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Article

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

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$[C_4H_3N(CH_2NMe_2)\text{-}2]AlMe_2$ (**1**) is prepared in 88% yield by the reaction of substituted pyrrole $[C_4H_4N(CH_2NMe_2)\text{-}2]$ with 1 equiv of $AlMe_3$ in methylene chloride. Reaction of compound **1** with 1 equiv of phenyl isocyanate in toluene generates a seven-membered cycloaluminum compound $\{C_4H_3N[CH_2NPh(CONMe_2)]\text{-}2\}AlMe_2$ (**2**). The phenyl isocyanate was inserted into the aluminum and dimethylamino nitrogen bond and induced an unusual rearrangement which results in C–N bond breaking and formation. A control experiment shows that the reaction of substituted pyrrole $[C_4H_4N(CH_2NMe_2)\text{-}2]$ with 1 equiv of phenyl isocyanate in diethyl ether yields a pyrrolyl attached urea derivative $\{C_4H_3N(CH_2NMe_2)\text{-}2\text{-}[C(=O)NHPh]\text{-}1\}$ (**3**). The demethanation reaction of $AlMe_3$ with 1 equiv of **3** in methylene chloride at 0 °C afforded O-bounded and N-bounded aluminum dimethyl compounds $\{C_4H_3N(CH_2NMe_2)\text{-}2\text{-}[C(=O)NPh]\text{-}1\}AlMe_2$ (**4a**) and $\{C_4H_3N(CH_2NMe_2)\text{-}2\text{-}[CO(=NPh)]\text{-}1\}AlMe_2$ (**4b**) in a total 78% yield after recrystallization. Both **4a** and **4b** are observed in ^1H NMR spectra; however, the relative ratio of **4a** and **4b** depends on the solvent used. Two equivalents of $AlMe_3$ was reacted with **3** in methylene chloride to yield a dinuclear aluminum compound $AlMe_3\{C_4H_3N(CH_2NMe_2)\text{-}2\text{-}[C(=O)NPh]\text{-}1\}AlMe_2$ (**5**). Reaction of **5** with another equivalent of ligand **3** results in the re-formation of compounds **4a** and **4b**.

Introduction

Regarding the organometallic compounds, aluminum compounds have been widely used in industry and research due to their availability and decreased expensiveness.[1] Large numbers of organoaluminum compounds have been synthesized from aluminum halide or aluminum alkyl precursors and converted to other aluminum compounds. Organic isocyanates represent an important class of reactive substances in organic synthesis[2] and polymer chemistry.[3] The synthesis and characterization of organic isocyanate compounds is of great interest because of their possible relevance in intermediates of catalytic reactions. Moreover, the organometallic isocyanate compounds can also serve as useful models for the chemical behavior of carbon dioxide.[4] The reactions of organic isocyanates with organometallic compounds generally involve insertion reactions,[5] coupling reactions,[6] and catalytic reactions.[7] We have been interested in the reactions of substituted pyrrolyl ligands[8] with group

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(1) (a) Murahashi, S.-I.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225. (b) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (c) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1. (d) Cucinella, S.; Mazzei, A.; Marconi, W. *Inorg. Chim. Acta Rev.* **1970**, *4*, 51. (e) Downs, A. J.; Pulham, C. R. *Adv. Inorg. Chem.* **1994**, *41*, 171. (f) Cowley, A. H.; Gabbaï, F. P.; Isom, H. S.; Decken, A. *J. Organomet. Chem.* **1995**, *500*, 81. (g) Wehmschulte, R. J.; Power, P. P. *Polyhedron* **2000**, *19*, 1649.

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10.1021/ic035261z CCC: $27.50

Scheme 1

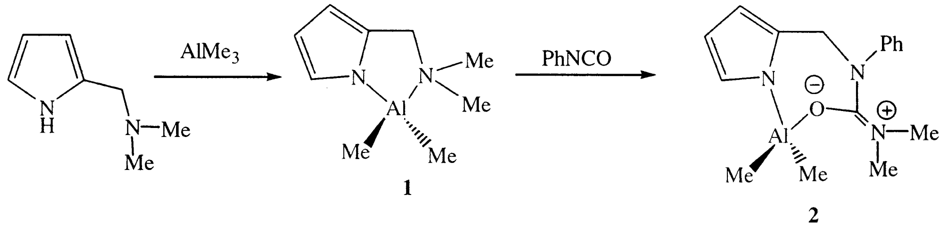

Table 1. Crystallographic Data for Compounds **1**, **2**, **3**, and **4b**, and **5**

