Carbodiimide Insertion into Organoaluminum Compounds and Thermal Rearrangement of the Products

Chung-Cheng Chang,*,† Chung-Sheng Hsiung,† Hsin-Lung Su,†
Bhamidi Srinivas,† Michael Y. Chiang,† Gene-Hsiang Lee,‡ and Yu Wang‡

Departments of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, Republic of China, and National Taiwan University, Taipei, Taiwan, Republic of China

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A series of carbodiimide insertion products were prepared using various aluminum reagents (viz., AlR_3 (R = Me, Et), AlX_2Y (X = Cl, R; Y = Cl, NR'_2)) and 1,3-diisopropyl- and 1,3-di-*tert*-butylcarbodiimides in various stoichiometric ratios. The resulting products **1**−**20** were isolated either as colorless liquids or as solids. These compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and mass spectral data. Elemental analysis data for some of the representative compounds were obtained. The crystal structures of two of the compounds (compounds **8″** and **10**) were determined by single-crystal X-ray diffraction. The competitive migration of the alkyl, chloro, or amino group attached to the aluminum atom onto the carbon of the carbodiimide is also reported.

Introduction

The reaction between carbon dioxide and organometallic compounds is of interest because it provides a carbon homologization of the organic group. Most of the studies of CO_2 activation have been reported for transition-metal compounds,[1] while main-group-metal compounds such as aluminum and magnesium alkyls have been studied to a lesser extent.[2] Synthetic and mechanistic studies of the insertion reactions of carbon dioxide and other heterocumulenes such as isothiocyanates, carbodiimides, etc. into M−C, M−O, M−H, and M−N bonds are of interest. The insertion reactions of isothiocyanates and carbodiimides have been well-documented in the literature.[3−5] The Grignard−CO_2 intermediate "RCO_2MgX" provides a variety of organic synthetic reagents, but the exact structural aspects of these intermediates have not been studied well.[6] Our aim is to study the structural and chemical properties of such intermediate complexes. Recently we reported a number of insertion products obtained from the insertion of CO_2, RNCNR, RNCO, and RNCS into M−X (X = C, N) bonds using polynuclear aluminum−magnesium compounds and organomagnesium reagents.[7] In the case of reactions involving CO_2 and aluminum−magnesium oligomers, the insertion occurs either at the metal−carbon center or at the metal−nitrogen bonds.[8] In continuation of work on these systems, we have extended our investigations to the insertion reactions of carbodiimides into Al−R (R = Me, Et) bond of AlR_3 and Al-X, Al−Y bonds of AlX_2Y (X = Cl, R; Y = Cl, NR'_2). The resulting insertion products could be good precur-

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† National Sun Yat-Sen University.

‡ National Taiwan University.

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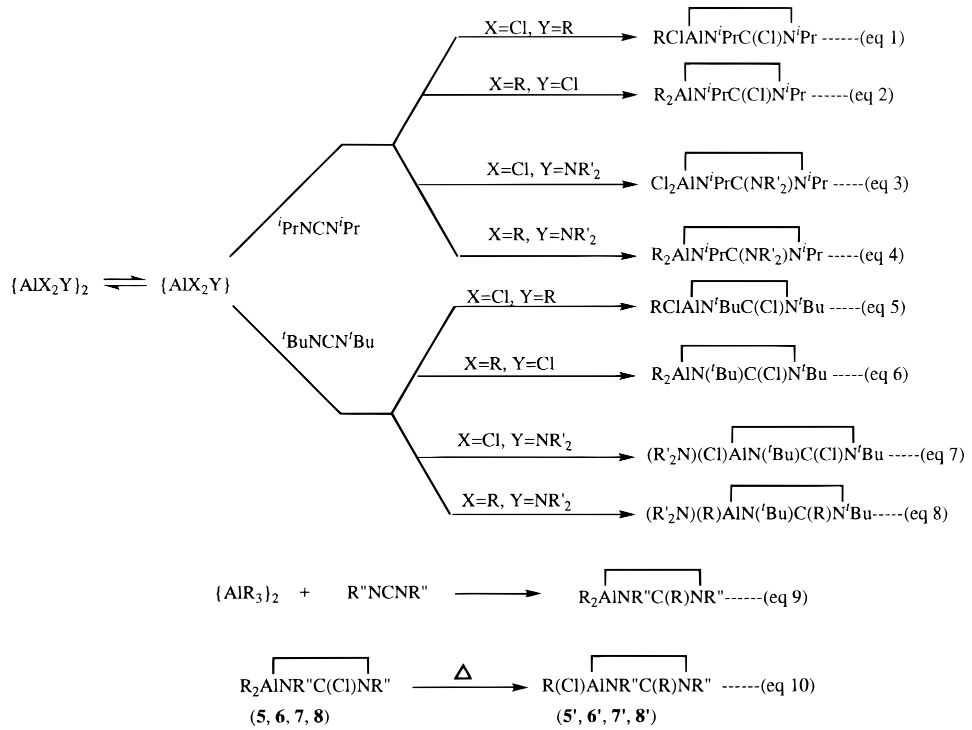
Scheme 1



sors in organic synthesis. Here we report on the synthesis, characterization and crystal structures of a number of carbodiimide insertion products using various organoaluminum reagents. The competitive migration abilities and order of migration of X and Y from Al to the carbon of the central carbodiimide are reported. Isomerization of the products upon thermolysis also is discussed.

Results and Discussion

Synthesis and Characterization. The compounds (**1**−**20**) of the general composition XYAlNR″C(X′)NR″ (X′ = migrating group) (X = Cl, R; Y = Cl, NR′$_2$) were obtained from the reaction of the aluminum complexes AlX$_2$Y and AlR$_3$ with 1,3-dialkylcarbodiimides (Scheme 1). All the compounds were characterized by mass spectrometry and ^{1}H and ^{13}C NMR and IR spectral data, which were in good agreement with the proposed structures. The structures of two compounds (**8″** and **10**) were determined using single-crystal X-ray diffraction. In their mass spectra, except for a few compounds, all the compounds showed the molecular ion peaks. Some of the typical compounds were analyzed for C, H, and N and the ^{1}H and ^{13}C NMR data were helpful in analyzing the variations in the ligand environment around the aluminum atom and the migrating groups X and Y. For instance, the reaction between Me$_2$AlCl and ^{t}BuNCN^{t}Bu produced two products, the initially formed Me$_2$AlN(^{t}Bu)C(Cl)N^{t}Bu (**5**) at room temperature and then MeClAlN(^{t}Bu)C(Me)N^{t}Bu (5′), formed by thermal rearrangement of **5** on vacuum distillation. The NMR data, which showed two different environments for the two kinds of methyl groups (one attached to the aluminum, the other attached to the carbon of the carbodiimide) confirmed the existence of two isomers: one at room temperature, the other upon thermolysis. Similarly, the isomerization products **6′**, **7′**, and **8′** were obtained upon microdistillation of **6**, **7**, and **8**, respectively. In the IR spectra, the band in the region 1550−1670 cm^{-1} was invariably assigned to the delocalized mode of −N$\overset{...}{-}$C$\overset{...}{-}$N− unit.

Description of the Structures. The reaction of 1,3-diisopropylcarbodiimide with Al(^{i}Pr$_2$N)Cl$_2$ yielded the mononuclear aluminum compound **10**. The crystal structure of **10** shows that the migration of a diisopropylamido anion from Al(^{i}Pr$_2$N)Cl$_2$ to the sp carbon of the carbodiimide has occurred during the reaction. The ligand species formed could be considered as the anion of *N*,*N*,*N*′,*N*″-tetraisopropylguanidine. A view of compound **10** is shown in Figure 1. Selected bond distances and angles are listed in Table 2.

