Synthesis, structure, and bridge-terminal alkyl exchange kinetics of pyrazolate-bridged dialuminum complexes containing bridging *n*-alkyl groups

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Abstract

Treatment of triethylaluminum with 3,5-diphenylpyrazole in a 2:1 stoichiometry afforded the ethyl-bridged complex $Et_2Al(\mu\text{-}Ph_2pz)$-$(\mu\text{-}Et)AlEt_2$ (79%) as a colorless crystalline solid. Treatment of tri-*n*-propylaluminum with 3,5-di-*tert*-butylpyrazole in a 2:1 stoichiometry afforded the *n*-propyl-bridged complex $(nPr)_2Al(\mu\text{-}tBu_2pz)(\mu\text{-}nPr)Al(nPr)_2$ (63%) and the dimeric complex $[(nPr)_2Al(\mu\text{-}tBu_2pz)]_2$ (3%), respectively, as colorless crystalline solids. Treatment of tri-*n*-propylaluminum (1 equiv.) or triisobutylaluminum (1 or 2 equiv.) with 3,5-di-*tert*-butylpyrazole afforded exclusively the dimeric complexes $[(nPr)_2Al(\mu\text{-}tBu_2pz)]_2$ (68%) or $[(iBu)_2Al(\mu\text{-}tBu_2pz)]_2$ (96%), respectively, as colorless crystalline solids. The solid state structures of $Et_2Al(\mu\text{-}Ph_2pz)(\mu\text{-}Et)AlEt_2$ and $(nPr)_2Al(\mu\text{-}tBu_2pz)$-$(\mu\text{-}nPr)Al(nPr)_2$ consist of 3,5-disubstituted pyrazolato ligands with a di-*n*-alkylalumino group bonded to each nitrogen atom. An ethyl or *n*-propyl group acts as a bridge between the two aluminum atoms. The kinetics of the bridge-terminal exchange was determined for the bridging *n*-alkyl complexes by ^{13}C NMR spectroscopy, and afforded $\Delta H^{\ddagger} = 1.5 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -46.8 \pm 39.0$ cal/K mol, and $\Delta G^{\ddagger}_{(298\ K)} = 15.4 \pm 11.7$ kcal/mol for $Et_2Al(\mu\text{-}Ph_2pz)(\mu\text{-}Et)AlEt_2$ and $\Delta H^{\ddagger} = 1.7 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -46.6 \pm 43.4$ cal/K mol, and $\Delta G^{\ddagger}_{(298\ K)} = 15.6 \pm 11.7$ kcal/molpz)$(\mu\text{-}nPr)Al(nPr)_2$. The negative values of $\Delta S^{\ddagger}$ imply ordered transition states relative to the ground states, and rotation along the $N\text{-}AlR_3$ vector without aluminum–nitrogen bond cleavage is proposed.
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Keywords: Aluminum; Trimethylaluminum; Triethylaluminum; Tri-*n*-propylaluminum

1. Introduction

It is broadly recognized that saturated hydrocarbon groups can bridge between two aluminum centers [1,2]. In spite of the fundamental importance of such interactions, structurally characterized complexes remain small in number and nearly all contain methyl bridges [2]. A few crystallographically characterized aluminum complexes have been reported that contain bridging ethyl [3] or cyclopropyl [4] ligands. Additionally, heterobimetallic compounds have been structurally characterized in which a methyl [5] or ethyl [6] group bridges between aluminum

and a transition metal, main group, or lanthanide ions. Recent advances in olefin polymerization catalysis have underscored the importance of bridging alkyl ligands in group 13 complexes. Methylalumoxane and aluminum alkyls are frequently employed as co-catalysts in alkene polymerization processes, but their exact roles are not well understood [7]. Cationic aluminum complexes are capable of polymerizing ethylene, epoxides, and lactide, and the highly electrophilic nature of the these species may promote the formation of alkyl-bridged complexes [3c,8]. Perfluoroaryl-substituted boranes and other boron-containing species act as methide/hydride abstracting agents and precatalyst activators in transition metal catalyzed single-site homogeneous olefin polymerization [9,10]. In the catalyst resting state, the boron center is often coordinated to the

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metal-bound methyl group, resulting in a bridging methyl ligand. Several groups have reported the use of boron compounds containing two Lewis acidic diarylboryl groups as effective activators for single-site olefin polymerization catalysis [11].

More recent research has shown that Lewis acids comprised of two closely-linked boron centers might be superior polymerization precatalyst activators [11a,12], since bidentate coordination of the abstracted alkyl group should afford a more weakly coordinating anion and higher polymerization activity. Finally, dinuclear complexes have been of considerable recent interest as Lewis acid catalysts [13]. Closely spaced metal centers may cooperatively bind Lewis bases, which could lead to new types of substrate activation compared to traditional mononuclear metal-based Lewis acids.

While the solution and solid state structures of trimethylaluminum have been intensively studied [2a,2b,2c,2e, 2j,14], less is known about the related structures of higher *n*-alkyl derivatives of aluminum. NMR studies have demonstrated that tri-*n*-alkylaluminum complexes exist predominantly as dimers in nonpolar organic solvents and possess structures that are similar to dimeric trimethylaluminum [15]. Solution molecular weight measurements have suggested that trialkylaluminum complexes with alkyl substitution on the α- or β-carbon atoms of the alkyl ligands are monomeric in solution [15f,16]. There have been no reports of X-ray crystal structures of dimeric tri-*n*-alkylaluminum complexes.

We have previously reported the synthesis, structure, molecular orbital calculations, and bridge-terminal methyl exchange kinetics of dialuminum pyrazolato complexes containing bridging methyl groups [2j]. In particular, molecular orbital calculations suggested that the bridging methyl group was stabilized by 6–7 kcal/mol, relative to dimeric trimethylaluminum, by extended orbital interactions involving the bridging methyl group and pyrazolato ligand-based orbitals. Such stabilization suggested that dialuminum pyrazolato complexes might stabilize other bridging alkyl ligands. Herein, we report the synthesis, structure, and bridge-terminal alkyl group exchange kinetics of dialuminum pyrazolato complexes that contain bridging ethyl or *n*-propyl groups. The strong aluminum–nitrogen bonds in these complexes stabilize them toward loss of triethylaluminum or tri-*n*-propylaluminum. We also report the synthesis and structural characterization of several dimeric dialkylaluminum complexes that contain bridging pyrazolato ligands. A portion of this work was communicated [3a].
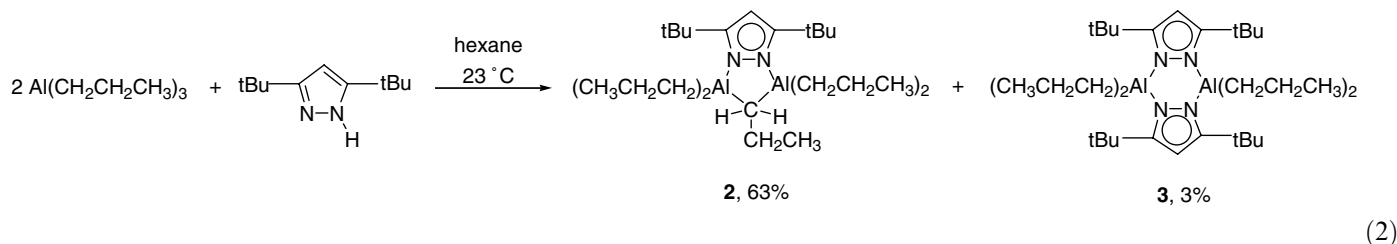
2. Results and discussion

