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Synthesis and structures of aluminium monohydride and chalcogenides bearing a bidentate [N,O] ligand

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The aluminium monohydride (3-tBu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-$i$$Pr_2C_6H_3$)AlH($NMe_3$) (**2**) was prepared by treatment of the bidentate salicylaldimine [3-tBu-5-Me-2-(OH)$C_6H_2CH{=}N$-2,6-$i$$Pr_2C_6H_3$] (**1**) with a small excess of $AlH_3{\cdot}NMe_3$ in high yield. Compound **2** reacted with sulfur and selenium respectively to afford the dimeric aluminium chalcogenide [(3-tBu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-$i$$Pr_2C_6H_3$)Al(μ-E)]$_2$ [E = S (**3**), E = Se (**4**)]. During the formation of **2** hydrogen migration from the aluminium centre to the ligand backbone occurred. A possible reaction mechanism for **3** and **4** is discussed and the molecular structures of compounds **2**–**4** were determined by X-ray structural analyses.

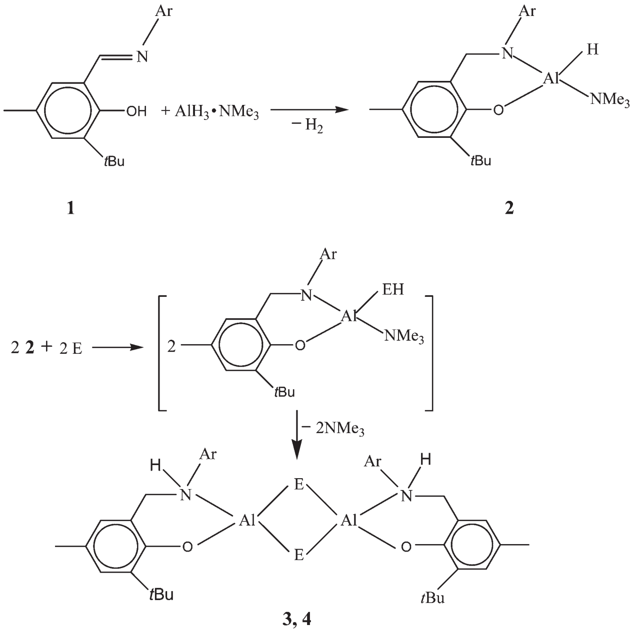
Introduction

Much attention is paid to the salicylaldiminato ligand family due to its easy accessibility and diversity as chelates with or without pendant arms. Moreover, salicylaldiminato ligands have played an important role in a range of olefin polymerization catalyst systems[1] and development of transition and main group metal coordination chemistry. This type of ligand was introduced to aluminium chemistry mainly to prepare the alkyl aluminium complexes[2] and their cationic derivatives by reaction with AlR_2X (R = alkyl group, X = alkyl group or Cl), which can be used as ethylene polymerization catalysts.[2d] To the best of our knowledge, there have been no reports on aluminium hydride species stabilized by Schiff base [N,O] chelate ligands.

Heavier Group 13 element chalcogenides have been widely studied due to their important applications in chemical vapor deposition (CVD) and catalysis,[3] and organoaluminium hydrides of low aggregation have proved to be effective reagents for preparing compounds with elemental chalcogens or organochalcogenides.[4] As an extension of this type of reaction, we explore a bidentate salicylaldimine [3-tBu-5-Me-2-(OH)$C_6H_2CH{=}N$-2,6-$i$$Pr_2C_6H_3$] (**1**)[5] and its reaction with $AlH_3{\cdot}NMe_3$ to afford an aluminium monohydride (3-tBu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-$i$$Pr_2C_6H_3$)AlH($NMe_3$) (**2**) by elimination of H_2 together with hydrogen migration from the metal to the ligand. In this paper we also describe its chalcogenide derivatives [(3-tBu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-$i$$Pr_2C_6H_3$)Al(μ-E)]$_2$ [E = S (**3**), Se (**4**)] from the reaction of **2** with sulfur and selenium, and the possible reaction mechanism is discussed as well.