The aluminum center is coordinated to two nitrogen atoms of the anionic ligand species and to two chloride ligands. The geometry of the aluminum center is distorted tetrahedral. The Al−Cl and Al−N bond distances are normal and are comparable to those in other organoaluminum chloride compounds.[9−13] The four-membered chelate ring is twisted, with the bite angle of the ligand being 108.9(4)°. The C−N bond distances associated with the central sp^2 carbon of the ligand anion are essentially equal (see Table 2) and are considerably shorter than a typical C−N single bond, suggesting that the three C−N bonds possess a partial double-bond character with typical C(1)−N(1), C(1)−

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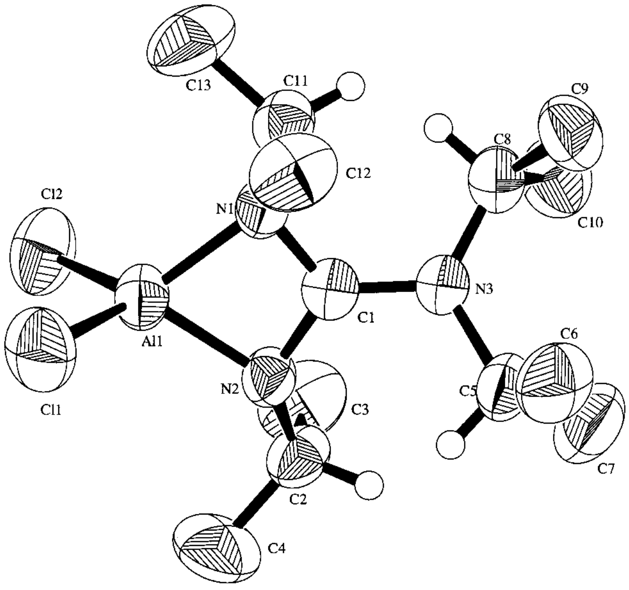

Figure 1. ORTEP view of the complex **10**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Crystal and Intensity Collection Data for Complexes 10 and 8″

	10	**8″**
formula	$C_{13}H_{28}N_3Cl_2Al$	$C_{13}H_{32}N_2OAl_2$
molar mass, g	324.27	286.37
cryst system	triclinic	monoclinic
diffractometer	Rigaku AFC7S	Nonius
space group	$P\bar{1}$ (No. 2)	$P2_1/n$
a /Å	8.953(3)	8.391(3)
b /Å	9.355(3)	16.360(4)
c /Å	12.220(4)	13.890(3)
α, deg	80.14(3)	
β, deg	77.83(3)	99.54(3)
γ, deg	69.21(2)	
V, Å^3	930.1(6)	1880.3(9)
Z	2	4
F(000)	348	633
D_{calcd}, g/cm^3	1.158	1.012
μ, cm^{-1}	3.89	1.442
2θ(max), deg	47.0	45.0
cryst dimens, mm	0.33 × 0.33 × 0.42	0.35 × 0.40 × 0.60
no. of measd rflns	2942	2446
no. of unique reflns	2743	2446
no. of obsd reflns	1537 [$(I > 3.0\sigma(I)$]	1579 [$(I > 2.0\sigma(I)$]
no. of variables	172	163
R_F, R_w	0.049, 0.057	0.050, 0.049
data collection temp, °C	25	25
goodness of fit (GOF)	2.04	2.16
radiation (graphite monoch)	Mo Kα	Mo Kα
intensity decay, %	0	16

N(2), and C(1)−N(3) distances of 1.355(5), 1.355(5), and 1.366(5) Å respectively.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 10 and 8″

$Cl_2\overline{AlN^iPrC(N^iPr_2)N^iPr}$ (**10**)			
Cl(1)−Al(1)	2.113(2)	N(2)−C(1)	1.355(5)
Cl(2)−Al(1)	2.117(2)	N(3)−C(1)	1.366(5)
Al(1)−N(1)	1.868(4)	N(2)−C(2)	1.468(6)
Al(1)−N(2)	1.868(4)	N(1)−C(11)	1.469(6)
Al(1)−C(1)	2.296(5)	N(3)−C(5)	1.489(6)
N(1)−C(1)	1.355(5)	N(3)−C(8)	1.478(6)
Cl(1)−Al(1)−Cl(2)	109.17(9)	Al(1)−N(2)−C(2)	133.3(3)
Cl(1)−Al(1)−N(2)	118.8(2)	C(1)−N(3)−C(8)	118.4(4)
Cl(2)−Al(1)−N(1)	117.7(1)	Al(1)−N(2)−C(1)	89.4(3)
N(1)−Al(1)−C(1)	36.2(2)	Al(1)−C(1)−N(1)	54.4(2)
N(1)−Al(1)−N(2)	72.3(2)	Al(1)−C(1)−N(3)	179.7(3)
N(2)−Al(1)−C(1)	36.2(2)	N(1)−C(1)−N(2)	108.9(4)
Al(1)−N(1)−C(11)	134.2(3)	N(1)−C(1)−N(3)	125.7(4)
C(1)−N(1)−C(11)	127.4(4)	N(2)−C(1)−N(3)	125.4(4)
$(Me_2Al)_2\{(\mu\text{-}OMe)(\mu\text{-}{}^iPrNC(Me)N^iPr)\}$(**8″**)			
Al(1)−O	1.823(3)	Al(2)−C(3)	1.965(3)
Al(1)−N(1)	1.922(3)	Al(2)−C(4)	1.962(5)
Al(1)−C(1)	1.973(5)	O−C(11)	1.425(5)
Al(1)−C(2)	1.962(5)	N(1)−C(5)	1.494(6)
Al(2)−O	1.828(3)	N(1)−C(12)	1.325(6)
Al(2)−N(2)	1.913(3)	N(2)−C(8)	1.485(6)
N(2)−C(12)	1.339(6)		
O−Al(1)−N(1)	98.29(14)	C(3)−Al(2)−C(4)	113.23(21)
O−Al(1)−C(1)	106.91(17)	Al(1)−O−Al(2)	116.06(15)
O−Al(1)−C(2)	111.82(17)	Al(1)−O−C(11)	123.1(3)
N(1)−Al(1)−C(1)	117.23(18)	Al(2)−O−C(11)	120.7(3)
N(1)−Al(1)−C(2)	109.73(17)	Al(1)−N(1)−C(5)	121.0(3)
C(1)−Al(1)−C(2)	112.03(20)	Al(1)−N(1)−C(12)	117.3(3)
O−Al(2)−N(2)	98.62(14)	Al(2)−N(2)−C(8)	121.8(3)
O−Al(2)−C(3)	110.77(18)	Al(2)−N(2)−C(12)	116.4(3)
O−Al(2)−C(4)	106.77(17)	C(8)−N(2)−C(12)	118.7(3)
N(2)−Al(2)−C(3)	108.87(18)	N(1)−C(12)−N(2)	118.0(4)
N(2)−Al(2)−C(4)	117.52(20)		

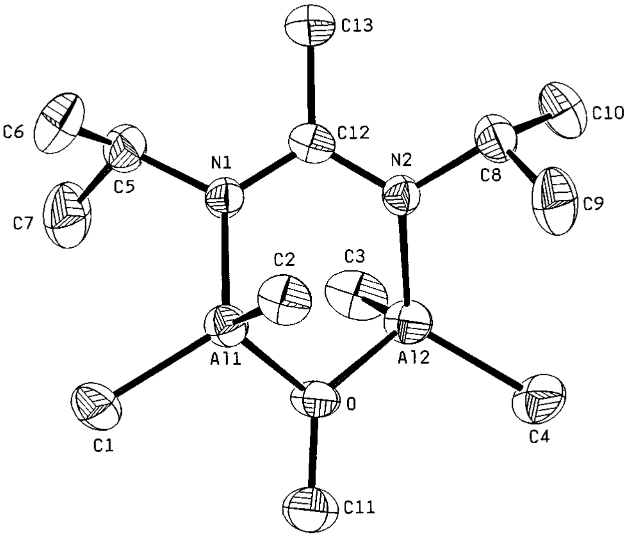

Figure 2. ORTEP view of the complex **8″**. Thermal ellipsoids are drawn at the 50% probability level.

