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# Lewis base adducts of diisobutylaluminum azide: synthesis and thermal stability

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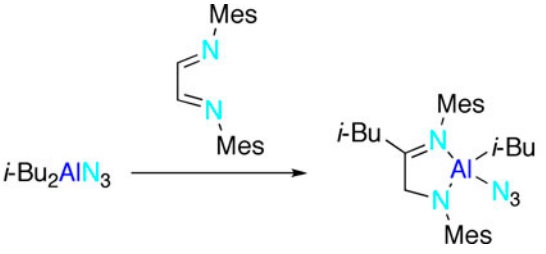


Diisobutylaluminum azide was prepared from the reaction of diisobutylaluminum hydride with trimethylsilyl azide, and it was reacted with five different Lewis bases. The monodentate ligands *p*-dimethylaminopyridine (DMAP) and the two N-heterocyclic carbenes IMes and IDipp afforded the expected adducts L·Al(*i*-Bu)$_2$N$_3$ in good yields. Reaction with the bidentate diimine (MesN=CH)$_2$ did not stop at the adduct stage, but continued to form the iminoamide compound {MesNCH$_2$C(*i*-Bu)NMes}Al(*i*-Bu)N$_3$ through formal Al-*i*-Bu addition to one of the N–C double bonds followed by *i*-Bu migration. The terdentate pincer ligand 2,6-bis(diethylaminomethyl)pyridine induces azide transfer and formation of the ionic compound [2,6-(Et$_2$NCH$_2$)$_2$C$_5$H$_3$NAl(*i*-Bu)$_2$][(*i*-Bu)$_2$Al(N$_3$)$_2$]. The compounds are thermally stable to at least 110 °C but decompose either into their precursors or into a mixture of unidentified products. All new compounds were characterized by $^1$H and $^{13}$C{$^1$H} spectroscopy, IR spectroscopy, and the iminoamide compound {MesNCH$_2$C(*i*-Bu)NMes}Al(*i*-Bu)N$_3$ was also analyzed by single-crystal X-ray diffraction.

*Keywords*: Aluminum; Azide; N-heterocyclic carbene; Thermolysis; Lewis acid; Main group

## 1. Introduction

Aluminum azides have been investigated as reagents for the synthesis of tetrazoles [1], for the ring opening of epoxides [2] or for the addition of azide to α,β-unsaturated carbonyl compounds [3]. They also have been employed as single-source precursors for the

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preparation of aluminum nitride, a hard ceramic that is both a thermal conductor and an electrical insulator [4]. Good results for the preparation of AlN thin films through CVD processes were obtained from the volatile four-coordinate precursors $(Et_2AlN_3)_3$ [5] and $[Me_2N(CH_2)_3]_2AlN_3$ [6]. There also has been interest in the synthesis of aluminum nitride nanoparticles under mild conditions from molecular precursors, and aluminum azides were among the materials investigated [7, 8]. As part of our activities in the development of precursors for the synthesis of nitride [9], oxynitride [10] and oxide[11] materials using routine bench top chemistry, we were interested in the potential of Lewis base adducts of *i*-$Bu_2AlN_3$ as such a precursor. We hypothesized that the combination of a Lewis base with the known facile β-butene elimination of butylalanes [12] and the lability of the azide substituent could lead to well-defined intermediates such as $(L{\cdot}AlN)_n$. Here, we report the synthesis of five adducts of *i*-$Bu_2AlN_3$ with different Lewis bases and the investigation of their thermal stability.



## 2. Experimental

### 2.1. *General methods*

All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres dry box unless otherwise noted. Dry, oxygen-free solvents were used unless otherwise indicated. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer and ATR-FTIR spectra were collected on a Nicolet IR200 FT-IR spectrometer with an ATR attachment (ATR = attenuated total reflection). NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. $^1$H NMR chemical shift values were determined relative to the residual protons in $C_6D_6$ as internal reference ($\delta$ = 7.16 ppm) and $^{13}$C NMR spectra were referenced to the solvent signal ($\delta$ = 128.39 ppm). 4-Dimethylaminopyridine (DMAP), *i*-$Bu_2AlH$, and $Me_3SiN_3$ were obtained from commercial sources and used as received. The ligands 2,6-bis(diethylaminomethyl)pyridine [13], glyoxal-bis(2,4,6-trimethylphenyl)imine [14], 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) [15] were prepared according to literature procedures.

