Journal of Organometallic Chemistry, *456* (1993) 161–166 161

JOM 23611

Synthesis and characterization of alkylaluminum imine complexes: the X-ray crystal structure of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$

James A. Jensen [1]

Hercules Incorporated, Research Center, 500 Hercules Road, Wilmington, DE 19808-1599 (USA)

(Received November 30, 1992; in revised form January 29, 1993)

Abstract

Organoaluminum imine complexes, $[RCH{=}NAlR_2]_2$, are formed by the action of dialkylaluminum hydrides on nitriles. The reaction of $HAl(i\text{-}C_4H_9)_2$ with nitriles, RCN, where R = CH_3, $(CH_3)_3C$, $CH_2{=}CHCH_2$, $CH_2{=}C(CH_3)$, C_6H_5, $C_6H_4\text{-}2\text{-}CH_3$, and $C_6H_3\text{-}2,6\text{-}(CH_3)_2$, has been conducted and spectroscopic data for the diisobutylaluminum imine products obtained. These complexes are dimeric both in solution and in the solid state. The X-ray crystal structure of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$ shows an Al_2N_2 core in which the imine moieties bridge aluminum centers: Al ··· Al 2.905(3) Å, Al–N 1.946(5) Å, Al–C 1.967(6) Å, N=C 1.248(7) Å, N–Al–N 80.6(2)°, and Al–N–Al 96.5(2)°. Crystal data for $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$: space group $C2/c$, monoclinic, $a = 21.556(5)$, $b = 9.3020(9)$, $c = 18.705(1)$ Å, $\beta = 108.09(1)°$, $V = 3565(2)$ Å³, $Z = 4$, $R_F = 6.4\%$, $R_{wF} = 8.3\%$.

1. Introduction

The reactions of aluminum alkyl reagents with amines have been extensively reported and a large body of spectroscopic and structural data exists [1]. Spectroscopic and structural details of alkylaluminum complexes derived from other nitrogen donor ligands, such as nitriles, are not as complete. This report describes a series of alkylaluminum imine complexes, their synthesis, and structure.

Organoaluminum imines are prepared by treating nitriles with trialkylaluminum reagents [2] and by the reduction of nitriles with aluminum hydride reagents [3]. Such aluminum imine complexes, which typically are not isolated, are utilized as intermediates in the preparation of aldehydes [3,4], primary amines [5,6], Schiff bases [7], and azacyclic compounds [8]. The use of metallo-imines in organic synthesis has been reviewed [1,9]. In addition, organoaluminum imines provide a useful route to aluminum-containing polymers which serve as precursors to aluminum nitride ceramics [10].

This report describes the synthesis and characterization of a series of alkylaluminum imine complexes of the form $[RCH{=}NAl(i\text{-}C_4H_9)_2]_2$, where R = CH_3, $(CH_3)_3C$, $CH_2{=}CHCH_2$, $CH_2{=}C(CH_3)$, C_6H_5, $C_6H_4\text{-}2\text{-}CH_3$, and $C_6H_3\text{-}2,6\text{-}(CH_3)_2$, prepared by diisobutylaluminum hydride reduction of the corresponding nitrile. Proton and carbon NMR spectroscopic data for these complexes and the X-ray crystal structure of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$, are reported.

2. Results and discussion

Diisobutylaluminum imine complexes were prepared by slow addition of a toluene solution of diisobutylaluminum hydride to the appropriate nitrile (eqn. (1)):

$$RC{\equiv}N + HAl(i\text{-}C_4H_9)_2 \xrightarrow{0°C} [RCH{=}NAl(i\text{-}C_4H_9)_2]_2 \quad (1)$$

1, R = CH_3; **2**, R = CD_3; **3**, R = $(CH_3)_3C$; **4**, R = $CH_2{=}CHCH_2$; **5**, R = $CH_2{=}C(CH_3)$; **6**, R = C_6H_5; **7**, R = $C_6H_4\text{-}2\text{-}CH_3$; **8**, R = $C_6H_3\text{-}2,6\text{-}(CH_3)_2$. Nitrile reduction proceeds cleanly and in quantitative yield. The reaction products obtained after solvent evaporation are liquids or low melting solids. Proton NMR spec-

---

[1] Present address: Lanxide Corporation, 1300 Marrows Road, P.O. Box 6077, Newark, DE 19714-6077, USA.

Elsevier Sequoia S.A.