Treatment of 3,5-diphenylpyrazole with triethylaluminum (2 equiv.) in hexane at ambient temperature led to slow ethane evolution over 18 h and afforded μ-diphenylpyrazolato-μ-ethyl-tetraethyldialuminum (**1**, 79%) as a colorless crystalline solid (Eq. (1)). The formulation of
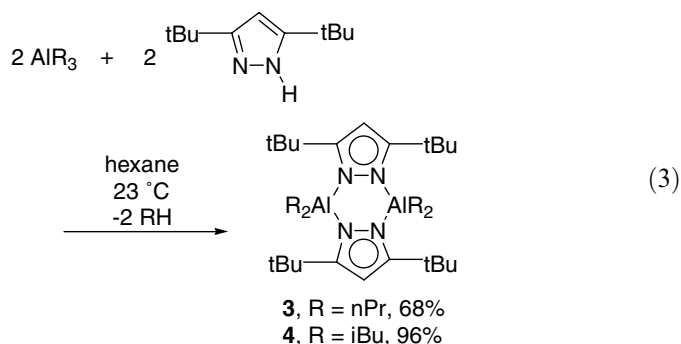
1 as the ethyl-bridged structure was based upon spectral and analytical data, and by X-ray crystallography. At $-40\,°C$ in toluene-d_8, resonances due to terminal ethyl groups were observed in the ^1H NMR spectrum at δ 1.27 (t) and -0.30 (q) while another set of ethyl resonances appeared at δ 1.00 (t) and 0.93 (q). The ratio of these two sets of peaks (δ 1.27, -0.30 and 1.00, 0.93) was 4:1, suggesting the presence of a bridging ethyl ligand. In the $^{13}C\{^1H\}$ NMR spectrum at $-40\,°C$, the terminal ethyl carbons resonated at 9.79 and 1.79 ppm while sharp bridging ethyl ligand resonances were observed at δ 7.35 and 4.08 ppm. Upon warming from -40 to $20\,°C$ in toluene-d_8, the methyl and methylene resonances of the bridging ethyl resonance gradually broadened and shifted downfield slightly. Above $20\,°C$, only one type of ethyl group was observed, suggesting rapid exchange of terminal and bridging ethyl sites.

(1)

1, 79%
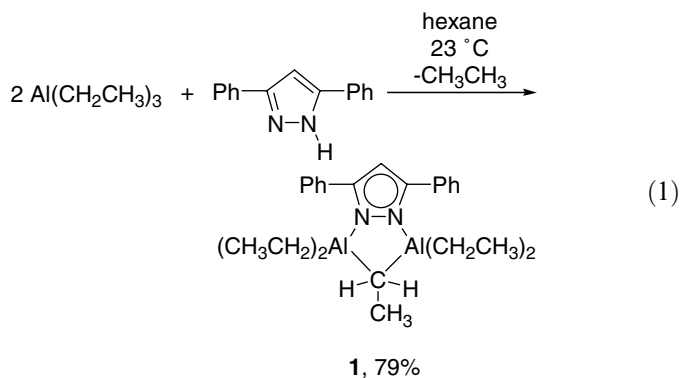
Treatment of 3,5-di-*tert*-butylpyrazole with tri-*n*-propylaluminum (2 equiv.) in hexane at ambient temperature afforded μ-3,5-di-*tert*-butylpyrazolato-μ-*n*-propyl-tetra-*n*-propyldialuminum (**2**, 63%) and bis(μ-3,5-di-*tert*-butylpyrazolato)tetra-*n*-propyldialuminum (**3**, 3%) as colorless crystalline solids (Eq. (2)). The formulations of **2** and **3** were assigned based upon their spectral and analytical data and by X-ray crystallography, as described below. The formulation of **2** as the *n*-propyl-bridged structure was suggested initially by the ^1H and $^{13}C\{^1H\}$ NMR spectra. At $23\,°C$ in toluene-d_8, resonances due to terminal *n*-propyl groups were observed in the ^1H NMR spectrum at δ 1.50 (m), 1.15 (t) and 0.40 (t) while another set of *n*-propyl group resonances appeared at δ 1.77 (m), 1.17 (t), 1.05 (br s). The ratio of these two sets of resonances (δ 1.50, 1.15, 0.40 and δ 1.77, 1.17, 1.05) was 4:1, suggesting the presence of a bridging *n*-propyl ligand. In the $^{13}C\{^1H\}$ NMR spectrum of **2** at $-70\,°C$ in toluene-d_8, the methylene resonances (Al–CH_2) of the terminal *n*-propyl group resonated at 16.56 ppm while the methylene resonance (Al–CH_2) of the bridging *n*-propyl group was observed at 16.73 ppm. Upon warming from -70 to $20\,°C$ in toluene-d_8, the methylene resonance (Al–CH_2) of the bridging *n*-propyl resonance gradually broadened and shifted downfield slightly. Above $20\,°C$, only one type of methylene resonance was observed, suggesting rapid exchange of terminal and bridging *n*-propyl sites.

$$2\,Al(CH_2CH_2CH_3)_3 \; + \; tBu\!-\!\!\diagup\!\!\diagdown\!\!-\!tBu \xrightarrow[\text{23 °C}]{\text{hexane}} (CH_3CH_2CH_2)_2Al \diagup\!\!\diagdown Al(CH_2CH_2CH_3)_2 \; + \; (CH_3CH_2CH_2)_2Al \diagup\!\!\diagdown Al(CH_2CH_2CH_3)_2$$

2, 63%   **3**, 3%

(2)

Treatment of 3,5-di-*tert*-butylpyrazole with tri-*n*-propylaluminum (1 equiv.) or triisobutylaluminum (1 or 2 equiv.) in hexane at ambient temperature afforded bis(μ-3,5-di-*tert*-butylpyrazolato)tetra-*n*-propyldialuminum (**3**, 68%), and bis(μ-3,5-di-*tert*-butylpyrazolato)tetra-isobutyldialuminum (**4**, 96%), respectively, as colorless crystalline solids (Eq. (3)). The formulations of **3** and **4** were assigned based upon their spectral and analytical data, as well as by X-ray crystallography. There was no evidence for a complex with a structure similar to **1** or **2** in the NMR spectra of crude **4**.

$$2\,AlR_3 \; + \; 2 \; tBu\!-\!\!\diagup\!\!\diagdown\!\!-\!tBu \xrightarrow[\substack{\text{23 °C} \\ -2\,RH}]{\text{hexane}} tBu\!-\!\!\diagup\!\!\diagdown\!\!-\!tBu$$

3, R = nPr, 68%
4, R = iBu, 96%

(3)

The X-ray crystal structures of **2**–**4** were determined to establish the solid state geometries. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2–4, and perspective views are presented in Figs. 1–3. We reported the X-ray crystal structure of **1** in a preliminary communication [3a].

