Hydroalumination of Carbon Dioxide, Carbon Disulfide, and Phenyl Isocyanate with an Aluminum Ketiminate Compound

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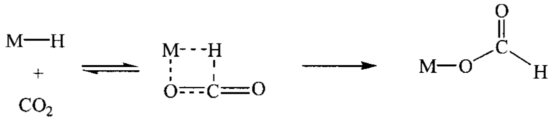
The reaction of MeC(O)C(H)=C(Me)NHAr (Ar = 2,6-diisopropylphenyl) (**1**) with excess $LiAlH_4$ in diethyl ether at –78 °C generates $[AlH(OCMeCHCMeNAr)_2]$ (**2**) in 76% yield. The aluminum formate compound $[Al(OCMeCHCMeNAr)_2(OCOH)]$ (**3**) can be isolated from the reaction of **2** with CO_2 in 93% yield. Compound **3** is thermally stable and remains unchanged when heated under vacuum at 100 °C for 24 h. Similarly, a solution of **2** in dichloromethane reacts with carbon disulfide or phenyl isocyanate at room temperature to yield the insertion products $[Al(OCMeCHCMeNAr)_2(SCHS)]$ (**4**) and $[Al(OCMeCHCMeNAr)_2(OCH{=}NPh)]$ (**5**), respectively, in 80% and 92% yield. Reaction of **2** with 1 equiv. of urethane in toluene at refluxing temperature for 1 h yields the aluminum isocyanate compound $[Al(OCMeCHCMeNAr)_2(NCO)]$ (**6**). The molecular structures of compounds **2**–**6** have been determined by X-ray crystallography. Density functional calculations show that the isomer of compound **2** with an N–N *trans* arrangement is 3.1 kcal·mol^{-1} lower in energy than the O–O *trans* isomer. Inserting CO_2 into the Al–H bond of compound **2** results in the formation of the formate compound **3**; this reaction is predicted to be exothermic by 29.8 kcal·mol^{-1}.

Introduction

Metal−hydride bonds are important in organometallic chemistry because a wide variety of unsaturated small organic molecules can insert into them to yield stable species or intermediates. Among these reactions, the insertion of CO_2 into metal−hydride bonds is particularly interesting. The use of carbon dioxide as a C_1 source is a current research area which is important not only for reducing the dependence on fossil-fuel consumption but also the reduction of greenhouse gases.[1,2] Various methods have been developed for CO_2 activation, and the use of transition-metal compounds as catalysts is common.[3−5] One way to convert CO_2 into functionalized organic molecules is by inserting CO_2 into a transition metal−hydride bond (Scheme 1). Reactions between CO_2 and transition metal hydrides have been reported for many metals, with the main focus on late transition metals.[6−13] The insertion of CO_2 into an aluminum hydride bond has not been reported so far.



Scheme 1

Highly reactive metal−hydrogen bonds also play an important role in catalytic reactions.[14−18] Among these, aluminum hydrides are well known and widely used due to their high reactivity and low cost.[19−27] In this paper we present the synthesis and characterization of aluminum hydride compounds containing substituted ketiminate ligands and their reactions with carbon dioxide, carbon disulfide, and phenyl isocyanate. A related reaction of the aluminum hydride compound with urethane to yield a novel aluminum isocyanate compound is also presented.

Results and Discussion

Reactivity Studies of Ketiminatoaluminum Hydride Compounds

Ketimine **1** [MeC(O)C(H)=C(Me)NHAr; Ar = 2,6-diisopropylphenyl] can be easily synthesized in high yield by an imine condensation reaction between 2,4-pentanedione and 2,6-diisopropylaniline in a 1:1 ratio in methanol.[28] The reaction of compound **1** with an excess of $LiAlH_4$ in diethyl ether at −78 °C, followed by stirring at −10 °C for 2 h, generates $[AlH(OCMeCHCMeNAr)_2]$ (**2**) in 76% yield after recrystallization of the crude solids from diethyl ether at −20 °C (Scheme 2). The ^1H NMR spectrum of compound **2** in C_6D_6 indicates C_2 symmetry of the molecule, with the two methyl resonances of the ligand backbone appearing at

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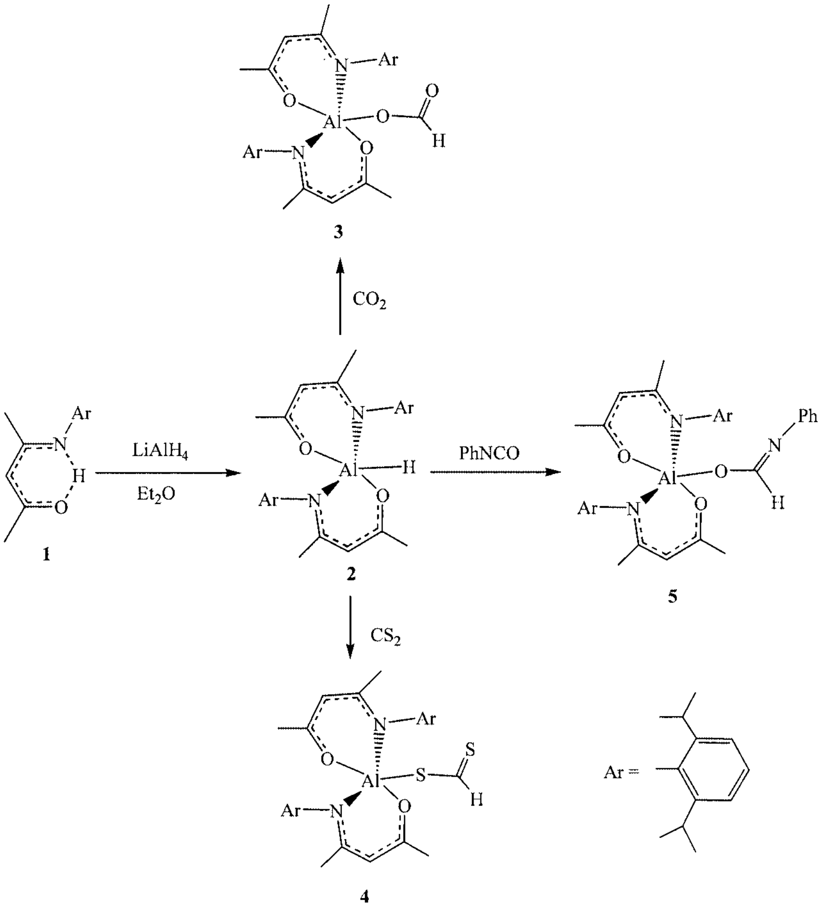