The reaction of 1,3-diisopropylcarbodiimide with Me_2AlCl, which apparently contained the oxidized impurity MeAl(OMe)Cl, yielded a dinuclear aluminum compound (**8″**). The crystal structure of **8″** revealed a novel cyclic structure. A view of the molecule is shown in Figure 2. Selected bond distances and angles are given in Table 2. This structure demonstrates the migration of a methyl anion to the sp carbon of the carbodiimide during the reaction. The anion of the methyl-substituted carbodiimide bridges two aluminum centers by ligation through its two nitrogen atoms. The aluminum centers also are bridged by a methoxy group, resulting in the formation of a six-membered cyclic core. The geometry of the tetracoordinated aluminum centers is distorted tetrahedral. Although the complex does not contain crystallographic 2-fold symmetry, the bond distances and bond angles associated with the two aluminum centers are comparable. The C−N distances of the methylated carbodiimide ligand are consistent with a partial double bond with distances of 1.325(6) Å and 1.339(6) Å. The associated C−C bond distance is 1.506(6) Å, a typical single-bond distance.

The migration of a methyl group from the aluminum reagent to the carbodiimide central carbon atom observed in this reaction could be compared to the migration of the *N*,*N*-diisopropylamido group in the former reaction. We assume that a product similar to **10** might have formed as the initial product in this reaction also. However, X-ray data indicate the presence of the methoxy group as a bridging unit. Cases of serendipitous oxygen-insertion have long been known in organometallic chemistry. We have previously reported oxygen inserted products in alkoxide compounds and oxygen-encapsulated aluminum and magnesium compounds.[14,15] A few other examples of main-group-metal oxo compounds have been reported. Parkin et al.[16] reported the formation of peroxo derivative of magnesium, while Mulvey et al.[17] have reported a Li$-$Mg mixed-metal oxo-bridged compound.

Competitive Migration. The reactions between the dimeric aluminum complexes and 1,3-dialkylcarbodiimides yielded the insertion products **1**$-$**20** with migration of alkyl, chloro, or amino groups onto the central carbon atom of carbodiimide to form the σ,σ-symmetric amidinoaluminum complexes as shown in Scheme 1. In an attempt to rationalize the migrating ability of these groups, we have carried out experiments using $[AlR_2(NR'_2)]_2$, $[AlCl_2(NR'_2)]_2$, $[AlR_2Cl]_2$, $[AlRCl_2]_2$, and $[AlR_3]_2$ and 1,3-diisopropylcarbodiimide under different experimental conditions. For instance, the reaction of $[AlR_2(NR'_2)]_2$ with carbodiimides went to completion only when the reaction mixture was heated to 130 °C, while the reactions of $[AlR_2Cl]$ with 1,3-dialkylcarbodiimides gave products even at room temperature. We obtained the following rationale from the above reactions. From eqs 1 and 2, which involve reaction of aluminum compounds with 1,3-diisopropylcarbodiimide, it is clear that the chloro group is preferred to the alkyl group for migration. Also, the results from eqs 3 and 4 indicates that the amino group is preferred to the alkyl or chloro groups for migration. Hence, the migration order is $NR'_2 > Cl > R$. Similarly, the reactions using 1,3-di-*tert*-butylcarbodiimide and aluminum compounds containing chloro and alkyl groups (eqs 5 and 6) indicate a tendency similar to that noticed in eqs 1 and 2. Interestingly, an opposite tendency was observed in the case of eqs 7 and 8.[18] In these, the alkyl or chloro groups are preferred to the amino group for migration. Hence, the migration order in this set of complexes is $Cl > R > NR'_2$. The presence of two *tert*-butyl groups makes the migration of alkyl groups easier than that of the amino group. Therefore, the carbodiimide was inserted into the Al$-$Cl or Al$-$C bond instead of the Al$-$N bond (See Figure 3).

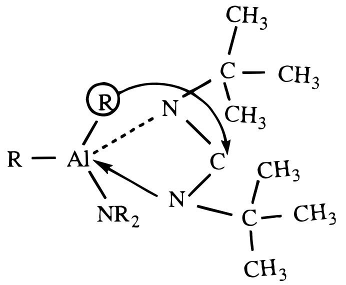

Figure 3.

Isomerization. When the dialkylaluminum chloride was treated with 1,3-di-*tert*-butylcarbodiimide, the product $R_2AlN(^tBu)C(Cl)N^tBu$ was obtained. Its ^1H NMR spectrum (R = Et) showed chemical shifts at δ 0.31 (quart, 4H, $AlCH_2CH_3$, J = 7.8 Hz), 1.11 (s, 18H, $C(CH_3)_3$), and 1.40 (t, $AlCH_2CH_3$, 6H, J = 7.8 Hz), indicating only one kind of environment for the ethyl group. However, products such as $Et_2AlN(^tBu)C(Cl)N^tBu$ (**6**), when heated or distilled, isomerized to the thermodynamically favored product $EtClAlN(^tBu)C(Et)N(^tBu)$ (**6′**). ^1H NMR spectrum of **6′** showed two environments for the ethyl groups. Two quartets at δ 0.29 (J = 8.0 Hz) and δ 3.43 (J = 7.2 Hz) were assigned to the methylene group of ethyl groups, two triplets at δ 0.79 (J = 7.2 Hz) and 1.38 (J = 8.0 Hz) were assigned to the methyl group of ethyl groups, and a singlet at δ 1.09 was assigned to the methyl of the *tert*-butyl group. Similar isomerization reactions of Et_2AlCl with 1,3-diisopropylcarbodiimide yielded two products, $Et_2AlN^iPrC(Cl)N^iPr$ (**7**) and $EtClAlN^iPrC(Et)N^iPr$ (**7′**), at room temperature and upon distillation, respectively.

Experimental Section

All experiments were carried out in a N_2-flushed glovebag, in a drybox, or in vacuo using standard Schlenk techniques.[19] All solvents were distilled and degassed prior to use. The aluminum reagents were purchased from Aldrich and were used as received, except for aluminum chloride, which was sublimed before use. All ^1H and ^{13}C NMR spectra were measured on a Varian-300 spectrometer. Chemical shifts are referenced to either $SiMe_4$ (^1H) or C_6D_6 (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.00). Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer. IR spectra were obtained as Nujol mulls between KBr disks on a Bio-Rad FTS-40 FT-IR spectrometer. Elemental analyses (C, H, and N) were performed at the Analytische Laboratorien of H. Malissa and G. Reuter GmbH, Lindlar, Germany. Deviations in the results from calculated values are attributed to the extremely air-sensitive and hygroscopic nature of the compounds.