The molecular structure of **2** is shown in Fig. 1. Consistent with the NMR analysis, the molecule consists of a 3,5-di-*tert*-butylpyrazolato ligand with a di-*n*-propylalumino group bonded to each nitrogen atom. An *n*-propyl group acts as a bridge between the two aluminum atoms. The two nitrogen atoms and two aluminum atoms occupy an approximate plane, but the methylene carbon atom of the bridging *n*-propyl group is situated 0.873(3) Å above this plane. The geometry about the aluminum centers is distorted tetrahedral. The aluminum–nitrogen bond lengths are 1.951(3) and 1.957(2) Å. The aluminum–carbon bond lengths range between 1.968(3) and 1.988(3) Å for the terminal *n*-propyl groups and are 2.156(4) and 2.166(4) Å for the bridging *n*-propyl group. These aluminum–carbon bond lengths are very similar to the related values in structurally characterized aluminum complexes with bridging methyl and ethyl groups [2,3]. In **1** [3a], the aluminum–nitrogen bond lengths are 1.928(2) and 1.936(2) Å, the

Table 1
Crystal data and data collection parameters for **2**–**4**

	2	**3**	**4**
Empirical formula	$C_{26}H_{54}Al_2N_2$	$C_{34}H_{66}Al_2N_4$	$C_{38}H_{74}Al_2N_4$
Formula weight	448.67	584.87	640.97
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	10.430(8)	10.004(2)	11.7375(17)
b (Å)	11.486(8)	12.474(3)	18.843(3)
c (Å)	14.164(11)	15.942(3)	19.910(3)
α (°)	82.151(17)	93.353(5)	
β (°)	70.402(14)	99.666(6)	105.376(3)
γ (°)	77.561(19)	102.722(6)	
V (Å³)	1557(2)	1903.5(7)	4245.9(11)
Z	2	2	4
T (K)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073
D_{calc} (g cm⁻³)	0.957	1.020	1.003
μ (mm⁻¹)	0.107	0.102	0.096
No. data used in refinement[a]	6983	8733	10009
$R(F)$[b] (%)	5.25	9.13	5.62
$Rw(F)$[c] (%)	12.15	26.94	11.92

[a] 2θ cutoff angle = 56°. All unique reflections, including the weak ones, were used in the refinements.
[b] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[c] $Rw(F)^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

terminal aluminum–carbon bond lengths range from 1.942(4) to 1.967(3) Å, and the bridging aluminum–carbon bond lengths are 2.144(4) and 2.150(4) Å. The methylene carbon atom of the bridging ethyl ligand in **1** lies 0.95 Å above the Al_2N_2 plane. These values in **1** are slightly shorter than the corresponding values in **2**, although the differences are probably within experimental uncertainty. It is possible that the increased steric crowding in **2** leads to slightly longer bond lengths compared to **1**.

The molecular structures of **3** and **4** are very similar and consist of dimers with central six-membered Al_2N_4 rings and four terminal *n*-alkyl groups per dimeric unit (Figs. 2, 3). A small family of dimeric aluminum pyrazolato complexes with core structures similar to **3** and **4** has been reported [17]. Two 3,5-di-*tert*-butylpyrazolato ligands serve as bridges between the two aluminum atoms, and the six-membered Al_2N_4 rings contain four nitrogen atoms from two 3,5-di-*tert*-butylpyrazolato ligands. The geometry about the aluminum centers is distorted tetrahedral. The angle between the pyrazolato C_3N_2 cores (**3**, 89.6(1)°; **4**, 86.87(12)°) are comparable to that observed in [Me₂Al-

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Al(1)–N(1)	1.957(2)
Al(2)–N(2)	1.951(3)
Al(1)–C(12)	1.968(3)
Al(1)–C(15)	1.988(3)
Al(1)–C(24)	2.166(4)
Al(2)–C(18)	1.986(3)
Al(2)–C(21)	1.975(3)
Al(2)–C(24)	2.166(4)
N(1)–Al(1)–C(12)	109.63(11)
N(1)–Al(1)–C(15)	114.52(11)
N(1)–Al(1)–C(24)	103.92(13)
Al(1)–C(24)–C(25)	114.3(2)
C(12)–Al(1)–C(15)	116.48(13)
C(12)–Al(1)–C(24)	109.05(12)
C(15)–Al(1)–C(24)	102.07(13)
N(2)–Al(2)–C(18)	114.61(12)
N(2)–Al(2)–C(21)	109.48(12)
N(2)–Al(2)–C(24)	103.49(11)
Al(2)–C(24)–C(25)	114.8(2)
C(18)–Al(2)–C(21)	117.04(14)
C(18)–Al(2)–C(24)	101.43(14)
C(21)–Al(2)–C(24)	109.50(15)
Al(1)–N(1)–N(2)	114.39(16)
Al(2)–N(2)–N(1)	115.04(15)
Al(1)–C(24)–Al(2)	89.43(12)

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Al(1)–N(1)	1.970(3)
Al(1)–N(3)	1.974(3)
Al(1)–C(23)	1.941(5)
Al(1)–C(26)	1.939(6)
Al(2)–N(2)	1.965(3)
Al(2)–N(4)	1.953(3)
Al(2)–C(29)	2.092(13)
Al(2)–C(32)	1.951(8)
N(1)–Al(1)–N(3)	99.40(13)
N(1)–Al(1)–C(23)	107.24(19)
N(1)–Al(1)–C(26)	118.2(2)
N(3)–Al(1)–C(23)	117.4(2)
N(3)–Al(1)–C(26)	106.05(18)
C(23)–Al(1)–C(26)	108.8(3)
N(2)–Al(2)–N(4)	100.73(14)
N(2)–Al(2)–C(29)	120.9(3)
N(2)–Al(2)–C(32)	107.5(2)
N(4)–Al(2)-C(29)	109.5(3)
N(4)–Al(2)–C(32)	118.0(3)
C(29)–Al(2)–C(32)	101.3(4)
Al(1)–N(1)–N(2)	107.27(19)
Al(1)–N(3)–N(4)	107.60(19)
Al(2)–N(2)–N(1)	107.5(2)
Al(2)–N(4)–N(3)	105.8(2)

