行政院國家科學委員會專題研究計畫　成果報告

酮胺配位基化合物：合成、鑑定和開環聚合(2/2)

計畫類別：個別型計畫
計畫編號：NSC92-2113-M-018-007-
執行期間：92 年 08 月 01 日至 93 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：完整報告

處理方式：本計畫可公開查詢

中　華　民　國 93 年 12 月 3 日

附件一

行政院國家科學委員會補助專題研究計畫 ■ 成 果 報 告 □期中進度報告

（計畫名稱）

酮胺配位基化合物：合成、鑑定和開環聚合(2/2)

計畫類別：■ 個別型計畫　　□ 整合型計畫
計畫編號：NSC 92－2113－M－　018 －　007－
執行期間：　92 年　8 月　1 日至　93 年　07 月　31 日

計畫主持人：黃瑞賢
共同主持人：
計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

本成果報告包括以下應繳交之附件：
□赴國外出差或研習心得報告一份
□赴大陸地區出差或研習心得報告一份
□出席國際學術會議心得報告及發表之論文各一份
□國際合作研究計畫國外研究報告書一份

處理方式：除產學合作研究計畫、提升產業技術及人才培育研究計畫、列管計畫及下列情形者外，得立即公開查詢
□涉及專利或其他智慧財產權，□一年□二年後可公開查詢

執行單位：國立彰化師範大學化學系暨研究所

中　華　民　國　93 年　12 月　3 日

Abstract

[$C_4H_3N(CH_2NMe_2)$-2]$AlMe_2$ (**1**) is prepared by the reaction of substituted pyrrole [$C_4H_4N(CH_2NMe_2)$-2] with 1 equiv of $AlMe_3$ in methylene chloride. Reaction of complex **1** with one equiv of phenyl isocyanate in toluene generates complex **2**. The phenyl isocyanate was inserted into the aluminum and dimethylamino nitrogen bond and induced an unusual rearrangement which results the C–N bond breaking and formation. The reaction of substituted pyrrole [$C_4H_4N(CH_2NMe_2)$-2] with 1 equiv of phenyl isocyanate in diethyl ether yields a pyrrolyl attached urea derivative **3**. The reaction of $AlMe_3$ with 1 equiv of **3** in methylene chloride afforded O-bounded and N-bounded aluminum dimethyl complexes **4a** and **4b**. Both **4a** and **4b** are observed in ^{1}H NMR spectra, however, the relative ratio of **4a** and **4b** depends on the deuterium solvent used.

中文摘要

化合物[$C_4H_3N(CH_2NMe_2)$-2]$AlMe_2$ (**1**) 可經由 [$C_4H_4N(CH_2NMe_2)$-2]與 1 當量之 $AlMe_3$ 於二氯甲烷中反應而得。 化合物 **1** 與 1 當量之 PhNCO 於甲苯中反應而得 **2**. PhNCO 可插入鋁及二甲基胺氮原子之間的鍵，並且經 C–N 鍵的斷裂及生成而引發一種不尋常的重排反應。 [$C_4H_4N(CH_2NMe_2)$-2] 與 1 當量之 PhNCO 於乙醚中反應生成具有仳各取代之尿素衍生物 **3**。 $AlMe_3$ 與 1 當量之 **3** 於二氯甲烷中反應得 O-鍵結 與 N-鍵結之二甲基鋁化合物 **4a** 和 **4b**. **4a** 和 **4b** 均可經由 1H NMR 光譜測得，但是其相對比例則與所使用之氘溶劑有關 。

Keywords: pyrrole, phenyl isocyanate, C–N bond breaking and formation, aluminum

關鍵字：仳各，C–N 鍵的斷裂及生成，鋁

Metal–Induced Coordination Inversion and Carbon–Nitrogen Bond Rearrangement. Structurally Characterized Phenyl Isocyanate Inserted into Aluminum Methyl Complexes and O- and N-Bound Aluminum Complexes

