Dinuclear Aminotroponiminate Compounds Containing Two Dialkyl Aluminum Substituents

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Reaction of the *n*-propyl-bridged bis(aminotroponimine) $H_2[(iPr)TP]$ with various dialkylaluminum hydrides R_2AlH, in hexane, led to novel bimetallic compounds of composition $[(R_2Al)_2\{(iPr)TP\}]$ (R = Me, Et, *i*Bu). Depending on the size of the substituents R bound to the Al centers the complexes crystallize either in a cisoid (R = Me) or a transoid (R = *i*Bu) conformation. The steric crowding at the aluminum centers is also observed in solution.

Introduction

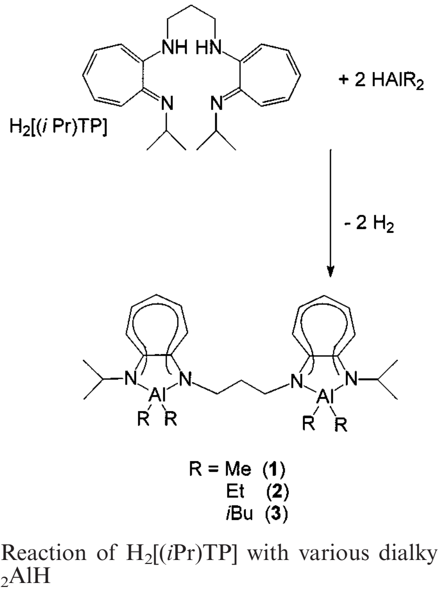
Organoaluminum compounds have attracted much attention due to their varied applications including, for example, organic syntheses, industrial catalytic processes, and chemical vapor deposition (CVD) processes.[1] Aluminum alkyls are employed as activators of group 4 complexes in Ziegler−Natta catalysis or related systems, and are known to act themselves as ethylene oligomerization and polymerization catalysts.[2] Recently, several classes of dialkylaluminum-substituted compounds, which include bidentate, monoanionic, and nitrogen-based ligands, including amidinates,[3] guadinates,[4] and aminotroponiminates,[5,6] were reacted with activators such as $[HNMe_2Ph][B(C_6F_5)_4]$, $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ to give aluminum cations. These cations, with weak counterion interactions, were used for the catalytic olefin polymerization.[3−5,7] Recent reports from our laboratory have described the preparation and characterization of monobridged aminotroponiminates as nitrogen-based ligands.[8] The tris(methylene)-bridged dianionic ligand 1,3-di[2-(isopropylamino)troponiminate]propane $[(iPr)TP]^{2-}$ was shown to coordinate in a chelating mode to various lanthanide ions.[8] Depending on the size of the lanthanide ion, products of composition $[\{(iPr)TP\}LnCl(THF)]_2$ (Ln = La, Nd) or $[\{(iPr)TP\}LnCl]_2$ (Ln = Er, Yb, Lu), in which the central atom has either a sevenfold (La, Nd) or a sixfold (Er, Yb, Lu) coordination sphere, were obtained.[8−10] Our interest in the coordination behavior of $[(iPr)TP]^{2-}$ with smaller metal ions than the lanthanides in the oxidation state +3 led us to group 13 metals. It has been demonstrated that in gallium and indium compounds of composition $[\{(iPr)TP\}MCl]$ (M = In, Ga), the structure reveals a chiral fivefold coordination sphere of the ligands around the center metal.[11] Analogous to the lanthanide complexes, the $[(iPr)TP]^{2-}$ ligand also coordinates in a chelating mode to indium and gallium.

Herein we report on the reaction of the neutral ligand $H_2[(iPr)TP]$ with various dialkylaluminum hydrides R_2AlH. We focused our attention mainly on the coordination behavior of $[(iPr)TP]^{2-}$ and its dependence on the size of the alkyl substituents.

Results

The bimetallic aluminum complexes $[(R_2Al)_2\{(iPr)TP\}]$ [R = Me (**1**), Et (**2**), *i*Bu (**3**)] were synthesized by reactions of the neutral ligand $H_2[(iPr)TP]$[8] with the corresponding dialkyl aluminum hydrides R_2AlH in hexane (Scheme 1). Upon cooling **1−3** were obtained as yellow crystalline solids with fairly high sensitivity towards air and moisture.

