable for x-ray structure determination, can be obtained from a saturated diethyl ether solution. ^1H NMR (CDCl_3): δ -0.94 (s, 12H, AlMe_2), 1.03 (d, 12H, CHMe_2), 1.12 (d, 12H, CHMe_2), 1.75 (s, 6H, CMe), 2.07 (s, 6H,

CMe), 2.87 (m, 4H, *CHMe*₂), 3.99 (s, 2H, *CH*₂), 5.33 (s, 2H, *CMeCHCMe*), 6.90 (s, 4H, Ph). ¹³C NMR (CDCl₃): -11.1 (q, J_{CH} = 112 Hz, *AlMe*₂), 23.1 (q, J_{CH} = 129 Hz, *CMe*), 24.4 (q, J_{CH} = 129 Hz, *CHMe*), 24.6 (q, J_{CH} = 129 Hz, *CHMe*), 25.8 (q, J_{CH} = 128 Hz, *CMe*), 27.9 (d, J_{CH} = 132 Hz, *CHMe*₂), 41.0 (t, J_{CH} = 130 Hz, *CH*₂), 100.5 (d, J_{CH} = 162 Hz, *CMeCHCMe*), 124.9 (d, J_{CH} = 154 Hz, phenyl CH), 136.9 (s, phenyl *C_{ipso}*), 139.4 (s, phenyl *C_{ipso}*), 142.7 (s, phenyl *C_{ipso}*), 176.3 (s, CN), 180.7 (s, CO).
Anal. Calcd. for C₃₉H₆₀N₂O₂Al₂: C, 72.86; H, 9.41; N, 4.36. Found: C, 72.19; H, 9.04; N, 4.27.

4.4. Synthesis of [OC(*Me*)CHC(*Me*)N(2,6-*i*-Pr₂C₆H₂-4)AlEt₂]₂CH₂ (**3**)

A solution of triethylaluminum (1.9 M in toluene, 9.93 mL, 18.87 mmol) was added dropwise at 0 °C to a stirred solution of **1** (5.0 g, 9.43 mmol) in methylene chloride (50 mL). The resulting solution was stirred at room temperature for 12 h. Volatiles were removed under vacuum to generate yellow solids; which were recrystallized from a diethyl ether solution to yield 6.45 g pale yellow solids in 98 % yield. ¹H NMR (CDCl₃): -0.23 (m, 8H, AlCH₂CH₃), 0.84 (t, 12H, AlCH₂CH₃), 1.05 (d, 12H, *CHMe*₂), 1.16 (d, 12H, *CHMe*₂), 1.75 (s, 6H, *CMe*), 2.09 (s, 6H, *CMe*), 2.89 (m, 4H, *CHMe*₂), 3.99(s, 2H, *CH*₂), 5.31 (s, 2H, *CMeCHCMe*), 6.93 (s, 4H, Ph). ¹³C NMR (CDCl₃): δ -1.1 (t, J_{CH} = 111 Hz, AlCH₂CH₃), 8.9 (qt, J_{CH} = 124 Hz, ²J_{CH} = 5 Hz, AlCH₂CH₃), 23.0 (q, J_{CH} = 129 Hz, *CMe*), 24.2 (q, J_{CH} = 126 Hz, *CHMe*), 24.6 (q, J_{CH}

= 126 Hz, CHMe), 25.7 (q, $J_{\text{CH}} = 128$ Hz, CMe), 27.8 (d, $J_{\text{CH}} = 129$ Hz, CHMe), 41.1 (t, $J_{\text{CH}} = 127$ Hz, CH₂), 100.6 (d, $J_{\text{CH}} = 162$ Hz, CMeCHCMe), 124.9 (d, $J_{\text{CH}} = 154$ Hz, phenyl CH), 137.1 (s, phenyl *C_{ipso}*), 139.5 (s, phenyl *C_{ipso}*), 142.7 (s, phenyl *C_{ipso}*), 176.4 (s, CN), 181.2 (s, CO).

