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Synthesis of (Hydrazonido)aluminum Complexes

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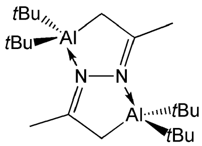
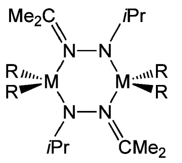
Complexes $[XAl\{CH_2CR{=}NNMe_2\}_2]$ {X = Cl and R = Me or *i*Pr, X = Me and R = Me, and X = $N(NMe_2)[CR{=}CH_2]$ and R = Me or *i*Pr} were synthesized by salt metathesis reactions involving lithium salts of hydrazones, $Li[CH_2CR{=}NNMe_2]$. X-ray crystallographic studies showed that all the complexes contain two chelating hydrazonido ligands bonding to aluminum through the methylene carbon and amine nitrogen ($-NMe_2$). For the complexes in which X = $N(NMe_2)[CR{=}CH_2]$ (R = Me or *i*Pr), the $N(NMe_2)[CR{=}CH_2]$ ligand represents a linkage isomer in which the hydrazonido ligand bonds through nitrogen rather than through carbon, thereby becoming a hydrazido ligand. In the single crystal containing $[Al\{CH_2C\textit{i}Pr{=}NNMe_2\}_2\{N(NMe_2)(C\textit{i}Pr{=}CH_2)\}]$, its isomer $[Al\{CH_2C\textit{i}Pr{=}NNMe_2\}_3]$, having two chelating hydrazonido and one monodentate hydrazonido ligands, is present 45 % of the time. In solution, the $[Al\{CH_2CR{=}NNMe_2\}_2\{N(NMe_2)(CR{=}CH_2)\}]$ (R = Me or *i*Pr) complexes are in equilibrium with $[Al\{CH_2CR{=}NNMe_2\}_3]$.

Introduction

In 2001, Uhl and co-workers reported the syntheses and structures of hydrazonido complexes of aluminum and gallium, in which the hydrazonido ligand functioned as a chelating alkyl ligand (**I**) or as a hydrazido (or amido) ligand (e.g. **II**).[1,2] Structurally characterized palladium complexes are also known in which the hydrazonido ligands function as chelating alkyl ligands (e.g. **III**).[3–5] In this paper, we describe the synthesis of (hydrazonido)aluminum complexes displaying linkage isomerism, wherein the hydrazonido ligands bond through carbon as an alkyl ligand or through nitrogen as a hydrazido (or amido) ligand. Our interest in hydrazonido complexes originates from recent papers by Nakamura et al., who demonstrated that olefins readily insert into the Zn–C bonds of proposed (hydrazonido)zinc intermediates.[6–8] The similar reactivity of Zn–C and Al–C bonds prompted us to synthesize (hydrazonido)aluminum complexes.

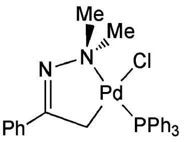


I



M = Al, R = Me
M = Ga, R = H

II

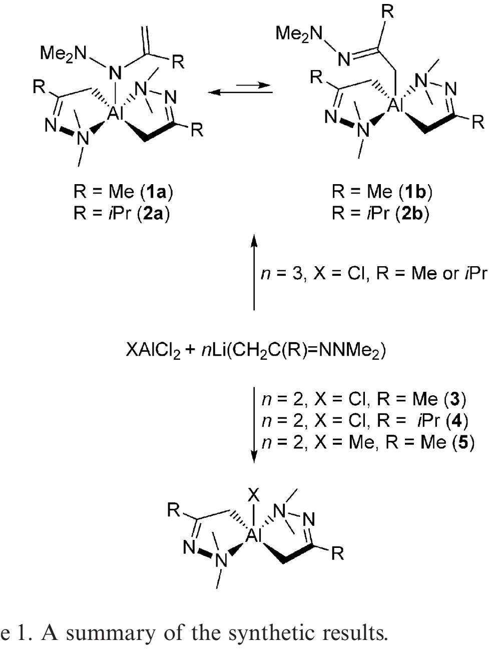


III

Results and Discussion

Synthesis

A summary of our synthetic results is presented in Scheme 1.



Scheme 1. A summary of the synthetic results.

Complexes $[Al\{CH_2CR{=}NNMe_2\}_2\{N(NMe_2)(CR{=}CH_2)\}]$ [R = Me (**1a**) or *i*Pr (**2a**)] were synthesized by allowing $AlCl_3$ to react with 3 equiv. of $Li[CH_2CR{=}NNMe_2]$ in diethyl ether. In the case of the isopropyl derivative, heating under reflux was necessary to replace all three chlorine atoms. Both complexes were very soluble in

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hydrocarbon solvents. As discussed below, crystals of **2a** obtained from toluene solution contain a mixture of **2a** and its isomer [Al{CH_2C*i*Pr=$NNMe_2$}$_3$] (**2b**), and in solution [Al{CH_2CR=$NNMe_2$}$_2${N(NMe_2)(CR=CH_2)}] and [Al{CH_2CR=$NNMe_2$}$_3$] {R = Me (**1b**) or *i*Pr} are in equilibrium.

