Alumoxanes

DOI: 10.1002/anie.200605081

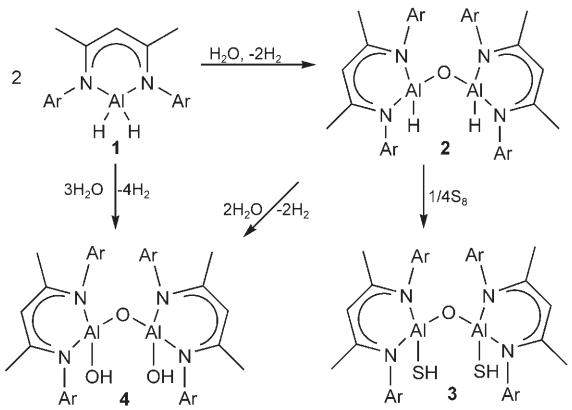
Preparation of Molecular Alumoxane Hydrides, Hydroxides, and Hydrogensulfides**

*Sandra González-Gallardo, Vojtech Jancik, Raymundo Cea-Olivares, Rubén A. Toscano, and Mónica Moya-Cabrera**

Research on the controlled hydrolysis of aluminum compounds has led to the isolation and structural characterization of several interesting alumoxanes.[1] Alumoxanes (entities containing Al-O-Al moieties) are known to easily undergo association, leading to oligomeric structures.[1a,b] Thus, the preparation of molecular alumoxanes with low degrees of association in a pure, crystalline form remains a synthetic challenge. Moreover, organically modified alumoxanes are not common,[1c,d] although they are highly desirable compounds owing to their potential application as cocatalysts in the polymerization of a wide range of organic monomers.[2] Aluminum hydride compounds have been demonstrated to be useful precursors for the preparation of organoalumoxanes[3] and aluminum chalcogenides.[4] Indeed, the aluminum hydride [$^{i\mathrm{Pr}}$LAlH$_2$] ($^{i\mathrm{Pr}}$L = HC[(CMe)N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2^-$)[4a] bearing the sterically encumbered β-diketiminate ligand $^{i\mathrm{Pr}}$L is easily transformed into the aluminum hydrogensulfide [$^{i\mathrm{Pr}}$LAl(SH)$_2$] upon reaction with elemental sulfur in the presence of a catalytic amount of P(NMe$_2$)$_3$.[4b] However, the preparation of the alumoxane hydroxide [{$^{i\mathrm{Pr}}$LAl(OH)}$_2$(μ-O)] requires an ammonia/toluene two-phase liquid system with [$^{i\mathrm{Pr}}$LAlI$_2$] as the starting material.[5a]

During our research with the sterically modified aluminum hydride [LAlH$_2$] (L = HC[(CMe)N(2,4,6-Me$_3$C$_6$H$_2$)]$_2^-$), we observed that this compound readily reacts with water, forming Al-O-Al moieties under very mild conditions. Herein, we describe the preparation of the unprecedented alumoxane hydride [{LAl(H)}$_2$(μ-O)] (**2**) and hydrogensulfide [{LAl(SH)}$_2$(μ-O)] (**3**), as well as the unique [{LAl(SH)}$_2$(μ-S)] (**5**) from the readily available aluminum hydride [LAlH$_2$] (**1**). To the best of our knowledge, **3** represents the first example of a structurally characterized alumoxane bearing terminal SH groups.

Reaction of LH in toluene with AlH$_3$·NMe$_3$ at room temperature yields **1** in 94% yield. Compound **1** reacts smoothly with one equivalent of water at ambient temperature to afford [{LAl(H)}$_2$(μ-O)] (**2**) in 90% yield (Scheme 1). The IR spectrum of **2** shows the Al–H valence vibration at 1799 cm^{-1}, while the mass spectrum exhibits the highest peak



Scheme 1. Formation of compounds **2**–**4**; Ar = 2,4,6-Me$_3$C$_6$H$_2$.

at [M^+–H], indicating the formation of the alumoxane hydride. The thermal stability of **2** and its unique structural arrangement make it an advantageous starting material for the preparation of alumoxanes containing aluminum atoms with terminal SH groups.