### 2.2. *i-Bu$_2$AlN$_3$*

Trimethylsilylazide (1.40 mL, 1.22 g, 10.6 g) was added slowly to a solution of *i*-$Bu_2AlH$ in hexanes (25% w/w, 6 g, 1.50 g *i*-$Bu_2AlH$, 10.6 mmol) at −15 °C. The clear colorless solution was allowed to warm to room temperature and stirred overnight. Removal of the solvent under reduced pressure afforded the product as a colorless mobile liquid. Yield: 1.8 g, 93%. $^1$H NMR (400.13 MHz, $C_6D_6$): 2.04 (m, $J$ = 6.7 Hz, C*H*, 2H cpd. 1), 2.00 (m, $J$ = 6.7 Hz, C*H*, 2H cpd. 2), 1.10 (d, $J$ = 6.5 Hz, C$H_3$, 12H, cpd. 1), 1.04 (d, $J$ = 6.5 Hz, C$H_3$, 12H, cpd. 2), 0.39 (d, $J$ = 7.4 Hz, C$H_2$, 2H, cpd. 1), 0.32 (d, $J$ = 7.0 Hz, C$H_3$, 2H, cpd. 2). Ratio of cpd. 1 to cpd. 2: 2.2 to 1. Addition of a slight excess of pyridine (10 μL, *ca.* 1.5 equiv) led to this spectrum: $^1$H NMR (400.13 MHz, $C_6D_6$): 8.25 (d, $J$ = 4.6 Hz, *o*-H (py), 3H), 6.87 (tt, $J$ = 8.4 Hz, $J$ = 1.5 Hz, *p*-H(py), 1.5H), 6.52 (t, $J$ = 6.1 Hz, *m*-H(py), 3H), 2.08 (m, $J$ = 6.6 Hz, C*H*, 2H), 1.17 (d, $J$ = 6.5 Hz, C$H_3$, 12H), 0.32 (d, $J$ = 7.0 Hz, C$H_2$, 4H).

### 2.3. *i-Bu$_2$AlN$_3$·DMAP (1)*

A solution of *i*-$Bu_2AlN_3$ (0.38 g, 2.1 mmol) in hexanes (8 mL) was added to a slurry of DMAP (0.26 g, 2.2 mmol) in hexanes (8 mL) with cooling in an ice bath. The mixture was warmed to room temperature and a colorless oil separated. Decanting of the mother liquor followed by drying of the remaining oil under reduced pressure gave **1** as a colorless viscous oil. Yield: 0.6 g, 90%. $^1$H NMR (400.13 MHz, $C_6D_6$): 7.81 (d, $J$ = 7.2 Hz, *o*-H, 2H), 5.55 (d, $J$ = 7.2 Hz, *m*-H, 2H), 2.23 (nonet, $J$ = 6.7 Hz, Al-$CH_2$-C*H*-$(CH_3)_2$, 2H), 1.94 (s, N-$(CH_3)_2$,2H), 1.28 (d, $J$ = 6.5 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 12H), 0.50 (d, $J$ = 7.0 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 4H). $^{13}$C NMR ($C_6D_6$, 100.62 MHz): 155.86 (*p*-C), 145.82 (*o*-C), 107.14 (*m*-C), 38.68 (N-$CH_3$), 28.89 (Al-$CH_2$-CH-($CH_3$)$_2$), 27.16 (Al-$CH_2$-CH-$(CH_3)_2$), 22.60 (s, br, $w_{1/2}$ = 20 Hz, Al-$CH_2$-CH-$(CH_3)_2$). IR: (thin film between NaCl plates), 2117s, 2030w cm$^{-1}$ ($\nu(N_3)$).