Complexes [XAl{CH_2CR=$NNMe_2$}$_2$] [X = Cl and R = Me (**3**) or *i*Pr (**4**) and X = Me and R = Me (**5**)] were synthesized in moderate yields by allowing $AlCl_3$ and $MeAlCl_2$, respectively, to react with 2 equiv. of Li[CH_2CR=$NNMe_2$]. Less conveniently, **3** and **4** were synthesized from $AlCl_3$ and [Al{CH_2CR=$NNMe_2$}$_2$-{N(NMe_2)(CR=CH_2)}] by ligand redistribution reactions carried out in benzene under conditions of reflux. When stored under vacuum or inert gas, the chloride derivatives decompose slowly, producing a material that is insoluble in hydrocarbon solvents.

Solid-State Structures

X-ray crystallographic studies were performed on single crystals of **1a** (Figure 1), on the isomeric mixture of **2a** (Figure 2) and **2b** (Figure 3), on **3** (Figure 4), and on **5** (Figure 5). Molecules of **2a** with a terminal monodentate hydrazido ligand (Figure 2) and **2b** with a terminal monodentate hydrazonido ligand (Figure 3) co-exist in the single crystal in a 55:45 ratio, respectively. A limited data set was collected for a crystal of **4**, and the structure was solved. This revealed a structure very similar to those of **3** and **5**; consequently, a full data set for **4** was not collected.

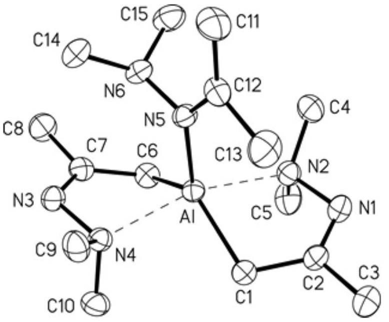


Figure 1. View of [Al{CH_2CMe=$NNMe_2$}$_2${N(NMe_2)-(CMe=CH_2)}] (**1a**) showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes; hydrogen atoms are omitted.

Selected bond lengths and angles for **1a**, **2a**, **3**, and **5** are presented in Table 1. The bond lengths and angles in **2b** associated with the chelating hydrazonido ligands are the same as those given in Table 1 for its isomer **2a**; selected bond lengths and angles associated with the monodentate hydrazonido ligand in **2b** are presented in the caption of Figure 3.

In the solid-state, all the molecules are five-coordinate and contain two bidentate hydrazonido ligands bound to the aluminum atom through the methylene carbon and the amine nitrogen, thereby forming five-member rings. The fifth coordination site is occupied by methyl, chlorido, monodentate hydrazido, or monodentate hydrazonido ligands. The coordination geometry at the five-coordinate aluminum centers may be described in each case as distorted trigonal bipyramidal; the apical positions are occupied by the amine groups of the chelating hydrazonido ligands (av. N–Al–N 161°). In each molecule, the angles at aluminum defining the trigonal planes sum up to approximately 360°.

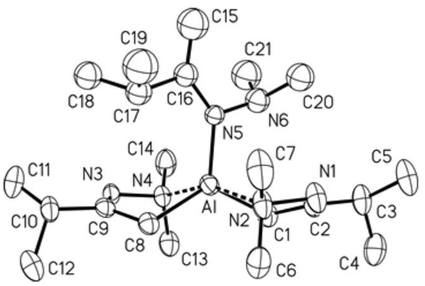


Figure 2. View of the [Al{CH_2C*i*Pr=$NNMe_2$}$_2${N(NMe_2)-(C(*i*Pr=CH_2)}] (**2a**) isomer showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes; hydrogen atoms are omitted.

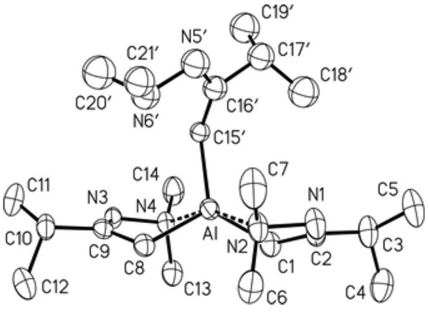


Figure 3. View of the [Al{CH_2C*i*Pr=$NNMe_2$}$_3$] (**2b**) isomer showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes; hydrogen atoms are omitted. The bond lengths and angles associated with the chelating hydrazonido ligands are the same as those given in Table 1 for its isomer **2a**. Selected bond lengths [Å] and angles [°] for the terminal hydrazonido ligand are as follows: Al–C15′ 2.068(9), C16′–N5′ 1.287(14), C15′–C16′ 1.399(14), N5′–N6′ 1.499(11), Al–C15′–C16′ 126.8(8); C15′–Al–C1 118.6(3), C15′–Al–C8 113.9(3), C15′–Al–N2 114.5(3), C15′–Al–N4 86.8(3).

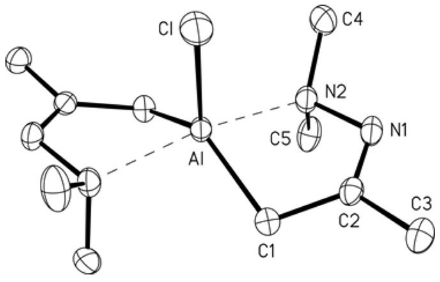


Figure 4. View of [ClAl{CH_2CMe=$NNMe_2$}$_2$] (**3**) showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes; hydrogen atoms are omitted.