TABLE 1. Properties of $[RCH{=}NAl(i\text{-}C_4H_9)_2]_2$ complexes

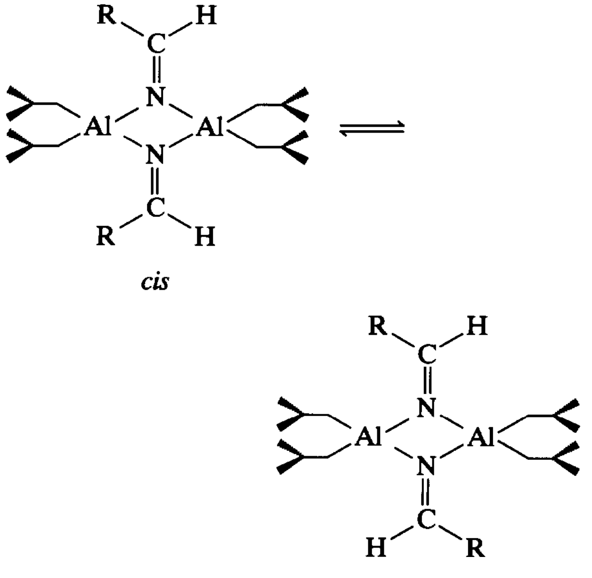
R	MP (°C)	^{1}H NMR δ CH=N	^{13}C NMR δ CH=N	IR ν C=N	*cis* : *trans* ratio
CH_3 (**1**)	liq	7.92	178.5	1669	1:1
CD_3 (**2**)	liq	7.92	178.6	1665	1:1
$(CH_3)_3C$ (**3**)	128	8.22	188.2	1655	1:6
$CH_2{=}CHCH_2$ (**4**)	liq	7.99	178.9	1670	1:1
$CH_2{=}C(CH_3)$ (**5**)	50	8.52	177.1	1670	1:5
C_6H_5 (**6**)	liq	8.95	175.0	1680	2:3
C_6H_4-2-CH_3 (**7**)	45	9.36	174.6	1635	2:3
C_6H_3-2,6-$(CH_3)_2$ (**8**)	140	8.93	180.9	1655	1:6

troscopy of these products shows no reaction side products. Infrared and NMR spectroscopic data for the imine groups and melting point data for the complexes are shown in Table 1. All of the imine complexes show characteristic CH=N stretches in the infrared spectrum centering about 1662 cm^{-1}. The CH=N proton resonances range from 7.9 to 9.3 ppm. Resonances for imine protons in compounds containing aryl substitution on the imine carbon are shifted downfield, to 9 ppm, relative to the alkyl substituted imine carbons which display proton resonances near 8 ppm. The imine carbon resonances appear between 174 and 188 ppm in the ^{13}C NMR spectra.

The NMR spectra of complexes **1**–**8** indicate both *cis* and *trans* isomers are present in benzene solution (eqn. (2)).

Cis and *trans* isomeric components are easily identified by the splitting patterns of the imine resonances in both the proton and carbon NMR spectra since the imine region is well separated from the rest of the peaks in the spectrum. The observed isomer ratios are recorded in Table 1. The reported *cis*/*trans* ratios were obtained from proton NMR integration.

Liquid complexes **1**, **2** and **4**, are approximately 1:1 isomer mixtures in benzene solution, while **6** shows a 2:3 ratio. Presumably, the dominant isomer in benzene solution for complexes **3** and **5**–**8** is the *trans* isomer. This is supported by the solid state structure for compound **8** (see below) that shows a *trans* geometry. In solution, complex **8** shows a *cis* : *trans* isomer ratio of 1:6. The isomer ratio for the series correlates roughly with the size of the alkyl- or aryl-imine group. When the imine carbon is substituted with small alkyl groups there is no preferred orientation and a 1:1 ratio results. However, in the more sterically demanding tert-butyl and 2,6-dimethylphenyl substituted imines, one geometry is strongly preferred over the other. The isomer ratios for **1** and **8** do not change over the



(2)

TABLE 2. Crystallographic data for **8**

a) Crystal parameters			
cryst. system	monoclinic	cryst. dimens., mm	0.50 × 0.50 × 0.24
space group	C2/c (No. 15)	Z	4
a, Å	21.556 (5)	V, Å^3	3565 (2)
b, Å	9.3020 (9)	Temp, °C	20
c, Å	18.705 (1)	ρ_{calc}, g cm^{-3}	1.231
β, deg	108.09 (1)		
b) Data collection			
diffractometer	Enraf-Nonius CAD4	rflns. collected	2515
monochromator	graphite	indpt. rflns.	2515
radiation	Mo Kα (0.71073Å)	rflns. with $I > 3\sigma$	1359
scan method	ω–2θ	no. of variables	182
2θ scan range, deg	4–45	transm. fact. (min, max)	0.60, 1.00
h, k, l limits	+23, +10, ±20	μ, cm^{-1}	1.10
c) Refinement			
$R(F_o)$	0.064	final ext. coeff.	4.311×10^{-7}
$R_w(F_o)$	0.083	GOF	2.143