The new complexes were characterized by standard analytical/spectroscopic techniques. Furthermore, the solid-state structures of **1** (Figure 1) and **3** (Figure 2) were investigated by single crystal X-ray diffraction. X-ray quality



Scheme 1. Reaction of $H_2[(iPr)TP]$ with various dialkylaluminum hydrides R_2AlH

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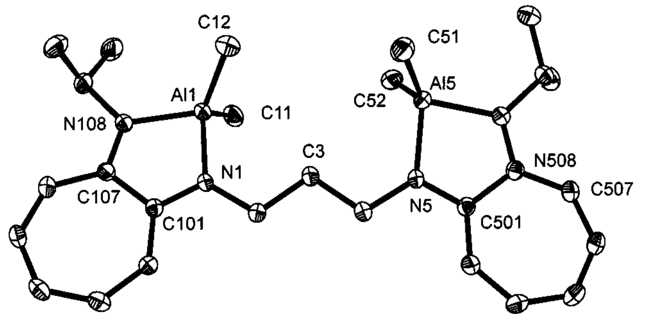

Figure 1. Perspective ORTEP view of the molecular structure of **1**; thermal ellipsoids are drawn to encompass at 50% probability; selected distances [pm] and angles [°]: Al(1)−N(1) 190.3(2), Al(1)−N(108) 191.0(2), Al(1)−C(11) 196.5(3), Al(1)−C(12) 196.8(3), N(1)−C(101) 134.4(3), N(108)−C(107) 134.5(3), N(5)−Al(5) 190.4(2), Al(5)−N(508) 191.4(2), Al(5)−C(51) 197.0(3), Al(5)−C(52) 196.7(3), N(5)−C(501) 134.9(3), N(508)−C(507) 133.5(3); N(1)−Al(1)−N(108) 84.0(1), N(1)−Al(1)−C(11) 112.0(1), N(108)−Al(1)−C(11) 114.5(1), N(1)−Al(1)−C(12) 115.4(1), N(108)−Al(1)−C(12) 112.9(1), C(11)−Al(1)−C(12) 114.5(1), N(5)−Al(5)−N(508) 84.0(1), N(5)−Al(5)−C(51) 114.7(1), N(508)−Al(5)−C(51) 112.0(1), N(5)−Al(5)−C(52) 112.0(1), N(508)−Al(5)−C(52) 113.3(1), C(51)−Al(5)−C(52) 116.6(1)

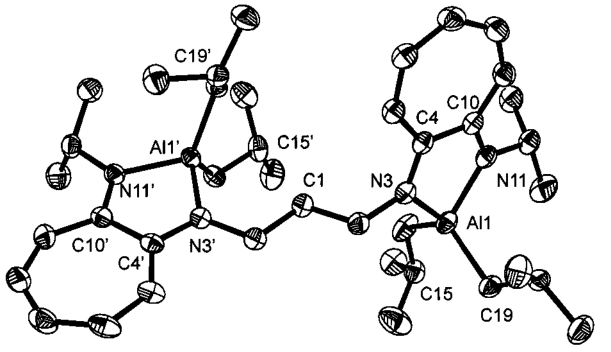

Figure 2. Perspective ORTEP view of the molecular structure of **3**; thermal ellipsoids are drawn to encompass at 50% probability; selected distances [pm] and angles [°]: Al(1)−N(3) 191.6(2), Al(1)−N(11) 191.7(2), Al(1)−C(19) 198.2(2), Al(1)−C(15) 198.4(2), N(3)−C(4) 133.9(2), N(11)−C(10) 134.0(2), Al(1′)−N(3′) 189.8(2), Al(1′)−N(11′) 191.8(2), Al(1′)−C(19′) 198.2(2), Al(1′)−C(15′) 198.2(2), N(3′)−C(4′) 133.7(2), N(11′)−C(10′) 134.0(2); N(3)−Al(1)−N(11) 83.2(1), N(3)−Al(1)−C(19) 111.7(1), N(11)−Al(1)−C(19) 111.4(1), N(3)−Al(1)−C(15) 111.3(1), N(11)−Al(1)−C(15) 116.1(1), N(3′)−Al(1′)−N(11′) 83.2(1), N(3′)−Al(1′)−C(19′) 112.1(1), N(11′)−Al(1′)−C(19′) 112.0(1), N(3′)−Al(1′)−C(15′) 111.9(1), N(11′)−Al(1′)−C(15′) 114.5(1)