Table 1. Selected bond lengths [Å] and angles [°] for [Al{$CH_2CMe{=}NNMe_2$}$_2${N(NMe_2)(CMe=CH_2)}] (**1a**), [Al{CH_2C*i*Pr=$NNMe_2$}$_2$-{N(NMe_2)(C*i*Pr=CH_2)}] (**2a**), [ClAl{$CH_2CMe{=}NNMe_2$}$_2$] (**3**), and [MeAl{$CH_2CMe{=}NNMe_2$}$_2$] (**5**).

	1a	**2a**	**3**	**5**
$Al–C_{methylene}$	2.003(2), 1.992(3)	2.000(4), 2.006(4)	1.9940(16)	2.0161(15)
$Al–N_{amine}$	2.173(2), 2.246(2)	2.186(4), 2.215(4)	2.1494(13)	2.1917(12)
Al–X	1.883(2) (X = $N_{hydrazido}$)	1.851(6) (X = $N_{hydrazido}$)	2.1925(9) (X = Cl)	1.984(2) (X = Me)
$C–N_{imine}$	1.285(3), 1.282(3)	1.282(5), 1.286(5)	1.280(2)	1.282(2)
$C–N_{hydrazido}$	1.386(3)	1.394(11)		
$C–CH_2$	1.475(3), 1.490(3)	1.469(6), 1.479(6)	1.491(2)	1.487(2)
$C–CH_{2(vinylic)}$	1.341(3)	1.352(14)		
$N_{imine}–N_{amine}$	1.476(3), 1.472(3)	1.482(5), 1.472(4)	1.4741(18)	1.4728(16)
$N–N_{hydrazido}$	1.444(3)	1.471(8)		
$C_{methylene}–Al–N_{amine}$	76.14(9), 78.00(9), 91.43(9), 96.69(9)	76.40(14), 77.15(16), 93.71(15), 93.15(15)	79.04(6), 95.70(6)	77.52(6), 94.40(5)
$C_{methylene}–Al–C_{methylene}$	126.83(11)	125.68(19)	132.89(11)	126.37(10)
$X–Al–C_{methylene}$	123.54(10), 109.62(10) (X = $N_{hydrazido}$)	119.8(2), 114.2(2) (X = $N_{hydrazido}$)	113.56(5) (X = Cl)	116.82(5) (X = Me)
$X–Al–N_{amine}$	100.45(8), 99.57(8) (X = $N_{hydrazido}$)	93.8(2), 107.6(2) (X = $N_{hydrazido}$)	96.52(4) (X = Cl)	98.89(4) (X = Me)
$N_{amine}–Al–N_{amine}$	159.92(8)	158.66(15)	166.97(8)	159.92(8)
$Cx–N_{hydrazido}–N_{amine}$	117.51(19) (*x* = 12)	115.8(6) (*x* = 16)		
$Al–N_{hydrazido}–Cx$	133.90(16) (*x* = 12)	137.3(6) (*x* = 16)		
$Al–N_{hydrazido}–N6$	108.48(14)	106.5(4)		

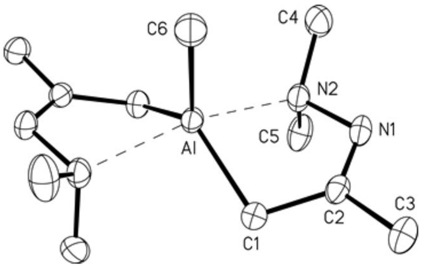
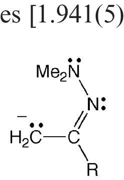


Figure 5. View of [MeAl{$CH_2CMe{=}NNMe_2$}$_2$] (**5**) showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes; hydrogen atoms are omitted.

Within the chelating hydrazonido ligands, the $C–CH_2$ lengths in **1a** [av. 1.483(3) Å], in the isomeric mixture **2a** and **2b** [av. 1.474(6) Å], in **3** (1.491 Å), and in **5** [1.487(2) Å] are slightly shorter than the common value for $C_{sp^2}–C_{sp^3}$ (1.51 Å).[9] The $C–N_{imine}$ lengths in **1a** [av. 1.284(3) Å], in the isomeric mixture **2a** and **2b** [av. 1.284(5) Å], in **3** [1.280(2) Å], and in **5** [1.282(2) Å] are very close to the common value for C=N (1.28 Å).[9] The observed lengths indicate that the charge on the chelating hydrazonido ligands is localized on the methylene carbon, as described by **IV**. The $Al–CH_2$ lengths involving the chelating hydrazonido ligands (av. 2.00 Å) are slightly longer than the $Al–CH_3$ lengths in **5** [1.984(2) Å] and in other reported five-coordinate aluminum complexes [1.941(5)–1.981(6) Å].[10–20]



IV

In the terminal hydrazonido ligand of **2b** (Figure 3), the $C–N_{imine}$ length [1.287(14) Å] is normal,[9] but the $H_2C–C$ length is short [C15′–C16′ = 1.399(14) Å] relative to a normal $C_{sp^2}–C_{sp^3}$ bond length (1.51 Å) and is 0.07–0.08 Å shorter than the analogous lengths in the chelating ligands (av. 1.482 Å). There was considerable disorder in the monodentate hydrazonido ligand of **2b**, which made the bond lengths and angles for the ligand dubious. The short CH_2–C length is consistent, however, with the associated large $Al–CH_2–C$ angle of 126.8(8)°; that is, an open angle at the methylene carbon would increase the s character at the methylene carbon and would thereby shorten the associated bond lengths.