Synthesis of $(R'_2N)(R)AlN(^tBu)C(R)N^tBu$ (R = Me, Et; R′ = Et, ^{i}Pr) (Eq 8). 1,3-Di-*tert*-butylcarbodiimide (7.4 mmol) was added into a tube containing $Al_2(NR'_2)_2R_4$ (3.7 mmol) under a nitrogen atmosphere. The tube was sealed in vacuo and heated in an oil bath at 130 °C for 48 h. The colorless product was obtained by vacuum distillation and characterized to be $(R'_2N)(R)AlN(^tBu)C(R)N^tBu$.

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[18] $(R'_2N)(Cl)AlN(^tBu)C(Cl)N^tBu$ (R′ = Et) ^1H NMR (C_6D_6): δ 0.65 (quart, 4H, $N(CH_2CH_3)_2$), 1.17 (s, 18H, $C(CH_3)_3$), 2.56 (t, 6H, NCH_2CH_3); ^{13}C NMR (C_6D_6) δ 12.54 ($N(CH_2CH_3)_2$), 31.46 ($C(CH_3)_3$), 42.66 ($N(CH_2CH_3)_2$), 54.60 ($C(CH_3)_3$), 139.29 ($^tBuNC(Cl)N^tBu$). $(R'_2N)(Cl)AlN(^tBu)C(Cl)N^tBu$ (R′ = ^{i}Pr): ^1H NMR (C_6D_6) δ 0.95 (d, 12H, $N(CH(CH_3)_2)_2$), 1.18 (s, 18H, $C(CH_3)_3$), 2.78 (sep, 2H, $N(CH(CH_3)_2)_2$); ^{13}C NMR (C_6D_6) δ 23.66 ($N(CH(CH_3)_2)_2$), 31.49 ($C(CH_3)_3$), 45.32 ($N(CH(CH_3)_2)_2$), 54.48 ($C(CH_3)_3$), 139.17 ($(^tBuN)C(Cl)(N^tBu)$).

[19] Shriver, D. F.; Dresdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(Et$_2$N)(Me)$\overline{\text{AlN(}^t\text{Bu)C(Me)N}}{}^t$Bu (1). Liquid (bp 32 °C; 0.01 Torr).Yield: 58%. Anal. Found: C, 63.47; H, 11.99; N, 14.94. Calcd: C, 63.60; H, 12.01; N; 14.94. Mass spectrum (EI, 70 eV); *m/z* relative intensity, %)): 283 (12, M$^+$), 268 (51, [M − Me]$^+$), 211 (94, [M − NEt$_2$]$^+$), 197 (10, [M − NEt$_2$ − MeH]$^+$), 155 (14, [(^{t}BuN)$_2$CH]$^+$), 114 (20, [MeAlNEt$_2$]$^+$), 98 (39, [AlNEt$_2$H]$^+$), 84 (13, [^{t}BuNCH]$^+$), 57 (100, [^{t}Bu]$^+$), 42 (15, [AlMe]$^+$). ^{1}H NMR (C$_6$D$_6$): δ −0.34 (s, 3H, AlC*H*$_3$), 1.14 (s, 18H, C(C*H*$_3$)$_3$), 1.24 (t, 6H, AlN(CH$_2$C*H*$_3$)$_2$), 1.71 (s, 3H, ^{t}BuNC(C*H*$_3$)^{t}Bu), 3.14 (quart, 4H, N(C*H*$_2$CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ −13.04 (AlCH$_3$), 16.96 (NCH$_2$*C*H$_3$)$_2$, 17.46 ((^{t}BuN)C(*C*H$_3$)(N^{t}Bu)), 31.37 (C(*C*H$_3$)$_3$), 41.98 (AlN(*C*H$_2$CH$_3$)$_2$), 50.40 (*C*(CH$_3$)$_3$), 173.86 ((^{t}BuN)*C*(CH$_3$) (N^{t}Bu)).

(^{i}Pr$_2$N)(Me)$\overline{\text{AlN(}^t\text{Bu)C(Me)N}}{}^t$Bu (2). Liquid (bp 34 °C, 0.01 Torr). Yield: 67%. Mass spectrum (EI, 70 eV); *m/z* (relative intensity, %)): 311 (<1, M$^+$), 211 (5), 170 (39), 155 (17), 114 (9), 99 (72), 86 (23), 72 (32), 58 (100), 42 (75). ^{1}H NMR (C$_6$D$_6$): δ −0.22 (s, 3H, AlC*H*$_3$), 1.17 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (d, 12H, N[CH(C*H*$_3$)$_2$]$_2$), 1.69 (s, 3H, (^{t}BuN)C(C*H*$_3$)(N^{t}Bu)), 3.30 (sep, 2H, N(C*H*(CH$_3$)$_2$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ −8.61 (Al*C*H$_3$), 17.08 (^{t}BuC(*C*H$_3$)N^{t}Bu), 26.66 (CH(*C*H$_3$)$_2$), 31.46 (C(*C*H$_3$)$_3$), 45.51 (*C*H(CH$_3$)$_2$), 50.56 (*C*(CH$_3$)$_3$), 173.34 ((^{t}BuN)*C*(CH$_3$)(N^{t}Bu)).

(Et$_2$N)(Et)$\overline{\text{AlN(}^t\text{Bu)C(Et)N}}{}^t$Bu (3). Liquid (bp 37 °C, 0.01 Torr). Yield 72%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 311 (17, M$^+$), 296 (22), 282 (82), 239 (39), 211 (23), 169 (5), 112 (30), 98 (34), 57 (100), 43 (75). ^{1}H NMR (C$_6$D$_6$): δ 0.36 (quart, 2H, AlC*H*$_2$CH$_3$), 0.99 (t, 3H, (^{t}BuN)C(CH$_2$C*H*$_3$)(N^{t}Bu)), 1.19 (s, 18H, C(CH$_3$)$_3$), 1.28 (t, 6H, AlN (CH$_2$C*H*$_3$)$_2$), 1.36 (t, 3H, AlCH$_2$C*H*$_3$), 2.17 (quart, 2H, (^{t}BuN)C(C*H*$_2$CH$_3$)(N^{t}Bu)), 3.12 (quart, 4H, AlN(C*H*$_2$CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 1.97 (Al*C*H$_2$CH$_3$), 10.04 ((^{t}BuN)C(CH$_2$*C*H$_3$) (N^{t}Bu)), 13.51 (AlCH$_2$*C*H$_3$), 17.27 ((^{t}BuN)C(*C*H$_2$CH$_3$)(N^{t}Bu)), 22.5 (AlN(CH$_2$*C*H$_3$)$_2$), 32.06 (C(*C*H$_3$)$_3$), 41.98 (Al N(*C*H$_2$CH$_3$)$_2$), 50.94 (*C*(CH$_3$)$_3$), 179.32 ((^{t}BuN)*C*(CH$_2$CH$_3$)(N^{t}Bu)).