Table 4
Selected bond lengths (Å) and angles (°) for **4**

Al(1)–N(1)	1.964(3)
Al(1)–N(3)	1.985(3)
Al(1)–C(23)	1.973(4)
Al(1)–C(27)	1.970(4)
Al(2)–N(2)	1.974(3)
Al(2)–N(4)	1.965(3)
Al(2)–C(31)	1.981(4)
Al(2)–C(35)	1.967(4)
N(1)–Al(1)–N(3)	101.38(14)
N(1)–Al(1)–C(23)	105.56(16)
N(1)–Al(1)–C(27)	112.80(16)
N(3)–Al(1)–C(23)	116.61(16)
N(3)–Al(1)–C(27)	98.60(15)
C(23)–Al(1)–C(27)	120.48(19)
N(2)–Al(2)–N(4)	101.12(14)
N(2)–Al(2)–C(31)	98.78(15)
N(2)–Al(2)–C(35)	114.04(16)
N(4)–Al(2)–C(31)	112.14(15)
N(4)–Al(2)–C(35)	107.67(16)
C(31)–Al(2)–C(35)	121.19(18)
Al(1)–N(1)–N(2)	111.1(2)
Al(1)–N(3)–N(4)	104.9(2)
Al(2)–N(2)–N(1)	106.3(2)
Al(2)–N(4)–N(3)	110.7(2)
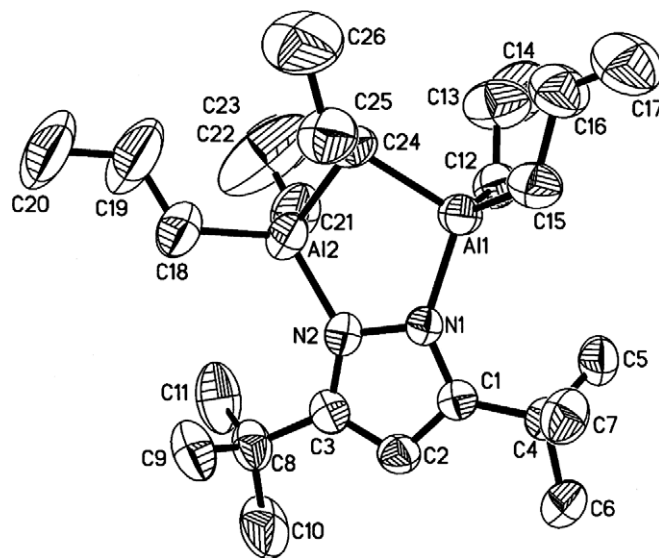
Fig. 1. Perspective view of nPr$_2$Al(μ-tBu$_2$pz)(μ-nPr)AlnPr$_2$ (**2**) with thermal ellipsoids at the 50% probability level.

(μ-η^1:η^1-3,5-tBu$_2$pz)]$_2$ (87.84°) [17g]. Most of the other reported dimeric aluminum pyrazolato complexes contain planar Al$_2$N$_4$ rings [17]. The twisted Al$_2$N$_4$ rings in **3** and **4** likely arise from accommodation of the bulky *tert*-butyl groups. The aluminum–nitrogen bond lengths (**3**, 1.953(3)–1.974(3) Å; **4**, 1.964(3)–1.985(3) Å) are similar to those observed in **1** [3a] and **2**. The aluminum–carbon bond lengths (**3**, 1.939(6)–1.952(8) Å; **4**, 1.967(4)–1.981(4) Å) are slightly shorter in **3** than in **4**, perhaps reflecting the increased steric congestion about the aluminum ions in **4**. One of the aluminum–carbon distances in **3** (Al(2)–C(29)) was found to be 2.092(13) Å. This value is much larger the other aluminum–carbon bond lengths. The long Al(2)–C(29) bond length in **3** is unreliable due to the very large thermal parameters associated with C(29), especially along the bond axis. This lack of reliability in the bond length reflects our inability to place atomic nuclei precisely in regions of extensive disorder. The nitrogen–aluminum–
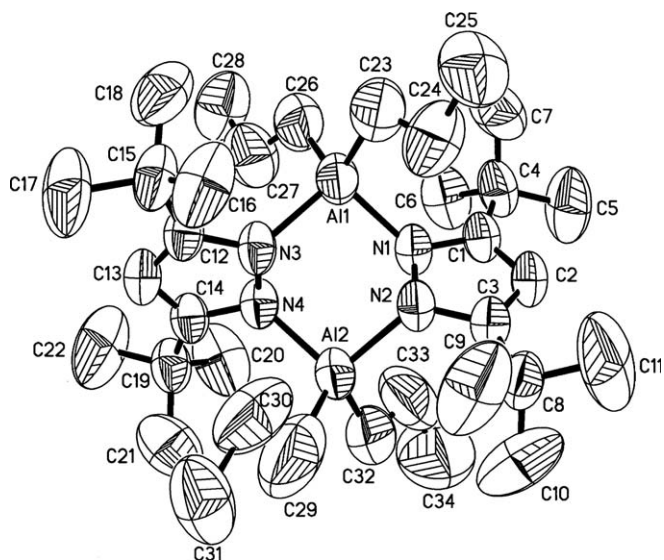
Fig. 2. Perspective view of nPr$_2$Al(μ-tBu$_2$pz)$_2$AlnPr$_2$ (**3**) with thermal ellipsoids at the 50% probability level.

nitrogen angles are 99.39(13)° and 100.74(14)° in **3** and are 101.12(14)° and 101.38(14)° in **4**. These bond lengths and angles for **3** and **4** are similar to the values observed in the related dimeric complexes [Me$_2$Al(μ-η^1:η^1-pz)]$_2$ [17e], [tBu$_2$Al(μ-η^1:η^1-pz)]$_2$ [17f], [Me$_2$Al(μ-η^1:η^1-Me$_2$pz)]$_2$ [17f], and [Me$_2$Al(μ-η^1:η^1-3,5-tBu$_2$pz)]$_2$ [17g].

The kinetics of the bridge-terminal ethyl and n-propyl site exchange processes in **1** and **2** was studied. Due to the complexity of the n-alkyl ligand resonances, it was not convenient to employ variable temperature ^{1}H NMR spectroscopy to measure the kinetics data. However, the ^{13}C{^{1}H} NMR spectra afforded singlets for each type of n-alkyl ligand in **1** and **2**. Thus, the kinetics data were obtained by ^{13}C{^{1}H} NMR spectroscopy in toluene-d_8. In **1**, variable temperature ^{13}C{^{1}H} NMR spectra indicated

that the terminal and bridging ethyl groups in **1** undergo site exchange between −70 and 20 °C. To gain further insight into the dynamic processes, the line-broadening kinetics was modeled as an AB$_4$ exchange. Rate constants were determined by simulating the ^{13}C{^{1}H} spectra of the ethyl group methylene resonances at various temperatures using the program gNMR [18]. Details of the analyses are presented in Section 3. Fig. 4 shows the ^{13}C{^{1}H} NMR spectra for **1** taken at various temperatures, while rate constants are presented in Table 5. Eyring analysis of the rate data for **1** afforded the activation parameters $\Delta H^{\ddagger} = 1.5 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -46.8 \pm 39.0$ cal/K mol, and $\Delta G^{\ddagger}_{(298\ \mathrm{K})} = 15.4 \pm 11.7$ kcal/mol. The kinetics of