	1	2	3	4b	5
empirical formula	$C_9H_{17}AlN_2$	$C_{16}H_{22}AlN_3O$	$C_{14}H_{17}N_3O$	$C_{16}H_{22}AlN_3O$	$C_{19}H_{31}Al_2N_3O$
formula weight	180.23	299.35	243.31	299.35	371.43
temp (K)	150(1)	293(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	8.6007(2)	8.3661(12)	10.8566(19)	13.274(2)	9.3229(10)
b, Å	8.9211(2)	21.722(3)	10.3255(18)	10.5400(17)	13.5500(15)
c, Å	14.3956(2)	9.7502(14)	12.663(2)	12.2178(19)	17.8097(19)
α, deg	90	90	90	90	90
β, deg	93.0406(9)	102.323(3)	105.494(3)	101.194(4)	91.595(2)
γ, deg	90	90	90	90	90
volume, Å^3	1102.99(4)	1731.1(4)	1367.9(4)	1676.9(5)	2248.9(4)
Z	4	4	4	4	4
density (calcd), mg/m^3	1.085	1.149	1.181	1.233	1.097
abs coeff, mm^{-1}	0.139	0.120	0.077	0.126	0.140
F(000)	392	640	520	664	800
crystal size	0.50 × 0.35 × 0.35	0.45 × 0.35 × 0.24	0.30 × 0.25 × 0.20	0.28 × 0.25 × 0.20	0.45 × 0.30 × 0.24
θ range, deg	2.37−27.50	1.87−20.82	1.95−27.52	1.56−27.56	1.89−27.53
reflns collected	16428	6135	8458	10379	14034
independent reflns	2523 ($R_{int} = 0.0483$)	1817 ($R_{int} = 0.0816$)	3140 ($R_{int} = 0.0312$)	3815 ($R_{int} = 0.1251$)	5139 ($R_{int} = 0.0576$)
data/restraints/params	2523/0/110	1817/0/195	3140/0/165	3815/0/194	5139/0/233
goodness-of-fit on F^2	1.084	0.982	0.853	0.802	0.725
final R indices [$I > 2\sigma(I)$]	R1 = 0.0399 wR2 = 0.1130	R1 = 0.0726 wR2 = 0.2072	R1 = 0.0512 wR2 = 0.1460	R1 = 0.0811 wR2 = 0.1891	R1 = 0.0421 wR2 = 0.0842
R indices (all data)	R1 = 0.0513 wR2 = 0.1225	0.1120 wR2 = 0.2200	0.0922 wR2 = 0.1665	0.1716 wR2 = 0.2292	R1 = 0.1081 wR2 = 0.0948
largest diff peak and hole, e Å^3	0.266 and −0.249	0.274 and −0.277	0.446 and −0.176	0.323 and −0.664	0.192 and −0.217

13[9] and early transition metals[10] and their reactivites toward small organic molecules. Herein we report the reactions of phenyl isocyanate with substituted pyrrolyl aluminum compounds, and an unusual rearrangement which results in nitrogen−carbon bond breaking and formation. Moreover, Lewis acid induced O- and N-bound inversion reactions of aluminum compounds are also reported.

Results and Discussion

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

Compound **1** was obtained in an oily form following workup. However, it solidified after immersion of the flask in liquid nitrogen, and the solid compound **1** remained as a solid after warming to room temperature. Solid compound **1** can be recrystallized from methylene chloride to yield crystallized product. The ^{1}H and ^{13}C NMR spectra of compound **1** in $CDCl_3$ are all as expected; the ^{1}H NMR spectra of methylene and dimethylamino groups of the substituted pyrrolyl exhibit singlet resonance at δ 3.88 and 2.56, respectively, and the dimethyl group of the $AlMe_2$ fragment appears at −0.68. The single-crystal structure of compound **1** was determined, and the molecular structure is depicted in Figure 1. The summaries of data collection parameters are shown in Table 1, and selected bond distances and angles are listed in Table 2. The four-coordinate compound **1** represents as a tetrahedral structure with the bite angle of the substituted pyrrolyl ligand N(1)−Al−N(2) of 85.40(5)°.

Reaction of compound **1** with 1 equiv of phenyl isocyanate in toluene generates an unusual seven-membered cycloaluminum compound {$C_4H_3N[CH_2NPh(CONMe_2)]$-2}$AlMe_2$ (**2**) as shown in Scheme 1. The ^{1}H NMR spectra of methylene and dimethylamino groups of the substituted pyrrolyl of **2** exhibit singlet resonances 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 161.5 which can be assigned to the NCO carbonyl. The proposed mechanism for the reaction of **1** with PhNCO is shown in

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[9] (a) Huang, J.-H.; Kuo, P.-C.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc.* **2000**, *27*, 1191. (b) Huang, J.-H.; Chi, L.-S.; Huang, F.-M.; Kuo, P.-C.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc.* **2000**, *27*, 895. (c) Huang, J.-H.; Chi, L.-S.; Yu, R.-C.; Jiang, G. J.; Yang, W.-T.; Lee, G.-H.; Peng, S.-M. *Organometallics* **2001**, *20*, 5788.