4.5. Synthesis of [OC(Me)CHC(Me)N(2,6-*i*Pr₂C₆H₂-4)AlMe]₂CH₂ (4)

To a 50 mL Schlenk flask containing **1** (3.6 g, 5.6 mmol) was added 20 mL toluene and iodine (2.9 g, 11.4 mmol) and heated at 100 °C for 48 h. Volatiles were removed under vacuum and the resulting yellow-brown solid was recrystallized from toluene to yield 4.50 g of yellow brown solids (yield 93%). ¹H NMR (CDCl₃): δ -0.55 (s, 6H, AlMe), 0.97 (d, 6H, CHMe₂), 1.07~1.17 (m, 18H, CHMe₂), 1.84 (s, 6H, CMe), 2.14 (s, 6H, CMe), 2.66 (m, 2H, CHMe₂), 3.25 (m, 2H, CHMe₂), 4.00 (s, 2H, CH₂), 5.65 (s, 2H, CMeCHCMe), 6.90 (s, 2H, Ph), 6.97 (s, 2H, Ph). ¹³C NMR (CDCl₃): δ -7.5 (q, $J_{\text{CH}} = 116$ Hz, AlMe₂), 23.2 (q, $J_{\text{CH}} = 128$ Hz, CHMe₂), 23.4 (q, $J_{\text{CH}} = 128$ Hz, CMe), 24.1 (q, $J_{\text{CH}} = 128$ Hz, CHMe₂), 24.7 (q, $J_{\text{CH}} = 126$ Hz, CHMe₂), 25.7 (q, $J_{\text{CH}} = 128$ Hz, CMe), 26.8 (q, $J_{\text{CH}} = 126$ Hz, CHMe₂), 28.0 (d, $J_{\text{CH}} = 128$ Hz, CHMe₂), 28.4 (d, $J_{\text{CH}} = 128$ Hz, CHMe₂), 40.9 (t, $J_{\text{CH}} = 127$ Hz, CH₂), 102.6 (d, $J_{\text{CH}} = 163$ Hz, CMeCHCMe), 124.9 (d, $J_{\text{CH}} = 155$ Hz, phenyl CH), 125.4 (d, $J_{\text{CH}} = 155$ Hz, phenyl CH), 135.4 (s, phenyl *C_{ipso}*), 140.0 (s, phenyl *C_{ipso}*), 142.5 (s, phenyl *C_{ipso}*), 143.7 (s, phenyl *C_{ipso}*), 178.7 (s, CN), 181.7 (s, CO). Anal. Calcd. For C₃₇H₅₄N₂O₂Al₂I₂: C, 51.28; H, 6.28;

N, 3.23. Found: C, 49.94; H, 6.12; N, 3.42.

4.6. Synthesis of $[OC(Me)CHC(Me)N(2,6\text{-}i\text{Pr}_2C_6H_2\text{-}4)AlI_2]_2CH_2$ (**5**)

By a similar procedure, the reaction of **2** (3.6 g, 5.6 mmol) with I_2 (5.8 g, 22.8 mmol) in toluene gave brown solids **4** in 98 % yield (6.0 g). 1H NMR ($CDCl_3$): δ 1.04 (d, 12H, $CHMe_2$), 1.21 (d, 12H, $CHMe_2$), 1.91 (s, 6H, CMe), 2.20 (s, 6H, CMe), 2.95 (m, 2H, $CHMe_2$), 4.01 (s, 2H, CH_2), 5.75 (s, 2H, $CMeCHCMe$), 6.96 (s, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 24.5 (q, $J_{CH} = 126$ Hz, CMe), 24.6 (q, $J_{CH} = 126$ Hz, $CHMe$), 25.4 (q, $J_{CH} = 127$ Hz, $CHMe$), 25.8 (q, $J_{CH} = 129$ Hz, CMe), 28.7 (d, $J_{CH} = 128$ Hz, $CHMe_2$), 41.1 (t, $J_{CH} = 130$ Hz, CH_2), 103.3 (d, $J_{CH} = 162$ Hz, $CMeCHCMe$), 125.5 (d, $J_{CH} = 154$ Hz, phenyl CH), 135.1 (s, phenyl C_{ipso}), 140.6 (s, phenyl C_{ipso}), 143.3 (s, phenyl C_{ipso}), 180.3 (s, CN), 182.5 (s, CO). Anal. Calcd. For $C_{35}H_{48}N_2O_2Al_2I_4$: C, 38.56; H, 4.44; N, 2.57. Found: C, 38.10; H, 4.38; N, 2.43.