Results and discussion

Reaction of **1** with a small excess of $AlH_3{\cdot}NMe_3$[6] in toluene at 0 °C or alternatively under refluxing conditions in toluene afforded the aluminium monohydride (3-tBu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-$i$$Pr_2C_6H_3$)AlH($NMe_3$) (**2**) in good yield under elimination of H_2 (Scheme 1). Furthermore, a hydrogen migration from the aluminium centre to the parent ligand backbone occurred at the CH=N double bond to give the CH_2N single bond. A migration reaction of a methyl group was not observed when $AlMe_3$ was used instead, and the CH=N double bond was retained within the bidentate salicylaldiminato ligand.[2a–c] We assume that this is due to the higher reactivity of $AlH_3{\cdot}NMe_3$ compared to that of $AlMe_3$. Moreover we believe that both the 2,6-$i$$Pr_2C_6H_3$ group on the aldimine nitrogen and the bulky *ortho* tBu group on the phenoxide ring of **1** prevent the dimerization of **2**. Compound **2** is well soluble in common organic solvents, such as toluene, benzene, hexane and pentane. The broad IR band at 1837 cm⁻¹ can be assigned to the Al–H stretching frequency.[7] The absorptions for the C=N double bond and O–H group are absent in the IR of **2**. Compound **2** crystallizes with one molecule of toluene. The structure of **2** shows the distorted tetrahedral aluminium centre (Fig. 1). Selected bond lengths and angles are listed in Table 1. The terminal Al–H bond length (1.479(2) Å) is similar to that in [ArN$(CH_2)_3$NAr]AlHNMe$_3$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (1.52 Å).[4a] The Al–N$_{\text{ligand}}$ bond distance (1.799(1) Å) is much shorter than those in [3,5-tBu$_2$-2(O)$C_6H_2CH{=}NR$]AlMe$_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-$i$$Pr_2C_6H_3$) (1.972(3), 1.972(3) Å) bearing the unchanged bidentate salicylaldiminato ligands.[2a] The Al–N$_{\text{NMe3}}$ bond length (2.000(1) Å) is comparable to those in [ArN$(CH_2)_3$NAr]AlRNMe$_3$ (Ar = 2,6-$i$$Pr_2C_6H_3$, R = H, F) (2.024(2), 2.000(2) Å).[4a] The Al–O distance (1.741(1) Å) is a little shorter than those in [3,5-tBu$_2$-2(O)$C_6H_2CH{=}NR$]AlMe$_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-$i$$Pr_2C_6H_3$) (1.755(3), 1.773(3) Å).[2a] The N(1)–C(24) bond length (1.478(2) Å) shows a typical C–N single bond character compared to the corresponding retained C=N double bond in {3,5-tBu$_2$-2(O)$C_6H_2CH{=}NR$}AlMe$_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-$i$$Pr_2C_6H_3$) (1.285(5), 1.300(5) Å).[2a]



Scheme 1 Synthesis of **2**, **3** (E = S) and **4** (E = Se), Ar = 2,6-$i$$Pr_2C_6H_3$.

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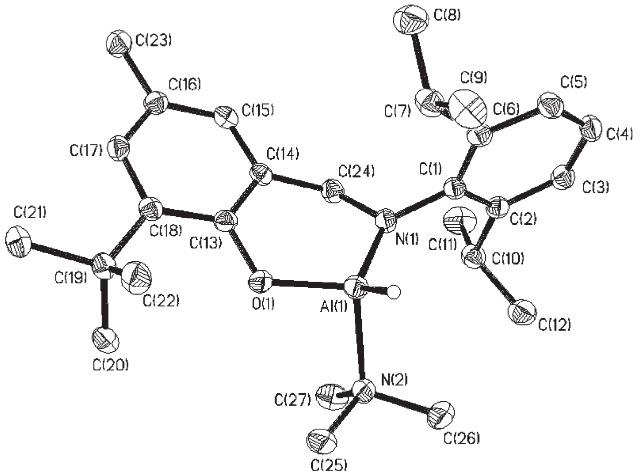

Fig. 1 The molecular structure of **2**. the solvent molecule and the hydrogen atoms are omitted for clarity except for the Al–H hydrogen atom.