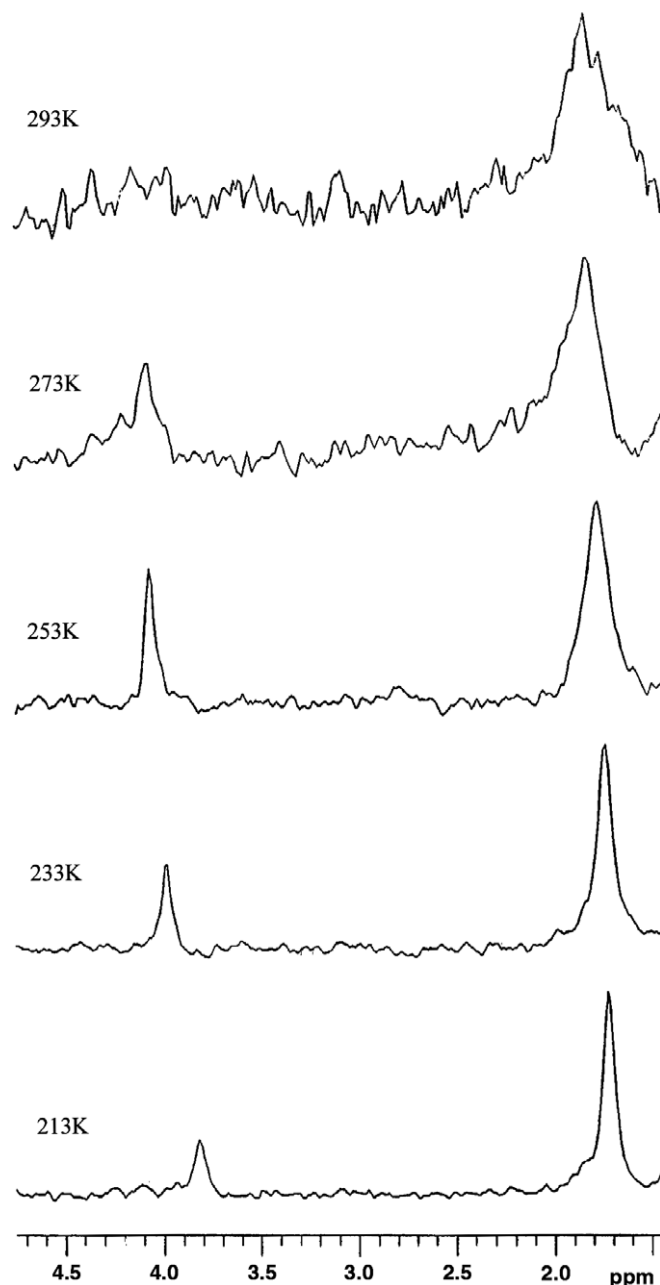Fig. 3. Perspective view of iBu$_2$Al(μ-tBu$_2$pz)$_2$AliBu$_2$ (**4**) with thermal ellipsoids at the 50% probability level.

Fig. 4. Variable temperature ^{13}C{^{1}H} NMR spectra for **1**.

Table 5
Rate constants for bridge-terminal ethyl group site exchange in **1**

Temperature (K)	Rate constant (s^{-1})
213.8	7.68
224.0	9.04
234.2	9.46
239.3	10.7
244.4	12.3
249.5	14.1
254.6	14.6
259.7	16.5
264.9	18.1
270.0	19.9
275.1	20.1
280.2	21.4
285.3	23.4
290.9	25.5
295.5	26.1

Fig. 5. Variable temperature $^{13}C\{^1H\}$ NMR spectra for **2**.

exchange between the terminal and bridging *n*-propyl groups of **2** was determined by analysis of the aluminum-bound methylene resonances in the variable temperature $^{13}C\{^1H\}$ NMR spectra in toluene-d_8. The terminal and bridging *n*-propyl groups in **2** undergo site exchange between −70 and 20 °C. Fig. 5 shows the $^{13}C\{^1H\}$ NMR spectra for **2** taken at various temperatures, while rate constants are presented in Table 6. Eyring analysis of the exchange process for **2** afforded the activation parameters $\Delta H^{\ddagger} = 1.7 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -46.6 \pm 43.4$ cal/K mol, and $\Delta G^{\ddagger}_{(298\ K)} = 15.6 \pm 11.7$ kcal/mol. The calculated exchange rates at 298 K are 27.3 s^{-1} for **1** and 21.5 s^{-1} for **2**. We have previously reported the kinetics of bridge-terminal methyl exchange in μ-diphenylpyrazolato-μ-methyl-tetramethyldialuminum [2j]. The activation parameters were $\Delta H^{\ddagger} = 15.4 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -3.2 \pm 0.1$ cal/K mol, and $\Delta G^{\ddagger}_{(298\ K)} = 16.4 \pm 0.4$ kcal/mol, and the calculated exchange rate at 298 K was 6.8 s^{-1}. The negative entropy of activation values in **1**, **2**, and μ-diphenylpyrazolato-μ-methyl-tetramethyldialuminum are consistent with ordered transition states, relative to the ground state, although the high uncertainties associated with the entropy of activation values in **1** and **2** limit a more definitive statement. Such transition states likely correspond to rotation of a trialkylalumino group along the aluminum–nitrogen bond. The aluminum–nitrogen bond energies should be much stronger than the bridging aluminum–carbon bond energies, and thus aluminum–nitrogen bond breaking does not occur in the transition state. The enthalpies of activation for the exchange processes in **1** and **2** represent the upper limit for the energy difference between the ground state and the transition state. The small enthalpy of activation values for **1** and **2**, compared to μ-diphenylpyrazolato-μ-methyl-tetramethyldialuminum, could be due to the increased steric crowding which would increase the energies of the ground states. The higher calculated exchange rates at 25 °C for **1** and **2**, compared to μ-diphenylpyrazolato-μ-methyl-tetramethyldialuminum [2j], are consistent with previous reports that dimeric trieth-
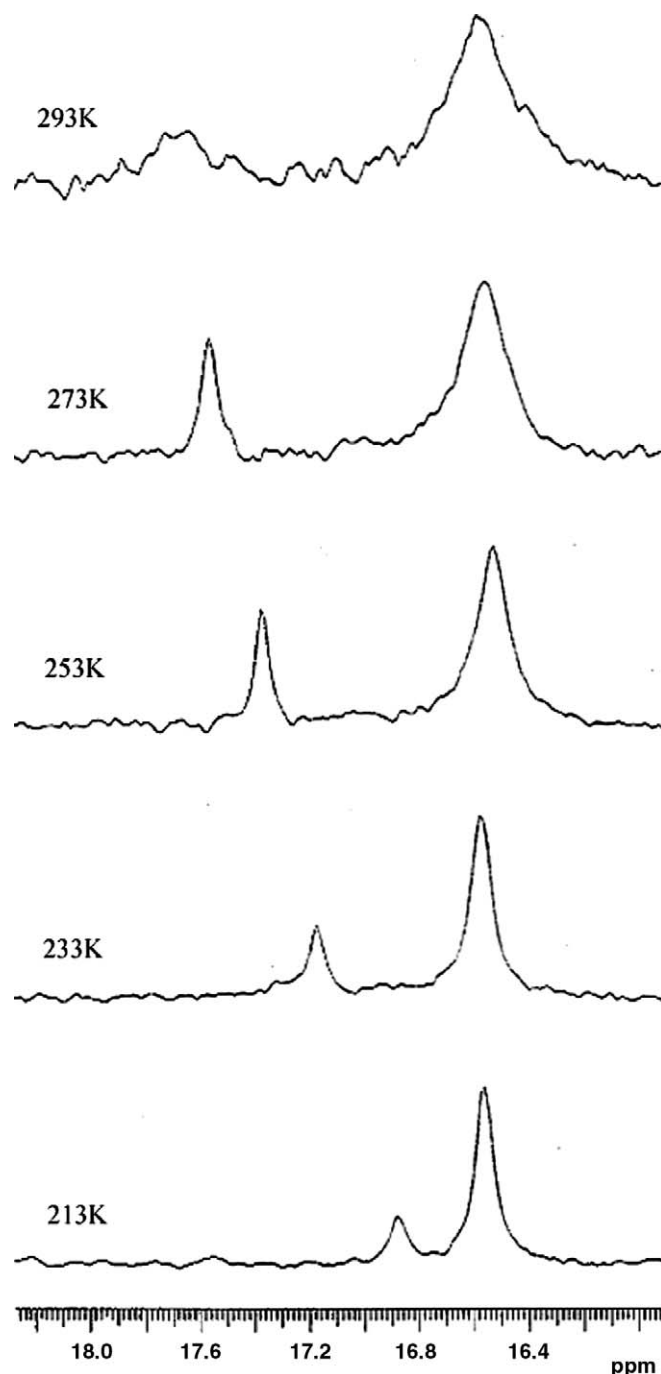
Table 6
Rate constants for bridge-terminal *n*-propyl group site exchange in **2**