In the hydrazido ligands of **1a** and **2a**, the sum of the angles about $N_{hydrazido}$ is approximately 360°, and the bulkier $CR{=}CH_2$ substituent on $N_{hydrazido}$ is bent away from Al more than the NMe_2 substituent (av. C–N–Al 135.6° vs. av. N–N–Al 107.5°). The $CR{=}CH_2$ substituents are *trans* coplanar with the Al–N bonds (the av. $Al–N_{hydrazido}–C{=}C$ torsion angle is 168°), suggesting the possibility of delocalization of the charge on $N_{hydrazido}$ into the vinyl group. The $CR{=}CH_2$ lengths, 1.341(3) Å (R = Me) and 1.352(14) Å (R = *i*Pr), however, are only slightly longer than a normal C=C length (1.32 Å).[9] The $Al–N_{hydrazido}$ lengths (av. 1.87 Å) are a little longer than reported terminal $Al–N_{amide}$ bond lengths [1.782(8)–1.822(2) Å].[21–25]

NMR Spectroscopic Characterization

In the solid state, monomers **3**–**5** have crystallographically imposed C_2 symmetry. For the chloride derivatives, the ^1H NMR spectra recorded at room temperature are consistent with the solid-state structures; for example, **3** gives rise to an AB quartet and three singlets arising from the methylene, C*Me*, and N*Me*$_2$ protons, respectively. Molecule **5**, however, is fluxional. At room temperature, the ^1H NMR spectrum consists of sharp singlets arising from the Al*Me* and C*Me* protons and very broad resonances arising from the methylene and N*Me*$_2$ protons. At –30 °C, the latter resonances resolve into a sharp AB quartet and two singlets, thereby producing a spectrum consistent with the solid-state structure. A mechanism involving $Al–NMe_2$ bond rupture, concomitant $Al–CH_2$ bond rotation to render the methylene protons equivalent, amine inversion and N–N bond rotation to render the amine methyl protons equivalent, and reformation of the Al–NMe$_2$ bond is a plausible explanation for the observed fluxionality.

Molecule **1a** is an asymmetric monomer in the solid state with one terminal hydrazido ligand and two bidentate hydrazonido ligands (Figure 1). The ^{1}H NMR spectrum for this complex recorded at room temperature is consistent with a fluxional molecule. A spectrum recorded at –30 °C reveals, for the hydrazido ligand, a singlet arising from the C*Me* protons, two singlets arising from the N*Me*$_2$ protons, and two singlets arising from the =CH_2 protons, while the chelating hydrazonido ligands produce one singlet arising from the C*Me* protons, two singlets arising from the N*Me*$_2$ protons, and an AB quartet arising from the CH_2 protons. These data are consistent with rapid Al–N$_{\mathrm{hydrazide}}$ bond rotation at –30 °C, rendering the molecule to have virtual C_2 symmetry.

Isomers **2a** and **2b** coexist in crystals grown from toluene. Not surprisingly, ^{1}H NMR spectra for solutions of the crystals were complex. At room temperature, the ^{1}H NMR spectrum was consistent with an approximately 3:1 mixture of **2a** and **2b**, respectively. Both of the isomers exhibit fluxional behavior. A subsequent variable-temperature NMR spectroscopic study showed that the fluxionality of **2a** was analogous to that observed for its methyl congener **1a** (see the previous paragraph). The fluxional process for **2b** was such that resonances for only one type of hydrazonido ligand were observed at all temperatures examined (i.e., two singlets, a doublet, and a septet in a 2:6:6:1 ratio, respectively, were observed at all temperatures).

The variable-temperature ^{1}H NMR spectroscopic study for the isomeric mixture of **2a** and **2b** also revealed that the two isomers were in equilibrium (Scheme 1, top). A van 't Hoff plot gave $\Delta H° = 1.0(1.8)$ kcal/mol, $\Delta S° = 1.2(2.1)$ eu, and $\Delta G°_{298\mathrm{K}} = 0.67(1.5)$ kcal/mol for the equilibrium written as **2a** ⇄ **2b**. The results indicate the amide isomer is slightly favored thermodynamically at room temperature, and $\Delta S°$ is small as expected for two monomers with similar structures in equilibrium. Using the enthalpy value from the van 't Hoff plot and assuming bond energies of 141 and 143 kcal/mol for C=C and C=N bonds,[9] the difference in energy between the Al–N$_{\mathrm{amide}}$ and Al–CH$_2$ bonds can be estimated to be about 1 kcal/mol.

In the ^{1}H NMR spectra for solutions of **1a** at temperatures above 60 °C, resonances consistent with the equilibrium **1a** ⇄ **1b** were observed; that is, an equilibrium analogous to the equilibrium involving **2a** and **2b** was observed. As in the case of the **2a**/**2b** equilibrium, the **1a** isomer is favored; for example, $K_{\mathrm{eq.}} = 0.0378$ and 0.064 at 60 and 80 °C, respectively.