Scheme 2

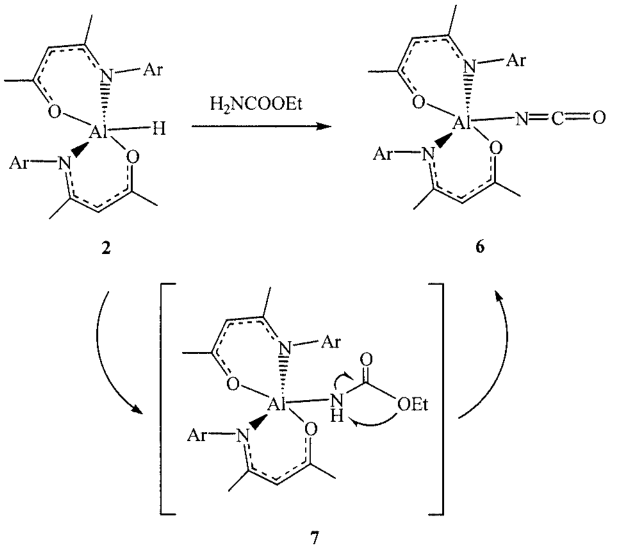
δ = 1.50 and 1.32 ppm. The N−Ar rotation of compound **2** in solution at ambient temperature is slow due to the high steric hindrance between the isopropyl group and the methyl groups of the ligand backbone. The ^{1}H and ^{13}C NMR spectra of compound **2** confirm this (two sets of isopropyl resonances). The hydride resonance was not observed, presumably due to the interaction of the hydrogen atom with ^{27}Al (I = 5/2).[29] The solid-state IR spectrum shows a $\nu_{\mathrm{Al-H}}$ band at 1788 cm^{-1}. Moreover, the deuterated compound [AlD(OCMeCHCMeNAr)$_2$] (**2D**), synthesized by treating compound **1** with LiAlD$_4$, exhibits exactly the same ^{1}H NMR spectrum as compound **2**. The $\nu_{\mathrm{Al-D}}$ band of this compound appears at 1297 cm^{-1} (calculated value 1287 cm^{-1} from the isotope shift). Compound **2** is thermally unstable and decomposes in C$_6$D$_6$ at 80 °C, forming unidentified compounds.

The aluminum hydride compound **2** is reactive toward the C=O, C=S, and C=N functional groups in carbon dioxide, carbon disulfide, and phenyl isocyanate, respectively. The reactions are summarized in Scheme 2. Reaction of compounds **2** or **2D** with CO$_2$ in dichloromethane solution were completed within minutes after admitting CO$_2$ gas into the solution. The reactions are exothermic. The aluminum formate compounds [Al(OCMeCHCMeNAr)$_2$(OCOH)] (**3**) and [Al(OCMeCHCMeNAr)$_2$(OCOD)] (**3D**) were isolated in 93% yield from diethyl ether solutions at −20 °C. Compound **3** is thermally stable and remains unchanged even when heated under vacuum at 100 °C for 24 h. The ketiminate backbone of **3** exhibits the same pattern of ^{1}H and ^{13}C NMR resonances as **2**. However, the ^{1}H NMR spectrum of **3** exhibits a singlet at δ = 8.0 ppm for the formate proton, which was not observed for compound **3D**. The ^{13}C{^{1}H} NMR spectrum of compound **3** shows a singlet at δ = 163.8 ppm for the formate carbon atom; this signal is a triplet for compound **3D** with a $^1J_{\mathrm{C,D}}$ coupling constant of 31 Hz.

Similarly, reactions of **2** with carbon disulfide and phenyl isocyanate in dichloromethane at room temperature yielded the insertion products [Al(OCMeCHCMeNAr)$_2$(SCHS)] (**4**) and [Al(OCMeCHCMeNAr)$_2$(OCH=NPh)] (**5**) in 80% and 92% yield, respectively. The ^{1}H NMR spectrum of **4** exhibits a downfield singlet at δ = 11.66 ppm for the dithioformate proton, comparable to the values of other metal dithioformate compounds.[30,31] The dithioformate proton resonance was not observed for the corresponding deuterated compound **4D**. In the ^{13}C{^{1}H} NMR spectrum, the carbon resonance of C=S for **4** appears at δ = 240.5 ppm, which is downfield relative to that of the C=O resonance of **3**, but similar to the values of reported metal dithioformate compounds.[30,31] Again, the ^{13}C{^{1}H} NMR spectrum shows that the carbon resonance of C=S for compound **4D** also appears as a triplet at δ = 240.5 ppm with a $^1J_{\mathrm{C,D}}$

coupling constant of 28 Hz. The ^1H NMR spectrum of **5** displays a singlet at δ = 7.74 ppm for the formimidato proton, which was not observed in **5D**. Similarly, the carbon resonance of the C=N fragment appears at δ = 157.8 ppm as a singlet for compound **5**. However, even with very high concentrations of **5D**, no signal was observed for the carbon resonance of the C=N fragment.

An intriguing reaction of **2** occurs with urethane, $H_2NCOOEt$. Reaction of **2** with 1 equiv. of urethane in refluxing toluene for 1 h yielded the aluminum isocyanate compound [Al(OCMeCHCMeNAr)$_2$(NCO)] (**6**) as white crystals in 57% yield (Scheme 3). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** show similar patterns for the ketiminate fragments as those of **3** and **4**. The isocyanate functional group exhibits two strong infrared absorptions at 2267 and 2206 cm^{-1}, which are similar to those of other M−NCO compounds in the literature.[32−34] The reaction was also monitored by ^1H NMR spectroscopy in a C_6D_6 solution. A possible mechanistic pathway for the formation of **6** is shown in Scheme 3. The first step involves hydrogen elimination to form the aluminum carbamidate intermediate **7**, followed by successive loss of ethanol to form the final aluminum isocyanate compound **6**. Precise control of the reaction time and recrystallization procedure are necessary to avoid further reaction of the by-product, ethanol, with the aluminum ketiminate compounds, which regenerates the ketimine ligands. A related reaction converting an NCO fragment to urethane was reported by Knoth[35] et al. in 1967. A boron compound containing B−NCO, derived from the reaction of B−CO with azide, was converted into $B-NHCO_2C_2H_5$ in the reactions of 1,12-$B_{12}H_{10}(NCO)_2^{2-}$ and 1,10-$B_{10}Cl_8(NCO)_2^{2-}$ with ethanol/hydrogen chloride, resulting in the formation of the urethanes 1,12-$B_{12}H_{10}(NHCO_2C_2H_5)_2^{2-}$ and 1,10-$B_{10}Cl_8(NHCO_2C_2H_5)_2^{2-}$, respectively.