crystals were grown either from hot hexane (**1**) or from pentane at −30 °C (**3**). In contrast to all other known structures in which the [(*i*Pr)TP]$^{2-}$ ligand coordinates in a chelating fashion, **1** and **3** only show a metal-bridging coordination mode. Since the cisoid arrangement of both metal atoms in **1** suggests that a chelating coordination of the ligand might be possible, $\mathrm{Me_2AlH}$ was reacted with an excess of $\mathrm{H_2}$[(*i*Pr)TP] at elevated temperature to force the ligand to coordinate in a chelating fashion. However, even under these reaction conditions only **1** was obtained. In contrast to **1** the two metal centers of **3** are located in a transoid conformation in the solid state which is mainly caused by the increased steric demand of the *i*Bu substituents of the aluminum atoms. Thus, **1** features a noncrystallographic C_2 symmetry through C3 (parallel to the planes of the seven-membered rings) whereas **3** has a noncrystallographic C_2 symmetry through C1. The heterocyclic five-membered ring systems (N, Al, N, C, C) are essentially planar with an average deviation from the least-square plane of 2 pm (**1**) and 1 pm (**3**). The four-coordinate aluminum centers in both **1** and **3** adopt a distorted tetrahedral geometry. The N−Al−N angles are 84.0(1)°, 84.0(1)° (**1**) and 83.2(1)°, 83.2(1)° (**3**). The larger steric demand of the *i*Bu substituents in **3** compared to Me in **1** leads to a slight decrease of the N−Al−N angle, while the C−Al−C angles are increased [114.5(1)°, 116.6(1)° (**1**) and 118.1(1)°, 118.1(1)° (**3**)]. The Al−N distances [190.3(2) pm to 191.4(2) pm (**1**); 191.6(2) pm, 191.7(2) pm (**3**)] are typical for four-coordinate Al, e.g. [(*i*Pr)$_2$ATI]$\mathrm{AlMe_2}$ [191.5(1) pm] and [(*i*Pr)$_2$ATI]$\mathrm{AlH_2}$ (ATI = aminotroponiminate) [188.2(4) pm, 188.6(4) pm] have similar bond lengths.[5] The $\mathrm{C_{ring}{-}N}$ distances [av. 134.3(3) pm (**1**); 133.9(2) pm and 134.0(2) pm (**3**)] are similar to the values observed for [(*i*Pr)$_2$ATI]H [131.4(3) pm and 134.2(3) pm] and [(*i*Pr)$_2$ATI]$\mathrm{AlMe_2}$ (av. 133.8 pm).[5]

For compound **1** one sharp $\mathrm{Al{-}CH_3}$ signal is observed in the ^{1}H and ^{13}C NMR spectra ($\delta = -0.25$ and $\delta = -6.1$, respectively). Due to the nonequivalence of the Al−αH in **2** and **3**, a splitting of the Al−αH resonance is seen in the ^{1}H NMR spectra [Al−C*H*$_2$: $\delta = 0.35$ and 0.36 (**2**); $\delta = 0.36$ and 0.38 (**3**)] but not in the ^{13}C NMR spectra [e.g. Al−*C*H$_2$: $\delta = 2.9$ (**2**); $\delta = 25.4$ (**3**)]. The ^{1}H and ^{13}C NMR spectra also point to a symmetrical coordination of the [(*i*Pr)TP]$^{2-}$ anion in solution. The signals of the isopropyl C*H* of **1−3** are well-resolved into a septet and show only a slight high-field shift [$\delta = 3.50$ (**1**), 3.51 (**2**) and 3.54 (**3**)] compared to that of the free ligand $\mathrm{H_2}$[(*i*Pr)TP] ($\delta = 3.55$).[8] This is in sharp contrast to comparable lanthanide alkyl compounds of composition [{(*i*Pr)TP}Ln−R] [Ln = La, Lu; R = $\mathrm{CH(SiMe_3)_2}$, $\mathrm{CH_2SiMe_3}$)] in which the isopropyl C*H* signal is strongly downfield shifted {$\delta = 3.67$ [{(*i*Pr)-TP}$_2$La$\mathrm{CH(SiMe_3)_2}$];[8] $\delta = 3.93$ [{(*i*Pr)TP}$_2$Lu$\mathrm{CH_2{-}SiMe_3}$][10]}. Besides the NMR investigations all new compounds were also characterized by elemental analyses and IR and EI mass spectroscopy. Compounds **1−3** show molecular ion peaks as well as characteristic fragmentation patterns.