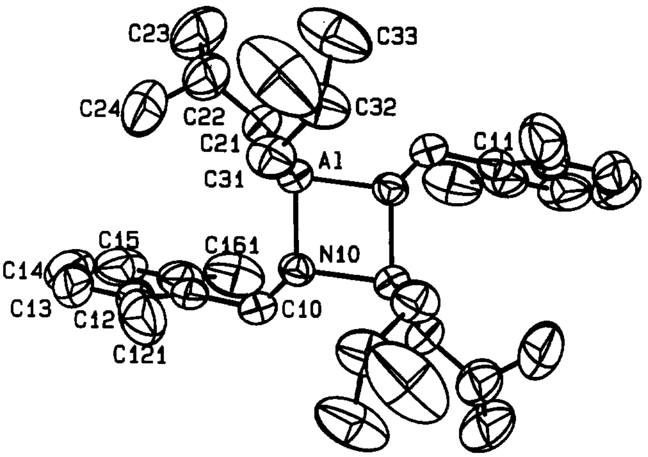


Fig. 1. ORTEP diagram of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl\ (i\text{-}C_4H_9)_2]_2$ (**8**) showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

temperature range −70°C to +70°C as indicated by proton NMR measurements.

Complexes **1**–**8** react rapidly with water and alcohols forming insoluble inorganic residues. Lewis bases do not cleave the dimers to form adducts. NMR spectra of samples treated with diethyl ether, tetrahydrofuran, or pyridine (eqn. (3)) do not differ in appearance from untreated samples. No evidence for monomeric adducts is observed.

$$[RCH{=}NAl(i\text{-}C_4H_9)_2]_2 + 2L \ \text{—X→}\ 2RCH{=}NAl(i\text{-}C_4H_9)_2 \cdot L \quad (3)$$

L = Lewis base

This behavior is in sharp contrast with that of complexes such as the silylamines $[i\text{-}Bu_2AlN(H)SiPh_3]_2$ and $[Me_2AlN(H)SiEt_3]_2$ which are readily cleaved by 4-methyl-pyridine to form monomeric adducts [11].

2.1. *X-ray crystal structure of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$ (8)*

The molecular structure of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$ is illustrated in Fig. 1. Single crystals were obtained by cooling saturated diethyl ether solutions to −20°C. Crystal data are given in Table 2, while final atomic parameters and important bond lengths and angles are given in Tables 3 and 4. The structure shows that the molecule has an Al_2N_2 core with the 2,6-dimethylphenyl substituted imine groups in a *trans* orientation. The molecule resides on a crystallographic 2-fold axis.

The Al···Al contact at 2.905 Å is significantly longer than the 2.66 Å distance reported for the Al–Al single bond in $[((CH_3)_3Si)_2CH]_2Al{-}Al[CH(Si(CH_3)_3)_2]_2$ [12], and is also slightly longer than that typically found in dimeric aluminumamide complexes. For example, values of 2.81 Å and 2.859 Å were reported for $[Me_2AlNMe_2]_2$ [13] and *trans*-$[Me_2AlNH\text{-}1\text{-}adamantyl]_2$ [14], respectively. The N–Al–N–Al torsion angle in complex **8** is 18°.