Scheme 3

Molecular Structures of Ketiminatoaluminum Compounds 2−6

The molecular structures of compounds **2−6** are shown in Figures 1−5, and selected bond lengths and angles are listed in Table 1. Compounds **2−6** are all five-coordinate trigonal-bipyramidal structures. The two nitrogen atoms of the ketiminate backbone for compound **2** occupy the axial positions while the two oxygen atoms and the hydrido ligand form the equatorial plane. However, the most distinct structural difference between **3−6** and **2** is that the two oxygen atoms of the two ketiminate backbones in **3−6** occupy the axial positions. A schematic description of the molecular structures of **2−6** is shown in Scheme 4. The molecular structures of a series of ketiminatoaluminum halide and alkyl compounds reported in the literature are all shown with an O−O *trans* geometry.[36] A theoretical calculation of the geometry of **2** was therefore performed (vide infra).

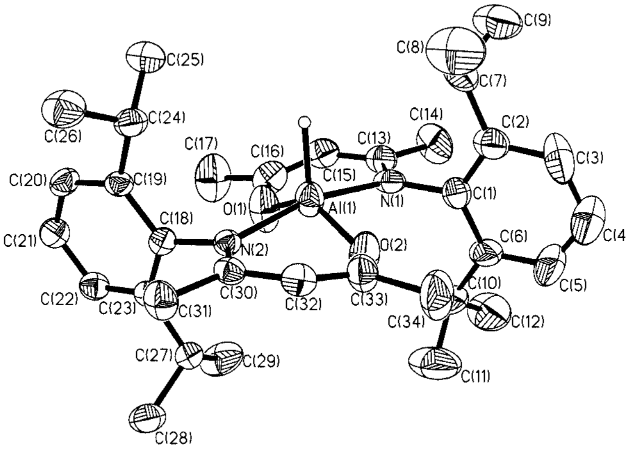


Figure 1. The molecular structure of compound **2**, with ellipsoids drawn at the 50% probability level; all hydrogen atoms except the aluminum hydride have been omitted for clarity

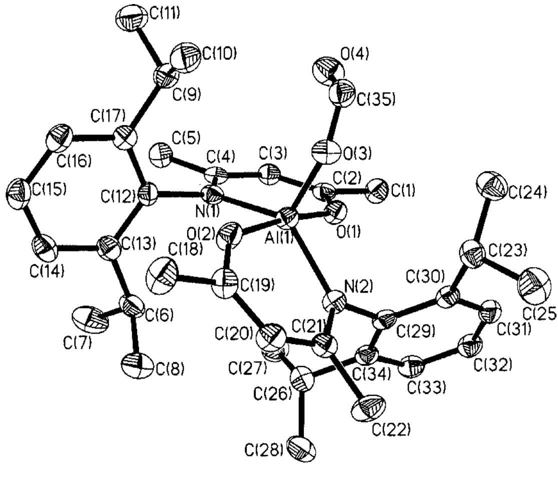


Figure 2. The molecular structure of compound **3**, with ellipsoids drawn at the 50% probability level; all hydrogen atoms have been omitted for clarity

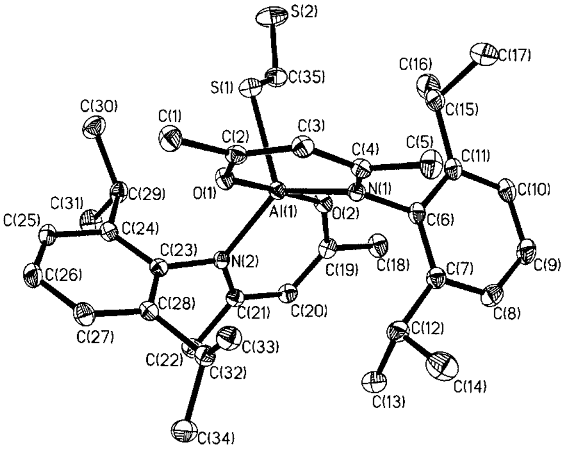


Figure 3. The molecular structure of compound **4**, with ellipsoids drawn at the 50% probability level; toluene and all hydrogen atoms have been omitted for clarity

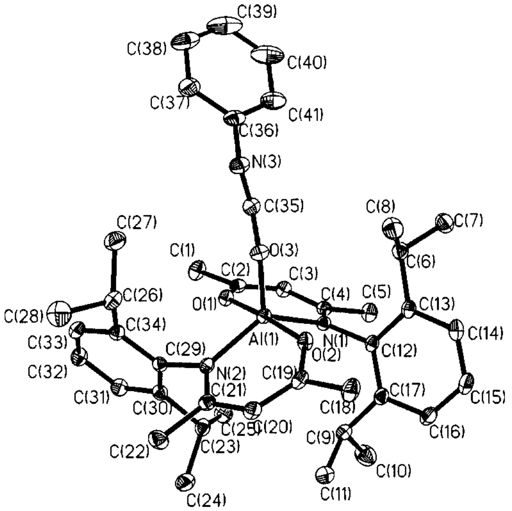


Figure 4. The molecular structure of compound **5**, with ellipsoids drawn at the 50% probability level; all hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2**−**6**