Temperature (K)	Rate constant (s^{-1})
214.7	5.52
225.1	6.24
235.4	8.39
245.7	8.78
256.1	10.1
287.0	19.9
291.6	20.9
297.4	22.2

ylaluminum and tri-*n*-propylaluminum have higher bridge-terminal alkyl group exchange rates than dimeric trimethylaluminum [15f].

As noted in Section 1, there have been very few crystallographically characterized aluminum complexes containing bridging *n*-alkyl groups other than methyl. The first example of a crystallographically characterized complex containing a bridging ethyl ligand was our preliminary account describing **1** [3a]. This work was followed by reports describing [Al(Si(Si(CH$_3$)$_3$)$_2$)Et(μ-Et)]$_2$ [3b] and [AlEt(μ-*i*Pr$_2$-ATI)(μ-Et)AlEt$_2$]B(C$_6$F$_5$)$_4$ (ATI = aminotroponiminate) [3c]. To date, there have been no reports of crystallographically characterized aluminum complexes containing bridging higher *n*-alkyl ligands. Thus, **2** represents the first structurally characterized aluminum complex containing a bridging *n*-propyl ligand. Attempts to prepare the analog of **2** containing a bridging isobutyl ligand were unsuccessful, and instead led to the dimeric complex **4**. It is very likely that the bridging *n*-alkyl ligand in structures such as **1** and **2** resides in a sterically congested pocket. Increased steric interactions associated with a bridging isobutyl ligand probably destabilize such a complex to the point where only **4** is produced.

A kinetics study of bridge-terminal ethyl exchange in triethylaluminum in toluene afforded $\Delta H^{\ddagger} = 15.0 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 16.1 \pm 3.7$ cal/K mol, and $\Delta G^{\ddagger}_{(298 \text{ K})} = 10.2 \pm 0.3$ kcal/mol [17f]. The large positive entropy of activation was interpreted in terms of a transition state that was less ordered than the ground state, i.e. some type of dissociative exchange mechanism. A similar dissociative mechanism is well established for bridge-terminal methyl group exchange in dimeric trimethylaluminum [2j,14]. As noted above, the large, negative entropies of activation for **1** and **2** are consistent with no breaking of the aluminum–nitrogen bonds in the transition states, and instead triethylalumino group rotation along the aluminum–nitrogen bond vector is proposed. The strong aluminum–nitrogen bonds also lead to much slower bridge-terminal exchange rates in **1** and **2**, compared to triethylaluminum and tri-*n*-propylaluminum. For example, separate resonances for the bridging and terminal ethyl groups in triethylaluminum are only observed below −50 °C in the ^{1}H NMR spectrum in cyclopentane [17f]. By contrast, separate resonances for the bridging and terminal ethyl groups in **1** are observed up to 15 °C.

A final comment relates to the structures of *n*-alkyl complexes of aluminum, such as triethylaluminum, tri-*n*-propylaluminum, and triisobutylaluminum. The crystallographic results with **2**–**4** suggest that aluminum complexes containing many higher *n*-alkyl ligands do not crystallize well, and those that do crystallize may lack a high degree of crystalline registry due to the many alkyl group interactions in the solid state. During this investigation, attempts were made to synthesize analogs of **1** and **2** containing a range of substituted pyrazolato ligands and different tri-*n*-alkylaluminum compounds. Of these many potential complexes, only **1**–**4** could be crystallized as pure complexes. The remainder afforded either inseparable mixtures of complexes or complexes that were liquids or greasy crystals. Such complexes were very difficult to handle. Accordingly, it is not surprising that triethylaluminum, tri-*n*-propylaluminum, and other tri-*n*-alkylaluminum derivatives have not been crystallized and structurally characterized to date.

3. Experimental

3.1. General considerations

All manipulations were carried out under argon using Schlenk line or glove box techniques. Hexane and toluene were distilled from sodium immediately prior to use. Triethylaluminum, tri-*n*-propylaluminum, triisobutylaluminum, and anhydrous benzene were purchased from Aldrich Chemical Company and were used as received. 3,5-Di-*tert*-butylpyrazole was prepared according to a published procedure [19]. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75 MHz, respectively, in benzene-d_6 or toluene-d_8, as indicated. Chemical shifts (δ, ppm) are given relative to residual protons or the carbon atoms of the solvent. Infrared spectra were obtained using Nujol as the medium. Microanalyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were determined in sealed capillary tubes under argon on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