TABLE 3. Positional parameters and estimated standard deviations for **8**

Atom	*x*	*y*	*z*	B (A²)
Al	0.07087(7)	0.1689(2)	0.27698(8)	4.02(3)
N(10)	0.0019(2)	0.1360(4)	0.1834(2)	3.8(1)
C(10)	−0.0003(2)	0.0851(6)	0.1210(3)	4.8(1)
C(11)	0.0571(2)	0.0442(7)	0.0965(3)	5.1(1)
C(12)	0.0878(3)	0.1521(8)	0.0670(3)	6.3(2)
C(13)	0.1409(3)	0.112(1)	0.0436(3)	9.2(2)
C(14)	0.1611(3)	−0.026(1)	0.0486(4)	10.1(3)
C(15)	0.1317(3)	−0.1297(9)	0.0767(4)	9.0(2)
C(16)	0.0774(3)	−0.0957(7)	0.1003(3)	6.7(2)
C(21)	0.1369(3)	0.0206(7)	0.3144(3)	5.2(1)
C(22)	0.2077(3)	0.0563(8)	0.3303(4)	7.2(2)
C(23)	0.2535(3)	−0.0581(9)	0.3739(5)	9.9(3)
C(24)	0.2236(3)	0.101(1)	0.2630(5)	11.9(3)
C(31)	0.0939(3)	0.3761(6)	0.2813(3)	5.3(2)
C(32)	0.0943(6)	0.452(1)	0.3510(6)	6.0(3)
C(35)	0.1399(7)	0.439(1)	0.3583(7)	7.6(4)
C(33)	0.1348(5)	0.3876(9)	0.4243(4)	10.6(3)
C(34)	0.1311(5)	0.6090(8)	0.3506(5)	12.3(3)
C(121)	0.0665(3)	0.3034(9)	0.0618(4)	8.6(2)
C(161)	0.0439(4)	−0.2097(8)	0.1318(4)	9.6(3)

The average Al–N bond distance of 1.946(5) Å is comparable to the bond lengths reported for aluminum ketimide species: 1.96 Å in $(^tBuC(Me){=}NAlMe_2)_2$ [15], 1.916 Å in $(BrC_6H_4C(Ph){=}NAlPh_2)_2 \cdot 2C_6H_6$ [16], and 1.941 Å in the heterobimetallic complex $[(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}N{=}CHCH_3)]_2$ [17]. The Al–N distance appears at the high end of the 1.88–1.94 Å range typical for Al–N bonds. It is significantly longer than the 1.78 Å distance reported for the Al–N bonds in the trimer $[MeAlN(2,6\text{-}^iPr_2C_6H_3)]_3$, in which multiple bond character between Al and N has been suggested [18].

The N=C bond length of 1.248(7) Å observed in complex **8** is slightly shorter than the imine distance

TABLE 4. Selected bond distances (Å) and bond angles (°) for $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl(i\text{-}C_4H_9)_2]_2$ (**8**)

Bond distances			
Al···Al	2.905(3)	Al–C(31)	1.986(6)
Al–N(10)	1.937(5)	N(10)–C(10)	1.248(7)
Al–N(10)′	1.955(5)	C(10)–C(11)	1.495(8)
Al–C(21)	1.949(6)		
Bond angles			
Al–N(10)–Al′	96.5(2)	N(10)–Al–C(31)	107.6(2)
Al–N(10)–C(10)	134.5(4)	N(10)′–Al–C(31)	110.9(2)
Al′–N(10)–C(10)	127.8(4)	C(21)–Al–C(31)	121.8(3)
N(10)–Al–N(10)′	80.6(2)	C(10)–C(11)–C(12)	118.3(7)
N(10)–Al–C(21)	118.9(2)	C(10)–C(11)–C(16)	120.5(7)
N(10)′–Al–C(21)	109.6(2)	C(10)–C(11)–C(121)	122.1(7)
N(10)–C(10)–C(11)	126.0(5)	C(10)–C(11)–C(161)	120.5(7)

recorded for the aluminum ketimide complexes: $({}^tBuC(Me){=}NAlMe_2)_2$, 1.27 Å [15]; $(BrC_6H_4C(Ph){=}NAlPh_2)_2 \cdot 2C_6H_6$, 1.282 Å [16]; and $[(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)\ (\mu\text{-}N{=}CHCH_3)]_2$, 1.260 Å [17]. The C–N bond distance does not vary significantly for RC(H)=N substituted complexes, such as **8**, compared to RR′C=N substituted ketimide complexes.

The coordination geometry around the aluminum atom is distorted from tetrahedral. The internal N–Al–N angles at 80.6° and Al–N–Al angles at 96.5° are in the range observed for dimeric aminoalanes and the dimeric aluminum ketimide complexes $({}^tBuC(Me){=}NAlMe_2)_2$ [15] and $(BrC_6H_4C(Ph){=}NAlPh_2)_2 \cdot 2C_6H_6$ [16]. The angle at aluminum in the latter is 82.9° and the angle at nitrogen is 97.1°.

2.2. *Concluding remarks*

A series of alkylaluminum imine dimers has been prepared by the reduction of nitriles with diisobutylaluminum hydride. *Cis/trans* isomer mixtures for all of the $[RCH{=}NAl(i\text{-}C_4H_9)_2]_2$ compounds **1–8** are observed. The solution *cis/trans* ratios at room temperature range from 1:1 for small R groups to 1:6 for sterically bulky R groups. While both *cis* and *trans* dimeric isomers are evident in solution, the solid state structure of **8** shows the imine groups oriented in a *trans* geometry.