2					
Al(1)−O(1)	1.763(3)	Al(1)−O(2)	1.757(3)	Al(1)−N(1)	2.079(3)
Al(1)−N(2)	2.064(3)	Al(1)−H(1)	1.61(3)		
O(1)−Al(1)−O(2)	133.6(2)	O(1)−Al(1)−N(1)	88.3(1)	O(1)−Al(1)−N(2)	86.96(13)
O(1)−Al(1)−H(1)	111.8(11)	O(2)−Al(1)−N(1)	85.31(14)	O(2)−Al(1)−N(2)	88.21(13)
O(2)−Al(1)−H(1)	114.5(11)	N(1)−Al(1)−H(1)	95.3(11)	N(1)−Al(1)−N(2)	165.69(13)
N(2)−Al(1)−H(1)	99.0(1)				
3					
Al(1)−O(1)	1.807(2)	Al(1)−O(2)	1.813(2)	Al(1)−O(3)	1.798(2)
Al(1)−N(1)	1.976(2)	Al(1)−N(2)	1.997(2)	O(4)−C(35)	1.213(3)
O(3)−C(35)	1.296(3)				
O(1)−Al(1)−O(2)	171.20(8)	O(1)−Al(1)−O(3)	96.95(8)	O(1)−Al(1)−N(1)	90.45(7)
O(1)−Al(1)−N(2)	87.00(7)	O(2)−Al(1)−O(3)	91.77(8)	O(2)−Al(1)−N(1)	86.73(7)
O(2)−Al(1)−N(2)	89.17(8)	O(3)−Al(1)−N(1)	116.10(8)	O(3)−Al(1)−N(2)	108.30(8)
N(1)−Al(1)−N(2)	135.50(8)	O(3)−C(35)−O(4)	127.6(3)		
4					
Al(1)−O(1)	1.8093(16)	Al(1)−O(2)	1.8018(16)	Al(1)−N(1)	1.9685(18)
Al(1)−N(2)	1.9864(17)	Al(1)−S(1)	2.3342(8)	S(2)−C(35)	1.642(2)
S(1)−C(35)	1.689(2)				
O(1)−Al(1)−O(2)	177.84(7)	O(1)−Al(1)−N(1)	91.24(7)	O(1)−Al(1)−N(2)	87.48(7)
O(1)−Al(1)−S(1)	85.58(5)	O(2)−Al(1)−N(1)	90.39(7)	O(2)−Al(1)−N(2)	90.39(7)
O(2)−Al(1)−S(1)	95.16(6)	N(1)−Al(1)−N(2)	129.30(7)	N(1)−Al(1)−S(1)	110.70(5)
N(2)−Al(1)−S(1)	119.69(6)	S(1)−C(35)−S(2)	126.35(15)		
5					
Al(1)−O(1)	1.8263(12)	Al(1)−O(2)	1.8054(12)	Al(1)−O(3)	1.7852(13)
Al(1)−N(1)	2.0019(14)	Al(1)−N(2)	1.9799(14)	O(3)−C(35)	1.305(2)
N(3)−C(35)	1.267(2)	N(3)−C(36)	1.418(2)		
O(1)−Al(1)−O(2)	174.26(6)	O(1)−Al(1)−N(1)	89.24(5)	O(1)−Al(1)−N(2)	88.31(6)
O(1)−Al(1)−O(3)	94.25(6)	O(2)−Al(1)−O(3)	91.41(6)	O(2)−Al(1)−N(1)	87.65(5)
O(2)−Al(1)−N(2)	90.18(6)	O(3)−Al(1)−N(1)	113.40(6)	O(3)−Al(1)−N(2)	114.59(6)
O(3)−C(35)−N(3)	122.95(17)	N(1)−Al(1)−N(2)	131.99(6)		
6					
Al(1)−O(1)	1.7875(15)	Al(1)−O(2)	1.7946 (15)	Al(1)−N(1)	1.9991(17)
Al(1)−N(2)	1.9961(18)	Al(1)−N(3)	1.837(2)	N(3)−C(35)	1.147(3)
O(3)−C(35)	1.189(3)				
O(1)−Al(1)−O(2)	168.17(9)	O(1)−Al(1)−N(1)	89.44(7)	O(1)−Al(1)−N(2)	86.73(7)
O(1)−Al(1)−N(3)	96.02(9)	O(2)−Al(1)−N(1)	86.22(7)	O(2)−Al(1)−N(2)	89.33(7)
O(2)−Al(1)−N(3)	95.81(8)	N(1)−Al(1)−N(2)	138.95(8)	N(1)−Al(1)−N(3)	111.70(9)
N(2)−Al(1)−N(3)	109.34(8)	N(3)−C(35)−O(3)	179.5(4)		

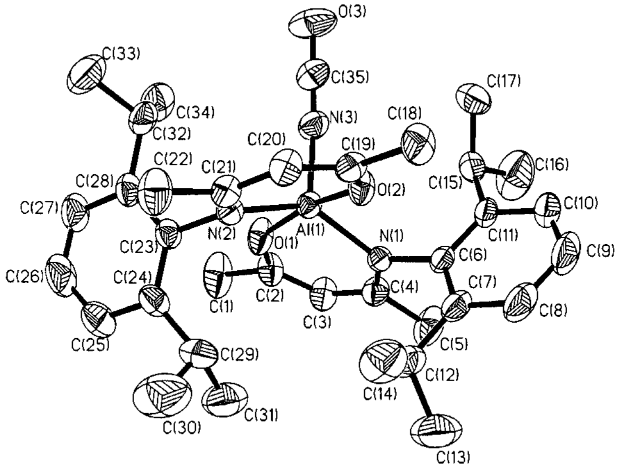


Figure 5. The molecular structure of compound **6**, with ellipsoids drawn at the 50% probability level; all hydrogen atoms have been omitted for clarity