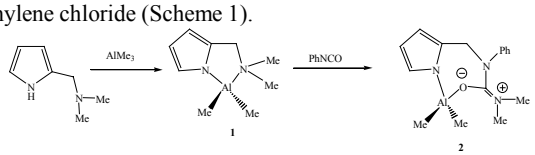
Chia-Fu Tsai, Hsing-Jen Chen, Jr-Chiuan Chang, Cheng-Hsiang Hung, Chun-Chia Lai, Ching-Han Hu, Jui-Hsien Huang*

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

juihuang@cc.ncue.edu.tw

Organic isocyanates represent an important character in organic synthesis[1] and polymer chemistry.[2] The synthesis and characterization of organic isocyanate complexes is of great interest because of their possible relevance to the intermediate of catalytic reactions. Moreover, the organometallic isocyanate complexes can also serve as useful models for the chemical behavior of carbon dioxide.[3] The reactions of organic isocyanates with organometallic complexes generally involve insertion reactions,[4] coupling reactions,[5] and catalytic reactions.[6] Here we report the reactions of phenyl isocyanate with aluminum complexes and an unusual rearrangement, which results the nitrogen–carbon bond breaking and formation. Moreover, Lewis acid induced O– and N–bound inversion reactions of aluminum complexes are also reported.

The dimethyl aluminum complex $[C_4H_3N(CH_2NMe_2)\text{-}2]AlMe_2$ (**1**) is readily prepared in 90 % yield by the reaction of substituted pyrrole $[C_4H_4N(CH_2NMe_2)\text{-}2]$ with 1 equiv of $AlMe_3$ in methylene chloride (Scheme 1).



Scheme 1

Complex **1** was obtained in an oily form after work-up procedure. However, it solidified after immersing the flask in liquid nitrogen and the solid complex **1** remained as solid after warming up to room temperature. Solid complex **1** can be recrystallized from methylene chloride to yield crystallized product. The ^1H and ^{13}C NMR spectra of complex **1** in $CDCl_3$ are all as expected; the ^1H NMR spectra of methylene and dimethylamino groups of the substituted pyrrolyl exhibit singlet resonance at δ 3.90 and 2.56, respectively and the dimethyl group of the $AlMe_2$ fragment appears at – 0.70. The single crystal structure of complex **1** was determined and the molecular structure is depicted in Figure 1. **1** represents as a tetrahedral structure with the biting angle of the substituted pyrrolyl ligand at 85.40(5)°.

Reaction of complex **1** with one equiv of phenyl isocyanate in toluene generates an unusual cycloheptaaluminum complex **2** as shown in Scheme 1. The ^1H NMR spectra of methylene and dimethylamino groups of the substituted pyrrolyl of **2** exhibit singlet resonance at δ 4.76 and 2.72, respectively and the dimethyl group of the $AlMe_2$ fragment appears as a singlet at δ – 0.64. The ^{13}C NMR gated decoupling spectrum exhibited a singlet resonance at δ 161.5 which can be assigned to the NCO carbonyl. The phenyl isocyanate was inserted into the aluminum and dimethylamino nitrogen bond and induced an unusual rearrangement which results the C–N bond breaking and formation.

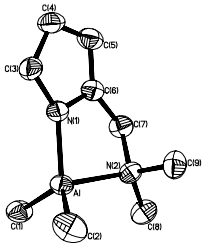
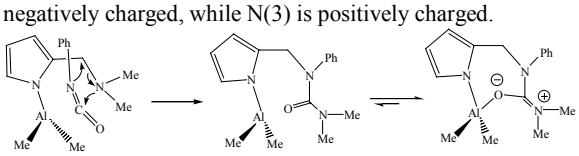


Figure 1. The molecular structure of compound **1**.

The proposed reaction mechanism is as shown in Scheme 2. The molecular geometry of **2** was confirmed by X-ray crystallography. The colorless crystals of **2** were obtained by cooling of its saturated methylene chloride solution. The molecular structure of **2** is shown in Figure 2. The molecular structure of N,N-dimethyl-N-phenyl urea (**DMPU**) was taken into account for comparisons. The bond lengths of C(12)–O(1) (1.276(8) Å) and C(12)–N(3) (1.339(8) Å) both are in the range between single and double bond while comparing with the bond lengths of C=O (1.239(3) Å) and C–N (1.378(3) and 1.360(4) Å) of **DMPU**. As suggested in Scheme 2, the unpaired electrons of the urea group of **2** are resonance between CN and CO bond, which results the partially doubly bonded C(12)–N(3) and C(12)–O(1). In the view of covalent model, the N(3) would be partially positive charge and the O(1) would be partially negative charge. Indeed, charge distribution (see Figure 3) derived from density functional theory (B3LYP/6-31G*) confirms that O(1) is negatively charged, while N(3) is positively charged.