Conclusions

(Hydrazonido)aluminum complexes exhibited isomerism in the solid state and in solution, including linkage isomerism. In complexes $[\mathrm{MeAl\{CH_2CMe{=}NNMe_2\}_2}]$ and $[\mathrm{ClAl\{CH_2CR{=}NNMe_2\}_2}]$ (R = Me or *i*Pr), the hydrazonido ligands act as chelating alkyl ligands, forming five-membered rings by bonding to aluminum through the methylene carbon and amine nitrogen. In contrast, in $[\mathrm{Al\{CH_2CR{=}NNMe_2\}_2\{N(NMe_2)(CR{=}CH_2)\}}]$ (R = Me or *i*Pr) one of the hydrazonido ligands bonds through nitrogen, becoming a monodentate hydrazido ligand, while the other two ligands bond as chelating hydrazonido ligands as in $[\mathrm{XAl\{CH_2CR{=}NNMe_2\}_2}]$ (X = Me or Cl). In the single crystal containing $[\mathrm{Al\{CH_2C}\mathit{i}\mathrm{Pr{=}NNMe_2\}_2\{N(NMe_2)(C}\mathit{i}\mathrm{Pr{=}CH_2)\}}]$, isomer $[\mathrm{Al\{CH_2C}\mathit{i}\mathrm{Pr{=}NNMe_2\}_3}]$, with a monodentate hydrazonido ligand and two chelating hydrazonido ligands, is present 45% of the time. In solution, complexes $[\mathrm{Al\{CH_2CR{=}NNMe_2\}_2\{N(NMe_2)(CR{=}CH_2)\}}]$ (R = Me or *i*Pr) are in equilibrium with their respective homoleptic hydrazonido isomers, $[\mathrm{Al\{CH_2CR{=}NNMe_2\}_3}]$.

Experimental Section

Synthesis: Manipulations of air-sensitive compounds were performed inside a nitrogen-filled glove box or by using Schlenk techniques. Solvents were purified according to standard methods and stored over molecular sieves inside the glove box. Hydrazones MeCR=NNMe$_2$ (R = Me and *i*Pr) were synthesized by following procedures based on those found in the literature.[26–29] Nuclear magnetic resonance spectra were recorded with a 300-MHz instrument at 25 °C unless stated otherwise. Midwest Microlab, Indianapolis, IN, USA performed the elemental analyses.

$[\mathbf{Al\{CH_2CMe{=}NNMe_2\}_2\{N(NMe_2)(CMe{=}CH_2)\}}]$ (1a): Li[CH$_2$CMe=NNMe$_2$] (1.13 g, 10.6 mmol) was added to a cold (–25 °C) solution of AlCl$_3$ (0.473 g, 3.55 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the ether was removed under vacuum to yield a yellow powder. Hexanes (20 mL) was added to the residue, and the mixture was filtered through Celite. The filtrate was concentrated under vacuum, and the resulting white powder was dissolved in a minimum amount of toluene. The flask was transferred to the freezer (–25 °C) for crystallization. Crystals formed within 24 h. For additional purification, the crystalline material may be sublimed (60 °C/0.01 Torr) (yield 0.680 g, 60%). C$_{15}$H$_{33}$AlN$_6$ (324.5): calcd. C 55.53, H 10.25, N 25.90; found C 54.91, H 9.87, N 25.19. ^{1}H NMR ([D$_8$]toluene at –30 °C): δ = 0.62 and 0.75 [d of an AB q, J = 14 Hz, 4 H, CH_2C(CH$_3$)=NN(CH$_3$)$_2$], 1.70 [s, 3 H, N(NMe$_2$)(C(CH_3)=CH$_2$)], 1.92 [s, 6 H, CH$_2$C(CH$_3$)=NN(CH_3)$_2$], 1.96 [s, 6 H, CH$_2$C(CH_3)=NN(CH$_3$)$_2$], 2.43 [s, 6 H, CH$_2$C(CH$_3$)=NN(CH_3)$_2$], 2.80 [s, 3 H, N{N(CH_3)$_2$)}{C(CH$_3$)=CH$_2$}], 2.92 [s, 3 H, N{N(CH_3)$_2$}{C(CH$_3$)=CH$_2$}], 3.80 [s, 1 H, N{N(CH$_3$)$_2$}{C(CH$_3$)=CH_2}], 3.94 [s, 1 H, N{N(CH$_3$)$_2$}{C(CH$_3$)=CH_2}] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 20.2 [br., CH$_2$C(CH$_3$)=NN(CH$_3$)$_2$], 23.7 [N{N(CH$_3$)$_2$}{C(CH$_3$)=CH$_2$}], 26.3 [CH$_2$C(CH$_3$)=NN(CH$_3$)$_2$], 43.8, 47.2, 47.6, and 48.05 [CH$_2$C(CH$_3$)=NN(CH$_3$)$_2$ and N{N(CH$_3$)$_2$}{C(CH$_3$)=CH$_2$}], 80.8 [N{N(CH$_3$)$_2$}{C(CH$_3$)=CH$_2$}], 148.2 [N{N(CH$_3$)$_2$}{C(CH$_3$)=CH$_2$}], 179.6 [CH$_2$$C$(CH$_3$)=NN(CH$_3$)$_2$] ppm. IR (Nujol, NaCl): $\tilde{\nu}$ = 1608 (s) [ν(C=N)], 1531 (w), 1290 (m), 1265 (m), 1218 (m), 1180 (m), 1156 (w), 1104 (vw), 1056 (m), 1033 (m), 1018 (m), 962 (w), 942 (m), 905 (w), 849 (w), 769 (m), 723 (w), 699 (w), 663 (m) cm^{-1}.