### 2.4. *i-Bu$_2$AlN$_3$·IMes (2a)*

A solution of *i*-$Bu_2AlN_3$ (0.19 g, 1.0 mmol) in hexanes (20 mL) was added dropwise via cannula to a stirred solution of IMes (0.30 g, 1.0 mmol) in hexanes (35 mL) at −78 °C. Upon addition, a white precipitate quickly formed. The reaction mixture was allowed to reach room temperature, and the mother liquor was removed via cannula. The remaining solid was dried in vacuo to afford **2** as a fine off-white powder. Yield: 0.10 g, 21%. Subsequent syntheses afforded higher yields, but the products contained about 10% of an unknown Mes-containing impurity, which could not be removed by crystallization. $^1$H NMR ($C_6D_6$, 400.13 MHz): 6.77 (s, *m*-H, 4H), 5.84 (s, N–C*H*=C*H*–N, 2H), 2.12 (s, *p*-$CH_3$, 6H), 1.98 (s, *o*-$CH_3$, 12H), 1.91 (m, $J$ = 6.6 Hz, Al-$CH_2$-C*H*-$(CH_3)_2$, 2H), 1.13 (d, $J$ = 6.4 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 12H), −0.32 and −0.40 (doublet of AB system, $^2J_{AB}$ = 13.9 Hz, $J$ = 6.7 and 7.4 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 4H). $^{13}$C NMR ($C_6D_6$, 100.62 MHz): 172.44 (N*C*N), 140.44 (*p*-*C*), 135.54 (*o*-*C*), 135.12 (*i*-*C*), 129.96 (*m*-*C*), 123.46 (N*C*=*C*N), 29.33 (Al-*C*$H_2$-CH-$(CH_3)_2$), 28.56 (Al-$CH_2$-CH-(*C*$H_3$)$_2$), 27.08 (Al-$CH_2$-*C*H-$(CH_3)_2$), 21.32 (*p*-*C*$H_3$), 17.84 (*o*-*C*$H_3$). IR-ATR: 2112s, 2097s cm$^{-1}$ ($\nu(N_3)$).

### 2.5. *i-Bu$_2$AlN$_3$·IDipp (2b)*

A solution of IDipp (0.85 g, 2.2 mmol) in toluene (30 mL) was added dropwise to a solution of *i*-$Bu_2AlN_3$ (0.40 g, 2.2 mmol) in toluene (10 mL) at 0 °C. The clear colorless reaction mixture was kept at 0 °C for 2 h, slowly warmed to room temperature and stirred for an additional 12 h. The resulting pale yellow solution was concentrated under reduced pressure to a volume of 3–4 mL, whereupon some solid precipitated. This solid was redissolved with gentle warming followed by crystallization at −20 °C for 2 d to afford **3** as colorless large (2–3 mm) crystals. Yield: 0.72 g, 58%. M.p. softens at 168 °C, melts at 178–184 °C. $^1$H NMR ($C_6D_6$, 400.13 MHz): 7.26 (t, $J$ = 7.8 Hz, *p*-H, 2H), 7,12 (d, $J$ = 7.8 Hz, *m*-H, 4H), 6.39 (s, N–C*H*=C*H*–N, 2H), 2.66 (sept, $J$ = 6.8 Hz, C*H*$(CH_3)_2$, 4H), 1.90 (m, Al-$CH_2$-C*H*-$(CH_3)_2$, 2H), 1.43 (d, $J$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.09 (d, $J$ = 6.4 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 6H), 1.08 (d, $J$ = 6.5 Hz, Al-$CH_2$-CH-$(CH_3)_2$, 6H), 0.96 (d, $J$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), −0.43 and −0.57 (doublet of AB system, $^2J_{AB}$ = 13.9 Hz, $J$ = 6.2 and 8.0 Hz, Al-C*H*$_2$-CH-$(CH_3)_2$, 4H). $^{13}$C NMR ($C_6D_6$, 100.62 MHz): 175.17 (N*C*N), 146.48 (*o*-C), 135.37 (*i*-C), 131.81 (*p*-C), 125.46 (N*C*=*C*N), 125.12 (*m*-C), 29.84 (*C*H$(CH_3)_2$), 29.82 (Al-$CH_2$-CH-$(CH_3)_2$), 28.78 (Al-$CH_2$-CH-(*C*$H_3$)$_2$), 27.20 (Al-$CH_2$-*C*H-$(CH_3)_2$), 26.65 (CH

($CH_3$)$_2$), 23.39 (CH($CH_3$)$_2$), 23.3 (broad, (Al-$CH_2$-CH-($CH_3$)$_2$). IR–ATR: 2100s, 2014s cm$^{-1}$ ($\nu$($N_3$)).