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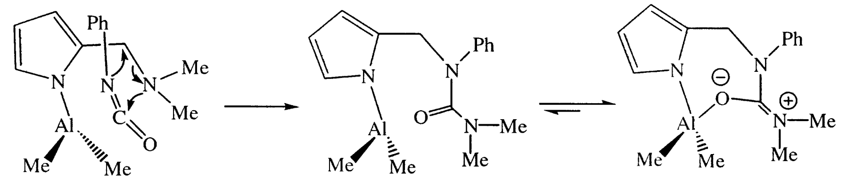
Scheme 2



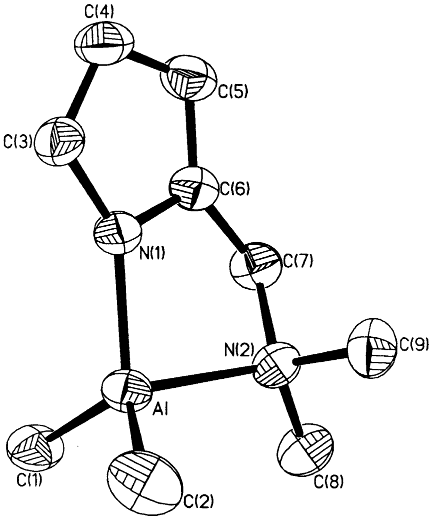


Figure 1. Molecular structure of compound **1**. The thermal ellipsoids were drawn at 50% probability, and all hydrogen atoms were omitted for clarity.

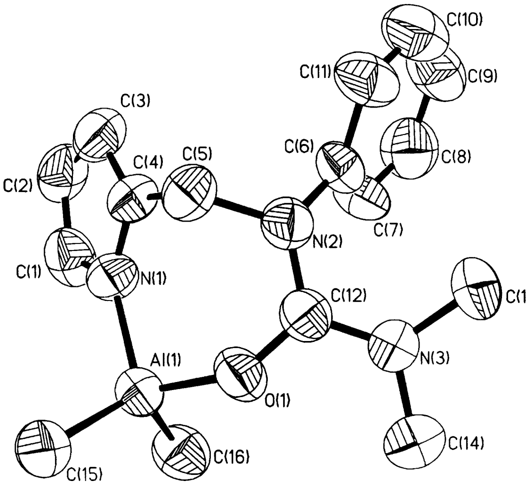


Figure 2. Molecular structure of compound **2**. The thermal ellipsoids were drawn at 50% probability, and all hydrogen atoms were omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, **3**, **4b**, and **5**

	1		
Al−N(1)	1.8785(13)	Al−N(2)	2.0242(13)
Al−C(1)	1.9632(17)	Al−C(2)	1.9556(18)
N(1)−Al−C(2)	117.31(7)	N(1)−Al−C(1)	112.12(7)
C(1)−Al−C(2)	119.46(8)	N(1)−Al−N(2)	85.40(5)
N(2)−Al−C(2)	109.88(7)	C(1)−Al−N(2)	106.67(7)
	2		
Al(1)−O(1)	1.828(5)	Al(1)−N(1)	1.898(6)
Al(1)−C(15)	1.932(7)	Al(1)−C(16)	1.956(7)
O(1)−C(12)	1.276(8)	N(2)−C(12)	1.362(9)
N(3)−C(12)	1.339(8)		
O(1)−Al(1)−N(1)	101.4(3)	O(1)−Al(1)−C(15)	105.4(3)
N(1)−Al(1)−C(15)	112.8(3)	O(1)−Al(1)−C(16)	106.6(3)
N(1)−Al(1)−C(16)	109.2(3)	C(15)−Al(1)−C(16)	119.5(3)
	3		
N(1)−C(8)	1.415(2)	C(8)−O(1)	1.213(2)
N(2)−C(8)	1.343(2)	N(2)−C(9)	1.415(2)
O(1)−C(8)−N(1)	119.42(17)	O(1)−C(8)−N(2)	125.96(18)
N(2)−C(8)−N(1)	114.58(15)	C(8)−N(2)−C(9)	124.57(14)
	4b		
Al(1)−O(1)	1.785(3)	Al(1)−N(2)	2.015(4)
C(10)−O(1)	1.317(5)	C(10)−N(1)	1.429(5)
C(10)−N(3)	1.270(5)		
O(1)−Al(1)−N(2)	97.30(16)	N(3)−C(10)−N(1)	116.2(4)
C(10)−N(3)−C(11)	119.0(4)		
	5		
Al(1)−N(3)	1.932(2)	Al(1)−N(2)	2.007(2)
Al(1)−C(1)	1.939(2)	Al(1)−C(2)	1.945(2)
Al(2)−O(1)	1.894(2)	Al(2)−C(3)	1.968(2)
Al(2)−C(4)	1.970(2)	Al(2)−C(5)	1.964(2)
C(13)−N(3)	1.314(2)	C(13)−O(1)	1.265(2)
N(3)−Al(1)−N(2)	98.16(7)	N(3)−C(13)−N(1)	116.60(18)
O(1)−C(13)−N(1)	125.85(19)	C(13)−O(1)−Al(2)	132.94(13)