Conclusions

In conclusion, it can be emphasized that the reactions of $\mathrm{H_2}$[(*i*Pr)TP] with various aluminum alkyl compounds $\mathrm{R_2AlH}$ lead to bimetallic complexes of composition [$\mathrm{(R_2Al)_2}${(*i*Pr)TP}] (R = Me, Et, *i*Bu). In contrast to other complexes of group 3, 13 and the lanthanide metals the TP ligand does not bind in a chelating fashion; instead, a metal-bridging coordination is observed. Obviously, due to the smaller ion radius of the aluminum(III) center, bis(aminotroponiminate) complexes cannot be formed. Depending on the steric size of the alkyl groups bound to Al either a cisoid or a transoid conformation of [$\mathrm{(R_2Al)_2}${(*i*Pr)TP}] is observed in the solid state. In summary, our results extend the series of the few known bimetallic complexes of group 13 elements such as salen complexes.[12−15]

Experimental Section

General: All manipulations were performed in a glovebox under an N_2 atmosphere or with standard Schlenk techniques. Solvents were dried over sodium/potassium and degassed prior to use. $i\mathrm{Bu_2AlH}$ was purchased from Aldrich and used as received. $\mathrm{Me_2AlH}$,[16] $\mathrm{Et_2AlH}$[17] and $\mathrm{H_2}[(i\mathrm{Pr})\mathrm{TP}]$[8] were prepared by literature methods. − A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to internal C_6D_5H (^{1}H: δ = 7.154; ^{13}C: δ = 128.0). − Infrared spectra were recorded in Nujol between KBr plates with a Nicolet Magna 550 and are reported in wave numbers. − Mass spectra were recorded at 70 eV on Varian MAT 711 spectrometer in the electron ionisation mode. − Melting points were observed in sealed capillaries and were not corrected. − Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

$[(\mathrm{Me_2Al})_2[(i\mathrm{Pr})\mathrm{TP}]]$ (1): $\mathrm{Me_2AlH}$ (0.12 g, 2.00 mmol) was dissolved in hexane (20 mL). At ambient temperature a solution of $\mathrm{H_2}[(i\mathrm{Pr})\mathrm{TP}]$ (0.36 g, 1.00 mmol) in hexane (30 mL) was added, immediately followed by gas evolution and precipitation of a yellow solid. After the gas evolution had stopped, the suspension was heated under reflux for 10 min, until the solid had dissolved. Cooling to −10 °C gave **1** as yellow crystals (0.45 g, 95%). Single crystals were formed from a solution of hot hexane. (60 °C to 25 °C within 8 h). M.p. 128 °C. − ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ = −0.25 (s, 12 H, Al−CH_3), 1.17 [d, $^3J_{H-H}$ = 6.4 Hz, 12 H, CH(CH_3)$_2$], 2.12 (m, 2 H, $CH_2-CH_2-CH_2$), 3.18 (m, 4 H, $CH_2-CH_2-CH_2$), 3.50 [dsept, $^3J_{H-H}$ = 6.4 Hz, $^5J_{H-H}$ = 0.7 Hz 2 H, $CH(CH_3)_2$], 6.21 (t, $^3J_{H-H}$ = 9.3 Hz, 2 H, H_{ring}), 6.31 (d, J_{H-H} = 11.4 Hz, 2 H, H_{ring}), 6.36 (d, J_{H-H} = 11.1 Hz, 2 H, H_{ring}), 6.71−6.84 (m, 4 H, H_{ring}). − ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ = −6.1 (Al−CH_3), 22.9 [CH(CH_3)$_2$], 27.6 ($CH_2-CH_2-CH_2$), 44.8 ($CH_2-CH_2-CH_2$), 47.6 [$CH(CH_3)_2$], 113.5 (C_{ring}), 114.0 (C_{ring}), 119.7 (C_{ring}), 136.8 (C_{ring}), 136.9 (C_{ring}), 161.4 (N−C_{ring}), 162.1 (N−C_{ring}). MS (EI, 20 eV): *m/z* (%) = 476 (2) [M^+], 461 (64) [$M^+ - CH_3$], 389 (100) [$M^+ - Al - 4CH_3$], 208 (7) [$M^+/2 - 2CH_3$]. − IR (nujol): ṽ = 2362, 2337, 1511, 1259, 1095, 1018, 798, 721 cm^{-1}. − $C_{27}H_{42}Al_2N_4$(476.6): calcd. C 68.04, H 8.88, N 11.76; found C 67.93, H 8.82, N 11.71.