Treatment of **2** with elemental sulfur and selenium in toluene yielded the dimeric aluminium chalcogenides [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-E)]$_2$ [E = S (**3**), Se (**4**)] bearing the hydrogenated bidentate salicylaldiminato ligand (Scheme 1). Compounds **3** and **4** are air and moisture sensitive and soluble in toluene, while sparingly soluble in benzene. They were characterized by IR and NMR spectroscopy and EI mass spectrometry, as well as elemental analyses. No bands for the C=N stretches were found in the IR spectrum. We assume that the formation of **3** and **4** might proceed through a reactive intermediate [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(EH)(NMe_3)] (E = S, Se) (Scheme 1). The conversion of Al–H to Al–EH was observed in compounds stabilized by the bulky β-diketiminato ligand.[8] The intermediate then dimerized to [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ with elimination of NMe_3. Under heating the unstable [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ was converted to the stable products **3** and **4** with hydrogen migration from μ-EH to nitrogen. The absorption bands at 3175 and 3220 cm^{-1} assigned to the NH stretching frequency in the IR spectrum of **3** and **4** respectively support the proposed hydrogen migration. The proton of the NH group was also found in the molecular structures by X-ray analyses and ^1H NMR spectroscopy. A comparable migration phenomena was observed in previous examples.[4a]

Compounds **3** and **4** crystallize with two molecules of toluene respectively. The molecular structures of **3** and **4** show that both of them have a dimeric structure featuring a fused planar four-membered ring with a central Al_2E_2 core (Figs. 2 and 3). Selected bond lengths and angles are shown in Table 1. The Al–N bond length (2.005(1) Å for **3**; 2.009(2) Å for **4**) is much longer than that in **2** (1.799(1) Å), however similar to those in {3,5-*t*Bu_2-2(O)C_6H_2CH=NR}AlMe_2 (R = 2,6-$Me_2C_6H_3$ or 2,6-*i*$Pr_2C_6H_3$) (1.972(3), 1.972(3) Å) bearing the unchanged bidentate salicylaldiminato ligand.[2a] The Al–O distance (1.750(1) Å for **3**; 1.749(2) Å for **4**) is comparable to that in **2** (1.741(1) Å). The N–C bond length (1.510(2) Å for **3**; 1.511(3) Å for **4**) shows single bond character like that of **2**. The Al–E distance (2.185(2), 2.232(2) Å for **3**; 2.314(1), 2.366(1) Å for **4**) is analogous to those of similar Al_2E_2 species.[4] The E(1)–Al–E(1A) angle (102.47(3)° E = S **3**; 104.50 (3)° E = Se **4**) is in the range of those reported.[4b]

Concluding remarks

This work provides an aluminium monohydride employing a bidentate salicylaldiminato ligand. During the formation of the aluminium monohydride, a hydrogen migration occurred together with the elimination of H_2. Reactions of aluminium hydride with chalcogens (S, Se) result in the dimeric products **3** and **4**. A possible mechanism for the latter reaction is discussed.

Table 1 Selected bond distances (Å) and bond angles (°) for compounds **2**, **3** and **4**

2·C_7H_8			
Al(1)–O(1)	1.741(1)	Al(1)–N(1)	1.799(1)
Al(1)–N(2)	2.000(1)	N(1)–C(24)	1.478(2)
Al(1)–H(1)	1.479(2)		
O(1)–Al(1)–N(1)	102.32(6)	N(1)–Al(1)–N(2)	117.07(6)
O(1)–Al(1)–N(2)	95.45(5)	H(1)–Al(1)–O(1)	121.2(6)
N(1)–C(24)–C(14)	115.63(1)	H(1)–Al(1)–N(2)	100.3(6)
H(1)–Al(1)–N(1)	118.9(6)		
3·2C_7H_8			
S(1)–Al(1)	2.185(2)	S(1)–Al(1A)	2.232(2)
O(1)–Al(1)	1.750(1)	Al(1)–N(1)	2.005(1)
N(1)–C(24)	1.510(2)		
Al(1)–S(1)–Al(1A)	77.53(3)	O(1)–Al(1)–N(1)	96.99(5)
O(1)–Al(1)–S(1)	119.92(4)	N(1)–Al(1)–S(1)	118.01(5)
O(1)–Al(1)–S(1A)	117.74(4)	N(1)–Al(1)–S(1A)	100.86(5)
S(1)–Al(1)–S(1A)	102.47(3)	C(14)–C(24)–N(1)	111.15(1)
4·2C_7H_8			
Se(1)–Al(1)	2.314(1)	Se(1)–Al(1A)	2.366(1)
Al(1)–O(1)	1.749(2)	Al(1)–N(1)	2.009(2)
N(1)–C(12)	1.511(3)		
O(1)–Al(1)–Se(1)	118.45(6)	O(1)–Al(1)–N(1)	96.43(8)
N(1)–Al(1)–Se(1)	118.48(7)	O(1)–Al(1)–Se(1A)	116.08(6)
N(1)–Al(1)–Se(1A)	102.25(7)	Al(1)–Se(1)–Al(1A)	75.50(3)
Se(1)–Al(1)–Se(1A)	104.50(3)	C(2)–C(12)–N(1)	110.7(2)