Scheme 2. The phenyl isocyanate was inserted into the aluminum and dimethylamino nitrogen bond and induced an unusual rearrangement which results in C−N bond breaking and formation.

The molecular geometry of **2** was confirmed by X-ray crystallography. The colorless crystals of **2** were obtained by cooling of a saturated solution in methylene chloride. The molecular structure of **2** is depicted in Figure 2. Selected bond distances and angles of **2** are shown in Table 2. The molecular structure of *N*,*N*-dimethyl-*N*-phenylurea (DMPU)[11] was taken into account for comparison. The bond lengths C(12)−O(1) (1.276(8) Å) and C(12)−N(3) (1.339(8) Å) are in the range between single and double bonds in comparison to the bond lengths of C═O (1.293(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 delocalized between the CN and CO bonds, which results in partially doubly bonded C(12)−N(3) and C(12)−O(1). In view of the covalent model, the N(3) would be partially positively charged and O(1) would be partially negatively charged. Indeed, the electrostatic potential on the electron isodensity surface derived from density functional theory using B3LYP/6-31G* confirms that O(1) is negatively charged, while N(3) is positively charged.[12] A figure representing the electrostatic potential of compound **2** is shown in Supporting Information.

The reaction of isocyanate with amine to form urethane is common.[13] Rearrangement involving C−N bond breaking

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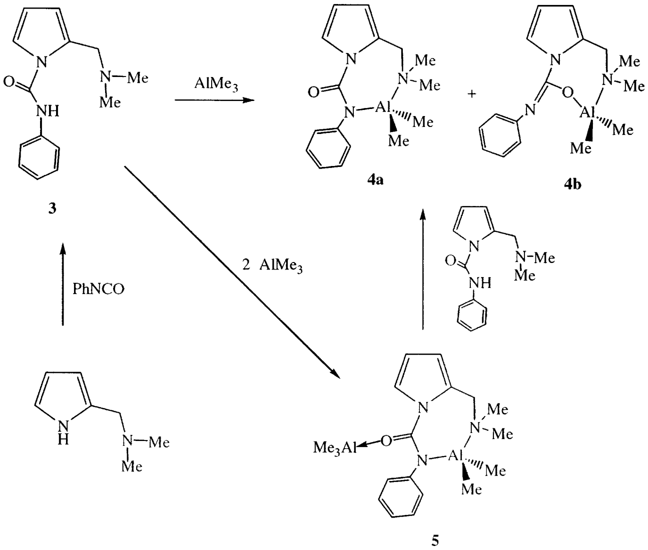
(11) The molecular structure of DMPU was solved, and CIF files can be found in the Supporting Information.

(12) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1.

Scheme 3



and formation can be found in the literature.[14] However, the metal induced rearrangement reaction in Scheme 1 was unusual. A control experiment was performed for comparison with the reactions in Scheme 1 using the nonmetal 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 {$C_4H_3N(CH_2NMe_2)$-2-[C(=O)-NHPh]-1} (**3**) (Scheme 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 3. Selected bond distances and angles are listed in Table 2. The bond distances of C(8)−O(1) (1.213(2) Å) and C(8)−N(2) (1.343(2) Å) are in the range of double and single bond, respectively, in comparison to DMPU.

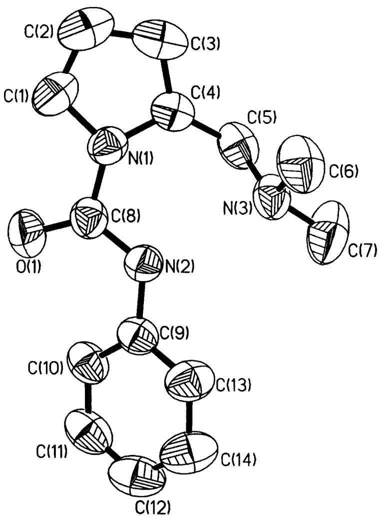


Figure 3. Molecular structure of compound **3**. The thermal ellipsoids were drawn at 50% probability, and all hydrogen atoms were omitted for clarity.