Compound **2** reacts cleanly in toluene with two equivalents of elemental sulfur to yield the first known alumoxane bearing two terminal SH groups, [{LAl(SH)}$_2$(μ-O)] (**3**; 85% yield). Furthermore, **2** reacts smoothly in toluene with two equivalents of water to produce the alumoxane hydroxide [{LAl(OH)}$_2$(μ-O)] (**4**; 82%). Compound **4** can also be obtained by the direct reaction of **1** with three equivalents of water at ambient temperature (73%).

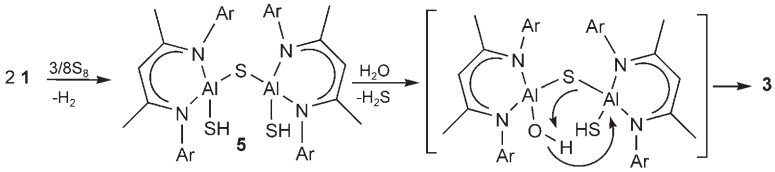
Compounds **2**–**4** are stable over a long period of time when stored under an inert atmosphere and are highly soluble in common organic solvents (benzene, toluene, CH_2Cl_2, THF) but insoluble in hexane and pentane. The facile hydrolysis of **1**, yielding alumoxanes **2** and **4**, contrasts significantly with the reaction conditions required for the preparation of the analogous [{$^{i\mathrm{Pr}}$LAl(OH)}$_2$(μ-O)].[5]

Treatment of **1** with 1.5 equivalents of elemental sulfur in toluene at ambient temperature gives [{LAl(SH)}$_2$(μ-S)] (**5**) in 75% yield (Scheme 2). No evidence was found to suggest the formation of the aluminum hydrogensulfide [LAl(SH)$_2$]. Moreover, the presence of P(NMe$_2$)$_3$ is not required for the formation of the terminal SH groups in **3** and **5**. However, the addition of a catalytic amount of P(NMe$_2$)$_3$ at ambient temperature substantially decreases the yield of **5** (36%),

[*] S. González-Gallardo, Dr. V. Jancik, Prof. Dr. R. Cea-Olivares, Dr. R. A. Toscano, Dr. M. Moya-Cabrera
Instituto de Química
Universidad Nacional Autónoma de México
Circuito Exterior
Ciudad Universitaria, México 04510 (Mexico)
Fax: (+52) 55-5616-2217
E-mail: monica.moya@correo.unam.mx

[**] We thank the UNAM (PAPIIT grant 209706) for financial support and T. Flores for technical assistance. V.J. acknowledges the UNAM for his postdoctoral fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 2. Formation of **5** and its hydrolysis to **3**; Ar = 2,4,6-$Me_3C_6H_2$.

giving insoluble [LAl(μ-S)$_2$AlL] as the only by-product. Compound **5** is air- and moisture-sensitive and reacts readily with one equivalent of water with subsequent elimination of H_2S to produce **3**.

Colorless single crystals of **1** (see the Supporting Information), **3** (Figure 1), **4** (Figure 2), and **5** (Figure 3) were grown from their saturated toluene solutions at −32 °C within several days.[6] Compound **3** crystallizes in the monoclinic