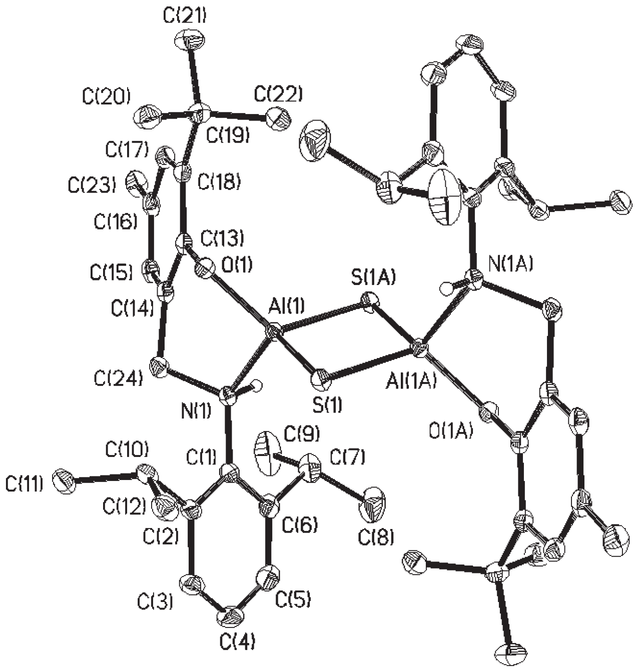

Fig. 2 The molecular structure of **3**. Solvent molecules and the hydrogen atoms are omitted for clarity except for the N–H hydrogen atoms.

Experimental

General

All manipulations were carried out using Schlenk line techniques or in a glove box under a purified nitrogen atmosphere. Solvents were dried according to standard methods and freshly distilled prior to use. Elemental sulfur, selenium were purchased

Table 2 Crystallographic data for compounds **2**, **3** and **4**

Compound	**2**·C_7H_8	**3**·$2C_7H_8$	**4**·$2C_7H_8$
Empirical formula	$C_{34}H_{51}AlN_2O$	$C_{62}H_{84}Al_2N_2O_2S_2$	$C_{62}H_{84}Al_2N_2O_2Se_2$
M	530.75	1007.39	1101.19
λ/Å	1.54178	1.54178	0.71073
T/K	100(2)	100(2)	133(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.100(1)	12.149(1)	10.048(4)
b/Å	9.632(1)	12.345(1)	12.4855(5)
c/Å	36.703(1)	12.554(1)	13.1473(6)
α/°	90	108.94(1)	77.061(3)
β/°	96.65(1)	118.62(1)	68.039(3)
γ/°	90	97.75(1)	89.284(3)
V/Å^3	3195(1)	1465(1)	1486.23(11)
Z	4	1	1
ρ_c/Mg m^{-3}	1.103	1.142	1.230
μ/mm^{-1}	0.746	1.431	1.315
F(000)	1160	544	580
No. of reflns collected	13836	11561	50725
No. of indep reflns	4447 (Rint = 0.0327)	4107 (Rint = 0.0299)	5105 (Rint = 0.0437)
Data/restaints/paramers	4447 / 0 / 61	4107 / 249 / 394	5105 / 0 / 292
GOF on F^2	1.045	1.047	1.020
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0338, 0.0845	0.0324, 0.0859	0.0345, 0.0878
$R1$,$wR2$ (all data)	0.0413, 0.0886	0.0369, 0.0891	0.0367,0.0891
Largest diff peak,hole/e Å^{-3}	0.169,−0.243	0.200,−0.232	0.920,−0.633