4.7. Synthesis of $[OC(Me)CHC(Me)N(2,6\text{-}i\text{Pr}_2C_6H_2\text{-}4)BF_2]_2CH_2$ (**6**)

To a 50 mL Schlenk flask containing **4** (0.5 g, 0.46 mmol) and $AgBF_4$ (0.18 g, 0.92 mmol) was added 20 mL toluene and heated at 90 °C for 8 h. The solution was filtered through Celite and volatiles were removed under vacuum. The resulting solids were recrystallized from a toluene solution to generate 0.050 g of yellow solids in 18% yield. 1H NMR ($CDCl_3$): δ 1.07 (d, 12H, $CHMe_2$), 1.20 (d, 12H, $CHMe_2$), 1.82 (m, THF), 1.88 (s, 6H, CMe), 2.19 (s, 6H, CMe), 2.80 (m, 2H, $CHMe_2$), 3.72 (m,

THF), 3.96 (s, 2H, CH₂), 5.56 (s, 2H, CMeCHCMe), 7.02 (s, 4H, Ph). ¹³C NMR (CDCl₃): δ 21.2 (q, J_{CH} = 129 Hz, CMe), 22.8 (q, J_{CH} = 130 Hz, CMe), 24.2 (q, J_{CH} = 132 Hz, CHMe), 24.5 (q, J_{CH} = 126 Hz, CHMe), 28.3 (d, J_{CH} = 131 Hz, CHMe₂), 41.6 (t, J_{CH} = 132 Hz, CH₂), 67.9 (t, THF), 98.7 (d, J_{CH} = 168 Hz, CMeCHCMe), 124.9 (d, J_{CH} = 153 Hz, phenyl CH), 132.5 (s, phenyl C_{ipso}), 140.8 (s, phenyl C_{ipso}), 144.6 (s, phenyl C_{ipso}), 172.9 (s, CN), 176.8 (s, CO). ¹¹B NMR (CDCl₃): δ 0.67 (t, J_{BF} = 15.4 Hz). MS (FAB): 607 (M–F), 320 (M–306)

4.8. X-Ray structure determination of complexes 2, 3, and 6.

Crystals of complex **2** were obtained from a concentrated diethyl ether solution of **2** at –20 °C. Crystals of **6** were obtained directly from the sublimation of viscous complex **6** by storing it in glove box. Crystals of **2** and **6** were mounted on a goniostat and data collections were preceded at 150(2) K and data of crystal of **3** were collected at 298(2) K. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo K_α 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 2.

Acknowledgments

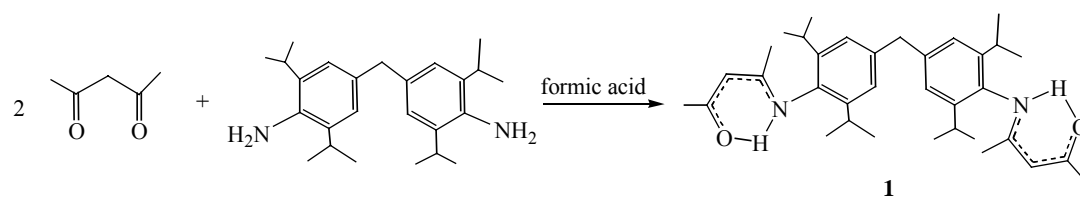
We thank the National Science Council of Taiwan for financial support and the National Center for High Performance Computing for databank search.