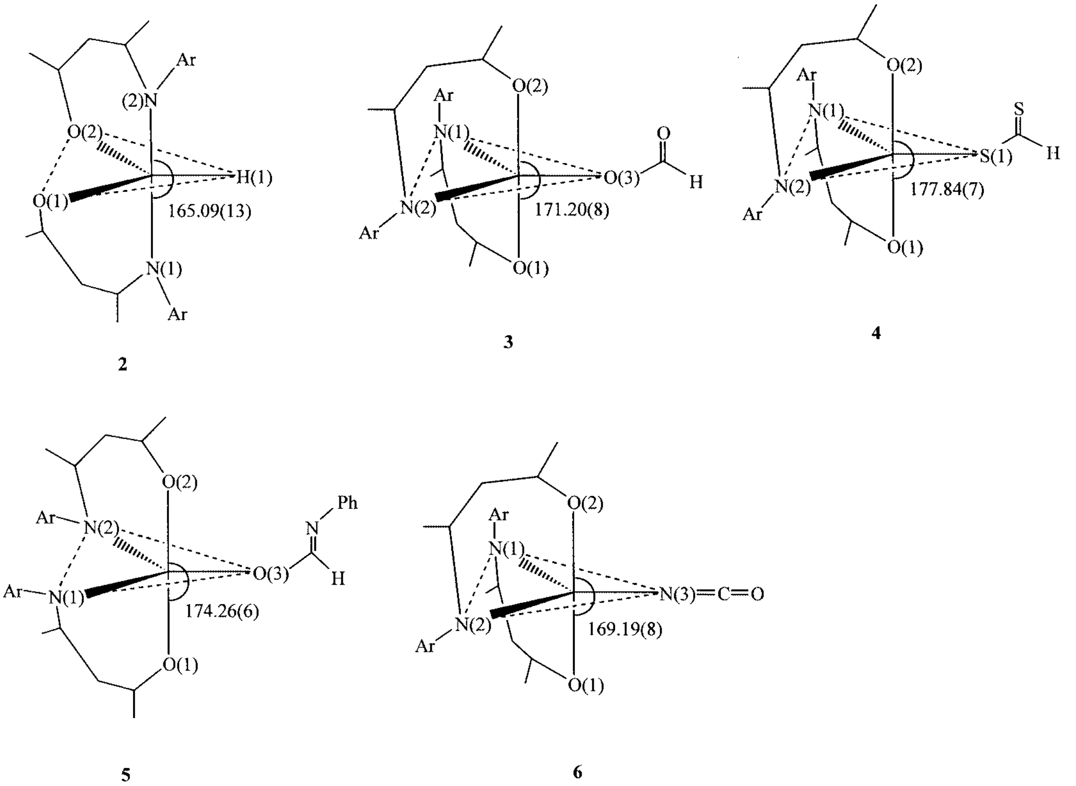
As described above, the molecular structure of **2** is trigonal-bipyramidal with two Al−N(axial) bond lengths of 2.079(3) and 2.064(3) Å. For comparison, the Al−N(equatorial) bonds in compounds **3**−**6**, which range from 1.976(2) to 2.002(1) Å, are generally shorter than the Al−N(axial) bonds. Similarly, the Al−O(equatorial) bonds in compound **2** [1.763(3) and 1.757(3) Å] are shorter than the Al−O(axial) bonds for compounds **3**−**6** [ranging from 1.795(1) to 1.826(1) Å]. A better hybridization of the trigonal-planar sp^2 orbitals of aluminum with the equatorial oxygen or nitrogen atoms forming σ-bonds may be the reason for these shorter distances.

Molecular Structures of Group 13 Metal−NCO Compounds

Compounds containing NCO ligands are very common for late transition metals. However, only a few group 13 metal NCO compounds have been structurally characterized. When searching the Cambridge Crystallographic Database, there are only three M(NCO) (M = group 13) compounds, two B−NCO compounds and one In−NCO compound.[37−39] A comparison of the bond angles and bond lengths of these M(NCO) (M = group 13) compounds is given in Table 2. The NCO angles for all the compounds listed in the table are almost linear [177.8(4)° to 179.5(4)°]. However, the M−NCO angles vary depending on the metals. The In−N−C angle of 147.1(8)° is much smaller than those of compound **6** and the B−N−C compounds; this is probably due to crystal packing effects.[37] The C−N and C−O bond lengths are very similar in all the compounds listed in Table 2 and can be viewed as C≡N triple bonds (normally at 1.16 Å) and C=O double bonds (normally at 1.22 Å), respectively.

Density Functional Theory (DFT) Calculations on the Reaction between CO_2 and 2

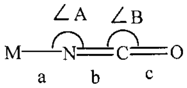
The intriguing reactivity of compound **2** toward CO_2 has been carefully calculated. Four structures were considered:



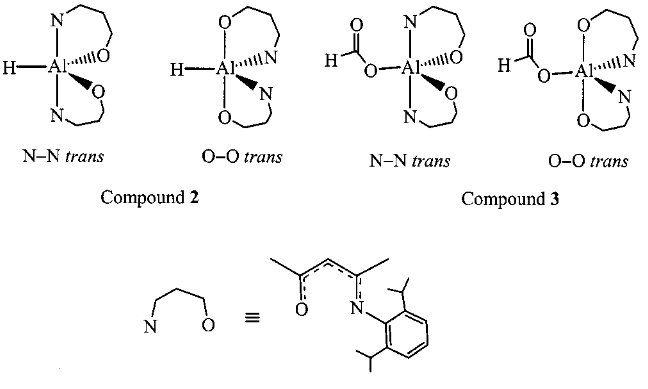
Scheme 4

Table 2. Comparisons of bond lengths and angles for M(NCO) (M = group 13) compounds

Compound	Bond angles [°]		Bond lengths [Å]			Ref.
	∠ A	∠ B	a	b	c	
$[closo\text{-}2\text{-}B_{10}H_9NCO]^{2-}$	172.3(3)	177.8(4)	1.498(7)	1.128(7)	1.187(7)	[37]
6	172.4(2)	179.5(4)	1.836(2)	1.151(3)	1.188(3)	this work
$[(Pc)_2In(NCO)_2][PNP]$	147.1(8)	178 (1)	2.155(9)	1.15(1)	1.17(2)	[39]
	164.4(9)	179(1)	2.165(9)	1.17(2)	1.23(2)	[39]



the N−N *trans* and O−O *trans* forms of compound **2**, and the N−N *trans* and O−O *trans* forms of compound **3**, as shown in Scheme 5.



Scheme 5

Density functional theory, which includes Becke's three-parameter nonlocal exchange potential and the nonlocal correlation functional of Lee, Yang, and Parr, was used, along with the 6-31G* basis sets.[40,41] For compound **2**, the isomer with the N−N *trans* arrangement is found to be 3.1 kcal·mol^{-1} lower in energy than the O−O *trans* isomer. This observation is consistent with the solid-state structure of compound **2**, in which the two nitrogen atoms of the ketiminate ligands are found in the axial positions. Inserting CO_2 into the Al−H bond of compound **2** results in the formation of the formate compound **3** in a reaction which was predicted to be exothermic by 29.8 kcal·mol^{-1}. For compound **3**, the N−N *trans* and O−O *trans* isomers are very close in energy, with the former being 0.05 kcal·mol^{-1} more stable. The predicted geometrical parameters at the B3LYP/6-31G* level[42] agree reasonably well with those obtained by X-ray crystallography.