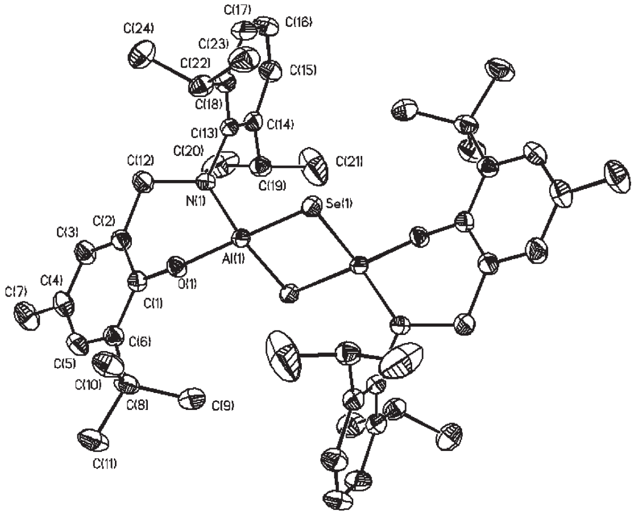

Fig. 3 The molecular structure of **4**. Solvent molecules and the hydrogen atoms including the N–H hydrogen atoms are omitted for clarity.

from Aldrich and used as received. $AlH_3·NMe_3$[6] was prepared as described in the literature.

NMR spectra were recorded on Bruker AM 200, AM 300 spectrometers. Chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^1H nuclei. Mass spectra were obtained on Finnigan MAT system 8230 or Varian MAT CH5 mass spectrometers by EI-MS methods. Melting points of all new compounds were measured on a Büchi melting point B-540 apparatus in sealed capillaries and are uncorrected. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer (only the characteristic absorptions are reported) and the samples were prepared as Nujol mulls between KBr plates. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Preparations

[3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$]AlH(NMe_3) (2). A solution of $AlH_3·NMe_3$ (17.2 mL of a 0.8 M solution in toluene, 13.76 mmol) was added at 0 °C to a solution of **1** (3.14 g, 8.95 mmol) in toluene (40 mL). The reaction mixture was slowly warmed to room temperature and stirred for an additional 15 h. The volatiles were removed *in vacuo*. The crude product was recrystallized from toluene, and the filtrate was kept at −20 °C to obtain colorless crystals (3.10 g, 79%). Mp 109–112 °C; IR (Nujol): $\tilde{\nu}$ = 1837 cm^{-1} (Al–H stretch); ^1H NMR (300.13 MHz, C_6D_6,): δ 1.02 (d, 3H, CH*Me*$_2$), 1.19 (d, 3H, CH*Me*$_2$), 1.43 (d, 6H, CH*Me*$_2$), 1.72 (s, 9H, C*Me*$_3$), 1.79 (s, 9H, N*Me*$_3$), 2.26 (s, 3H, *Me*), 3.72 (sept, 2H, C*H*Me$_2$), 3.86 (d, 1H, C*H*$_2$N), 4.69 (d, 1H, C*H*$_2$N), 6.65 (d, 1H, OAr–*H*), 6.99–7.18 (m, 4H, NAr–*H*, OAr–*H*); EI -MS (70 eV): *m*/*z* (%) only CH fragments; elemental analysis (%) calcd. for $C_{27}H_{43}AlN_2O$ (438.62): C, 73.93; H, 9.88; N, 6.39; Found: C, 74.29; H 9.51; N, 5.53.