3. Experimental section

All manipulations were carried out using standard vacuum line and dry box techniques under inert atmospheres or vacuum. Solvents were dried using standard techniques [19]. The reagents diisobutylaluminum hydride (Aldrich, 1.0 *M* in toluene), acetonitrile (Aldrich), acetonitrile-d_3 (Aldrich), benzonitrile (Aldrich), butenenitrile (Aldrich), methacrylonitrile (Aldrich), trimethylacetonitrile (Aldrich), 2-methylbenzonitrile (Lancaster), and 2,6-dimethylbenzonitrile (Lancaster) were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 or AM 500 spectrometer. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS. Chemical shifts for the major isomer are reported. The IR spectra were recorded on a Perkin-Elmer 597 either neat or as Nujol mulls. Melting points were recorded in sealed capillaries under argon on a Thomas-Hoover Capillary Melting Point Apparatus. Elemental analyses on selected compounds were performed by Galbraith Laboratories, Knoxville, TN.

3.1. *Preparation of* $[CH_3CH{=}NAl^iBu_2]_2$ *(1)*

A 250 ml Schlenk round bottom flask was fitted with a pressure equalized dropping addition funnel and purged with nitrogen. Acetonitrile (25 ml, 479 mmol) was added to the flask. The funnel was charged with diisobutylaluminum hydride (100 ml, 100 mmol) and the flask was cooled to 0°C. The DIBAL-H was added dropwise over 30 minutes and stirred at 0°C for an additional hour. The flask was warmed to room temperature and the colorless solution was stirred overnight. After about 12 h a yellow color developed. The solvent was removed under vacuum, leaving 18.5 g (100%) $[CH_3CH{=}NAl^iBu_2]_2$. The product can be vacuum distilled at 87°C/0.35 mm Hg. ^1H NMR (C_6D_6, 500 MHz) of the 1:1 isomer mixture: δ 7.92 (m, 1H, HC=N), 1.98 (t of septets, 2H, CH), 1.57 (d of d, 3H, $CH_3C{=}N$), 1.12 (m, 12H, CH_3–CH), 0.25 (m, 4H, CH_2Al). $^{13}C\{^1H\}$NMR (C_6D_6, 75 MHz): δ 178.5 (C=N), 28.6 ($CH_3C{=}N$), 28.5 (Al–C–C–CH_3), 26.6 (Al–C–C), 22.6 (Al–CH_2) ppm. IR (neat, KBr): 3345w, 3070vw, 2965sh, 2950s, 2925s, 2895s, 2865s, 2845sh, 2790sh, 2775m, 2750sh, 2725w, 2615w, 1685sh, 1669s [C=N], 1655sh, 1590m, 1462s, 1432s, 1400m, 1378m, 1362s, 1320m, 1263w, 1205w, 1180s, 1163m, 1123m, 1067s, 1018m, 970w, 950w, 825m, 685s br, 585sh, 512sh, 485m, 460m, 410w cm^{-1}.

3.2. *Preparation of* $[CD_3CH{=}NAl^iBu_2]_2$ *(2)*

Compound **2** was obtained from acetonitrile-d_3 (5.0 g, 113.7 mmol) and DIBAL-H (100 ml, 100 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving 18.3 g (98%) of yellow liquid **2**, $[CD_3CH{=}NAl^iBu_2]_2$. ^1H NMR (C_6D_6, 300 MHz) of the 1:1 isomer mixture: δ 7.91 (d, 1H, CH=N), 1.99 (m, 2H, CH), 1.10 (m, 12H, CH_3), 0.26 (m, 4H, $AlCH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 178.6 (C=N), 27.9 ($CD_3C{=}N$), 27.7 (Al–C–C–CH_3), 26.6 (Al–C–C), 22.6 (Al–CH_2) ppm. IR (neat, KBr): 2940s, 2860s, 2760w, 2600w, 1665s [C=N], 1455m, 1390m, 1370m, 1355m, 1315m, 1255w, 1200w, 1170m, 1150w, 1130m, 1055m, 1030m, 1010m, 970m, 940w, 810m, 620s, 500w, 450m cm^{-1}.