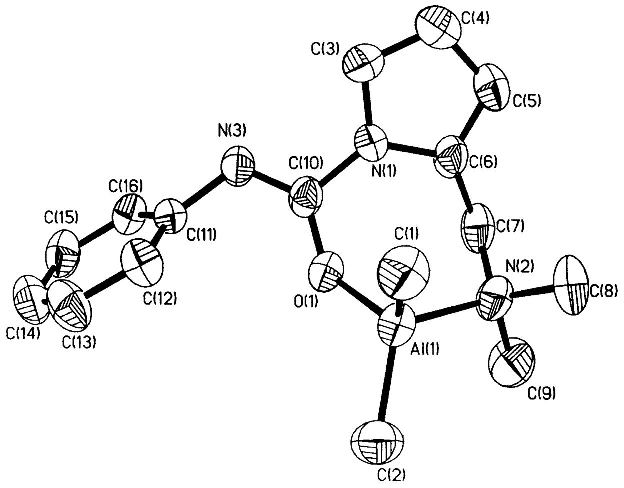


Figure 4. Molecular structure of compound **4b**. The thermal ellipsoids were drawn at 50% probability, and all hydrogen atoms were omitted for clarity.

Compound **3** represents a new type of polydentate ligand with multiple coordination sites which may bond to metal(s) via sigma or coordinating bonds. Scheme 4 represents some possible metal complex geometries. The reactions of the polydentate ligand **3** with trimethyl aluminum are summarized in Scheme 3. 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 compounds {$C_4H_3N(CH_2NMe_2)$-2-[C(=O)NPh]-1}$AlMe_2$ (**4a**) and {$C_4H_3N(CH_2NMe_2)$-2-[CO-(=NPh)]-1}$AlMe_2$ (**4b**) (types **A** and **B** in Scheme 4) in a total 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 average 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 interconverting at room temperature and that the ratio is 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 were not able to distinguish which went with which compound due to the 1:1 ratio.

The molecular structure of **4b** was determined by X-ray crystallography, and the molecular structure is depicted in Figure 4. Selected bond distances and angles are listed in Table 2. The structure of **4b** 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,

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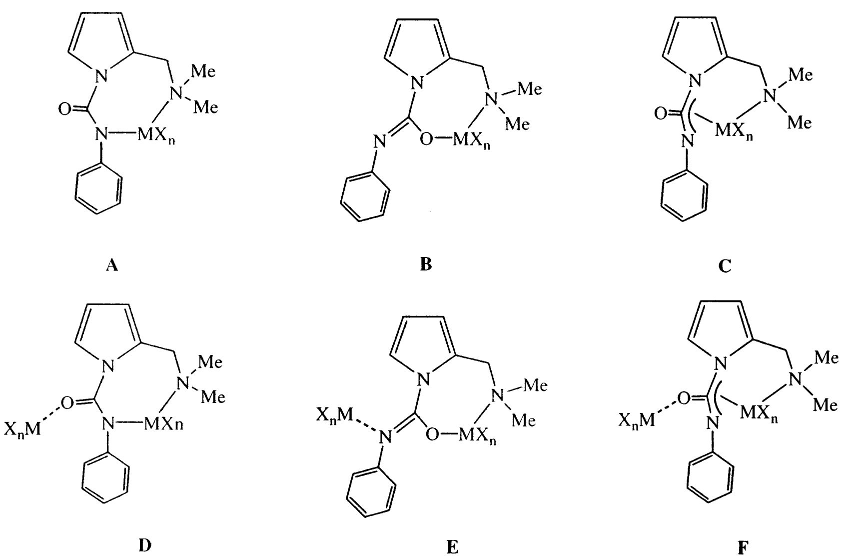
(14) For examples of C−N bond breaking and formation, see: (a) Bhattacharyya, S.; Weakley, T. J. R.; Chaudhury, M. *Inorg. Chem.* **1999**, *38*, 5453. (b) Saha, A.; Ghosh, A. K.; Majumdar, P.; Mitra, K. N.; Mondal, S.; Rajak, K. K.; Falvello, L. R.; Goswami, S. *Organometallics* **1999**, *18*, 3772. (c) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pérez-Priede, M. *J. Am. Chem. Soc.* **1999**, *121*, 3065. (d) Khumtaveeporn, K.; Alper, H. *Acc. Chem. Res.* **1995**, *28*, 414. (e) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (f) Izod, K.; O'Shaughnessy, P.; Clegg, W. *Organometallics* **2002**, *21*, 641. (g) Ishikawa, T.; Kawakami, M.; Fukui, M.; Yamashita, A.; Urano, J.; Saito, S. *J. Am. Chem. Soc.* **2001**, *123*, 7734.