Isomeric Mixture of $[\mathbf{Al\{CH_2C}\boldsymbol{i}\mathbf{Pr{=}NNMe_2\}_2\{N(NMe_2)(C}\boldsymbol{i}\mathbf{Pr{=}CH_2)\}}]$ (2a) and $[\mathbf{Al\{CH_2C}\boldsymbol{i}\mathbf{Pr{=}NNMe_2\}_3}]$ (2b): Li[CH$_2$C*i*Pr=NNMe$_2$] (1.50 g, 11.2 mmol) was added to a solution of

$AlCl_3$ (0.496 g, 3.73 mmol) in diethyl ether (25 mL). The mixture was heated at reflux under argon for 12 h before the ether was removed under vacuum to yield a yellow solid. Hexanes (20 mL) was added to the residue, and the mixture was filtered through Celite. The filtrate was concentrated under vacuum, and the resulting yellow powder was dissolved in the minimum amount of toluene. The flask was transferred to the freezer (–25 °C) for crystallization. After 24 h, colorless crystals were isolated (yield 0.78 g, 52%). $C_{21}H_{45}AlN_6$ (408.6): calcd. C 61.73, H 11.10, N 20.57; found C 61.63, H 10.90, N 20.44. **2a**: ^1H NMR ($[D_8]$toluene at –40 °C): δ = 0.72 and 0.78 [d of an AB q, J = 15.5 Hz, 4 H, $C\mathit{H}_2C\{CH(CH_3)_2\}=NNMe_2$], 1.198 [d, J = 6.9 Hz, 6 H, $CH_2C\{CH(C\mathit{H}_3)_2\}=NNMe_2$], 1.201 (d, J = 6.3 Hz, 3 H, $N(NMe_2)\{C[CH(C\mathit{H}_3)_2]=CH_2\}$), 1.25 {d, J = 6.6 Hz, 6 H, $CH_2C[CH(C\mathit{H}_3)_2]=NNMe_2$}, 1.30 (d, J = 6.3 Hz, 3 H, $N(NMe_2)\{C[CH(C\mathit{H}_3)_2]=CH_2\}$), 1.77 (sept, J = 6.3 Hz, 1 H, $N[N(CH_3)_2]\{C[C\mathit{H}(CH_3)_2]=CH_2\}$), 2.08 {s, 6 H, $CH_2C[CH(CH_3)_2]=NN(C\mathit{H}_3)_2$}, 2.40–2.46 {overlapping sept, J = 7 Hz, 2 H, $CH_2C[C\mathit{H}(CH_3)_2]=NN(CH_3)_2$}, 2.46 {s, 6 H, $CH_2C[CH(CH_3)_2]=NN(C\mathit{H}_3)_2$}, 2.77 (s, 3 H, $N[N(C\mathit{H}_3)_2]\{C[CH(CH_3)_2]=CH_2\}$), 2.87 (s, 3 H, $N[N(C\mathit{H}_3)_2]\{C[CH(CH_3)_2]=CH_2\}$), 3.83 (s, 1 H, $N[N(CH_3)_2]\{C[CH(CH_3)_2]=C\mathit{H}_2\}$), 4.02 (s, 1 H, $N[N(CH_3)_2]\{C[CH(CH_3)_2]=C\mathit{H}_2\}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 20.5 {br., $\mathit{C}H_2C[CH(CH_3)_2]=NN(CH_3)_2$}, 21.0 ($CH_2C[CH(\mathit{C}H_3)_2]=NN(CH_3)_2$ and $N[N(CH_3)_2]\{C[CH(\mathit{C}H_3)_2]=CH_2\}$), 32.9 {$CH_2C[\mathit{C}H(CH_3)_2]=NN(CH_3)_2$}, 37.7 {$CH_2C[\mathit{C}H(CH_3)_2]=NN(CH_3)_2$}, 44.1 {$CH_2C[CH(CH_3)_2]=NN(\mathit{C}H_3)_2$}, 46.9 ($N[N(\mathit{C}H_3)_2]\{C[CH(CH_3)_2]=CH_2\}$), 76.3 ($N[N(CH_3)_2]\{C[CH(CH_3)_2]=\mathit{C}H_2\}$), 159.6 ($N[N(CH_3)_2]\{\mathit{C}[CH(CH_3)_2]=CH_2\}$), 185.0 {$CH_2\mathit{C}[CH(CH_3)_2]=NN(CH_3)_2$} ppm. **2b**: ^1H NMR ($[D_8]$toluene at 18 °C): δ = 0.98 {s, 6 H, $C\mathit{H}_2C[CH(CH_3)_2]=NNMe_2$}, 1.20 {d, J = 7 Hz, 18 H, $CH_2C[CH(C\mathit{H}_3)_2]=NNMe_2$}, 2.31 {s, 18 H, $CH_2C[CH(CH_3)_2]=NN(C\mathit{H}_3)_2$}, 2.39 {sept, J = 6.6 Hz, 3 H, $CH_2C[C\mathit{H}(CH_3)_2]=NN(CH_3)_2$} ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.8 {br., $\mathit{C}H_2C[CH(CH_3)_2]=NN(CH_3)_2$}, 21.0 {$CH_2C[CH(\mathit{C}H_3)_2]=NN(CH_3)_2$}, 37.4 {$CH_2C[\mathit{C}H(CH_3)_2]=NN(CH_3)_2$}, 48.0 {$CH_2C[CH(CH_3)_2]=NN(\mathit{C}H_3)_2$}, 183.3 {$CH_2\mathit{C}[CH(CH_3)_2]=NN(CH_3)_2$} ppm. IR (Nujol, NaCl): $\tilde{\nu}$ = 1619 (s) [$\nu(C=N)$], 1546 (w), 1349 (s), 1325 (s), 1210 (s), 1152 (m), 1118 (m), 1079 (s), 1053 (s), 1008 (s), 966 (s), 929 (s), 897 (vs), 833 (m), 783 (w) cm^{-1}.