3.2. Synthesis of Et$_2$Al(μ-3,5-Ph$_2$pz)(μ-Et)AlEt$_2$ (**1**)

To a stirred solution of triethylaluminum (0.737 g, 6.0 mmol) in hexane (40 mL) was added 3,5-diphenylpyrazole (0.661 g, 3.0 mmol) in small portions over a period of 0.25 h. The mixture was stirred at room temperature overnight. Then the volatile components were removed under reduced pressure. The white residue was dissolved in hexane (30 mL) and the resultant solution was filtered through a 2 cm pad of Celite on a coarse glass frit. The resultant filtrate was placed in a −20 °C freezer for 24 h, during which time crystallization occurred. The supernatant solution was removed with a cannula and the crystals were vacuum dried to afford **1** as colorless crystals (0.990 g, 79%): mp 66–67 °C; IR (Nujol, cm^{-1}) 3119 (w), 1541 (m), 1471 (s), 1418 (m), 1321 (w), 1298 (w), 1276 (w), 1194 (w), 1071 (s), 981 (s), 914 (m), 817 (m), 761 (s), 698 (s), 646 (s), 526 (m), 474 (s); ^{1}H NMR (C$_6$D$_6$, 23 °C, δ) 7.42 (m, 4H, *ortho*-C*H* of phenyl rings), 7.09 (m, 6H, *meta*- and *para*-C*H* of phenyl rings), 6.24 (s, 1H, Ph$_2$pz ring C*H*), 1.13 (t, $J = 7.8$ Hz, 15H, CH$_2$C*H*$_3$), 0.22 (q, $J = 7.8$ Hz, 10H, C*H*$_2$CH$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, −40 °C, ppm) 155.25 (s, pz ring *C*-Ph), 131.29 (s, *ipso*-*C* of phenyl rings), 129.54 (s, para-*C*H of phenyl rings), 128.82 (s, ipso-*C*H of phenyl rings), 128.50 (s, meta-*C*H of phenyl rings), 106.89 (s, Ph$_2$pz ring *C*H), 9.78 (s, terminal *C*H$_2$CH$_3$), 7.34 (s, bridging CH$_2$*C*H$_3$), 4.07 (s, bridging *C*H$_2$CH$_3$), 1.79

(s, terminal CH_2CH_3); MS (EI, 70 ev) m/z 304 ([M–AlEt$_3$]$^+$, 16%), 220 ([Ph$_2$pz]$^+$, 100%).

Anal. Calcd for C$_{25}$H$_{36}$Al$_2$N$_2$: C, 71.74; H, 8.67; N, 6.69. Found: C, 71.48; H, 8.60; N, 6.52%.

3.3. Synthesis of nPr$_2$Al(μ-tBu$_2$pz)(μ-nPr)AlnPr$_2$ (2) and nPr$_2$Al(μ-tBu$_2$pz)$_2$AlnPr$_2$ (3)

A 100-mL Schlenk flask was charged with tri-*n*-propylaluminum (1.25 g, 8.00 mmol) and hexane (50 mL). To this stirred solution at ambient temperature was added a solution of 3,5-di-*tert*-butylpyrazole (0.721 g, 4.00 mmol) in hexane (50 mL) dropwise with a cannula. The reaction mixture was stirred at ambient temperature for 18 h and then the volatile components were removed under reduced pressure to afford a viscous colorless liquid with solid particles. This oil was extracted with hexane (70 mL) and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The clear, colorless filtrate was concentrated to a volume of about 20 mL and was placed in a −20 °C freezer for 24 h to allow crystallization. The supernatant solution was removed with a cannula and the crystals were vacuum dried to afford **2** as colorless crystals (1.13 g, 63%): mp 53–54 °C; IR (Nujol, cm^{-1}) 3195 (w), 1727 (m), 1517 (s), 1410 (w), 1311 (m), 1253 (m), 1215 (w), 1163 (w), 1046 (s), 975 (w), 883 (w), 671 (s), 643 (s), 540 (w), 485 (w); ^{1}H NMR (C$_6$D$_6$, 23 °C, δ) 6.00 (s, 1H, *t*Bu$_2$pz ring-CH), 1.78 (m, 2H, bridging CH$_2$CH_2CH$_3$), 1.53 (m, 8H, terminal CH$_2$CH_2CH$_3$), 1.26 (s, 18H, C(CH$_3$)$_3$), 1.20 (t, J = 6.6 Hz, 3H, bridging CH$_2$CH$_2$CH_3), 1.17 (t, J = 6.6 Hz, 12H, terminal CH$_2$CH$_2$CH_3), 1.04 (broad s, 2H, bridging CH_2CH$_2$CH$_3$), 0.40 (t, 8H, terminal CH_2CH$_2$CH$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, −70 °C, ppm) 164.54 (s, CC(CH$_3$)$_3$), 103.95 (s, *t*Bu$_2$pz ring-CH), 32.10 (s, CC(CH$_3$)$_3$), 30.81 (s, CC(CH$_3$)$_3$), 21.87 (s, terminal CH$_2$$CH_2CH_3$), 21.10 (s, bridging CH$_2$$CH_2CH_3$), 20.84 (s, bridging CH$_2$$CH_2CH_3$), 20.45 (s, terminal CH$_2$$CH_2CH_3$), 16.70 (s, bridging CH$_2CH_2CH_3$), 16.34 (s, terminal CH$_2CH_2CH_3$).

Anal. Calcd for C$_{26}$H$_{54}$Al$_2$N$_2$: C, 69.60; H, 12.13; N, 6.24. Found: C, 69.80; H, 12.23; N, 6.43%.

The crude product was extracted with benzene (70 mL) and filtered through a 2-cm pad of Celite. The clear, colorless filtrate was concentrated and left at 23 °C to afford **3** as colorless crystals (0.071 g, 3%). See below for spectroscopic and analytical data.

3.4. Synthesis of nPr$_2$Al(μ-tBu$_2$pz)$_2$AlnPr$_2$ (3)

A 100-mL Schlenk flask was charged with tri-*n*-propylaluminum (0.625 g, 4.00 mmol) and hexane (50 mL). To this stirred solution was added a solution of 3,5-di-*tert*-butylpyrazole (0.721 g, 4.00 mmol) in hexane (50 mL). The resultant colorless solution was stirred for 18 h at ambient temperature. The volatile components were then removed under reduced pressure and the resultant white solid was extracted with hexane (70 mL). The hexane

extract was filtered through a 2-cm pad of Celite on a coarse glass frit to afford a colorless solution. The filtrate was concentrated to about 20 mL and was placed in a −20 °C freezer for 24 h. The supernatant solution was removed with a cannula and the crystals were vacuum dried to afford **3** as colorless crystals (0.799 g, 68%): mp 184–186 °C; IR (Nujol, cm^{-1}) 1513 (s), 1404 (m), 1365 (s), 1323 (m), 1290 (m), 1247 (m), 1212 (m), 1169 (w), 1047 (s), 1016 (m), 976 (m), 930 (w), 887 (w), 811 (m), 776 (w), 732 (w), 637 (s); ^{1}H NMR (C$_6$D$_6$, 23 °C, δ) 6.28 (s, 2H, *t*Bu$_2$pz ring-CH), 1.39 (s, 36H, C(CH_3)$_3$), 1.17 (m, 8H, CH$_2$CH_2CH$_3$), 1.07 (t, J = 6.0 Hz, 12H, CH$_2$CH$_2$-CH_3), 0.14 (broad m, 8H, CH_2CH$_2$CH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 23 °C, ppm) 171.90 (s, CC(CH$_3$)$_3$), 107.97 (s, *t*Bu$_2$pz ring-CH), 32.74 (s, CC(CH$_3$)$_3$), 30.85 (s, CC(CH$_3$)$_3$), 21.22 (s, CH$_2$$CH_2CH_3$), 18.59 (s, CH$_2CH_2$$CH_3$), 16.69 (s, CH$_2CH_2CH_3$).