Scheme 4



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 of electrons left noncoordinated.

The PhNC=O and PhN=C moieties of **4a** and **4b** provide good electron-donating sites which might act as good candidates for coordinating to another Lewis acid metal center. In this regard, 2 equiv of $AlMe_3$ was reacted with **3** in methylene chloride at 0 °C to yield a dinuclear aluminum compound $AlMe_3\{C_4H_3N(CH_2NMe_2)\text{-}2\text{-}[C(=O)NPh]\text{-}1\}\text{-}AlMe_2$ (**5**) (Scheme 3). Compound **5** can be classified as type **D** geometry of Scheme 4, and no type **E** was observed spectroscopically. The ^{1}H NMR spectra of methylene and dimethylamino groups of the substituted pyrrolyl of **5** exhibit singlet resonances at δ 3.92 and 2.56, respectively. The methyl groups of the $AlMe_3$ and $AlMe_2$ fragment appear as two singlets at δ −1.23 and −1.27 with the relative ratio of 2:3. Further studies show that reaction of **5** with another equivalent of ligand **3** results in the re-formation of compounds **4a** and **4b**.

The colorless single crystals of **5** were obtained from a solution of concentrated methylene chloride, and its structure was determined by X-ray crystallography. The X-ray structure is shown in Figure 5, and a selection of bond distances and angles are collected in Table 2. The structure contains two aluminum atoms, an $AlMe_2$ moiety and an $AlMe_3$ molecule, both bonded to the multidentate ligand **3**. The $AlMe_2$ moiety is bonded to the nitrogen atoms of dimethylamino and PhNCO fragments, leading to a tetrahedral geometry around Al(1). The bond angle of N(3)−Al(1)−N(2) at 98.16(7)° is smaller than the average sp^3 bond angle (average 109.28°), which was attributed to the ring constraints of the seven-membered cycloaluminum fragment. The Lewis acidic $AlMe_3$ molecule forms an acid−base compound with the oxygen atom of the PhNCO fragment which also results in a tetrahedral geometry around Al(2). The bond lengths of Al−N and Al−C are all in the normal range as compared to other aluminum compounds in the literature.[15]

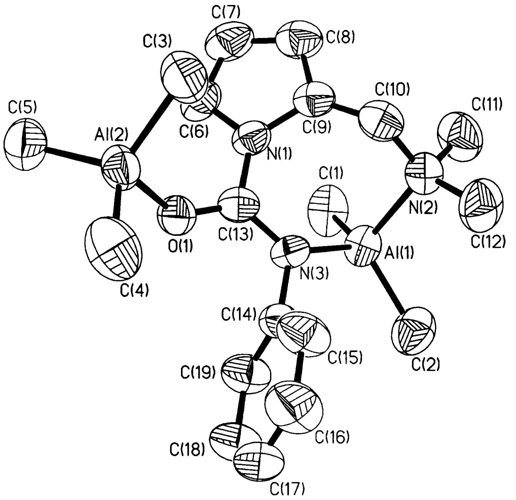


Figure 5. Molecular structure of compound **5**. The thermal ellipsoids were drawn at 50% probability, and all hydrogen atoms were omitted for clarity.

Conclusions

We have found a novel metal induced carbon−nitrogen bond rearrangement in the reaction of **1** and PhNCO with the formation of a seven-membered-ring aluminum compound. A control experiment proved that the C−N bond rearrangement can only occur in the presence of aluminum. Compound **3**, obtained from the reaction of substituted pyrrole and PhNCO, represents a new type of polydentate ligand which can coordinate to metals in a variety of binding modes. Again, Lewis acidic aluminum metal plays an important role for the bonding geometry of **3**. The potential ability for the versatile ligand **3** to bring two different metals simultaneously and their reaction activities toward small organic molecules are under investigation.

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Experimental Section

General Procedure. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Toluene, diethyl ether, and tetrahydrofuran 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 4 Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in parts per million (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). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. $[C_4H_3NH(CH_2NMe_2)$-2] was prepared according to a previously reported procedure.[8] $AlMe_3$ and phenyl isocyanate (Aldrich) were used as received.