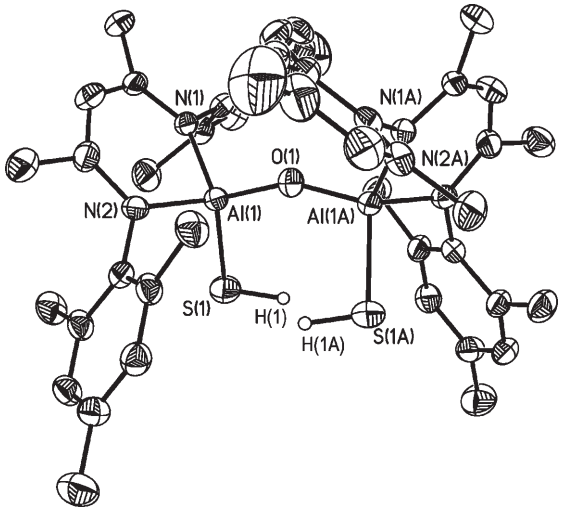


Figure 1. Molecular structure of **3**; hydrogen atoms (except SH) and solvent atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.687(1), Al(1)-S(1) 2.231(1), Al(1)-N(1) 1.895(3), Al(1)-N(2) 1.894(3), S(1)-H(1) 1.21(1); Al(1)-O(1)-Al(1A) 155.2(2), O(1)-Al(1)-S(1) 111.0(1), N(1)-Al(1)-N(2) 96.6(1), Al(1)-S(1)-H(1) 95(3).

space group *I*2/*a* with one half of the molecule of **3** and one molecule of toluene in the asymmetric unit, whereas compound **4** crystallizes in the monoclinic space group $P2_1/n$ as a nonmerohedral twin with one molecule of **4** in the asymmetric unit. Compound **5** crystallizes in the orthorhombic space group $Pna2_1$ with one molecule in the asymmetric unit. Unfortunately, we were not able to crystallize pure **5**, thus data for **5** which contains about 25% of **4** were used.

In all three compounds (**3**–**5**), the aluminum center possesses a distorted tetrahedral geometry and is coordinated to two nitrogen atoms from the β-diketiminato ligand. The remaining two coordination sites are occupied by sulfur and oxygen atoms (**3**), two oxygen atoms (**4**), or two sulfur atoms (**5**). The Al-O-Al angle in **3** (155.2°), is more obtuse than that in **4** (136.8°) and those found in [{$^{i\mathrm{Pr}}$LAl(OH)}$_2$(μ-O)] (112.3°) and [(μ-O){$^{i\mathrm{Pr}}$LAl(μ-O)}$_2$(AlMe)] (125.7°),[5a] but significantly smaller than those reported for [{(tBu)$_2$Al(3,5-Me$_2$py)}$_2$(μ-O)] (180°; 3,5-Me$_2$py = 3,5-dimethylpyridine)[5b] and for [{(tBu)$_2$Al[NH(Me)CH$_2$CH$_2$NMe$_2$]}$_2$(μ-O)](180°).[5c] The Al–(μ-O) distances in **3** (1.687 Å) are only slightly longer than those in **4** (1.691, 1.701 Å), which are comparable to those in [{$^{i\mathrm{Pr}}$LAl(OH)}$_2$(μ-O)] (1.698, 1.694 Å), but shorter than that reported for [(μ-O){$^{i\mathrm{Pr}}$LAl(μ-O)}$_2$-(AlMe)] (av 1.715 Å).[5a] The Al-S-Al angle in **5**