### 2.6. *{MesNCH$_2$C(i-Bu)NMes}Al(i-Bu)N$_3$ (3)*

A solution of *i*-$Bu_2AlN_3$ (0.199 g, 1.1 mmol) in hexane (5 mL) was added dropwise via cannula to a stirred solution of glyoxal-bis(2,4,6-trimethylphenyl)imine (0.297 g, 1.0 mmol) in hexane (20 mL) with cooling in an ice bath. Upon addition, the solution turned from the characteristic bright yellow to a bright orange color. After 10 min, the ice bath was removed and the reaction was stirred for 72 h at room temperature. The orange solution was concentrated under reduced pressure and then cooled at −20 °C for crystallization. Compound **3** was obtained as amber crystals after 3 d in sufficient quality for X-ray diffraction analysis. Yield: 0.30 g, 62%. $^1$H NMR ($C_6D_6$, 400.13 MHz): 6.99 (s, *m*-H, 2H), 6.66 (s, *m*-H, 1H), 6.64 (s, *m*-H, 1H), 4.10 (d, $J$ = 24.3 Hz, NC$H_2$C=N, 1H), 3.86 (d, $J$ = 24.3 Hz, NC$H_2$C=N, 1H), 2.55 (s, broad, $w_{1/2}$ = 9 Hz, *o*-C$H_3$, 6H), 2.26 (s, C$H_3$, 3H), 2.25 (s, p-C$H_3$, 3H), 2.01 (s, C$H_3$, 3H), 1.96 (s, C$H_3$, 3H), 2.03 (m, AlC$H_2$C$H$($CH_3$)$_2$, 1H), 1.64 (dd, $J$ = 7.9 Hz, 2 Hz, CC$H_2$CH($CH_3$)$_2$, 2H), 1.28 (m, 1H, CCH$_2$C$H$($CH_3$)$_2$, 1H), 0.93 (d, $J$ = 6.9 Hz, AlCH$_2$CH(C$H_3$)$_2$, 3H), 0.88 (d, $J$ = 6.9 Hz, AlCH$_2$CH(C$H_3$)$_2$, 3H), 0.42 (d, $J$ = 6.9 Hz, CCH$_2$CH(C$H_3$)$_2$, 3H), 0.40 (d, $J$ = 6.6 Hz, CCH$_2$CH(C$H_3$)$_2$, 3H), 0.33 (d, $J$ = 6.6 Hz, AlC$H_2$CH($CH_3$)$_2$, 2H). $^{13}$C NMR ($C_6D_6$, 100.62 MHz): 196.28 (NCH$_2$*C*=N), 144.74 (*i*-C), 137.51, 137.41, 137.27 (*o*-C), 133.71(*p*-C), 130.82 (*m*-C), 130.09 (*m*-C), 130.03 (*m*-C), 129.94, 60.18 (N*C*H$_2$C=N), 41.45 (C*C*H$_2$CH($CH_3$)$_2$), 28.43 (AlCH$_2$CH(*C*H$_3$)$_2$), 28.36 (AlCH$_2$CH(*C*H$_3$)$_2$), 26.32 (AlCH$_2$*C*H($CH_3$)$_2$), 26.16 (*CC*H$_2$CH($CH_3$)$_2$), 22.90 (CCH$_2$CH (*C*H$_3$)$_2$), 22.86 (CCH$_2$CH(*C*H$_3$)$_2$), 21.7 (Al–C), 21.39 (*p*-*C*H$_3$), 21.06 (*C*H$_3$), 19.14 (*o*-*C*H$_3$), 18.60 (*C*H$_3$), 18.11 (*C*H$_3$). IR–ATR: 2125s cm$^{-1}$ ($\nu$($N_3$)).

### 2.7. *[2,6-(Et$_2$NCH$_2$)$_2$C$_5$H$_3$NAl(i-Bu)$_2$][(i-Bu)$_2$Al(N$_3$)$_2$] (4)*

A solution of 2,6-bis(diethylaminomethyl)pyridine (0.26 g, 1.0 mmol) in hexane (5 mL) was added via cannula to a stirred solution of *i*-$Bu_2AlN_3$ (0.38 g, 2.1 mmol) in hexane (4 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and a dense yellow-amber layer separated. The mother liquor was removed via cannula. The remaining volatiles were removed in vacuo to yield **4** as a viscous, yellow-amber oil. Yield: 0.35 g, 86%. $^1$H NMR ($C_6D_6$, 400.13 MHz): 7.77 (t, $J$ = 7.8 Hz, *p*-H, 1H), 7.31 (d, $J$ = 7.8 Hz, *p*-H, 2H), 3.61 (s, Py-C$H_2$-N, 4H), 2.41 (q, $J$ = 7.3 Hz, NC$H_2$CH$_3$, 8H), 2.40 (m, $J$ = 6.9 Hz, AlCH$_2$C$H$($CH_3$)$_2$, 2H), 1.78 (m, $J$ = 6.6 Hz, AlCH$_2$C$H$($CH_3$)$_2$, 2H), 1.37 (d, 12H, $J$ = 6.6 Hz, AlCH$_2$CH(C$H_3$)$_2$), 1.01 (d, $J$ = 6.5 Hz, AlCH$_2$CH(C$H_3$)$_2$, 12H), 0.78 (t, $J$ = 7.2 Hz, NCH$_2$C$H_3$, 12H), 0.48 (d, $J$ = 7.0 Hz, AlC$H_2$CH-($CH_3$)$_2$, 4H), 0.05 (d, 4H, $J$ = 6.9 Hz, AlC$H_2$CH($CH_3$)$_2$, 4H). $^{13}$C NMR ($C_6D_6$, 100.62 MHz): 156.54 (*o*-C), 145.46 (*p*-C), 124.62 (*m*-C), 55.90 (Py-*C*H$_2$-N), 46.67 (N*C*H$_2$CH$_3$), 29.18 (AlCH$_2$CH(*C*H$_3$)$_2$), 28.93 (AlCH$_2$CH(*C*H$_3$)$_2$), 27.43 (AlCH$_2$*C*H($CH_3$)$_2$), 26.66 (AlCH$_2$*C*H($CH_3$)$_2$), 23.38 (broad, AlCH$_2$CH($CH_3$)$_2$), 20.06 (broad, AlCH$_2$CH($CH_3$)$_2$), 9.27 (NCH$_2$*C*H$_3$). IR–ATR: 2113s, 2093s, 2030m cm$^{-1}$ ($\nu$($N_3$)).