In conclusion, we have synthesized aluminum hydride compounds containing ketiminate ligands. These aluminum hydride compounds show novel reactivity toward CO_2, CS_2, and phenyl isocyanate insertion, which has not been seen before in main-group chemistry. A first example of an aluminum NCO compound, $[Al(OCMeCHCMeNAr)_2(NCO)]$ (**6**), has also been structurally characterized from the reaction of aluminum hydride with urethane. A theoretical calculation proved that the CO_2 insertion product has a lower energy than that of the corresponding aluminum hydride compounds.

Experimental Section

General Procedures: All reactions were performed under dry nitrogen using standard Schlenk techniques or in a glove box. Toluene and diethyl ether were dried by refluxing in the presence of sodium benzophenone ketyl. CH_2Cl_2 was dried with P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained molecular sieves (4 Å) and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC200 or an Avance 300 M Hz spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the internal deuterated solvent ($CDCl_3$: ^1H: $\delta = 7.24$ ppm; ^{13}C: $\delta = 77.0$ ppm). Elemental analyses were performed with a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. Ketimine **1** [MeC(O)C(H)=C(Me)NHAr; Ar = 2,6-diisopropylphenyl] was prepared according to a previously reported procedure.[36] $AlCl_3$ (Strem), MeLi, and EtLi (Aldrich) were used as received.

$[AlH(OCMeCHCMeNAr)_2]$ (2): A diethyl ether solution (30 mL) of **1** (10.0 g, 38.6 mmol) was added dropwise whilst stirring at −78 °C to a 100-mL Schlenk flask containing a suspension of $LiAlH_4$ (0.73 g, 19.2 mmol) in diethyl ether (20 mL). The mixture was allowed to warm to −10 °C and then stirred for 2 h. The resulting suspension was filtered through Celite. The filtrate was dried under vacuum to remove volatiles, and the resulting solid was recrystallized from diethyl ether to give 8.0 g of **2** (76% yield). ^1H NMR (C_6D_6): δ = 1.08 (d, 6 H, CH*Me₂*), 1.12 (d, 6 H, CH*Me₂*), 1.32 (s, 6 H, C*Me*), 1.34 (d, 6 H, CH*Me₂*), 1.38 (d, 6 H, CH*Me₂*), 1.50 (s, 6 H, C*Me*), 3.13 (m, 2 H, C*H*Me₂), 3.40 (m, 2 H, C*H*Me₂), 5.06 (s, 2 H, CMeC*H*CMe), 7.15 (m, 6 H, *Ph*) ppm. ^{13}C NMR (C_6D_6): δ = 23.4 (q, $J_{C,H}$ = 128 Hz, CH*Me₂*), 24.0 (q, $J_{C,H}$ = 126 Hz, CH*Me₂*), 24.3 (q, $J_{C,H}$ = 126 Hz, CH*Me₂*), 24.5 (q, $J_{C,H}$ = 128 Hz, CH*Me₂*), 24.6 (q, $J_{C,H}$ = 125 Hz,), 25.9 (q, $J_{C,H}$ = 125 Hz,), 28.2 (q, $J_{C,H}$ = 133 Hz,), 28.5 (q, $J_{C,H}$ = 130 Hz,), 100.1 (d, $J_{C,H}$ = 160 Hz,), 123.5 (d, $J_{C,H}$ = 152 Hz,), 123.9 (d, $J_{C,H}$ = 153 Hz,), 125.6 (d, $J_{C,H}$ = 158 Hz,), 129.4 (s), 142.0 (s, Ph C_{ipso}), 145.2 (s, Ph C_{ipso}), 173.0 (s, *C*N), 177.2 (s, *C*O) ppm. IR (KBr): ν_{Al-H} = 1788 cm^{-1}. $C_{34}H_{49}AlN_2O_2$ (544.75): calcd. C 74.96, H 9.07, N 5.14; found C 74.14, H 8.92, N 6.20. **2D** was synthesized following the same procedure except that $LiAlD_4$ was used. The ^1H and ^{13}C

NMR spectra of **2D** and **2** are identical. IR (KBr): $\nu_{\text{Al-D}}$ = 1297 cm^{-1}.

[Al(OCMeCHCMeNAr)$_2$(OCOH)] (3): Carbon dioxide was bubbled through a 30-mL Schlenk flask charged with 15 mL of dichloromethane and **2** (1.0 g, 1.8 mmol) at room temperature for 1 min. The solution was then stirred for 3 min and the volatiles were removed under vacuum to yield a pure white solid (1.0 g) of **3** in 92.6% yield. ^{1}H NMR (CDCl$_3$): δ = 1.05 (d, 6 H, CH*Me$_2$*), 1.08 (d, 6 H, CH*Me$_2$*), 1.10 (d, 6 H, CH*Me$_2$*), 1.16 (d, 6 H, CH*Me$_2$*), 1.18 (s, 6 H, C*Me*), 1.65 (s, 6 H, C*Me*), 2.85 (m, 2 H, C*H*Me$_2$), 3.05 (m, 2 H, C*H*Me$_2$), 5.21 (s, 2 H, CMeC*H*CMe), 7.03−7.23 (m, 6 H, *Ph*), 8.23 (s, CO*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 23.7 (q, $J_{\text{C,H}}$ = 127 Hz, C*Me*), 23.9 (q, CH*Me$_2$*), 24.3 (q, CH*Me$_2$*), 24.8 (br. q, two overlapping peaks, CH*Me$_2$*), 25.3 (q, $J_{\text{C,H}}$ = 128 Hz, *C*Me), 27.3 (d, $J_{\text{C,H}}$ = 126 Hz, *C*HMe$_2$), 28.2 (d, $J_{\text{C,H}}$ = 127 Hz, *C*HMe$_2$), 100.1 (d, $J_{\text{C,H}}$ = 159 Hz, CMe*C*HCMe), 123.1(d, $J_{\text{C,H}}$ = 158 Hz, Ph *C*H), 123.9 (d, $J_{\text{C,H}}$ = 158 Hz, Ph *C*H), 125.6 (d, $J_{\text{C,H}}$ = 159 Hz, Ph *C*H), 140.6 (s, Ph C_{ipso}), 143.0 (s, Ph C_{ipso}), 145.1 (s, Ph C_{ipso}), 163.8 (d, $J_{\text{C,H}}$ = 204 Hz, *C*HO), 177.8 (s, *C*N), 180.6 (s, *C*O) ppm. $C_{35}H_{49}AlN_2O_4$ (588.756): calcd. C 71.40, H 8.39, N 4.76; found C 71.83, H 8.90, N 5.05. The ^{1}H and ^{13}C NMR spectra of **3D** are similar to those of **3** except that the formate proton of **3** (δ = 8.01 ppm) is not present in **3D** and the formate carbon atom (δ = 163.8 ppm) for **3D** appears as a triplet ($^1J_{\text{C,D}}$ = 31 Hz).