(^{i}Pr$_2$N)(Et)$\overline{\text{AlN(}^t\text{Bu)C(Et)N}}{}^t$Bu (4). Liquid (bp 42 °C, 0.01 Torr). Yield: 76%. Anal. Found: C, 67.14; H, 12.43; N, 12.22. Calcd: C, 67.26; H, 12.39; N, 12.39. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 339 (6, M$^+$), 324 (26), 310 (33), 239 (56), 225 (15), 184 (11), 112 (44), 86 (50), 72 (21), 57 (100), 44 (68). ^{1}H NMR (C$_6$D$_6$): δ 0.39 (quart, 2H, AlC*H*$_2$CH$_3$), 1.02 (t, 3H, (^{t}BuN)C(CH$_2$C*H*$_3$)(N^{t}Bu)), 1.22 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (d, 12H, Al(NCH(C*H*$_3$)$_2$)$_2$), 1.31 (t, 3H, AlCH$_2$C*H*$_3$), 2.16 (quart, 2H, (^{t}BuN)C(C*H*$_2$CH$_3$)(N^{t}Bu)), 3.27 (sep, 2H, Al(N(C*H*(CH$_3$)$_2$)$_2$)). ^{13}C NMR (C$_6$D$_6$): δ 2.13 (Al*C*H$_2$CH$_3$), 10.32 ((^{t}BuN)C(CH$_2$*C*H$_3$)(N^{t}Bu)), 13.67 (AlCH$_2$*C*H$_3$), 22.49 ((^{t}BuN)C(*C*H$_2$CH$_3$)(N^{t}Bu)), 26.57 (AlN(CH(*C*H$_3$)$_2$)$_2$), 32.13 (C(*C*H$_3$)$_3$), 45.40 (AlN(*C*H(CH$_3$)$_2$)$_2$), 51.05 (*C*(CH$_3$)$_3$), 178.99 ((^{t}BuN)*C*(CH$_2$CH$_3$)(N^{t}Bu)).

Synthesis of (R$_2$)$\overline{\text{AlNR}''\text{C(R}')\text{N}}$R″ (R = Me, Et; R′ = Cl; R″ = ^{t}Bu) and RCl$\overline{\text{AlN(R}'')\text{C(R}')\text{N}}$(R″) (R = R′ = Me, Et; R″ = ^{t}Bu, ^{i}Pr) (Eqs 2, 5, and 6). A solution of 1,3-di-*tert*-butylcarbodiimide (6.02 mmol) in diethyl ether (30 mL) was added to a hexane solution of dialkylaluminum chloride (3.0 mmol) in ether (20 mL) under nitrogen at room temperature. The reaction mixture was stirred for 8 h. A colorless liquid was obtained upon removal of solvent in vacuo to yield compounds **5**−**8**, respectively.

Me$_2$$\overline{\text{AlN(}^t\text{Bu)C(Cl)N}}{}^t$Bu (5). Yield: 85%. Anal. Found: C, 53.55; H, 9.56; N, 11.34. Calcd: C, 53.54; H, 9.72; N, 11.34. Mass spectrum (EI, 70 eV; *m/z* relative intensity, %)): 195 (9, [MeAl(^{t}BuN)$_2$C]$^+$), 165 (31, [Al(^{t}BuN)$_2$C − Me]$^+$), 154 (17, [(^{t}BuN)$_2$C]$^+$), 139 (68, [(^{t}BuN)C(NCMe$_2$)]$^+$), 99 (27, [(^{t}BuN)CMeH]$^+$), 83 (100, [^{t}BuNC]$^+$), 77 (60, [ClAlMe]$^+$), 57 (95, [^{t}Bu]$^+$), 56 (42, [^{t}Bu − H]$^+$), 43 (13, [AlMeH]$^+$). ^{1}H NMR (C$_6$D$_6$): δ −0.21 (s, 6H, AlC*H*$_3$), 1.09 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$): δ −5.24 (AlCH$_3$), 30.70 (C(*C*H$_3$)$_3$), 58.21 (*C*(CH$_3$)$_3$), 136.37 (^{t}BuN*C*(Cl)N^{t}Bu).

MeCl$\overline{\text{AlN(}^t\text{Bu)C(Me)N}}{}^t$Bu (5′). Microdistillation of compound **5** at 40 °C(0.01 Torr) yielded the isomer MeCl$\overline{\text{AlN(}^t\text{Bu)C(Me)N}}{}^t$Bu (5′) in quantitative yield (90%). Anal. Calcd: C, 53.54; H, 9.72; N, 11.34. Found: C, 53.27; H, 9.68; N, 11.04. ^{1}H NMR (C$_6$D$_6$): δ −0.224 (s, 3H, AlC*H*$_3$), 1.17 (s, 18H, C(C*H*$_3$)$_3$), 1.69 (s, 3H, ^{t}BuNC(C*H*$_3$)N^{t}Bu). ^{13}C NMR (C$_6$D$_6$): δ −8.61 (AlCH$_3$), 23.74 (^{t}BuNC(*C*H$_3$)N^{t}Bu), 31.46 (C(*C*H$_3$)$_3$), 50.56 (*C*(CH$_3$)$_3$), 173.33 (^{t}BuN*C*(CH$_3$)N^{t}Bu).

Et$_2$$\overline{\text{AlN(}^t\text{Bu)C(Cl)N}}{}^t$Bu (6). Yield: 92%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 245 (13), 237 (26), 215 (8), 120 (11), 91 (48), 85 (36), 83 (39), 71 (72), 57 (100), 56 (41), 43 (58). ^{1}H NMR (C$_6$D$_6$): δ 0.31 (quart, 4H, AlC*H*$_2$CH$_3$), 1.11 (s, 18H, C(C*H*$_3$)$_3$), 1.40 (t, 6H, AlCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 3.54 (Al*C*H$_2$CH$_3$), 9.53 (AlCH$_2$*C*H$_3$), 30.31 (C(*C*H$_3$)$_3$), 60.07 (*C*(CH$_3$)$_3$), 134.97 ((^{t}BuN)*C*(Cl)(N^{t}Bu)).

EtCl$\overline{\text{AlN(}^t\text{Bu)C(Et)N}}$(^{t}Bu) (6′). Microdistillation of **6** at 45 °C (0.01 Torr) yielded the isomer **6′**. Yield: 95%. Anal. Calcd: C, 52.36; H, 10.18; N, 10.18. Found: C, 52.32; H, 10.02; N, 10.76. ^{1}H NMR (C$_6$D$_6$): δ 0.29 (quart, 2H, AlC*H*$_2$CH$_3$), 0.79 (t, 3H, CCH$_2$C*H*$_3$), 1.09 (s, 18H, C(C*H*$_3$)$_3$), 1.38 (t, 3H, AlCH$_2$C*H*$_3$), 3.43 (quart, 2H, CC*H*$_2$CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 1.25 (Al*C*H$_2$CH$_3$), 9.95 (C(CH$_2$*C*H$_3$)), 13.57 (AlCH$_2$*C*H$_3$), 22.84 (C(*C*H$_2$CH$_3$)), 32.00 (C(*C*H$_3$)$_3$), 50.77 (*C*(CH$_3$)$_3$), 178.30 (^{t}BuN*C*(Et)N^{t}Bu). Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 273 (20), 246 (89), 217 (10), 155 (3), 112 (43), 98 (17), 84 (10), 71 (7), 57 (100), 43 (14).

Et$_2$$\overline{\text{AlN}^i\text{PrC(Cl)N}}{}^i$Pr (7). Yield: 86%. Anal. Calcd: C, 53.55; H, 9.74; N, 11.36. Found: C, 53.12, H, 9.58; N, 11.32. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (quart, 4H, AlC*H*$_2$CH$_3$), 0.97 (d, 6H, NCH(C*H*$_3$)$_2$), 1.14 (d, 6H, NCH(C*H*$_3$)$_2$), 1.26 (t, 6H, AlCH$_2$C*H*$_3$), 3.34 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 3.72 (Al*C*H$_2$CH$_3$), 11.52 (AlCH$_2$*C*H$_3$), 18.85 (NCH(*C*H$_3$)$_2$), 46.00 (N*C*H(CH$_3$)$_2$), 178.63 (N^{i}Pr*C*(Cl)N^{i}Pr).