### 2.8. *X-ray diffraction analysis of 3*

An orange block-shaped crystal of dimensions 0.48 × 0.36 × 0.30 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector [16, 17] and graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a nonlinear least-squares fit of 6993 peaks in the range $2.2 < \theta < 27.6°$. A total of 61,829 data were measured in the range $1.78 < \theta < 20.82°$ using $\phi$ and $\omega$ oscillation frames. The data were corrected for absorption by the empirical method [18] giving minimum and maximum transmission factors of 0.9552 and 0.9716. The data were merged to form a set of 2921 independent data with $R$(int) = 0.1002 and a coverage of 100.0%. The monoclinic space group $P2_1/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ [19]. Hydrogen positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. The crystal was split by a rotation of about 8.0° rotation about the $b$ axis. The intensity data were truncated to 1.0 Å resolution because data in higher resolution shells all had $\langle I/\sigma \rangle$ <2.0. The isobutyl group bonded to the metal atom was disordered and modeled in three orientations with occupancies of 0.380(4), 0.319(7), and 0.301(7). Restraints on the positional and displacement parameters of the disordered atoms were required. A total of 382 parameters were refined against 247 restraints and 2921 data to give $wR(F^2) = 0.2090$ and $S = 1.017$ for weights of $w = 1/[\sigma^2 (F^2) + (0.1000\ \mathrm{P})^2 + 3.1000\ \mathrm{P}]$, where $\mathrm{P} = [F_o^2 + 2F_c^2]/3$. The final $R$

Table 1. Crystal data and structure refinement for **3**.

| | |
|---|---|
| Empirical formula | $C_{28}H_{42}AlN_5$ |
| Formula weight | 475.65 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | $a$ = 9.417(3) Å; $\alpha$ = 90° |
| | $b$ = 12.992(4) Å; $\beta$ = 98.42(8)° |
| | $c$ = 23.139(8) Å; $\gamma$ = 90° |
| Volume | 2800.4(16) Å$^3$ |
| $Z$, $Z'$ | 4, 1 |
| Density (calculated) | 1.128 Mg m$^{-3}$ |
| Wavelength | 0.71073 Å |
| Temperature | 100(2) K |
| $F$(0 0 0) | 1032 |
| Absorption coefficient | 0.096 mm$^{-1}$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9716 and 0.9552 |
| Theta range for data collection | 1.78–20.82° |
| Reflections collected | 61,829 |
| Independent reflections | 2921 [$R$(int) = 0.1002] |
| Data/restraints/parameters | 2921/247/382 |
| $wR$ ($F^2$ all data) | $wR2$ = 0.2090 |
| $R$ ($F$ obsd. data) | $R1$ = 0.0809 |
| Goodness of fit on $F^2$ | 1.017 |
| Observed data [$I > 2\sigma(I)$] | 1821 |
| Largest and mean shift/s.u. | 0.006 and 0.000 |
| Largest diff. peak and hole | 0.290 and −0.283 e Å$^{-3}$ |

$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

($F$) was 0.0809 for the 1821 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.006 in the final refinement cycle. The final difference map had maxima and minima of 0.290 and −0.283 e Å$^{-3}$, respectively. Although the low crystal quality resulted in a weak data set, the connectivity and the metric data are of sufficient quality for this study. Crystal data and structure refinement parameters are in table 1.