[Al(OCMeCHCMeNAr)$_2$(SCSH)] (4): An excess of carbon disulfide was added at room temperature to a 30-mL Schlenk flask containing 15 mL of dichloromethane and **2** (1.0 g, 1.8 mmol). The solution was stirred for 1 h and the volatiles were removed under vacuum to yield **4** (0.91 g) as a yellow solid in 80% yield. ^{1}H NMR (CDCl$_3$): δ = 1.03 (d, 6 H, CH*Me$_2$*), 1.10 (two overlapping doublets, 12 H, CH*Me$_2$*), 1.18 (d, 6 H, CH*Me$_2$*), 1.24 (s, 6 H, C*Me*), 1.71 (s, 6 H, C*Me*), 2.89 (m, 2 H, C*H*Me$_2$), 3.07 (m, 2 H, C*H*Me$_2$), 5.20 (s, 2 H, CMeC*H*CMe), 7.06−7.24 (m, 6 H, *Ph*), 11.66 (s, CS*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 23.6 (q, $J_{\text{C,H}}$ = 128 Hz, C*Me*), 23.9 (q, CH*Me$_2$*), 24.7 (q, CH*Me$_2$*), 25.0 (q, CH*Me$_2$*), 25.1 (q, CH*Me$_2$*), 25.3 (q, $J_{\text{C,H}}$ = 129 Hz, *C*Me), 28.1 (d, *C*HMe$_2$), 28.4 (d, *C*HMe$_2$), 100.4 (d, $J_{\text{C,H}}$ = 162 Hz, CMe*C*HCMe), 123.1 (d, $J_{\text{C,H}}$ = 159 Hz, Ph *C*H), 124.3 (d, $J_{\text{C,H}}$ = 156 Hz, Ph *C*H), 126.1 (d, $J_{\text{C,H}}$ = 160 Hz, Ph *C*H), 140.8 (s, Ph C_{ipso}), 143.6 (s, Ph C_{ipso}), 143.7 (s, Ph C_{ipso}), 178.9 (s, *C*N), 180.9 (s, *C*O), 240.5 (d, $J_{\text{C,H}}$ = 178 Hz, S*C*SH) ppm. $C_{35}H_{49}AlN_2O_2S_2$ (620.89): calcd. C 67.71, H 7.95, N 4.51; found C 67.36, H 9.05, N 4.49. The ^{1}H and ^{13}C NMR spectra of **4D** are similar to those of **4** except that the resonance of the dithioformate proton of **4** at δ = 11.66 ppm is not observed in **4D** and the resonance of the dithioformate carbon atom (δ = 240.5 ppm) of **4D** appears as a triplet ($^1J_{\text{C,D}}$ = 28 Hz).

[Al(OCMeCHCMeNAr)$_2$(OCHNPh)] (5): Phenyl isocyanate (0.40 mL, 3.69 mmol) was added with a syringe at room temperature to a 30-mL Schlenk flask containing 15 mL of dichloromethane and **2** (2.0 g, 3.67 mmol). The solution was stirred for 1 h and volatiles were removed under vacuum to yield a yellow solid. The solid was washed with heptane in several portions to remove unreacted phenyl isocyanate, and was then dried under vacuum to give 2.25 g of **5** (92% yield). ^{1}H NMR (CDCl$_3$): δ = 1.06 (d, 6 H, CH*Me$_2$*), 1.10 (d, 6 H, CH*Me$_2$*), 1.11 (d, 6 H, CH*Me$_2$*), 1.20 (s, 6 H, C*Me*), 1.22 (d, 6 H, CH*Me$_2$*), 1.65 (s, 6 H, C*Me*), 2.82 (m, 2 H, C*H*Me$_2$), 3.17 (m, 2 H, C*H*Me$_2$), 5.18 (s, 2 H, CMeC*H*CMe), 6.81−7.25 (m, 6 H, *Ph*), 7.74 (s, CNPh*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 23.6 (q, $J_{\text{C,H}}$ = 127 Hz, C*Me*), 23.8 (q, CH*Me$_2$*), 24.3 (q,

Table 3. Summary of crystallographic data for compounds **2**−**6**

	2	3	4	5	6
Empirical formula	$C_{34}H_{49}AlN_2O_2$	$C_{35}H_{49}AlN_2O_4$	$C_{42}H_{57}AlN_2O_2S_2$	$C_{41}H_{54}AlN_3O_3$	$C_{35}H_{48}AlN_3O_3$
Formula mass	544.73	588.74	713.00	663.85	585.74
Crystal system	rhombohedral	triclinic	triclinic	monoclinic	triclinic
Space group	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	35.358(3)	10.4508(13)	12.433(1)	11.2660(7)	11.0971(9)
b [Å]	36.358(3)	12.1431(14)	12.494(1)	11.6265(8)	13.2319(10)
c [Å]	13.0454(14)	14.4459(17)	15.031(1)	29.8774(19)	13.8907(11)
α [°]	90	69.713(2)	101.124(2)	90	71.086(2)
β [°]	90	84.803(2)	111.020(2)	99.793(1)	88.583(2)
γ [°]	120	71.539(2)	102.898(2)	90	66.344(2)
Volume [Å^3]/Z	14935(2)/18	1630.7(3)/2	2026.7(3)/2	3856.4(4)/4	1754.3(2)/2
D_{calcd} [Mg/m^3]	1.090	1.199	1.168	1.143	1.109
μ [mm^{-1}]	0.091	0.102	0.189	0.092	0.093
F(000)	5328	636	768	1432	632
Crystal size [mm]	0.47 × 0.30 × 0.22	0.28 × 0.24 × 0.20	0.35 × 0.30 × 0.25	0.35 × 0.28 × 0.22	0.47 × 0.43 × 0.34
θ(min)−θ(max) [°]	1.12−27.52	1.50−27.57	1.52−27.55	1.38−27.52	2.07−27.51
Reflections collected	31448	10381	13027	23811	11319
Independent reflections	7566 (R_{int} = 0.1037)	7215 (R_{int} = 0.0401)	9009 (R_{int} = 0.0506)	8794 (R_{int} = 0.0395)	7807 (R_{int} = 0.0696)
Max./min. transmission	0.9486/0.7467	0.9486/0.5879	0.9486/0.7267	0.9486/0.5620	
Data/restraints/parameters	7566/0/368	7215/ 0 /391	9009/ 0 /455	8794/ 0 /445	7807/0 /379
Goodness-of-fit on F^2	0.996	0.809	0.611	0.816	0.706
R [$I > 2\sigma(I)$]	$R1$ = 0.0586 $wR2$ = 0.1180	$R1$ = 0.0510 $wR2$ = 0.1111	$R1$ = 0.0497 $wR2$ = 0.1441	$R1$ = 0.0420 $wR2$ = 0.0948	$R1$ = 0.0470 $wR2$ = 0.1084
R (all data)	$R1$ = 0.1998 $wR2$ = 0.1729	$R1$ = 0.0991 $wR2$ = 0.1244	$R1$ = 0.0809 $wR2$ = 0.1702	$R1$ = 0.0798 $wR2$ = 0.1140	$R1$ = 0.1193 $wR2$ = 0.1219
Largest difference peak/hole [eÅ^3]	0.423/−0.302	0.320/−0.429	0.579/−0.361	0.224/−0.325	0.198/−0.171