References

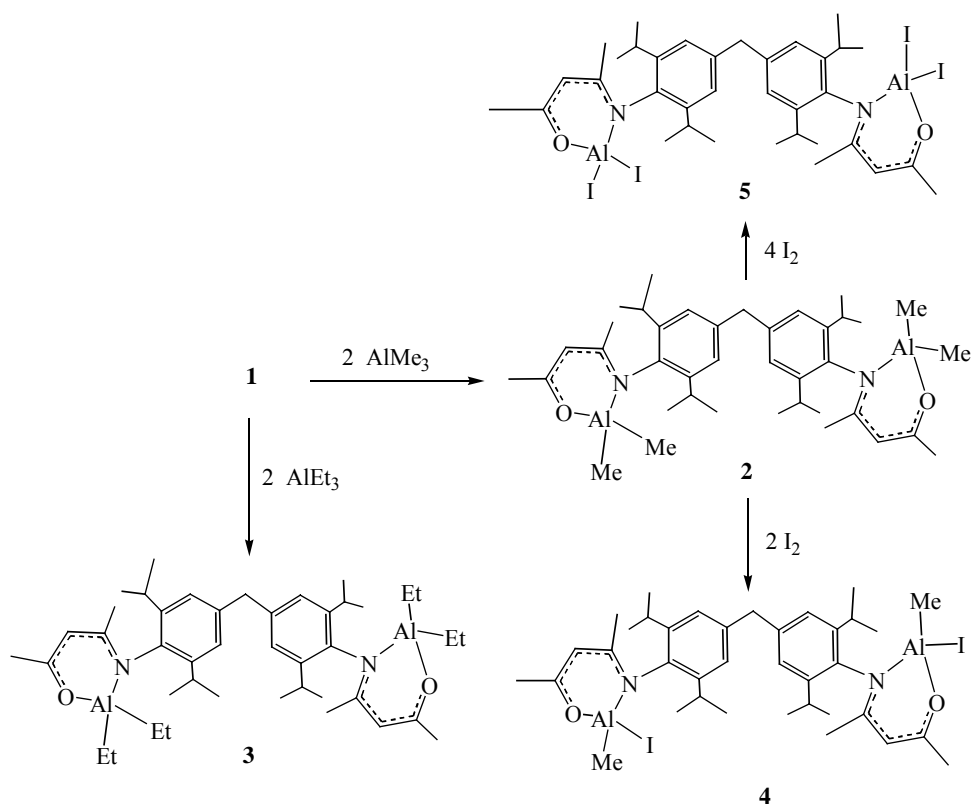
1. C. P. Casey, J. D. Audett, *Chem. Rev.* 86 (1986) 339–352.
2. J. Holton, M. F. Lappert, R. Pearce, P. I. W. Yarrow, *Chem. Rev.* 83 (1983) 135–201.
3. D. Zhang, G. -X. Jin, *Organometallics* 22 (2003) 2851–2854.
4. N. H. Williams, B. Takasaki, M. Wall, J. Chin, *Acc. Chem. Res.* 32 (1999) 485–493.
5. B. J. Wallar, J. D. Lipscomb, *Chem. Rev.* 96 (1996) 2625–2657.
6. B. Bosnich, *Inorg. Chem.* 38 (1999) 2554–2562.
7. S. A. Schuetz, V. W. Day, A. L. Rheingold, J. A. Belot, *J. Chem. Soc. Dalton Trans.* (2003) 4303–4306.
8. Y. Kasahara, Y. Hoshino, M. Kajitani, K. Shimizu, G. P. Sato, *Organometallics* 11 (1992) 1968–1971.
9. Z. Li, C. Jablonski, *Inorg. Chem.* 39 (2000) 2456–2461.
10. C. Incarvito, A. L. Rheingold, C. J. Qin, A. L. Gavrilova, B. Bosnich, *Inorg. Chem.*