$[(\mathrm{Et_2Al})_2[(i\mathrm{Pr})\mathrm{TP}]]$ (2): $\mathrm{Et_2AlH}$ (0.17 g, 2.00 mmol) was dissolved in hexane (20 mL) and added at ambient temperature to a solution of $\mathrm{H_2}[(i\mathrm{Pr})\mathrm{TP}]$ (0.36 g, 1.00 mmol) in hexane (30 mL). After the gas evolution had stopped the solution was heated under reflux for 15 min. Cooling to −30 °C gave **2** as a yellow solid (0.45 g, 85%). M.p. 111 °C. − ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ = 0.35 (q, $^3J_{H-H}$ = 8.2 Hz, 4 H, CH_2Al), 0.36 (q, $^3J_{H-H}$ = 8.1 Hz, 4 H, CH_2Al), 1.18 [d, $^3J_{H-H}$ = 6.4 Hz, 12 H, CH(CH_3)$_2$], 1.33 (t, $^3J_{H-H}$ = 8.1 Hz, 12 H, CH_3CH_2Al), 2.13 (m, 2 H, $CH_2-CH_2-CH_2$), 3.27 (m, 4 H, $CH_2-CH_2-CH_2$), 3.51 [dsept, $^3J_{H-H}$ = 6.4 Hz, $^5J_{H-H}$ = 0.8 Hz, 2 H, $CH(CH_3)_2$], 6.21 (t, $^3J_{H-H}$ = 9.3 Hz, 2 H, H_{ring}), 6.33 (d, J_{H-H} = 11.4 Hz, 2 H, H_{ring}), 6.43 (d, J_{H-H} = 11.0 Hz, 2 H, H_{ring}), 6.71−6.87 (m, 4 H, H_{ring}). − ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ = 2.9 (CH_2Al), 10.2 (CH_3CH_2Al), 22.7 [CH(CH_3)$_2$], 27.0 ($CH_2-CH_2-CH_2$), 44.8 ($CH_2-CH_2-CH_2$), 47.5 [$CH(CH_3)_2$], 113.4 (C_{ring}), 114.1 (C_{ring}), 119.8 (C_{ring}), 136.8 (C_{ring}), 136.9 (C_{ring}), 161.8 (N−C_{ring}), 162.5 (N−C_{ring}). − MS (EI, 20 eV): *m/z* (%) = 532 (4) [M^+], 503 (100) [$M^+ - Et$], 389 (70) [$M^+ - Al - 4Et$]. − IR (nujol): ṽ = 1595, 1511, 1423, 1274, 1234, 1160, 1043, 989, 962, 881, 731, 630, 576 cm^{-1}. − $C_{31}H_{50}Al_2N_4$ (532.7): C 69.89, H 9.46, N 10.52; found C 69.63, H 9.39, N 10.50.