3.3. *Preparation of* $[(CH_3)_3CCH{=}NAl^iBu_2]_2$ *(3)*

Compound **3** was obtained from trimethylacetonitrile (7 ml, 63.3 mmol) and DIBAL-H (63 ml, 63 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving 13.3 g (93%) of white solid $[(CH_3)_3CCH{=}NAl^iBu_2]_2$. The compound is readily soluble in aprotic organic solvents. It can be crystallized from diethyl ether, hexane, toluene, and acetonitrile. ^1H NMR (C_6D_6, 300 MHz): δ 8.22 (s, 1H, CH=N), 1.99 (sept, 2H, CH), 1.14 (d, 12H, Al–C–C–CH_3), 0.91 (s, 9H, CCH_3) 0.36 (m, 4H, $AlCH_2$) ppm. $^{13}C\{^1H\}$ NMR(C_6H_6, 75 MHz): δ 188.3 (s, CH=N), 40.6 (s, $(CH_3)_3C$), 28.7 (s, $(CH_3)_3C$), 26.6 (s, Al–C–C), 25.4 (s, Al–C–C–CH_3), 24.3 (s, $AlCH_2$)

ppm. IR (Nujol, KBr): 1680sh, 1655s [C=N], 1320w, 1270m, 1210w, 1180w, 1100w br, 1060m, 1030m, 900w, 820m, 800m, 780m, 730w, 690m, 530m, 460m cm^{-1}.

3.4. Preparation of $[CH_2{=}CHCH_2CH{=}NAl^iBu_2]_2$ (4)

Compound **4** was obtained from 3-butenenitrile (2.4 ml, 29.8 mmol) and DIBAL-H (29.8 ml, 29.8 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving 5.7 g (92%) of the yellow liquid $[CH_2{=}CHCH_2{-}CH{=}NAl^iBu_2]_2$. ^1H NMR (C_6D_6, 300 MHz) of the 1 : 1 mixture: δ 8.03 (d of t, 1H, CH=N), 5.56 (m, 1H, $CH_2{=}CH$), 5.00 (m, 2H, $CH_2{=}CH$), 2.73 (m, 2H, $={CHCH_2}$), 1.85 (m, 2H, Al–C–CH), 1.04 (m, 12H, CH_3), 0.18 (m, 4H, $AlCH_2$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6, 75 MHz): δ 178.9 (C=N), 129.8 (C=C), 119.6 (C=C), 46.6 (=$CHCH_2CH$=), 28.6 and 28.4 (Al–C–C–CH_3), 26.4 (Al–C–C), 22.4 (Al–CH_2) ppm. IR (neat, KBr): 3100w, 3000sh, 2960s, 2880s, 2780m, 2620w, 1850w, 1650s [C=N], 1620s [C=C], 1460m, 1430m, 1400m, 1380m, 1360m, 1320m, 1260w, 1200w, 1180m, 1160m, 1060m, 1020m, 995m, 930m, 820m, 680s, 500m, 460m cm^{-1}.

3.5. Preparation of $[CH_2{=}C(CH_3)CH{=}NAl^iBu_2]_2$ (5)

Compound **5** was obtained from methacrylonitrile (2.5 ml, 29.8 mmol) and DIBAL-H (29.8 ml, 29.8 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving 5.7 g (92%) of the light green, waxy solid $[CH_2{=}C(CH_3){-}CH{=}NAl^iBu_2]_2$. Mp: 50°C. ^1H NMR (C_6D_6, 300 MHz): δ 8.52 (s, 1H, CH=N), 5.37 (s, 1H, CH=C), 5.19 (s, 1H, CH=C), 2.0 (m, 2H, Al–C–CH), 1.87 (s, 3H, $=CCH_3$), 1.13 (m, 12H, Al–C–C–CH_3), 0.37 (m, 4H, $AlCH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 177.1 (C=N), 144.7, 131.7 (C=C), 28.6 and 28.5 (Al–C–C–CH_3), 26.6 (Al–C–C), 24.1 ($AlCH_2$), 16.4 (=CCH_3) ppm. IR (Nujol, KBr): 3100w, 2780w, 2620w, 1870w, 1670m, 1630m, 1370m, 1320m, 1270m, 1180m, 1100sh br, 1080m, 1020m, 940w, 870w, 840w, 820m, 805m, 730m, 680m, 540w, 480w, 460w cm^{-1}.