- 40 (2001) 1386–1390.
11. P. E. Kruger, N. Martin, M. Nieuwenhuyzen, *J. Chem. Soc. Dalton Trans.* (2001) 1966–1970.
12. N. Yoshida, H. Oshio, T. Ito, *Chem. Commun.* (1998) 63–64.
13. N. Yoshida, K. Ichikawa, *Chem. Commun.* (1997) 1091–1092.
14. D. A. Atwood, M. J. Harvey, *Chem. Rev.* 101 (2001) 37–52.
15. M. S. Hill, P. Wei, D. A. Atwood, *Polyhedron* 17 (1998) 811–819.
16. M. A. van Aelstyn, T. S. Keizer, D. L. Klopotek, S. Liu, M. –A. Munoz-Hernandez, P. Wei, D. A. Atwood, *Organometallics* 19 (2000) 1796–1801.
17. R. –C. Yu, C. –H. Hung, J. –H. Huang, H. –Y. Lee, J. –T. Chen, *Inorg. Chem.* 41 (2002) 6450–6455.
18. J. E. Parks, R. H. Holm, *Inorg. Chem.* 7 (1968) 1408–1416.
19. J. Chen, A. Burghart, C. –W. Wan, L. Thai, C. Ortiz, J. Reibenspies, K. Burgess, *Tetrahedron Lett.* 41 (2000) 2303–2307.
20. J. Chen, A. Burghart, A. Derecskei-Kovacs, K. Burgess, *J. Org. Chem.* 65 (2000) 2900–2906.

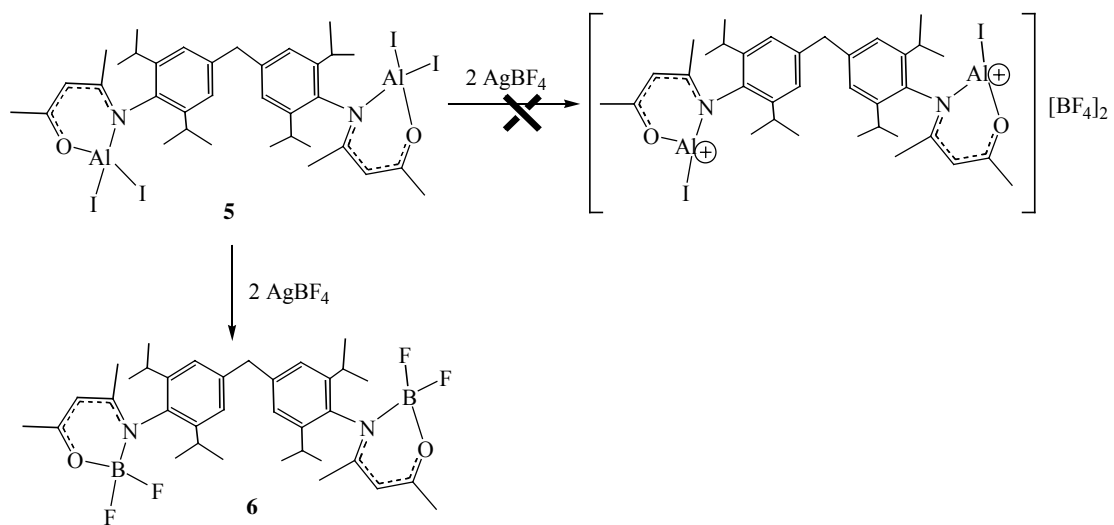
Scheme 1.



Scheme 2



Scheme 3



Captions to figures

Figure 1. The molecular structure of complex **2**. Thermal ellipsoids were drawn at 30 % probability and all hydrogen atoms were omitted for clarity.

Figure 2. The molecular structure of complex **3**. Thermal ellipsoids were drawn at 30 % probability and all hydrogen atoms were omitted for clarity.