EtCl$\overline{\text{AlN}i\text{PrC(Et)N}}{}^i$Pr (7′). Microdistillation of compound **7** at 42 °C (0.01 Torr) yielded the isomer **7′** in 80% yield. Anal. Calcd: C, 53.55; H, 9.74; N, 11.36. Found: C, 53.25; H, 9.64; N, 11.37. ^{1}H NMR (C$_6$D$_6$): δ 0.43 (quart, 2H, AlC*H*$_2$CH$_3$), 0.68 (t, 3H, CCH$_2$C*H*$_3$), 0.91 (d, 6H, NCH(C*H*$_3$)$_2$), 1.05 (d, 6H, NCH(C*H*$_3$)$_2$), 1.36 (t, 2H, AlCH$_2$C*H*$_3$), 1.71 (quart, 2H, CC*H*$_2$CH$_3$), 3.08 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 0.55 (Al*C*H$_2$CH$_3$), 8.77 (CCH$_2$*C*H$_3$), 11.39 (AlCH$_2$*C*H$_3$), 18.31 (C*C*H$_2$CH$_3$), 25.24 (NCH(*C*H$_3$)$_2$), 44.83 (N*C*H(CH$_3$)$_2$), 179.30 (N^{i}Pr*C*(Et)N^{i}Pr). Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 246 (4), 219 (21), 217 (89), 211 (21), 183 (9), 156 (10), 118 (9), 98 (45), 58 (9), 56 (100), 43 (20).

Me$_2$$\overline{\text{AlN}^i\text{PrC(Cl)N}}{}^i$Pr (8). Yield: 71%. Anal. Calcd: C, 49.43; H, 9.15; N, 12.81. Found: C, 49.30; H, 9.07; N, 12.85. ^{1}H NMR (C$_6$D$_6$): δ 0.22 (s, 6H, Al(C*H*$_3$)$_2$), 0.89 (d, 12H, NCH(C*H*$_3$)$_2$), 3.26 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 7.48 (Al(*C*H$_3$)$_2$), 20.13 (NCH(*C*H$_3$)$_2$), 45.03 (N*C*H(CH$_3$)$_2$), 179.66 (N^{i}Pr*C*(Cl)N^{i}Pr).

MeCl$\overline{\text{AlN}^i\text{PrC(Me)N}}{}^i$Pr (8′). This compound was obtained upon microdistillation of **8** at 34 °C (0.01 Torr). Yield: 68%. Anal. Calcd: C, 49.43; H, 9.15; N, 12.81. Found: C, 49.25; H, 9.27; N, 12.94. ^{1}H NMR (C$_6$D$_6$): δ 0.21 (s, 3H, AlC*H*$_3$), 0.94 (d, 12H, NCH(C*H*$_3$)$_2$), 1.25 (s, ^{i}PrNC(C*H*$_3$)N^{i}Pr), 3.05 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 9.54 (Al*C*H$_3$Cl), 10.59 (^{i}PrNC(*C*H$_3$)N^{i}Pr), 24.84 (NCH(*C*H$_3$)$_2$), 45.04 (N*C*H(CH$_3$)$_2$), 175.34 (^{i}PrN*C*(CH$_3$)N^{i}Pr).

(Me$_2$Al)$_2${(*μ*-OMe)(*μ*-^{i}PrNC(Me)N^{i}Pr)} (8″). This compound was obtained as colorless crystals upon microdistillation of the crude product obtained from the reaction for compound **8**. Unlike compound **8′**, this compound contains a methoxy group. Rigorous exclusion of oxygen produced compound **8′** under identical experimental conditions (see above). Compound **8″**: mp 56 °C; Yield 30%. Anal. Calcd: C, 54.47; H, 11.17; N, 9.77. Found: C, 54.25; H, 11.05; N, 9.82. ^{1}H NMR (C$_6$D$_6$): δ −0.50 (s, 12H, Al(C*H*$_3$)$_2$), 1.16 (d, 12H, NCH(C*H*$_3$)$_2$), 1.44 (s, 3H, (^{i}Pr)NC(C*H*$_3$)N(^{i}Pr)), 3.22 (sep, 2H, NC*H*(CH$_3$)$_2$), 3.44 (s, 3H, ((CH$_3$)$_2$Al)$_2$(OC*H*$_3$)). ^{13}C NMR (C$_6$D$_6$): δ 11.35 (Al(*C*H$_3$)$_2$), 20.04 (NCH(*C*H$_3$)$_2$), 46.14 (N*C*H(CH$_3$)$_2$), 51.85 (Al(O*C*H$_3$)Al).

(Cl$_2$)AlN^{i}PrC(NR$_2$)N^{i}Pr (R = Et, ^{i}Pr) (Eq 3). (Dialkylamino)aluminum chloride (1.012 g, 2.98 mmol) and 1,3-diisopropylcarbodiimide (0.814 g, 6.35 mmol) were added into a glass tube. The tube was evacuated and sealed under vacuum. The reaction mixture was subjected to pyrolysis at 100 °C (for diethylamino)aluminum chloride) and 150 °C (for (diisoproplyamino)aluminum chloride) for 4 h. After removal of excess carbodiimide, sublimation at 145 and 100 °C respectively yielded colorless crystals of compounds **9** and **10**.

Cl$_2$AlN^{i}PrC(NEt$_2$)N^{i}Pr (9). Yield 28%. Mass spectrum (EI, 70 eV; *m/z* relative intensity, %)): 156 (40), 84 (34), 71 (25), 69 (16), 58 (45), 56 (100), 44 (40). ^{1}H NMR (C$_6$D$_6$): δ 0.61 (t, 6H, N(CH$_2$C*H*$_3$)), 1.11 (d, 12H, NCH(C*H*$_3$)$_2$), 2.58 (quart, 4H, N(C*H*$_2$CH$_3$)), 3.08 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 12.40 (N(CH$_2$*C*H$_3$)$_2$), 23.91 (NCH(*C*H$_3$)$_2$), 42.35 (N(*C*H$_2$CH$_3$)$_2$), 45.62 (N*C*H(CH$_3$)$_2$), 168.48 (Et$_2$N*C*(N^{i}Pr$_2$) (N^{i}Pr)).

Cl$_2$AlN^{i}PrC(N^{i}Pr$_2$)NiPr (10). Yield 35%. Anal. Found: C, 47.97; H, 8.63; N, 12.88; Cl, 21.66. Calcd: C, 48.15; H, 8.70; N, 12.96; Cl, 21.87. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 184 (100), 169 (10), 127 (12), 100 (52), 85 (71), 69 (32), 43 (44). ^{1}H NMR (C$_6$D$_6$): δ 0.88 (d, 12H, N(CH(C*H*$_3$)$_2$)$_2$), 1.12 (d, 12H, N(CH(C*H*$_3$)$_2$), 3.29 (sep, 4H, NC*H*(CH$_3$)$_2$, N(C*H*(CH$_3$)$_2$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 22.81 (N(CH$_2$*C*H$_3$)$_2$), 24.57 (NCH(*C*H$_3$)$_2$), 45.61 (N(*C*H$_2$CH$_3$)$_2$), 50.06 (N*C*H(CH$_3$)$_2$), 172.18 (^{i}PrN*C*(N^{i}Pr)$_2$ (N^{i}Pr)).