$[C_4H_3N(CH_2NMe_2)$-2]$AlMe_2$ (1). A 100 mL Schlenk flask containing $[C_4H_3NH(CH_2NMe_2)$-2] (2.0 g, 16 mmol) was cooled to 0 °C and 20 mL of methylene chloride was added. To the methylene chloride solution $AlMe_3$ (2 M, 8.0 mL, 16 mmol) was added dropwise through a syringe with stirring. The solution was stirred at room temperature for 12 h after the addition was completed. The resulting solution was vacuum-dried to yield 2.50 g of white solid in 88% yield. ^1H NMR($CDCl_3$): 6.81 (s, 1H, pyrrole C*H*), 6.23 (m, 1H, pyrrole C*H*), 6.06 (m, 1H, pyrrole C*H*), 3.88 (s, 2H, C*H*$_2$), 2.56 (s, 6H, N*Me*$_2$), −0.68 (s, 6H, Al*Me*$_2$). ^{13}C NMR ($CDCl_3$): 131.6 (s, pyrrole C_{ipos}), 123.2 (d, J_{CH} = 180 Hz, pyrrole *C*H), 109.9 (d, J_{CH} = 166 Hz, pyrrole *C*H), 104.3 (d, J_{CH} = 167 Hz, pyrrole *C*H), 59.9 (t, J_{CH} = 140 Hz, *C*H$_2$N), 45.7 (q, J_{CH} = 139 Hz, N*Me*$_2$), −11.9 (q, J_{CH} = 114 Hz, Al*Me*$_2$). Anal. Calcd for $C_9H_{17}AlN_2$: C, 59.98; H, 9.51; N, 15.54. Found: C, 60.03; H, 9.42; N, 15.32.

{$C_4H_3N[CH_2NPh(CONMe_2)]$-2}$AlMe_2$ (2). To a 100 mL Schlenk flask containing **1** (1.23 g, 6.8 mmol) was added 20 mL of toluene and the solution was cooled to 0 °C. To the toluene solution PhNCO (0.81 g, 6.8 mmol) in 20 mL of toluene in another flask was added dropwise with stirring. The solution was stirred at room temperature for 24 h after the addition was completed. The resulting solution was vacuum-dried to yield a brick red solid, which was recrystallized from methylene chloride to afford 1.12 g of brick crystals in 55% yield. ^1H NMR ($CDCl_3$): 7.35−7.24 (m, 2H, phenyl C*H*), 6.93 (m, 3H, phenyl C*H*), 6.83 (s, 1H, pyrrole C*H*), 6.00 (m, 1H, C_4*H*$_3$N), 5.72 (m, 1H, pyrrole C*H*), 4.76 (s, 2H, C*H*$_2$N), 2.72 (s, 6H, N*Me*$_2$), −0.64 (s, 6H, Al*Me*$_2$). ^{13}C NMR ($CDCl_3$): 161.5 (s, N*C*O), 141.9 (s, phenyl C_{ipso}), 130.9 (s, pyrrole C_{ipso}), 129.9 (d, J_{CH} = 166 Hz, phenyl *C*H), 127.1 (d, J_{CH} = 163 Hz, phenyl *C*H), 126.0 (d, J_{CH} = 171 Hz, phenyl *C*H), 125.8 (d, J_{CH} = 157 Hz, pyrrole *C*H), 109.2 (d, J_{CH} = 166 Hz, pyrrole *C*H), 107.3 (d, J_{CH} = 167 Hz, pyrrole *C*H), 52.1 (t, J_{CH} = 140 Hz, *C*H$_2$N), 39.1 (q, J_{CH} = 140 Hz, N*Me*$_2$), −9.6 (q, J_{CH} = 112 Hz,Al*Me*$_2$). Anal. Calcd for $C_{16}H_{21}N_3OAl$: C, 64.20; H, 7.41; N, 14.04. Found: C, 63.25; H, 7.30; N, 13.91.

{$C_4H_3N(CH_2NMe_2)$-2-[C(=O)NHPh]-1} (3). A 100 mL Erlenmeyer flask was charged with $[C_4H_3NH(CH_2NMe_2)$-2] (4.0 g, 32.2 mmol) and 20 mL of diethyl ether. To the stirred solution, excess phenyl isocyanate (4.5 g, 37.8 mmol) was added dropwise and the combined solution was stirred for 1 h. The solution was vacuum-dried and the resulting solid was washed with heptane to remove excess phenyl isocyanate. Yield: 88% (6.91 g). ^1H NMR ($CDCl_3$): 12.91 (s, br, 1H, PhN*H*), 7.60−7.32 (m, 5H, phenyl C*H*), 7.10 (m, 1H, pyrrole C*H*), 6.12 (m, 2H, pyrrole C*H*), 3.46 (s, 2H, C*H*$_2$), 2.31 (s, 6H, N*Me*$_2$). ^{13}C NMR ($CDCl_3$): 149.1 (s, *C*ON), 138.7 (s, phenyl C_{ipos}), 128.6 (d, J_{CH} = 158 Hz, phenyl *C*H), 126.2 (s, pyrrole C_{ipso}), 123.2 (d, J_{CH} = 162 Hz, phenyl *C*H), 122.9 (d, J_{CH} = 162 Hz, phenyl *C*H),119.2 (d, J_{CH} = 175 Hz, pyrrole *C*H), 115.4 (d, J_{CH} = 170 Hz, pyrrole *C*H), 108.4 (d, J_{CH} = 173 Hz, pyrrole *C*H), 55.3 (t, J_{CH} = 136 Hz, *C*H$_2$N), 43.0 (q, J_{CH} = 135 Hz, N*Me*$_2$). Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.25; H, 6.72; N, 17.46.