CHMe_2), 24.6 (q, CHMe_2), 25.0 (q, CHMe_2), 25.1 (q, $J_{\mathrm{C,H}}$ = 127 Hz, C*Me*), 27.3 (d, $J_{\mathrm{C,H}}$ = 129 Hz, *C*HMe$_2$), 28.1 (d, $J_{\mathrm{C,H}}$ = 127 Hz, *C*HMe$_2$), 100.0 (d, $J_{\mathrm{C,H}}$ = 162 Hz, CMe*C*HCMe), 121.5 (d, $J_{\mathrm{C,H}}$ = 161 Hz, Ph *C*H), 122.2 (d, $J_{\mathrm{C,H}}$ = 161 Hz, Ph *C*H), 122.9 (d, $J_{\mathrm{C,H}}$ = 155 Hz, Ph *C*H), 123.8 (d, $J_{\mathrm{C,H}}$ = 154 Hz, Ph *C*H), 125.4 (d, $J_{\mathrm{C,H}}$ = 159 Hz, Ph *C*H), 128.6 (d, $J_{\mathrm{C,H}}$ = 160 Hz, Ph *C*H), 140.6 (s, Ph C_{ipso}), 142.9 (s, Ph C_{ipso}), 145.3 (s, Ph C_{ipso}), 151.2 (s, Ph C_{ipso}), 157.8 (d, $J_{\mathrm{C,H}}$ = 180 Hz, *C*NPhH), 177.3 (s, *C*N), 180.2(s, *C*O) ppm. A small amount of phenyl isocyanate was present in the product which resulted in inaccuracy of the elemental analysis. The ^{1}H and ^{13}C NMR spectra of **5D** are similar to those of **5** except that the resonance of the *N*-phenyl formimidato proton of **5** at δ = 7.74 ppm was not observed for **5D**.

[Al(OCMeCHCMeNAr)$_2$(NCO)] (6): A toluene (10 mL) solution of $H_2NCOOEt$ (0.32 g, 3.67 mmol) was added dropwise at room temperature to a 50-mL Schlenk flask containing 20 mL of toluene and **2** (2.0 g, 3.67 mmol). The solution was refluxed for 1 h and the volatiles were removed under vacuum to yield an off-white solid. The solid was washed with a small amount of heptane in several portions to remove free ketiminate ligand. The resulting solid was recrystallized from a toluene solution at −20 °C to yield colorless crystals of **6** (1.23 g) in 57% yield. ^{1}H NMR (CDCl$_3$): δ = 1.05 (2 d, overlapping, 12 H, CHMe_2), 1.17 (d, 6 H, CHMe_2), 1.19 (s, 6 H, C*Me*), 1.28 (d, 6 H, CHMe_2), 1.65 (s, 6 H, C*Me*), 2.75 (m, 2 H, C*H*Me$_2$), 3.14 (m, 2 H, C*H*Me$_2$), 5.17 (s, 2 H, CMeC*H*CMe), 7.03−7.17 (m, 6 H, *Ph*) ppm. ^{13}C NMR (CDCl$_3$): δ = 23.6 (q, $J_{\mathrm{C,H}}$ = 127 Hz, C*Me*), 23.7 (q, $J_{\mathrm{C,H}}$ = 128 Hz, CHMe_2), 24.3 (q, $J_{\mathrm{C,H}}$ = 127 Hz, CHMe_2), 24.7 (q, $J_{\mathrm{C,H}}$ = 127 Hz, CHMe_2), 24.8 (q, $J_{\mathrm{C,H}}$ = 127 Hz, CHMe_2), 24.9 (q, $J_{\mathrm{C,H}}$ = 128 Hz, C*Me*), 27.9 (d, $J_{\mathrm{C,H}}$ = 130 Hz, *C*HMe$_2$), 28.3 (d, $J_{\mathrm{C,H}}$ = 130 Hz, *C*HMe$_2$), 100.0 (d, JC,H = Hz, CMe*C*HCMe), 123.0, 123.8, 125.4, 140.0, 142.5, 145.3, 176.7 (s, *C*N), 178.9 (s, *C*O) ppm. $C_{35}H_{48}AlN_3O_3$ (585.35): calcd. C 71.75, H 8.26, N 7.18; found C 71.24, H 7.72, N 7.05.

X-ray Structure Determination of Compounds 2−6: Crystals of compound **2** were obtained from a concentrated diethyl ether solution at −20 °C. Crystals of **4** and **6** were obtained from saturated toluene solutions at −20 °C. Crystals of **3** and **5** were obtained from saturated dichloromethane/diethyl ether solutions at −20 °C. The crystals were sealed in glass capillaries and mounted on a goniostat. All data sets were collected at 150(2) K, except for **6**, which was measured at 298(2) K. Data were collected with a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation. Structural determinations were performed 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 were placed geometrically and included through the use of a riding model. The crystal data are summarized in Table 3. CCDC-234262 (**2**), -234264 (**3**), -234265 (**4**), -234263 (**5**) and -234261 (**6**) contain the crystallohgraphic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[42] A comparison of bond lengths and angles between the calculated structures and the crystal structures can be found in the Supporting Information.

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