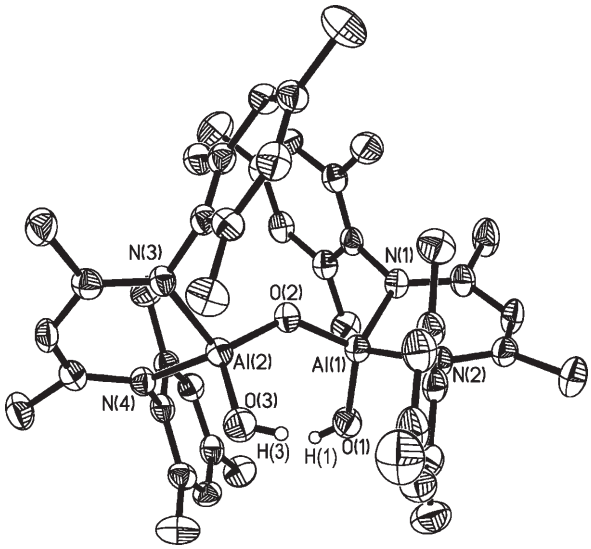


Figure 2. Molecular structure of **4**; hydrogen atoms except OH are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.707(2), Al(1)-O(2) 1.691(2), Al(2)-O(2) 1.701(2), Al(2)-O(3) 1.710(2), Al(1)-N(1) 1.900(2), Al(1)-N(2) 1.889(2), Al(2)-N(3) 1.890(2), Al(2)-N(4) 1.896(2); Al(1)-O(2)-Al(2) 136.8(1), O(1)-Al(1)-O(2) 118.0(1), O(2)-Al(1)-O(3) 117.6(1), N(1)-Al(1)-N(2) 95.4(1), N(3)-Al(1)-N(4) 95.2(1).

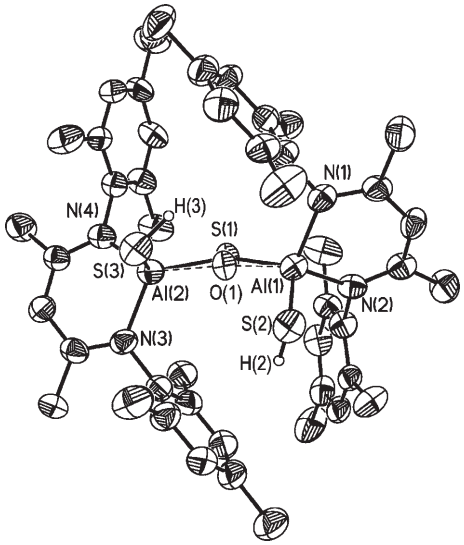


Figure 3. Molecular structure of **5**; hydrogen atoms except SH are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Al(1)-S(1) 2.150(3), Al(1)-S(2) 2.206(2), Al(2)-S(1) 2.163(3), Al(2)-S(3) 2.214(2), Al(1)-S(1)-Al(2) 110.8(1); S1(1)-Al(1)-S(2) 120.7(1), S(1)-Al(2)-S(3) 119.5(1), N(1)-Al(1)-N(2) 96.9(2), N(3)-Al(1)-N(4) 96.4(2).

(110.8°) is less obtuse than the Al-O-Al angles in compounds **3** and **4**, most probably because of the longer Al–(μ-S) distances (2.150, 2.163 Å) and the resulting larger separation between the organic ligands. The Al–S(H) bond length in **3** (2.231 Å) is larger than the terminal Al–S(H) bond lengths in **5** (2.206, 2.214 Å). The above-mentioned Al–(μ-S) distances for **4** are shorter than those reported for [$^{i\mathrm{Pr}}$LAl(μ-S)$_2$Al$^{i\mathrm{Pr}}$L] (2.237, 2.245 Å),[7a] [$^{i\mathrm{Pr}}$LAl(μ-S$_3$)$_2$Al$^{i\mathrm{Pr}}$L] (2.223, 2.248 Å),[7b] and [$^{i\mathrm{Pr}}$LAl(μ-S)(μ-C(SiMe$_3$)=C=C(SiMe$_3$)S)Al$^{i\mathrm{Pr}}$L] (2.230, 2.219 Å).[7c] In all three compounds, the XH groups (X = O, S) from the HX^1-Al^1-X^2-Al^2-X^{3}H moiety are in a *cis* conformation with an angle between the X^1–Al^1–X^2 and X^2-Al^2-X^3 planes of 58° (**3**), 72° (**4**), and 50° (**5**).

The facile synthesis of **2** allows access to the preparation of unprecedented molecular alumoxanes bearing two different Group 16 atoms covalently bonded to the same aluminum center, as well as to the modified alumoxane hydroxide [{LAl(OH)}$_2$(μ-O)], on a large scale. Furthermore, the *cis* conformation of the terminal SH and OH groups makes these compounds ideal precursors for further synthesis of heterometallic compounds. The preparation of such multimetallic systems is the subject of ongoing research.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2) by using Schlenk-line and glovebox techniques.