Anal. Calcd for C$_{34}$H$_{66}$Al$_2$N$_4$: C, 69.82; H, 11.37; N, 9.58. Found: C, 69.75, H, 11.48; N, 9.50%.

3.5. Synthesis of iBu$_2$Al(μ-tBu$_2$pz)$_2$AliBu$_2$ (4)

In a fashion similar to the synthesis of **3**, a solution of triisobutylaluminum (0.595 g, 3.00 mmol) in hexane (40 mL) was treated with 3,5-di-*tert*-butylpyrazole (0.541 g, 3.00 mmol) in hexane (40 mL) to afford **4** as a white crystalline solid (0.926 g, 96%): mp 131–132 °C; IR (Nujol, cm^{-1}) 1716 (w), 1518 (s), 1399 (w), 1322 (w), 1285 (w), 1250 (m), 1212 (m), 1182 (m), 1071 (m), 1045 (m), 1015 (s), 946 (w), 814 (m), 666 (s), 651 (s); ^{1}H NMR (C$_6$D$_6$, 23 °C, δ) 6.32 (s, 2H, *t*Bu$_2$pz ring-CH), 1.56 (m, 4H, CH$_2$CH(CH$_3$)$_2$), 1.43 (s, 36H, C(CH_3)$_3$), 1.03 (d, J = 6.6 Hz, 24H, CH$_2$CH(CH_3)$_2$), 0.14 (broad s, 8H, CH_2CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 23 °C, ppm) 172.48 (s, CC(CH$_3$)$_3$), 108.84 (s, *t*Bu$_2$pz ring-CH), 33.05 (s, CC(CH$_3$)$_3$), 31.30 (s, CC(CH$_3$)$_3$), 28.71 (s, CH$_2$$C$H(CH$_3$)$_2$), 26.01 (s, CH$_2$CH($CH_3$)$_2$), 24.65 (s, CH$_2$CH(CH$_3$)$_2$).

Anal. Calcd for C$_{38}$H$_{74}$Al$_2$N$_4$: C, 71.20; H, 11.64; N, 8.74. Found: C, 70.45; H, 11.48; N, 8.24%.

3.6. Kinetics measurements on 1

A 5-mm NMR tube was charged with **1** (0.046 g, 0.11 mmol) and toluene-d_8 (0.80 mL) and was sealed with a plastic cap. The tube was transferred to the NMR probe and the ^{13}C{^{1}H} NMR spectra were recorded between −70 and 20 °C. At −70 °C, sharp methylene resonances due to bridging and terminal ethyl groups were observed at 3.71 and 1.73 ppm. Upon warming from −70 to 15 °C, the methylene resonances of the bridging and terminal ethyl groups gradually broadened and shifted downfield slightly. At 20 °C, only one broad methylene resonance was observed at 1.85 ppm, suggesting exchange of the terminal and bridging ethyl groups. The dynamic process was modeled as an AB$_4$ exchange using the program gNMR [18]. The kinetics data were used to calculate the bridge-terminal

ethyl exchange rate constant at 25 °C in **1**. Errors in the kinetics data are reported at the 95% confidence level.

3.7. Kinetics measurements on 2

A 5-mm NMR tube was charged with **2** (0.052 g, 0.12 mmol) and toluene-d_8 (0.80 mL) and was sealed with a plastic cap. The tube was transferred to the NMR probe and the $^{13}C\{^1H\}$ NMR spectra were recorded between −70 and 20 °C. At −70 °C, methylene resonances (Al-CH_2) due to bridging and terminal *n*-propyl groups were observed at 16.73 and 16.56 ppm. Upon warming from −70 to 20 °C the methylene resonances of the bridging and terminal *n*-propyl groups gradually broadened and the bridging methylene resonance showed a slight downfield shift. At 20 °C, two broad bridging and terminal methylene resonances were observed at 17.68 and 16.56 ppm. The dynamic process was modeled as an AB_4 exchange using the program gNMR [18]. The kinetics data were used to calculate the bridge-terminal *n*-propyl exchange rate constant of **2** at 25 °C. Errors in kinetic data are reported at the 95% confidence level.

3.8. Crystallographic structural determinations of 2–4

Diffraction data were measured on a Bruker P4/CCD diffractometer equipped with Mo radiation and a graphite monochromator at 25 °C. The samples were mounted in thin-walled capillaries under an inert atmosphere. A sphere of data was measured at 10 s/frame and 0.2° between frames for each complex. The frame data were indexed and integrated with the manufacturer's SMART software [20]. All structures were refined using Sheldrick's SHELX-97 software [21]. Each of the following structures was collected multiple times on different samples and only the best refinements are presented here. The structural models are unambiguous in their gross correctness, but the many *n*-propyl and *tert*-butyl substituents all were disordered to some degree, resulting in unreliable geometric details in these groups. Poor packing and few significant van der Waals contacts contribute the low crystallinity of these crystals, and low observed:measured reflection ratios (35%, 37% and 21% for **2**, **3**, and **4**, respectively) for the size of the samples are evidence of the disorder.

Complex **2** crystallized as colorless pitted plates. A sample of dimensions $0.4 \times 0.2 \times 0.1$ mm^3 was used for data collection. 2450 frames were collected, yielding 11 049 reflections, of which 6983 were independent. Of these independent reflections, only 2489 were observed ($I > 2\sigma I$), attesting to the poor crystallinity of the sample. Hydrogen atom positions were calculated or observed. The pendant *n*-propyl groups showed a great deal of disorder, and extensive attempts were made to place partial atomic positions in these regions. However, even with multiple partial occupancies (sometimes as many as 4 for a single carbon atom), it remained obvious that the disorder was not satisfactorily described by discrete reasonably tight atoms, and

refinement became increasingly difficult. The simple solution of allowing the thermal ellipsoids to become very large produced the lowest *R*-values ($wR_2 = 0.12$ as compared to 0.24 with partial occupancies) and the conceptually simplest models. These crystals contain the kind of graduated disorder in the *n*-propyl substituents that is appropriately described by large thermal parameters.

Complex **3** crystallized as colorless flat rods and a crystal with dimensions of $0.6 \times 0.4 \times 0.3$ mm^3 was used for data collection. 2450 frames were collected, yielding 27 208 reflections, of which 8733 were independent. Of these, 3243 were observed ($I > 2\sigma I$). Hydrogen atom positions were observed or calculated. The asymmetric unit contains one neutral molecule. The same problems with disorder in *n*-propyl and *tert*-butyl substituents were observed as in **2**.

Complex **4** crystallized as colorless irregular fragments and a crystal with dimensions of $0.2 \times 0.2 \times 0.2$ mm^3 was used for data collection. 2450 frames were collected, yielding 30 147 reflections, of which 10 009 were independent and 2117 were observed ($I > 2\sigma I$). Hydrogen atoms were placed in calculated positions. Similar disorder problems to **2** and **3** were observed.

Acknowledgment

Appendix A. Supplementary data

X-ray crystallographic files in CIF format for the structure determinations of **2**–**4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 295466 (**2**), 295467 (**3**), and 295468 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336 033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.040.

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