Figure 3. The molecular structure of complex **6**. Thermal ellipsoids were drawn at 30 % probability and all hydrogen atoms were omitted for clarity.

Figure 1

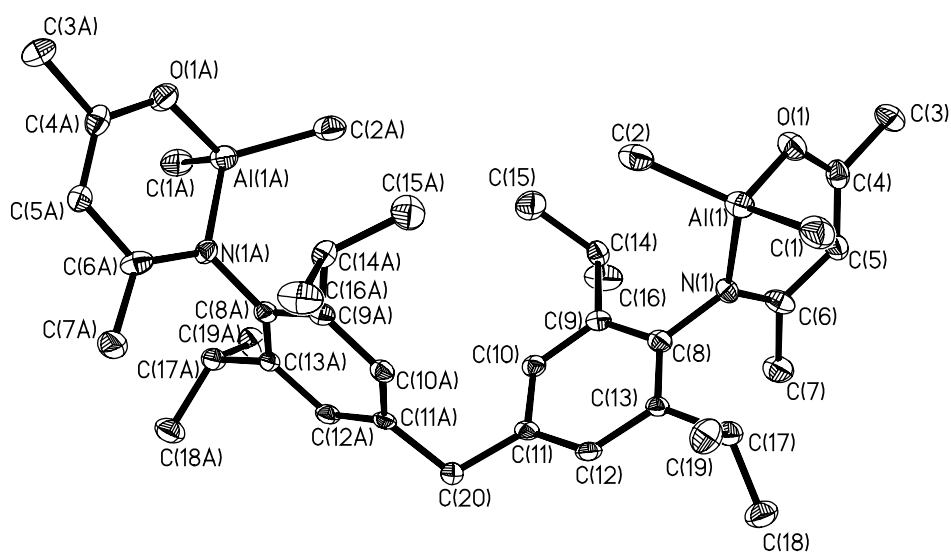


Figure 2.