## 3. Results and discussion

Diorganoaluminum azides can be obtained from the reaction of diorganoaluminum chlorides with sodium azide in aliphatic or aromatic solvents [20, 21]. They aggregate as dimers or trimers $(R_2AlN_3)_{2\ or\ 3}$ with bridging azides [22]. Due to the type of chemicals available in our laboratory, the starting material $i$-$Bu_2AlN_3$ [23] was synthesized according to equation (1) from $i$-$Bu_2AlH$ and $Me_3SiN_3$. The latter reagent has been applied previously for the synthesis of aluminum azides from $Me_2AlI$ [24] and $Me_3Al$ [25].

$$i\text{-}Bu_2AlH + Me_3SiN_3 \longrightarrow i\text{-}Bu_2AlN_3 + Me_3SiH \quad (1)$$

$i$-$Bu_2AlN_3$ was isolated as a colorless mobile liquid whose $^1$H NMR spectrum displays two sets of signals which may be attributed to the presence of $(i\text{-}Bu_2AlN_3)_2$ and $(i\text{-}Bu_2AlN_3)_3$. Addition of pyridine led to a simplified spectrum in agreement with the formation of the adduct $i$-$Bu_2AlN_3$·py.

$i$-$Bu_2AlN_3$ was then reacted with four different ligands, the tridentate diaminopyridine **A**, the bidentate diimine **B**, the monodentate pyridine **C** (DMAP), and the N-heterocyclic carbenes **D** (scheme 1). Whereas the reaction with the monodentate ligands **C** and **D** afforded the expected adducts $i$-$Bu_2AlN_3$·L, the reaction with ligands **A** and **B** led to substituent exchange and redox reactions.

Adduct **1** was isolated as a viscous, colorless, hexane insoluble oil, and the adducts **2a** and **2b** were obtained as off-white, crystalline solids. Interestingly, compound **2a** could not be isolated as a pure product despite numerous attempts. The large surface area of its yellowish feathery crystals may have contributed to this. On the other hand, compound **2b** forms large colorless crystals in good purity. The $^1$H NMR spectra of **1** and **2** clearly confirm the 1 : 1 stoichiometry, and the IR spectra display strong azide absorptions around 2100 cm$^{-1}$. The $^{13}$C chemical shifts of the coordinated carbene carbons are a bit more upfield (**2a**: 172.4 ppm, **2b**: 175.2 ppm) than those of the related carbene complexes IMes·$AlMe_3$ (178.2) [26] and IDipp·Al($n$-Bu)$_3$ (191.0 ppm) [27]. The reaction of the diimine **B** with $i$-$Bu_2AlN_3$ afforded the iminoamide complex **3**. The putative intermediates, adducts **5** or **6** (scheme 2) with four- or five-coordinate aluminum centers, were not detected.

The reaction of diimines with metal alkyls is a convenient route to iminoamine ligands [28, 29]. For diimines with unsubstituted backbones, the initial R-M addition across one imine double bond is followed by a hydrogen migration, so that the imine carbon bears the new substituent. Although the identity of **3** was established by $^1$H and $^{13}$C NMR and FTIR spectroscopy, a single-crystal X-ray diffraction experiment confirmed the spectroscopic analyses (figure 1). The aluminum center is four coordinate in a distorted tetrahedron. The Al–C and Al–N distances fall into the typical range for these bonds. As expected, the aluminum amide bond distance (Al1–N2) is the shortest followed by the aluminum azide (Al–N3) and the aluminum imine nitrogen bonds (Al–N1) with values of 1.785(5), 1.823(6), and 1.953(5) Å.