[(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-S)]$_2$ (3). Toluene (20 mL) was added to a mixture of **2** (0.558 g, 1.28 mmol) and S (0.042 g, 1.28 mmol), and the resulting solution was warmed to 60 °C and stirred for 15 h. After cooling to room temperature the yellow-green solution was filtered and the filtrate was concentrated to *ca.* 8 mL. Yellow crystals were obtained after storing the resulting solution at −20 °C for 5 days (0.72 g, 62%). Mp 121 °C decomp.; IR (Nujol): $\tilde{\nu}$ = 3175 cm^{-1} (N–H stretch); ^1H NMR (300.13 MHz, C_6D_6,): δ 0.88, 0.92, 1.09, 1.14 (d, 24H, CH*Me*$_2$), 1.52 (s, 2H, N*H*), 1.45, 1.71 (s, 18H, C*Me*$_3$), 2.10, 2.18 (s, 6H, *Me*), 3.15, 3.25, 3.41, 3.57 (sept, 4H, C*H*Me$_2$), 4.58, 4.64 (d, 4H, C*H*$_2$N), 5.80 (d, 1H, OAr–*H*), 6.01 (d, 1H, OAr–*H*), 6.40 (d, 1H, OAr–*H*), 6.51 (d, 1H, OAr–*H*), 7.01–7.15 (m, 6H, NAr–*H*); EI-MS (70 eV): *m*/*z* (%) 822 (12) [M$^+$ − H], 162 (100) [*i*$Pr_2C_6H_4$]; elemental analysis (%) calcd. for $C_{48}H_{68}Al_2N_2O_2S_2$ (823.16): C 70.04, H 8.33, N 3.40. Found C 70.75, H 8.46, N 3.50.

[(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-Se)]$_2$ (4). Toluene (30 mL) was added to a mixture of **2** (0.768 g, 1.75 mmol) and Se (0.28 g, 3.54 mmol). The solution was refluxed for 2 h. The unreacted Se was removed by filtration. The filtrate was concentrated to *ca.* 8 mL and kept at 0 °C to obtain yellow crystals (1.06 g, 60%). Mp 118 °C decomp.; IR (Nujol): $\tilde{\nu}$ = 3220 cm^{-1}(N–H stretch); ^1H NMR (300.13 MHz, C_6D_6,): δ 0.87, 0.94, 1.14, 1.44 (d, 24H, CH*Me*$_2$), 1.50, 1.56 (s, 18H, C*Me*$_3$), 1.88 (s, 2H, N*H*), 2.10, 2.15 (s, 6H, *Me*), 2.64, 3.25, 3.43, 3.57 (sept, 4H, C*H*Me$_2$), 4.35, 4.39 (d, 4H, C*H*$_2$N), 6.05 (d, 1H, OAr–*H*), 6.21 (d, 1H, OAr–*H*), 6.33 (d, 1H, OAr–*H*), 6.47 (d, 1H, OAr–*H*), 7.01–7.15 (m, 6H, NAr–*H*); EI-MS (70 eV): *m*/*z* (%) 916 (4) [M$^+$ − H], 162 (100) [*i*$Pr_2C_6H_4$]; elemental analysis (%) calcd. for $C_{62}H_{84}Al_2N_2O_2Se_2$ (1101.23): C, 67.62; H, 7.69; N, 2.54. Found: C, 67.25; H, 7.81; N, 2.72.

X-Ray structural determination and refinement for 2, 3, 4

Data for compounds **2** and **3** were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and for **4** on a Stoe IPDS II two-circle diffractometer. All structures were solved by direct methods (SHELXS-97)[9] and refined with all data by full-matrix least-squares methods on F^2.[10] The non-hydrogen atoms were refined anisotropically, except those of the highly disordered toluene molecules in **4** which were refined isotropically. The hydrogen atoms were included at geometrically idealized positions and refined with the riding model, except for the Al–H and N–H hydrogen atoms which were located by difference Fourier synthesis and refined isotropically. The toluene molecules in **2** were disordered over two positions and refined with distance restraints and restraints for the anisotropic displacement parameters.

CCDC reference numbers 245956 (**2**), 245957 (**3**) and 245958 (**4**).

See http://www.rsc.org/suppdata/dt/b4/b411617h/ for crystallographic data in CIF or other electronic format.

See Table 2 for crystallograpic details.

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