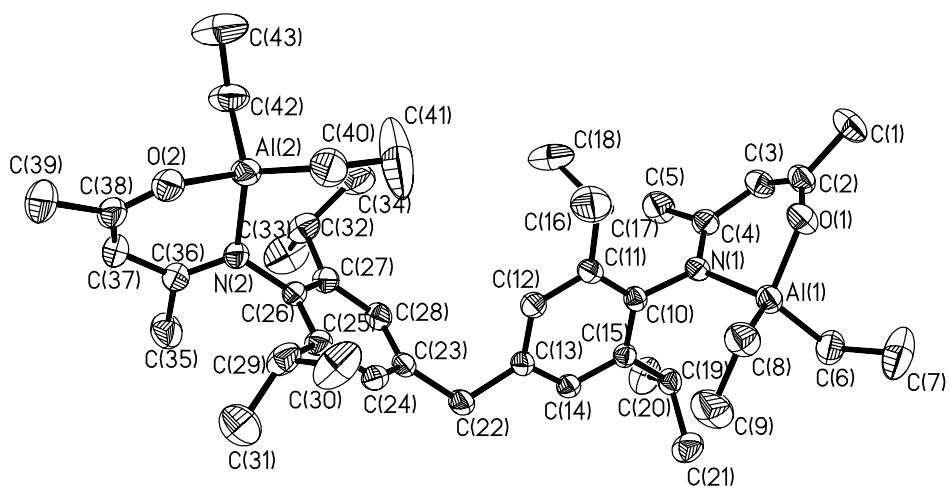


Figure 3

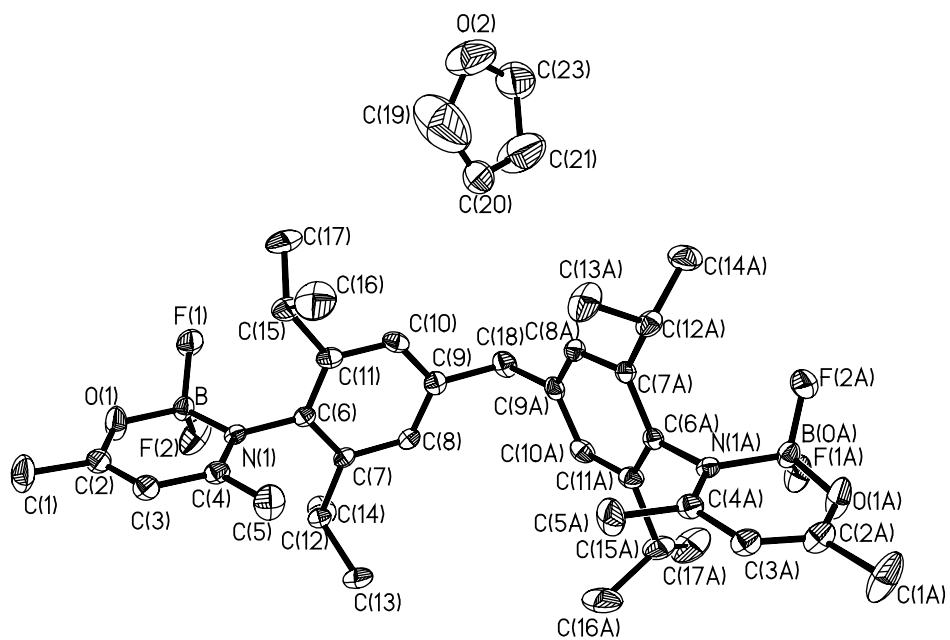


Table 1. Selected bond distances and angles of complexes 2, 3, and 6

2			
Al(1)–O(1)	1.784(4)	Al(1)–N(1)	1.934(4)
Al(1)–C(1)	1.972(6)	Al(1)–C(2)	1.937(5)
O(1)–C(4)	1.305(5)	N(1)–C(6)	1.334(5)
C(3)–C(4)	1.511(6)	C(4)–C(5)	1.355(6)
O(1)–Al(1)–N(1)	94.58(17)	O(1)–Al(1)–C(2)	111.8(2)
N(1)–Al(1)–C(2)	111.6(2)	O(1)–Al(1)–C(1)	107.9(2)
N(1)–Al(1)–C(1)	111.3(2)	C(2)–Al(1)–C(1)	117.3(2)
3			
Al(1)–O(1)	1.7990(18)	Al(1)–N(1)	1.9356(19)
Al(1)–C(8)	1.955(3)	Al(1)–C(6)	1.962(3)
Al(2)–O(2)	1.7957(18)	Al(2)–N(2)	1.9316(19)
Al(2)–C(40)	1.948(3)	Al(2)–C(42)	1.964(3)
N(1)–C(4)	1.317(3)	N(1)–C(10)	1.463(3)
N(2)–C(36)	1.316(3)	N(2)–C(26)	1.453(2)
O(1)–C(2)	1.303(3)	O(2)–C(38)	1.303(3)
C(2)–C(3)	1.354(3)	C(3)–C(4)	1.427(3)
C(37)–C(38)	1.361(3)	C(36)–C(37)	1.423(3)

O(1)–Al(1)–N(1)	93.26(8)	O(1)–Al(1)–C(8)	111.53(10)
N(1)–Al(1)–C(8)	113.03(11)	O(1)–Al(1)–C(6)	107.63(11)
N(1)–Al(1)–C(6)	112.21(10)	C(8)–Al(1)–C(6)	116.62(13)
O(2)–Al(2)–N(2)	94.26(8)	O(2)–Al(2)–C(40)	109.20(13)
N(2)–Al(2)–C(40)	114.77(11)	O(2)–Al(2)–C(42)	118.39(15)
N(2)–Al(2)–C(42)	108.83(11)	C(40)–Al(2)–C(42)	118.39(15)