$[ClAl\{CH_2CMe=NNMe_2\}_2]$ (3): $Li[CH_2CMe=NNMe_2]$ (1.50 g, 14.1 mmol) was added to a cold (–25 °C) solution of $AlCl_3$ (0.943 g, 7.07 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the ether was removed under vacuum to yield a yellow powder. Hexanes (20 mL) was added to the residue, and the mixture was filtered through Celite. The filtrate was concentrated under vacuum, and the resulting white powder was dissolved in a minimum amount of toluene. The flask was transferred to the freezer (–25 °C) for crystallization. After 24 h, colorless crystals were isolated (yield 1.20 g, 65%). The complex is unstable at room temperature, which precluded obtaining chemical analysis. ^1H NMR (CD_2Cl_2): δ = 0.92 and 1.07 [d of an AB q, J = 15 Hz, 4 H, $C\mathit{H}_2C(CH_3)=NN(CH_3)_2$], 1.96 [s, 6 H, $CH_2C(C\mathit{H}_3)=NN(CH_3)_2$], 2.36 [s, 6 H, $CH_2C(CH_3)=NN(C\mathit{H}_3)_2$], 2.60 [s, 6 H, $CH_2C(CH_3)=NN(C\mathit{H}_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 18.0 [br., $\mathit{C}H_2C(CH_3)=NN(CH_3)_2$], 25.4 [$CH_2C(\mathit{C}H_3)=NN(CH_3)_2$], 46.0 [$CH_2C(CH_3)=NN(\mathit{C}H_3)_2$], 47.5 [$CH_2C(CH_3)=NN(\mathit{C}H_3)_2$], 178.7 [$CH_2\mathit{C}(CH_3)=NN(CH_3)_2$] ppm. IR (neat, KBr): $\tilde{\nu}$ = 1648 (s) [$\nu(C=N)$], 1540 (w), 1523 (w), 1468 (m), 1440 (m), 1371 (m), 1298 (vw), 1276 (w), 1253 (vw), 1223 (vw), 1161 (w), 1082 (vw), 993 (m), 908 (w), 878 (vw), 846 (vw), 811 (vw) cm^{-1}.

$[ClAl\{CH_2C\mathit{i}Pr=NNMe_2\}_2]$ (4): This compound was isolated as a white crystalline solid by following the method used for $[ClAl\{CH_2C(CH_3)=NNMe_2\}_2]$ (yield 0.23 g, 79%). The complex is unstable at room temperature, which precluded obtaining a satisfactory chemical analysis: $C_{14}H_{30}AlClN_4$ (316.9): calcd. C 53.07, H 9.54, N 17.68; found C 50.88, H 9.25, N 17.72. ^1H NMR (C_6D_6): δ = 0.69 and 0.82 {d of an AB q, J = 15 Hz, 4 H, $C\mathit{H}_2C[CH(CH_3)_2]=NNMe_2$}, 1.09 {d, J = 7 Hz, 6 H, $CH_2C[CH(C\mathit{H}_3)_2]=NNMe_2$}, 1.13 {d, J = 7 Hz, 6 H, $CH_2C[CH(C\mathit{H}_3)_2]=NNMe_2$}, 2.09 {s, 6 H, $CH_2C[CH(CH_3)_2]=NN(C\mathit{H}_3)_2$}, 2.56 {s, 6 H, $CH_2C[CH(CH_3)_2]=NN(C\mathit{H}_3)_2$}, 2.57 {sept, J = 7 Hz, 2 H, $CH_2C[C\mathit{H}(CH_3)_2]=NN(CH_3)_2$} ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.3 {br., $\mathit{C}H_2C[CH(CH_3)_2]=NN(CH_3)_2$}, 20.1 {$CH_2C[CH(\mathit{C}H_3)_2]=NN(CH_3)_2$}, 20.3 {$CH_2C[CH(\mathit{C}H_3)_2]=NN(CH_3)_2$}, 37.2 {$CH_2C[\mathit{C}H(CH_3)_2]=NN(CH_3)_2$}, 45.9 {$CH_2C[CH(CH_3)_2]=NN(\mathit{C}H_3)_2$}, 47.6 {$CH_2C[CH(CH_3)_2]=NN(\mathit{C}H_3)_2$}, 185.7 {$CH_2\mathit{C}[CH(CH_3)_2]=NN(CH_3)_2$} ppm. IR (neat, NaCl): $\tilde{\nu}$ = 1620 (vs) [$\nu(C=N)$], 1507 (w), 1467 (w), 1425 (w), 1396 (w), 1370 (w), 1328 (w), 1234 (w), 1203 (w), 1177 (w), 1141 (w), 1089 (w), 1041 (w), 988 (w), 902 (s), 858 (w), 836 (w), 716 (vs) cm^{-1}.