1: A solution of AlH$_3$·NMe$_3$ (1.0 M, 70 mL, 70 mmol) in toluene was slowly added to a solution of LH (20.00 g, 60 mmol) in toluene (50 mL). The reaction mixture was stirred for 24 h, after which any insoluble material was filtered off and the volatiles were removed under vacuum. An oily residue remained, which solidified upon treatment with cold hexane (40 mL). After filtration and drying under vacuum, **1** was obtained as a white powder. Yield: 20.40 g (94%); m.p. 200 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.47$ (s, 6H, CH$_3$), 2.09 (s, 6H, *p*-ArCH$_3$), 2.32 (s, 12H, *o*-ArCH$_3$), 4.79 (s, 1H, γ-CH), 6.74 ppm (m, 4H, *m*-ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 25 °C): $\delta = 18.2$ (CH$_3$), 20.6 (*p*-ArCH$_3$), 21.8 (*o*-ArCH$_3$), 95.5 (γ-CH), 129.7, 133.3, 135.6, 139.5 (*i*-, *o*-, *m*-, *p*-C(Ar)), 169.4 ppm (C=N); IR (CsI): $\tilde{\nu} = 1815$, 1775 cm^{-1} (s, AlH$_2$); EI-MS (70 eV): *m*/*z* (%): 361 (100) [M^+–H]. Elemental analysis (%) calcd for $C_{23}H_{31}AlN_2$ (362.49): C 76.2, H 8.6, N 7.7; found: C 75.9, H 8.6, N 7.5.

2: A solution of H_2O (1.0 M, 6.9 mL, 6.9 mmol) in THF was slowly added to a solution of **1** (5.00 g, 13.8 mmol) in toluene (30 mL) at room temperature. The reaction mixture was stirred for 12 h and filtered. All volatiles were removed under vacuum to leave a viscous white residue, which was treated with hexane (10 mL). After filtration and drying under vacuum, **2** was obtained as a white powder. Yield: 4.59 g (90%); m.p. 215 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.56$ (s, 12H, CH$_3$), 2.09 (s, 12H, *p*-ArCH$_3$), 2.24–2.27 (s, 24H, *o*-ArCH$_3$), 3.99 (br, 2H, AlH), 4.95 (s, 2H, γ-CH), 6.72–6.76 ppm (m, 8H, *m*-ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 25 °C): $\delta = 18.8$ (CH$_3$), 20.7 (*p*-ArCH$_3$), 22.2 (*o*-ArCH$_3$), 95.9 (γ-CH), 129.4, 132.8, 134.7, 140.9 (*i*-, *o*-, *m*-, *p*-C(Ar)), 168.1 ppm (C=N); IR (CsI): $\tilde{\nu} = 1799$ cm^{-1} (m, AlH); EI-MS (70 eV): *m*/*z* (%): 738 (100) [M^+–H]. Elemental analysis (%) calcd for $C_{46}H_{60}Al_2N_4O$ (738.96): C 74.8, H 8.2, N 7.6; found: C 74.0, H 8.1, N 7.5.

3: Compound **2** (2.77 g, 3.75 mmol) and elemental sulfur (0.30 g, 9.38 mmol) were dissolved in toluene (30 mL) at ambient temperature. The reaction mixture was stirred for 5 h and filtered to remove the insoluble material. All volatiles were evaporated under vacuum to leave a white residue, which was washed with hexane (10 mL). After filtration and drying under vacuum, **3** was obtained as a white powder. Yield: 2.56 g (85%); m.p. 150 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -1.47$ (s, 2H, AlSH), 1.46 (s, 12H, CH$_3$), 2.06–2.15 (s, 24H, *o*-ArCH$_3$), 2.35 (s, 12H, *p*-ArCH$_3$), 4.92 (s, 2H, γ-CH), 6.76–6.83 ppm (m, 8H, *m*-ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 25 °C): $\delta = 19.4$ (CH$_3$), 20.7 (*p*-ArCH$_3$), 22.5 (*o*-ArCH$_3$), 96.9 (γ-CH), 129.3, 134.0, 135.1, 140.7 (*i*-, *o*-, *m*-, *p*-C(Ar)), 169.3 ppm (C=N); IR (CsI): $\tilde{\nu} = 2561$ cm^{-1} (w, AlS–H); EI-MS (70 eV): *m*/*z* (%): 802 (20) [M^+–H]. Elemental analysis (%) calcd for $C_{46}H_{60}Al_2N_4OS_2$ (803.09): C 68.8, H 7.5, N 7.0; found: C 69.1, H 7.7, N 6.9.