6

B–O(1)	1.462(5)	B–N(1)	1.572(5)
B–F(1)	1.367(5)	B–F(2)	1.365(5)
N(1)–C(4)	1.313(4)	O(1)–C(2)	1.311(5)
C(2)–C(3)	1.344(6)	C(3)–C(4)	1.412(5)
O(1)–B–N(1)	109.8(3)	F(2)–B–O(1)	110.0(3)
F(2)–B–N(1)	109.6(3)	F(1)–B–O(1)	108.6(3)
F(1)–B–N(1)	110.0(3)	F(2)–B–F(1)	108.9(3)

Table 2. The summary of crystallographic data for complexes 2, 3, and 6.THF

	2	3	6.THF
Empirical formula	C ₃₉ H ₆₀ Al ₂ N ₂ O ₂	C ₄₃ H ₆₈ Al ₂ N ₂ O ₂	C ₄₃ H ₆₄ B ₂ F ₄ N ₂ O ₃
Formula weight	642.85	698.95	754.58
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /c	C2/c
a, Å	26.197(15)	17.5663(12)	25.446(9)
b, Å	8.897(5)	14.5083(10)	6.951(2)
c, Å	16.620(9)	17.5663(12)	25.287(8)
β, °	97.177(12)	90.0170(10)	90.931(11)
Volume, Å ³ / Z	3843(4) / 4	4421.6(5) / 4	4472(3) / 4

Density (cald.), Mg/m ³	1.111	1.050	1.121
Absorption coefficient	0.109 mm ⁻¹	0.099	0.080 mm ⁻¹
F(000)	1400	1528	1624
Crystal size	0.33 x 0.29 x 0.26 mm	0.65 x 0.53 x 0.45 mm	0.31 x 0.77 x 0.26 mm
θ range for data collection	2.42 to 27.65°	1.17 to 27.54°	2.25 to 24.00°
Reflections collected	11858	27426	11394
Independent reflections	4398 (R _{int} = 0.1669)	11095 (R _{int} = 0.0673)	3490 (R _{int} = 0.0952)
Max. and min. transmission	0.9486 and 0.5667		
Data / restraints / parameters	4398 / 01 / 208	10095 / 01 / 458	3490 / 0 / 249
Goodness-of-fit on F ²	0.675	0.729	1.009
R indices [I>2σ(I)]	R1=0.0725, wR2=0.1521	R1=0.0456, wR2=0.1076	R1=0.0865, wR2=0.2397

R indices (all data)	R1=0.2637, wR2=0.1933	R1=0.1304, wR2=0.1359	R1=0.1168, wR2=0.2626
Largest diff. Peak and hole	0.473 and $-0.361 \text{ e}\text{\AA}^3$	0.232 and $-0.184 \text{ e}\text{\AA}^3$	0.663 and $-0.410 \text{ e}\text{\AA}^3$

出席第 228 次美國化學會全國大會會議報告

報告人：彰化師大化學系黃瑞賢

第 228 次美國化學會全國大會於 2004 年八月 22-26 日於美國東岸的費城舉行。本人於台北時間八月 20 日星期五從台北出發，並於八月 21 日星期六到達費城。本次所發表之論文 “ Zirconium and Hafnium Complexes Bearing Substituted Pyrrolyl Ligands. Synthesis, Characterization, and Ring-Opening Polymerization of Lactide and ϵ -Caprolactone ” 是以壁報方式呈現。本論文於會議中共報告兩次，第一次是在八月 22 日(星期日)晚上七至十時的無機組論文發表會，第二次是在八月 23 日晚上七至十時(星期一)的 SCI-MIX 論文發表會。在會議期間除論文發表外，亦利用有限的時間盡量聽取其他頂尖科學家的最新結果。

會議於八月 26 日星期四結束，本人於八月 27 日星期五啟程返台並於八月 28 日星期六深夜到達。綜觀本次會議，除成功報告所發表之論文，亦獲得許多新的知識及靈感，對於研究有莫大的幫助。