3.6. Preparation of $[C_6H_5CH{=}NAl^iBu_2]_2$ (6)

Compound **6** was obtained from benzonitrile (19.4 g, 188.1 mmol) and DIBAL-H (188 ml, 188 mmol) in a manner analogous to the preparation of **1**. Removal of the solvent gave 45 g (97%) of yellow liquid **6**, $[C_6H_5CH{=}NAl^iBu_2]_2$. ^1H NMR (C_6D_6, 300 MHz): δ 8.95 (s, 1H, CH=N), 7.55 and 7.07 (m, 5H, C_6H_5), 2.07 (t of septets, 2H, CH), 1.15 (d of d, 12H, CH_3), 0.55 (m, 4H, CH_2), ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 175.0 (C=N), 137.2, 132.7, 129.6, 129.4, 129.0, 128.9 (C_6H_5), 28.4 and 28.1 (Al–C–C–CH_3), 26.7 (Al–C–C), 23.2 ($AlCH_2$) ppm. IR (neat, KBr): 3200w, 3060w, 3020w, 2950s, 2860s, 2780m, 2600w, 2200w, 1940w, 1850w, 1810w, 1680m, 1640s, 1590s, 1570s, 1460m, 1390m, 1370m, 1350m, 1310m, 1280w, 1260w, 1190m, 1170m, 1150m, 1050m, 1000m, 970w, 930w, 900w, 840s, 800m, 740s, 700s, 670s, 610sh, 510m, 460m, 440m cm^{-1}.

3.7. Preparation of $[(C_6H_4\text{-}2\text{-}(CH_3))CH{=}NAl^iBu_2]_2$ (7)

Compound **7** was obtained from 2-methylbenzonitrile (2.0 g, 17.1 mmol) and DIBAL-H (17.1 ml, 17.1 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving pale yellow solid $[(C_6H_4\text{-}2\text{-}(CH_3))CH{=}NAl^iBu_2]_2$ (**7**). Yield 4.2 g (94%). Mp: 45°C. Elemental analysis for $C_{16}H_{26}NAl$: Calcd: C, 74.0; H, 10.1; N, 5.4; Al, 10.4. Found: C, 72.7; H, 10.1; N, 4.7; Al, 9.8%. ^1H NMR (C_6D_6, 300 MHz): δ 9.37 (s, 1H, CH=N), 8.1, 7.3 and 7.0 (m, 4H, C_6H_4), 2.13 (s, 3H, C_6CH_3), 2.02 (t of septets, 2H, CH), 1.12 (m, 12H, Al–C–C–CH_3), 0.50 (m, 4H, $AlCH_2$), ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 174.6 (CH=N), 138.8, 136.9, 132.3, 131.3, 126.6, 126.4 (C_6H_4), 28.7 (Al–C–C–CH_3), 28.3 (Al–C–C–CH_3), 26.8 (Al–C–CH), 23.6 ($AlCH_2$), 18.6 ($C_6H_4CH_3$) ppm. IR (Nujol, KBr): 1630s, 1600m, 1590m, 1320w, 1290w, 1220w, 1180w, 1060w, 1020w, 970w, 940w, 850w, 800w, 750m, 720w, 530w, 460w cm^{-1}.

3.8. Preparation of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2)CH{=}NAl^iBu_2]_2$ (8)

Compound **8** was obtained from 2,6-dimethylbenzonitrile (2.0 g, 15.2 mmol) and DIBAL-H (15.2 ml, 15.2 mmol) in a manner analogous to the preparation of **1**. The solvent was removed under vacuum leaving an off-white solid. The solid residue was extracted with diethyl ether, filtered, concentrated, and cooled to −20°C to yield 3.0 g (73%) of white prisms. Mp: 140°C. Elemental analysis for $C_{17}H_{28}NAl$: Calcd; C, 74.7; H, 10.3; N, 5.1; Al, 9.9. Found; C, 75.2; H, 10.0; N, 4.6; Al, 8.6%. ^1H NMR (C_6D_6, 300 MHz): δ 8.94 (s, 1H, CH=N), 6.9 and 6.7 (m, 3H, C_6H_3), 2.17 (s, 6H, C_6CH_3), 1.87 (sept, 2H, CH), 1.05 (m, 12H, Al–C–C–CH_3), 0.19 (m, 4H, $AlCH_2$), ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 180.9 (C=N), 140.2, 134.2, 129.2 (C_6), 28.8 (Al–C–C–CH_3), 28.4 (Al–C–C–CH_3), 26.7 (Al–C–CH), 22.3 (Al–CH_2), 19.8, 19.7 ($C_6H_3CH_3$) ppm.