$[(i\mathrm{Bu_2Al})_2\{(i\mathrm{Pr})\mathrm{TP}\}]$ (3): In a procedure similar that for **2**, compound **3** was obtained as a yellow solid (0.45 g, 70%) at −30 °C. Single crystals were formed from a pentane solution at −30 °C. M.p. 113 °C (dec). − ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ = 0.36 (d, $^3J_{H-H}$ = 6.8 Hz, 4 H, CH_2Al), 0.38 (d, $^3J_{H-H}$ = 6.9 Hz, 4 H, CH_2Al), 1.12 [d, $^3J_{H-H}$ = 6.3 Hz, 12 H, (CH_3)$_2$CHCH$_2$Al], 1.14 [d, $^3J_{H-H}$ = 6.3 Hz, 12 H, (CH_3)$_2$CHCH$_2$Al], 1.23 [d, $^3J_{H-H}$ = 6.5 Hz, 12 H, NCH(CH_3)$_2$], 2.01 [sept, 2 H, $^3J_{H-H}$ = 6.5 Hz, 4 H, (CH_3)$_2$CHCH$_2$Al], 2.16 (m, 2 H, $CH_2-CH_2-CH_2$), 3.30 (m, 4 H, $CH_2-CH_2-CH_2$), 3.54 [dsept, $^3J_{H-H}$ = 6.4 Hz, $^5J_{H-H}$ = 0.6 Hz, 2 H, NCH(CH_3)$_2$], 6.23 (t, $^3J_{H-H}$ = 9.3 Hz, 2 H, H_{ring}), 6.34 (d, J_{H-H} = 11.5 Hz, 2 H, H_{ring}), 6.45 (d, J_{H-H} = 11.1 Hz, 2 H, H_{ring}), 6.76 (m, 2 H, H_{ring}), 6.93 (m, 2 H, H_{ring}). − ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ = 22.7 [CH(CH_3)$_2$], 25.4 (CH_2Al), 26.6 ($CH_2-CH_2-CH_2$), 27.5 [(CH_3)$_2$CHCH$_2$Al], 28.8 [(CH_3)$_2$CHCH$_2$Al], 29.0 [(CH_3)$_2$CHCH$_2$Al], 45.0 ($CH_2-CH_2-CH_2$), 47.6 [$CH(CH_3)_2$], 113.8 (C_{ring}), 114.6 (C_{ring}),

Table 1. Crystallographic details for $[(\mathrm{Me_2Al})_2[(i\mathrm{Pr})\mathrm{TP}]]$ (**1**) and $[(i\mathrm{Bu_2Al})_2[(i\mathrm{Pr})\mathrm{TP}]]$ (**3**)

	1	3
Formula	$C_{27}H_{42}Al_2N_4$	$C_{39}H_{66}Al_2N_4$
Formula weight	476.6	644.9
Space group	$P2_1/c$ (Na 14)	$P\bar{1}$ (No. 2)
a, pm	735.04(2)	1165.11(4)
b, pm	1873.28(6)	1270.21(5)
c, pm	2005.54(5)	1493.67(6)
α,°		91.630(2)
β, °	98.250(2)	112.803(2)
γ, °		101.484(2)
V, 10^6 pm^3	2732.92(13)	1983.28(13)
Z	4	2
T, K	123(2)	123(2)
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
μ, mm^{-1}	0.128	0.103
Reflections collected	24437	30770
Unique reflections	4804 [R_{int} = 0.050]	9450 [R_{int} = 0.040]
Parameters	302	406
$R1$ for $I > 2\sigma(I)$	0.054	0.053
w$R2$ (all data)	0.134	0.148

119.9 (C_{ring}), 136.9 (C_{ring}), 137.0 (C_{ring}), 161.7 ($N-C_{ring}$), 162.2 ($N-C_{ring}$). − MS (EI, 20 eV): m/z (%) = 644 (0.03) [M^+], 587 (100) [$M^+ - i$Bu], 389 (31) [$M^+ - 4i$Bu], 322 (14) [$M^+/2$]. − IR (Nujol): $\tilde{\nu}$ = 2360, 2337, 1594, 1511, 1421, 1274, 1223, 1172, 1052, 727, 667, 619 cm^{-1}. − $C_{39}H_{66}Al_2N_4$ (644.9): C 72.63, H 8.37, N 8.69; found C 72.58, H 8.34, N 8.68.

X-ray Structure Solution and Refinement: Crystallographic data are summarized in Table 1. Figure 1 shows the ORTEP diagram of the solid state structure of **1** and Figure 2 that of **3**. Data were collected on a Nonius Kappa-CCD diffractometer. Structures of **1** and **3** were solved by direct methods (SHELXS-97)[18] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[19]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138108 (**1**) and CCDC-138109 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + (44)-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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