$[MeAl\{CH_2CMe=NNMe_2\}_2]$ (5): $Li[CH_2CMe=NNMe_2]$ (1.0 g, 9.4 mmol) was added to a cold (–25 °C) solution of $MeAlCl_2$ (4.7 mL of a 1.0 M solution, 4.7 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the

Table 2. Crystal data for **1a**, the mixture **2a** and **2b**, **3**, and **5**.

	1a	**2a/2b**	**3**	**5**
Chem. formula	$C_{15}H_{33}AlN_6$	$C_{21}H_{45}AlN_6$	$C_{10}H_{22}AlClN_4$	$C_{11}H_{25}AlN_4$
F.w. [$g\,mol^{-1}$]	324.45	408.61	260.75	240.33
Crystal dimensions [mm]	0.40 × 0.15 × 0.15	0.40 × 0.35 × 0.15	0.50 × 0.30 × 0.25	0.40 × 0.30 × 0.10
Space group	$P2_1/n$ (monoclinic)	$P2_1/c$ (monoclinic)	$C2/c$ (monoclinic)	$C2/c$ (monoclinic)
a [Å]	11.1567(10)	9.263(2)	16.3025(13)	16.2887(10)
b [Å]	12.0133(11)	16.515(3)	6.9365(5)	7.0982(4)
c [Å]	15.2560(14)	16.866(3)	12.9481(8)	12.9436(8)
α [°]	90	90	90	90
β [°]	109.423(1)	93.774(3)	104.404(1)	103.985(1)
γ [°]	90	90	90	90
T [K]	223(2)	223(2)	223(2)	223(2)
Z	4	4	4	4
V [Å^3]	1928.4(3)	2574.6(8)	1418.17(18)	1452.19(15)
$D_{calcd.}$ [$g\,cm^{-3}$]	1.118	1.054	1.221	1.099
$\mu(Mo\text{-}K_\alpha)$ [mm^{-1}]	0.112	0.096	0.314	0.124
R, R_w[a]	0.0365, 0.0926	0.0623, 0.1575	0.0286, 0.0792	0.0334, 0.0956

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

ether was removed under vacuum to yield a yellow powder. Hexanes (20 mL) was added to the residue, and the mixture was filtered through Celite. The filtrate was concentrated under vacuum, and the resulting white powder was dissolved in the minimum amount of toluene. The flask was transferred to the freezer (–25 °C) for crystallization. After 2 d, colorless crystals were isolated (yield 0.45 g, 40%). $C_{11}H_{25}AlN_4$ (240.3): calcd. C 54.98, H 10.48, N 23.31; found C 54.66, H 10.32, N 23.18. ^{1}H NMR ([D$_8$]toluene at –30 °C): δ = –0.70 [s, 2 H, $\mathrm{Al(C}H_3\mathrm{)}$], 0.66 and 0.92 {d of an AB q, J = 14.7 Hz, 4 H, $[\mathrm{C}H_2\mathrm{C(CH_3)=NN(CH_3)_2}]$}, 2.00 {s, 6 H, $[\mathrm{CH_2C(C}H_3\mathrm{)=NN(CH_3)_2}]$}, 2.04 {s, 6 H, $[\mathrm{CH_2C(CH_3)=NN(C}H_3\mathrm{)_2}]$}, 2.36 {s, 6 H, $[\mathrm{CH_2C(CH_3)=NN(C}H_3\mathrm{)_2}]$} ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.7 [br., $\mathit{C}\mathrm{H_2C(CH_3)=NN(CH_3)_2}$], 25.5 [$\mathrm{Al(}\mathit{C}\mathrm{H_3)}$], 25.7 $[\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)=NN(CH_3)_2}]$, 46.7 $[\mathrm{CH_2C(CH_3)=NN(}\mathit{C}\mathrm{H_3)_2}]$, 179.3 $[\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)=NN(CH_3)_2}]$ ppm. IR (neat, NaCl): $\tilde{\nu}$ = 1636 (s) [ν(C=N)], 1557 (m), 1507 (m), 1456 (m), 1437 (m), 858 (vs) cm^{-1}.

X-ray Crystallography: All measurements were made with a Siemens SMART platform diffractometer equipped with a CCD area detector. The programs used in the X-ray crystallographic analyses were as follows: data collection, Siemens APEX2 v1.0–27;[30] cell refinement and data reduction, Bruker SAINT v7.12A;[31] structure solution, SHELXS v6.12;[32] and structure refinement, SHELXL v6.12.[33] Crystal data are presented in Table 2. Crystals of **1a**, **3**, and **5** were colorless square columns, colorless prismatic blocks, and colorless diamond-shaped plates, respectively. The single crystal composed of **2a** and **2b** was a colorless thick plate. In the crystals of **3** and **5**, each asymmetric unit consisted of one-half molecule situated about a twofold axis. In the crystal containing both **2a** and **2b**, the molecules are present in the ratio 55:45, respectively. CCDC-696329, -696330, -696331, and -696332 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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