Synthesis of (R$_2$)AlN^{i}PrC(NR″$_2$)N^{i}Pr (R = Me, Et; R″ = Et, ^{i}Pr) (Eq 4). Dialkylamino dialkylaluminum (0.997 g, 3.86 mmol) and 1,3-diisopropyl carbodiimide (0.814 g, 6.35 mmol) were added into a glass tube. The tube was sealed under vacuum and the mixture was pyrolyzed in oil bath at 140 °C for 2 h. After removal of excess carbodiimide, vacuum distillation yielded a colorless liquid.

(Me$_2$)AlN^{i}PrC(NEt$_2$)N^{i}Pr (11). Liquid (bp 55 °C, 0.01 Torr). Yield: 56%. Anal. Found: C, 60.80; H, 11.84; N, 16.45. Calcd: C, 61.14; H, 11.84; N, 16.45. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 240 (100, [M − Me]$^+$), 183 (40, [(CH$_3$CHN)C(NEt$_2$)N^{i}Pr]$^+$), 169 (13, [EtNC(N^{i}Pr)$_2$]$^+$), 141 (34, [(Et$_2$N)C(N^{i}Pr)]$^+$), 127 (25, [C(N^{i}Pr)$_2$]$^+$), 99 (45, [Me$_2$AlN(CHCH$_3$)]$^+$, 84 (16, [Me$_2$AlNCH]$^+$), 56 (12, [N^{i}Pr]$^+$), 43 (18, [^{i}Pr]$^+$), 42 (40, [AlMe]$^+$). ^{1}H NMR (C$_6$D$_6$): δ −0.23 (s, 6H, AlC*H*$_3$), 0.77 (t, 6H, N(CH$_2$C*H*$_3$)), 1.08 (d, 12H, NCH(C*H*$_3$)$_2$), 2.76 (quart, 4H, N(C*H*$_2$CH$_3$)$_2$), 3.26 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ −8.05 (AlCH$_3$), 12.90 (N (CH$_2$*C*H$_3$)$_2$), 24.68 (NCH(*C*H$_3$)$_2$), 42.33 (N(*C*H$_2$CH$_3$)$_2$), 45.22 (N*C*H(CH$_3$)$_2$), 166.96 (Et$_2$N*C*(N^{i}Pr)$_2$).

Me$_2$AlN^{i}PrC(N^{i}Pr$_2$)N^{i}Pr (12). Liquid (bp 28 °C, 0.01 Torr). Yield: 52%. Mass spectrum (EI, 30 eV; *m/z* (relative intensity, %)): 268 (100, [M − Me]$^+$), 184 (39), 183 (81), 169(84), 127 (55), 100 (18), 85 (36), 84 (26), 58 (19), 43 (82). ^{1}H NMR (C$_6$D$_6$): δ −0.34 (s, 6H, AlC*H*$_3$), 0.99 (d, 12H, CN(CH(C*H*$_3$)$_2$)$_2$), 1.06 (d, 12H, AlNCH(C*H*$_3$)$_2$), 3.22 (sep, 2H, AlNC*H*(CH$_3$)$_2$), 3.49 (sep, 2H, CN(C*H*(CH$_3$)$_2$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ −8.99 (Al*C*H$_3$), 23.05 (CN(CH(*C*H$_3$)$_2$), 25.56 (AlNCH(*C*H$_3$)$_2$), 44.97 (AlN*C*H(CH$_3$)$_2$), 48.69 (CN(*C*H(CH$_3$)$_2$)$_2$), 167.50 (^{i}Pr$_2$N*C*(N^{i}Pr)$_2$).

(Et$_2$)AlN^{i}PrC(NEt$_2$)N^{i}Pr (13). Liquid (bp 37 °C, 0.01 Torr). Yield, 70%. Anal. Found: C, 63.40; H, 11.87; N, 14.81. Calcd: C, 63.60; H, 12.03; N, 14.84. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 282 (6), 254 (100), 226 (20), 211 (19), 183 (25), 141 (42), 127 (37), 99 (92), 56 (44), 43 (70). ^{1}H NMR (C$_6$D$_6$): δ 0.41 (quart, 4H, AlC*H*$_2$CH$_3$), 0.76 (t, 6H, N(CH$_2$C*H*$_3$)$_2$), 1.08 (d, 12H, N(CH(C*H*$_3$)$_2$)), 1.51 (t, 6H, AlCH$_2$C*H*$_3$), 2.73 (quart, 4H, N(C*H*$_2$CH$_3$)$_2$), 3.24 (sep, 2H, N(C*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 1.27 (Al*C*H$_2$CH$_3$), 10.14 (N(CH$_2$*C*H$_3$)$_2$), 13.00 (Al*C*H$_2$CH$_3$), 24.86 (NCH (*C*H$_3$)$_2$), 42.66 (N(*C*H$_2$CH$_3$)$_2$), 44.96 (N(*C*H(CH$_3$)$_2$), 167.04 ((^{i}PrN)*C*(NEt$_2$)(N^{i}Pr)).

(Et$_2$)AlN^{i}PrC(N^{i}Pr$_2$)NiPr (14). Liquid (bp 39 °C, 0.01 Torr). Yield: 65%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 296 (6), 282 (74), 211 (36), 184 (96), 169 (51), 127 (36), 100 (52), 85 (100), 58 (73), 43 (89). ^{1}H NMR (C$_6$D$_6$): δ 0.33 (quart, 4H, AlC*H*$_2$CH$_3$), 0.96, 0.98 (d, 12H, N(CH(C*H*$_3$)$_2$)$_2$), 1.06 (d, 12H, NCH(C*H*$_3$)$_2$), 1.30, 1.44 (t, 6H, AlCH$_2$C*H*$_3$), 3.18, 3.48 (sep, 4H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 0.74 (Al*C*H$_2$CH$_3$), 9.96 (AlCH$_2$*C*H$_3$), 22.96 (N(CH(*C*H$_3$)$_2$)$_2$), 25.52 (NCH(*C*H$_3$)$_2$), 44.66 (N*C*H(CH$_3$)$_2$), 48.51 (N(*C*H(CH$_3$)$_2$)$_2$), 167.82 ((^{i}PrN)*C* (N^{i}Pr$_2$)(N^{i}Pr).

Synthesis of RClAlNR″C(Cl)NR″ (R = Me, Et; R″ = ^{t}Bu, ^{i}Pr) (Eqs 1 and 5). A solution of 1,3-dialkylcarbodiimide (6.01 mmol) in ether (30 mL) was added to a hexane solution of alkylaluminum chloride (3 mL, 0.1 M, 3 mmol) in ether (20 mL) under nitrogen at room temperature. The reaction mixture was stirred for 2 h, and colorless liquids were obtained after removal of solvent.

ElClAlN^{t}BuC(Cl)N^{t}Bu (15). Yield: 87%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 154 (6, [(^{t}BuN)$_2$C]$^+$), 139 (26, [EtAl(^{t}BuN)C]$^+$), 99 (8, [Al(^{t}BuN)H]$^+$), 97 (7, [Al(^{t}BuN)H]$^+$), 83 (70, [(^{t}BuN)C]$^+$), 71 (2, [N^{t}Bu]$^+$), 57 (100, [^{t}Bu]$^+$), 56 (24, [AlEt]$^+$), 43 (14, [AlMeH]$^+$), 41 (30, [AlMe-H]$^+$). ^{1}H NMR (C$_6$D$_6$): δ 0.38 (quart, 2H, AlC*H*$_2$CH$_3$), 1.13 (s, 18H, C(CH$_3$)$_3$), 1.33 (t, 3H, AlCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 5.23 (Al*C*H$_2$CH$_3$), 8.90 (AlCH$_2$*C*H$_3$), 30.26 (C(*C*H$_3$)$_3$), 60.93 (*C*(CH$_3$)$_3$), 131.21 ((^{t}BuN)*C*(Cl)(N^{t}Bu)).