Scheme 2

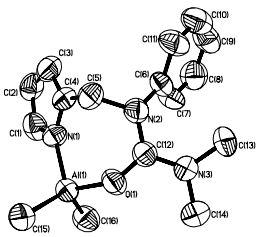


Figure 2. The molecular structure of compound **2**.

The reaction of isocyanate with amine to form urethane was common.[9] Rearrangement involving C–N bond-breaking and formation can be found in the literature.[10] However, the metal

induced rearrangement reactions in scheme 1 were unusual. A controlled experiment was performed for comparison the reactions in Scheme 1 with the non-metal existence reaction of phenyl isocyanate with substituted pyrrolyl ligand. The reaction of substituted pyrrole [$C_4H_4N(CH_2NMe_2)$-2] with 1 equiv of phenyl isocyanate in diethyl ether yields a pyrrolyl attached urea derivative **3**. No rearrangement as shown in Scheme 2 was observed. The ^{1}H NMR spectra of **3** showed a downfield singlet (δ 12.91) which can be assigned to the NH proton. The ^{13}C NMR spectrum exhibited a high field singlet at δ 149.1 that is assigned to the carbonyl group of the urea of **3**. However, the unambiguous molecular geometry was determined by X-ray single crystal structure determination. The molecular structure of **3** is shown in Figure 4. The bond distances of C(8)–O(1) (1.2132 Å) and C(8)–N(2) (1.343(2) Å) are in the range of double and single bond, respectively while comparing with that of **DMPU**.

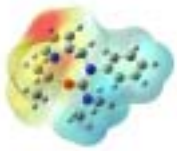


Figure 3. The electron charge distribution of compound **2**. Red and blue colors represent negative and positive charges on the electron density isosurface respectively.

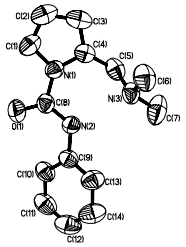
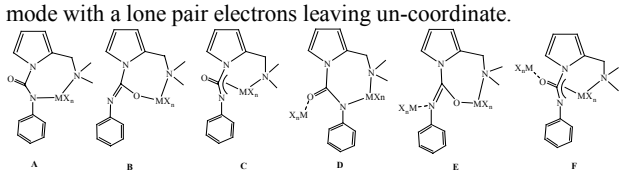
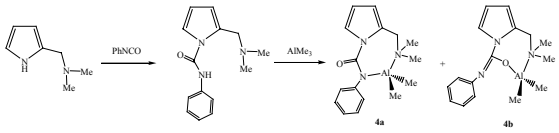


Figure 4. The molecular structure of compound **3**.

Compound **3** represents a new type of polydentate ligand with multiple coordination sites which may bind to metal(s) via sigma or coordinating bond. Scheme 3 represents some possible metal complexes geometry. The demethanation reaction of trimethyl aluminum with 1 equiv of **3** in methylene chloride at room temperature afforded O-bounded and N-bounded aluminum dimethyl complexes **4a** and **4b** (type **A** and **B**) in total of 78 % yield after recrystallization. Both **4a** and **4b** are observed in ^{1}H NMR spectra, however, the relative ratio of **4a** and **4b** depends on the deuterium solvent used. The general ratio of **4a**/**4b** is ca 1.0 in $CDCl_3$ and ca 0.5 in C_6D_6 at room temperature, which indicates that **4a** and **4b** are inter-converting at room temperature and affected by the polarity of solvents. Two singlets for the NMe_2 moiety at δ 2.47 and 2.43 and two singlets for the $AlMe_2$ at δ – 0.98 and – 1.29 are observed for **4a** and **4b** in $CDCl_3$, however, we are not able to distinguish them. The molecular structure of **4b** was determined by X-ray crystallography (Figure 5) and revealed an unsymmetrical geometry with the aluminum bonded with **3** forming a puckered seven-member ring. The bond distances of C(10)–N(3) (1.270(5) Å) and C(10)–O(1) (1.317(5) Å) are clearly identified as a C=N double bond and a C-O single bond, respectively. The bond angle of C(10)–N(3)–C(11) (119.0(4)°) represents the N(3) belonging to a sp^2 hybridization mode with a lone pair electrons leaving un-coordinate.