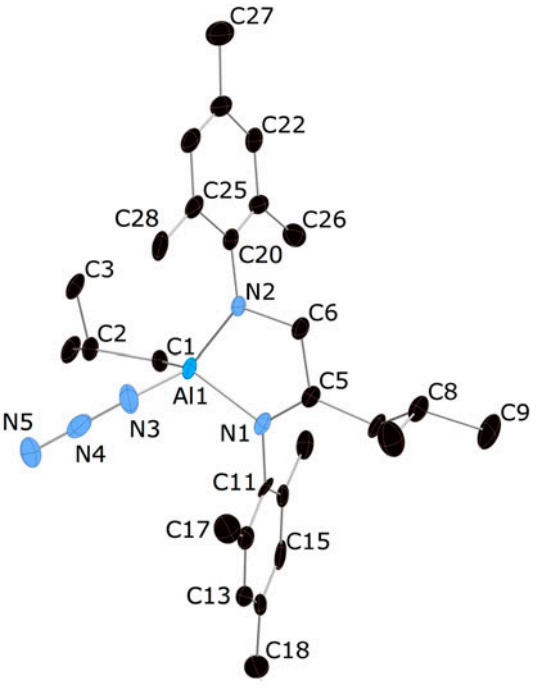
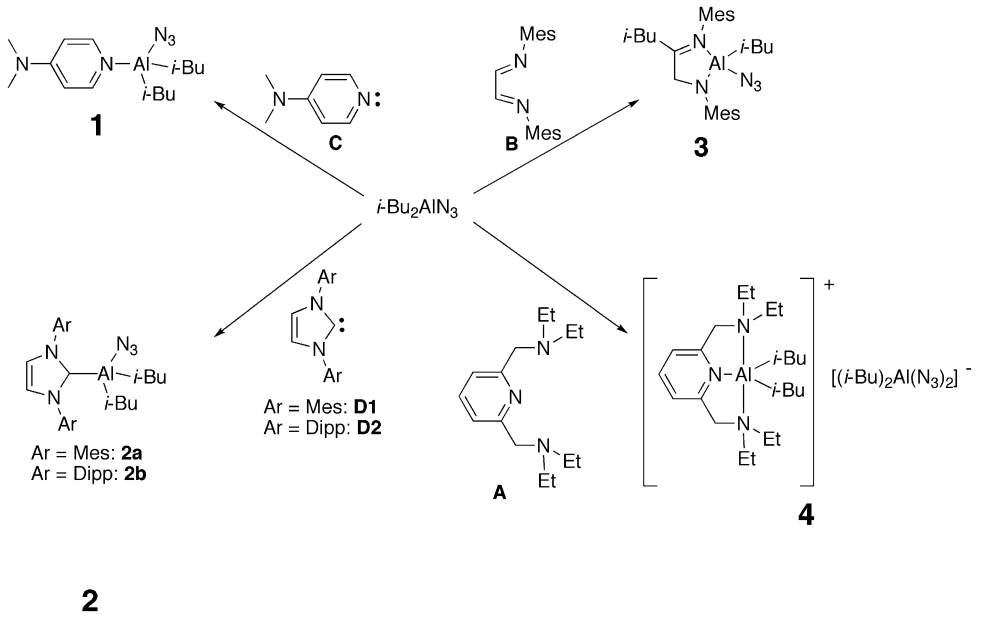


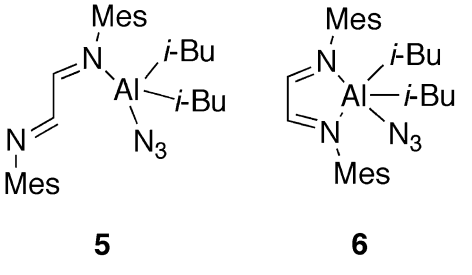

Figure 1. Thermal ellipsoidal plot (30%) of **3**. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.953(5), Al(1)–N(2) 1.785(5), Al(1)–N(3) 1.823(6), Al(1)–C(1) 1.945(7), N(3)–N(4) 1.190 (8), N(4)–N(5) 1.149(8), N(1)–C(5) 1.278(7), N(1)–C(11) 1.444(8), N(2)–C(6) 1.451(7), N(2)–C(20) 1.407(7), C (5)–C(6) 1.471(8), N(1)–Al(1)–N(2) 85.8(2), N(1)–Al(1)–N(2) 103.4(2), N(2)–Al(1)–N(3) 113.5(3), N(3)–Al(1)–C (1) 113.4(7), N(4)–N(3)–Al(1) 132.8(5), N(3)–N(4)–N(5) 175.8(8).

The azide is essentially linear (N(3)–N(4)–N(5) 175.8(8)°) and is bent away from the aluminum center (∠(Al1–N3–N4) = 132.8(5)°) as is typical for aluminum azides [21]. Interestingly, only five neutral aluminum azides featuring a four-coordinate aluminum center with a terminal azide [6, 30–33] and two anionic species $[Me_3AlN_3]M$ (M = Rb and Cs) [34, 35] have been crystallographically characterized to date. The Al–N and Al–C bond distances observed for **3** are at the lower end of those reported for the above-mentioned species. The values for $\{(pip)Al(N_3)(\mu\text{-}pip)\}_2$ (pip = piperidine) [30] come closest to those for **3** with $Al–N_{terminal}$ = 1.765, $Al–N_{bridging}$ = 1.935 (avg.), and $Al–N_{azide}$ = 1.805 Å.