{$C_4H_3N(CH_2NMe_2)$-2-[C(=O)NPh]-1}$AlMe_2$ (4a) and {$C_4H_3N(CH_2NMe_2)$-2- [CO(=NPh)]-1}$AlMe_2$ (4b). A 100 mL Schlenk flask containing **3** (4.20 g, 17.2 mmol) was cooled to 0 °C and 20 mL of methylene chloride was added. To the methylene chloride solution $AlMe_3$ (2 M, 8.6 mL, 17.2 mmol) was added dropwise through a syringe with stirring. The solution was stirred at room temperature for 12 h after the addition was completed. The resulting solution was vacuum-dried and crystallized again from methylene chloride to yield 4.0 g of white solid in 78% yield. ^1H NMR ($CDCl_3$): 7.62, 7.38−7.07, 6.19, 3.86, 3.79, 2.47, 2.43, −0.98, −1.29. ^{13}C NMR ($CDCl_3$): 156.7, 147.2, 144.2, 129.2, 128.8, 128.4, 127.5, 123.9, 123.5, 122.7, 122.5, 121.8, 116.7, 115.6, 109.1, 108.9, 57.8, 57.2, 46.2, 45.7, −11.9. Anal. Calcd for $C_{16}H_{22}AlN_3O$: C, 64.20; H, 7.41; N, 14.04. Found: C, 64.03; H, 7.16; N, 13.91.

$AlMe_3${$C_4H_3N(CH_2NMe_2)$-2-[C(=O)NPh]-1}$AlMe_2$ (5). A 100 mL Schlenk flask containing **3** (2.60 g, 10.7 mmol) was cooled to 0 °C and 20 mL of methylene chloride was added. To the methylene chloride solution $AlMe_3$ (2 M, 10.7 mL, 21.4 mmol) was added dropwise through a syringe with stirring. The solution was stirred at room temperature for 12 h after the addition was completed. The resulting solution was vacuum-dried and crystallized again from methylene chloride to yield 2.76 g of white solid in 70% yield. ^1H NMR ($CDCl_3$): 7.39−7.27 (m, 4H, phenyl and pyrrole C*H*), 7.05−7.01 (m, 2H, phenyl C*H*), 6.39 (m,1H, pyrrole C*H*), 6.28 (m, 1H, pyrrole C*H*), 3.92 (s, 2H, C*H*$_2$N), 2.56 (s, 6H, N*Me*$_2$), −1.23 and −1.27 (Al*Me*$_2$ and Al*Me*$_3$, 15H). ^{13}C NMR ($CDCl_3$): 158.9 (s, *C*ON), 141.5 (s, phenyl C_{ipso}), 129.3 (d, J_{CH} = 162 Hz, phenyl *C*H), 126.8 (d, J_{CH} = 162 Hz, phenyl *C*H), 126.3 (d, J_{CH} = 160 Hz, phenyl *C*H), 124.8 (d, J_{CH} = 194 Hz, pyrrole *C*H), 122.5 (s, pyrrole C_{ipso}), 118.1 (d, J_{CH} = 174 Hz, pyrrole *C*H), 111.1 (d, J_{CH} = 176 Hz, pyrrole *C*H), 57.0 (t, J_{CH} = 141 Hz, *C*H$_2$N), 46.1 (q, J_{CH} = 141 Hz, N*Me*$_2$), −8.3 (q, J_{CH} = 111 Hz, Al*Me*), −11.9 (q, J_{CH} = 108 Hz, Al*Me*). DEPT-135 ^{13}C NMR spectra were used for identifying the C_{ipso} and CH of phenyl and pyrrole groups. Anal. Calcd for $C_{19}H_{31}Al_2N_3O$: C, 61.44; H, 8.41; N, 11.31. Found: C, 61.02; H, 8.61; N, 10.79.

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Supporting Information Available: Theoretical calculation results and X-ray crystallographic files in CIF format for compounds **1**, **2**, **3**, **4b**, **5**, and DMPU. This material is available free of charge via the Internet at http://pubs.acs.org.

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