MeClAlN^{i}PrC(Cl)N^{i}Pr (16). Yield: 79%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 223 (47), 203 (44), 181 (28), 139 (73), 126 (55), 111 (91), 97 (37), 83 (20), 69 (100), 43 (82). ^{1}H NMR (C$_6$D$_6$): δ −0.14 (s, 3H, AlC*H*$_3$), 0.86 (d, 12H, N(CH(C*H*$_3$)$_2$)$_2$), 3.30 (sep, 2H, N(C*H*(CH$_3$)$_2$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 23.06 (N(CH(*C*H$_3$)$_2$)$_2$), 52.18 (N(*C*H(CH$_3$)$_2$)$_2$), 130.77 (^{i}PrN*C*(Cl)N^{i}Pr).

EtClAlN^{i}PrC(Cl)N^{i}Pr (17). Yield: 66%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 223 (26), 217 (10), 181 (10), 139 (36), 126 (34), 111 (68), 99 (24), 83 (14), 69 (100), 43 (75). ^{1}H NMR (C$_6$D$_6$): δ 0.42 (quart, 2H, AlC*H*$_2$CH$_3$), 0.88 (d, 12H, N(CH(C*H*$_3$)$_2$), 1.37 (t, 3H, AlCH$_2$C*H*$_3$), 3.32 (sep, 2H, N(C*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 1.68 (Al*C*H$_2$CH$_3$), 8.85 (AlCH$_2$*C*H$_3$), 23.06 (NCH (*C*H$_3$)$_2$), 52.23 (N*C*H(CH$_3$)$_2$), 130.43 (^{i}PrN*C*(Cl)N^{i}Pr).

Synthesis of (R$_2$)AlNR″C(R)NR″ (R = Me, Et; R″ = ^{t}Bu, ^{i}Pr) (Eq 9). A solution of 1,3-dialkylcarbodiimide (7.60 mmol) in ether (30 mL) was added to a toluene solution of trialkylaluminum (2.0 mL, 1.9 M, 3.8 mmol) in ether (15 mL) under nitrogen at room temperature. The reaction mixture was stirred for 2 h, and the solvent was removed. Vacuum distillation yielded a colorless liquid.

Et$_2$AlN^{t}BuC(Et)N^{t}Bu (18). Liquid (bp 28 °C, 0.01 Torr). Yield: 56%. Anal. Found: C, 67.03; H, 12.19; N, 10.57. Calcd: C, 67.16; H, 12.31; N, 10.45. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 267 (19, [M − H]$^+$), 239 (89, [M − Et]$^+$), 211 (10, [M − 2Et]$^+$), 155 (3, [(^{t}BuN)$_2$CH]$^+$), 112 (43, [^{t}BuNCEt]$^+$), 98 (17), 84 (10), 71 (7), 57 (100), 43 (14). ^{1}H NMR (C$_6$D$_6$): δ 0.34 (quart, 4H, AlC*H*$_2$CH$_3$), 0.98 (t, 3H, C(CH$_2$C*H*$_3$)), 1.14 (s, 18H, C(C*H*$_3$)$_3$), 1.40 (t, 6H, AlCH$_2$C*H*$_3$), 2.14 (quart, 2H, C(C*H*$_2$CH$_3$)). ^{13}C NMR (C$_6$D$_6$): δ 9.95

(C(CH$_2$*C*H$_3$)), 13.57 (AlCH$_2$*C*H$_3$), 22.84 (C(*C*H$_2$CH$_3$)), 32.00 (C(*C*H$_3$)$_3$), 50.77 (*C*(CH$_3$)$_3$), 178.30 (^{t}BuN*C*(Et)N^{t}Bu).

(Et$_2$)AlN^{i}PrC(Et)N^{i}Pr (19). Liquid (bp 31 °C, 0.01 Torr). Yield: 44%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 239 (6), 211 (68), 183 (18), 156 (11), 113 (14), 98 (27), 84 (28), 71 (13), 56 (100), 43 (26). ^{1}H NMR (C$_6$D$_6$): δ 0.33 (quart, 4H, AlC*H*$_2$CH$_3$), 0.77 (t, 3H, C(CH$_2$C*H*$_3$)), 0.99 (d, 12H, NCH(C*H*$_3$)$_2$), 1.40 (t, 6H, Al(CH$_2$C*H*$_3$)), 1.81 (quart, 2H, C(C*H*$_2$CH$_3$)), 3.18 (sep, 2H, N(C*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 0.34 (Al*C*H$_2$CH$_3$), 9.65 (C(CH$_2$*C*H$_3$)), 11.91 (AlCH$_2$*C*H$_3$), 18.01 (C (*C*H$_2$CH$_3$)), 25.65 (N(CH(*C*H$_3$)$_2$), 44.64 (N*C*H(CH$_3$)$_2$), 176.35 (^{i}PrN*C*(Et)N^{i}Pr).

(Me$_2$)AlN^{i}PrC(Me)N^{i}Pr (20). Liquid (bp 34 °C; 0.01 Torr). Yield: 63%. Mass spectrum (EI, 70 eV; *m/z* (relative intensity, %)): 198 (2), 184 (10), 183 (94), 84 (100), 70 (15), 58 (35), 57 (22), 44 (11), 43 (36), 42 (98). Anal. Calcd: C; 60.45; H, 11.58; N, 14.10. Found: C, 59.85; H, 11.47; N, 14.00. ^{1}H NMR (C$_6$D$_6$): δ −0.29 (s, 6H, Al(C*H*$_3$)$_2$), 0.96 (d, 12H, NCH(C*H*$_3$)$_2$), 1.30 (s, 3H, C*H*$_3$C(N^{i}Pr$_2$)), 3.14 (sep, 2H, NC*H*(CH$_3$)$_2$). ^{13}C NMR (C$_6$D$_6$): δ −0.959 (Al(*C*H$_3$)$_2$), 10.23 (*C*H$_3$C(N^{i}Pr)$_2$), 25.13 (NCH(*C*H$_3$)$_2$), 45.01 (N*C*H(CH$_3$)$_2$), 171.82 (CH$_3$*C*(N^{i}Pr)$_2$).

Structure Determination. Suitable single crystals of complexes **10** and **8″** were sealed in glass capillaries. Preliminary examination and intensity data collections were carried out with either a Rigaku AFC7S diffractometer (for complex **10**) or an Enraf-Nonius CAD-4 automatic diffractometer (for complex **8″**) using graphite-monochromatized Mo Kα ($\lambda = 0.710\ 69$ Å) radiation. Intensity data were collected using the $\theta-2\theta$ scan mode and corrected for absorption and decay. The structures were solved by SIR92[20] (for **10**) or by MULTAN[21] (for **8″**) and refined with full-matrix least squares on *F*. In the final cycles all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions. All calculations were carried out with either a SGI R4000 computer using the teXsan program package[22] (for **10**) or a Microvax 3600 computer using the NRCVAX program package[23] (for **8″**). A summary of the data collection and structure solution is given in Table 1; selected bond lengths and bond angles are given in Table 2.

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Supporting Information Available: Tables of crystal data, atomic coordinates and temperature factors, hydrogen coordinates, and intramolecular bond distances and angles for **10** and **8″**, figures showing the NMR spectra of unanalyzed compounds, and text giving IR data for all of the compounds (43 pages). Ordering information is given on any current masthead page.

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