Scheme 3



Scheme 4

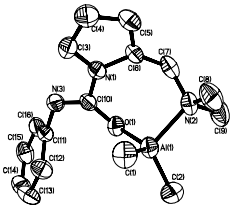


Figure 5. The molecular structure of compound **4b**.

In conclusion, we have found a novel metal induced carbon-nitrogen bond rearrangement of an aluminum complex. The pyrrolyl ligand **3** represents a new type of polydentate ligand which can bound to metals in various binding modes. A more detailed study of reactions **3** with metal alkyl complexes, where M = group 13 and early transition metals, in different stoichiometric ratios is under investigation.

Acknowledgement. We thank the National Science Council of Taiwan for financial support and the National Center for High Performance Computing for databank searches. We also thank Gene-Hsiang Lee of National Taiwan University for solving the molecular structure of compound **1**.

REFERENCES

(1) Lábbé, G. *Synthesis* **1987**, 525.
(2) Sanuder, J. H.; Frisch, K. C. Polyurethane; Wiely-Interscience: New York, 1962.
(3) (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev*. **1988**, *88*, 747. (b) Behr, A. *Angew. Chem. Int. Ed. Engl*. **1988**, *27*, 661. (c) Floriani, C. *Pure Appl. Chem*. **1982**, *54*, 661
(4) (a) Lappert, M. F.; Prokai, B. *Adv. Org. Chem.* **1967**, *5*, 225.(b) Zhou, X.; Zhang, L.; Cai, R.; Weng, L.; Huang, Z.; Wu, Q. *Organometallics* **2001**, *20*, 5700.
(5) Braunsteim, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927 and references therein.
(6) (a) Ulrich, H.; Tucker, B.; Sayigh, A. A. R. *Tetrahedron Lett.* **1967**, 1731. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539
(7) (a)Herz, W.; Dittmer, K. *J. Am. Chem. Soc.* **1947**, *69*, 1698. (b)Kim, H.; Elsenbaumer, R. L. *Tetrahedron Letters* **1998**, *39*, 1087.
(8) The molecular structure of **DMPU** was solved and CIF files can be found in the Supporting Information.
(9) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*, Volume 1, **1967**.
(10) (a) Izod, K.; O'Shaughnessy, P/; Clegg, W. *Organometallics* **2002**, *21*, 641. (b) Bhattacharyya, S.; Weakley, T. J. R.; Chaudhury, M. *Inorg. Chem.* **1999**, *38*, 5453. (c) Ishikawa, T.; Kawakami, M.; Fukui, M.; Yamashita, A.; Urano, J.; Saito, S. *J. Am. Chem. Soc.* **2001**, *123*, 7734. (d) Saha, A.; Ghosh, A. K.; Majumdar, P.; Mitra, K. N.; Mondal, S.; Rajak, K. K.; Falvello, L. R.; Goswami, S. *Organometallics* **1999**, *18*, 3772.

附件二

可供推廣之研發成果資料表

☐ 可申請專利　☐ 可技術移轉　日期：__年__月__日

國科會補助計畫	計畫名稱： 計畫主持人： 計畫編號：　學門領域：
技術/創作名稱	
發明人/創作人	
技術說明	中文： （100~500 字）
	英文：
可利用之產業及可開發之產品	
技術特點	
推廣及運用的價值	

※　1.每項研發成果請填寫一式二份，一份隨成果報告送繳本會，一份送　貴單位研發成果推廣單位（如技術移轉中心）。

※　**2.本項研發成果若尚未申請專利，請勿揭露可申請專利之主要內容。**

※　3.本表若不敷使用，請自行影印使用。