3.9. Crystallographic study

Colorless single crystals of $[(C_6H_3\text{-}2,6\text{-}(CH_3)_2){-}CH{=}NAl(i\text{-}C_4H_9)_2]_2$ were grown from diethyl ether at −20°C and were sealed in glass capillaries. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $13 < \theta < 18°$. Lorentz and polarization corrections were applied to the data. Empirical absorption [20] and secondary extinction corrections [21] were applied. The structure was solved using direct methods SHELX-86 [22]. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma_w(|F_o| - |F_c|)^2$ and the weight w is defined as per the Killean and Lawrence method with terms of 0.020 and 1.0 [23]. The final cycle of refinement gave unweighted and weighted agreement factors of $R(F_o) = \Sigma |F_o - F_c| / \Sigma F_o = 0.064$ and $R_w(F_o) = [\sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2} = 0.083$. The highest peak in the final difference Fourier had a height of 0.30 e/Å^3 with an estimated error based on δF of 0.05 [24]. All calculations were performed on a VAX computer using MOLEN [25].

4. Supplementary material available

A listing of the anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, complete listings of bond distances, bond angles, and torsion angles (7 pages), and listings of observed and calculated structure factors (6 pages) are available for complex **8** from the Cambridge Crystallographic Data Centre.

Acknowledgments

Acknowledgment is made to L.J. Hanna for technical assistance, to Dr. T.G. Neiss for help in recording the NMR spectra, and to Dr. P.E. Fanwick, Purdue University, for assistance with the X-ray structure determination.

References

1 (a) T. Mole and E.A. Jeffery, *Organoaluminium Compounds*, Elsevier, New York, 1972; (b) J.J. Eisch, *Aluminum*, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry, Vol. 1*, Chap. 6, Pergamon, Oxford, 1982, pp. 555–683; (c) M.J. Taylor, *Aluminum and Gallium*, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry, Vol. 3*, Chap. 25.1, Pergamon, Oxford, 1987, pp. 105–152.
2 (a) J.E. Lloyd and K. Wade, *J. Chem. Soc.*, (1965) 2662; (b) J.R. Jennings, J.E. Lloyd and K. Wade, *J. Chem. Soc.*, (1965) 5083.
3 L.I. Zakharkin and I.M. Khorlina, *Proc. Acad. Sci. USSR, 116* (1957) 879.
4 H.L. Goering and C.C. Tseng, *J. Org. Chem., 46* (1981) 5252.
5 L.I. Zakharkin and I.M. Khorlina, *Bull. Acad. Sci. USSR, Engl. Transl.*, (1959) 523.
6 P. Andreoli, L. Billi, G. Cainelli, M. Panunzio, G. Martelli and G. Spunta, *J. Org. Chem., 55* (1990) 4199.
7 B. Bogdanovic and S. Konstantinovic, *Liebigs Ann. Chem., 738* (1970) 202.
8 L.E. Overman and R.M. Burk, *Tetrahedron Lett., 25* (1984) 5737.
9 G. Cainelli, M. Panunzio, P. Andreoli, G. Martelli, G. Spunta, D. Giacomini and E. Bandini, *Pure Appl. Chem., 62* (1990) 605.
10 J.A. Jensen, *Mater. Res. Soc. Symp. Proc., 271* (1992) 845.
11 D.M. Choquette, M.J. Timm, J.L. Hobbs, M.M. Rahim, K.J. Ahmed and R.P. Planalp, *Organometallics, 11* (1992) 529.
12 W. Uhl, *Z. Naturforsch., 43B* (1988) 1113.
13 (a) G.M. McLaughlin, G.A. Sim and J.D. Smith, *J. Chem. Soc., Dalton Trans.*, (1972) 2197; (b) H. Hess, A. Hinderer and S. Steinhauser, *Z. Anorg. Allg. Chem., 377* (1970) 1.
14 K.M. Waggoner and P.P. Power, *J. Am. Chem. Soc., 113* (1991) 3385.
15 G.E. Coates and K. Wade, *Organometallic Compounds, Vol. I, The Main Group Elements*, Methuen, London, 1967, p. 311.
16 W.S. McDonald, *Acta Cryst., B25* (1969) 1385.
17 A.R. Baron, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1987) 837.
18 K.M. Waggoner, H. Hope and P.P. Power, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1699.
19 D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969.
20 N. Walker and D. Stuart, *Acta Cryst., A39* (1983) 158.
21 W.H. Zachariasen, *Acta Cryst., 16* (1963) 1139.
22 G.M. Sheldrick, Institut für Anorganische Chemie der Universität Göttingen, Germany, 1986.
23 R.C.G. Killean and J.L. Lawrence, *Acta Cryst., 25B* (1969) 1750.
24 D.W.J. Cruickshank, *Acta Cryst., 2* (1949) 154.
25 MOLEN, An Interactive Structure Solution Procedure, Enraf–Nonius, Delft, Netherlands (1990).