The reaction of the tridentate ligand **A** with $i\text{-}Bu_2AlN_3$ in a 1 : 1 ratio gave a hexane insoluble oil, whose $^1H$ NMR spectrum showed the presence of two sets of *i*-butyl signals and a ligand to *i*-butyl ratio of 1 : 2. Adjustment of the reactant ratio **A**:$i\text{-}Bu_2AlN_3$ to 1 : 2 gave **4** in good yields as an amber oil. Based on spectroscopic data, **4** may be formulated as the ionic species $[2,6\text{-}(Et_2NCH_2)_2C_5H_3NAl(i\text{-}Bu)_2][(i\text{-}Bu)_2Al(N_3)_2]$ (see scheme 1). The reaction of alkylaluminum halides $R_nAlX_{3-n}$ (R = alkyl, X = halide, *n* = 1,2) with polydentate ligands often leads to asymmetric cleavage of the halide bridges and formation of ionic species such as $[(12\text{-crown-}4)AlCl_2]^+[EtAlCl_3]^-$ [36] or $[t\text{-}Bu_2Al(TMEDA)]^+[t\text{-}Bu_2AlX_2]^-$ (X = Cl, Br; TMEDA = $Me_2NCH_2CH_2NMe_2$) [37]. Attempts to prevent the azide exchange by using THF as solvent, in which $i\text{-}Bu_2AlN_3$ should be present as the adduct $i\text{-}Bu_2AlN_3{\cdot}THF$, were unsuccessful, and compound **4** was obtained as well.




Scheme 1. Synthesis of **1**–**4**.




Scheme 2. Possible intermediates.

### 3.1. *Thermal stability*

The thermal stability of **1**, **2a**, **2b**, and **3** was probed using neat samples and/or solutions. Solutions of **2a** and **3** in $C_6D_5Br$ were heated in J. Young type NMR tubes at 190 °C for 3 and 7 days. During this time, the $^1H$ NMR signals of the starting materials disappeared and a plethora of new signals was observed indicating decomposition into numerous compounds. Due to this complexity, solution decomposition was not pursued further. Compound **1** was heated in a nitrogen atmosphere, and no change was observed until 250 °C when DMAP began to sublime. In contrast, **2a** experienced slow gas evolution when heated at 120 °C. The experiment was repeated under dynamic vacuum in order to collect the volatiles in a liquid nitrogen cooled trap. At 130 °C, a colorless condensate appeared in the cold trap, and at 165 °C, a yellow solid began to form on the cold finger. After 3 h at 165 °C, almost all of the substrate sublimed, and only a small amount of brown oil was left behind.

The sublimate consisted mostly of **2a** in addition to some unidentified Mes and *i*-BuAl containing species. The volatile material was identified as isobutane by $^{1}$H NMR spectroscopy. Finally, no changes were observed for **2b** until 240 °C.

Typically, organoaluminum compounds are thermally stable, and many compounds can be treated at temperatures in excess of 200 °C [12]. Notable exceptions include alkyl aluminum compounds with hydrogens in β-position to the aluminum center and aluminum hydrides. The former can undergo facile β-hydrogen elimination to afford an olefin and an aluminum hydride, whereas the latter suffer from homolytic Al–H bond breakage. An increase in the coordination number of the aluminum center [12] and the presence of good donors such as NHC's [38] can increase the stability of such aluminum compounds, and this was also observed in this study.



## 4. Conclusion

*i*-$Bu_2AlN_3$ readily reacts with Lewis bases to form the adducts L·Al(*i*-Bu)$_2N_3$. Reaction with the bidentate diimine $(MesN{=}CH)_2$ does not stop at the adduct stage, but continues to form the iminoamide compound **3** through formal Al-*i*-Bu addition to one of the N–C double bonds followed by *i*-Bu migration. The terdentate ligand **A** induces azide transfer and formation of the ionic compound **4**. The adducts **1–3** are thermally stable to at least 110 °C, but decompose into their precursors (**1**) or numerous unidentified species (**2a** and **3**) when heated to higher temperatures.

## Supplementary material

$^{1}$H and $^{13}$C NMR spectra of compounds **1**-**4**. Full details of the crystal structure of **3** (CCDC 1040893) in cif format are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, or E-mail: deposit@ccdc.cam.ac.uk.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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## Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1044447].

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