4: A solution of H_2O (1.0 M, 2.8 mL, 2.8 mmol) in THF was slowly added to a solution of **2** (2.10 g, 2.8 mmol) in toluene (30 mL) at room temperature. The reaction mixture was stirred for 12 h and filtered. All volatiles were removed under vacuum to leave a white residue, which was treated with hexane (10 mL). After filtration and drying under vacuum, **4** was obtained as a white powder. Yield: 1.77 g (82%); m.p. 160 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -0.64$ (s, 2H, AlOH), 1.43 (s, 12H, CH$_3$), 1.89 (s, 12H, *p*-ArCH$_3$), 2.22 (s, 12H, *o*-ArCH$_3$), 2.45 (s, 12H, *o*-ArCH$_3$), 4.82 (s, 2H, γ-CH), 6.81–6.85 ppm (m, 8H, *m*-ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 25 °C): $\delta = 18.8$ (CH$_3$), 20.8 (*p*-ArCH$_3$), 22.0 (*o*-ArCH$_3$), 95.8 (γ-CH), 127.8, 129.1, 134.5, 141.3 (*i*-, *o*-, *m*-, *p*-C(Ar)), 168.4 ppm (C=N); IR (CsI): $\tilde{\nu} = 3650$ cm^{-1} (m, AlO–H); EI-MS (70 eV): *m*/*z* (%): 770 (100) [M^+–H]. Elemental analysis (%) calcd for $C_{46}H_{60}Al_2N_4O_3$ (770.96): C 71.7, H 7.8, N 7.3; found: C 71.2, H 7.6, N 7.0.

5: Compound **1** (3.00 g, 8.29 mmol) and elemental sulfur (0.66 g, 20.7 mmol) were dissolved in toluene (30 mL) at ambient temperature. The reaction mixture was stirred for 4 h and filtered. All volatiles were removed under vacuum, leaving a white residue, which was treated with hexane (10 mL). After filtration and drying under vacuum, **5** was obtained as a white powder. Yield: 2.48 g (75%); m.p. 188 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -0.81$ (s, 2H, AlSH), 1.42 (s, 12H, CH$_3$), 2.07 (s, 12H, *p*-ArCH$_3$), 2.36 (s, 24H, *o*-ArCH$_3$), 4.86 (s, 2H, γ-CH), 6.76 ppm (m, 8H, *m*-ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 25 °C): $\delta = 18.7$ (CH$_3$), 20.6 (*p*-ArCH$_3$), 22.6 (*o*-ArCH$_3$), 97.7 (γ-CH), 129.9, 133.6, 135.9, 139.0 (*i*-, *o*-, *m*-, *p*-C(Ar)), 170.8 ppm (C=N); IR (CsI): $\tilde{\nu} = 2559$ cm^{-1} (m, AlS–H); EI-MS (70 eV): *m*/*z* (%): 819 (13) [M^+]. Elemental analysis (%) calcd for $C_{46}H_{60}Al_2N_4S_3$ (819.15): C 67.4, H 7.4, N 6.8; found: C 66.9, H 7.1, N 6.7.

Received: December 15, 2006
Published online: March 20, 2007

Keywords: aluminum · alumoxanes · hydrides · hydrogensulfides · hydrolysis

[1] a) S. Pasynkiewicz, *Polyhedron* **1990**, *9*, 429–453, and references therein; b) M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **1993**, *115*, 4971–4984; c) C. J. Harlan, M. R. Mason, A. R. Barron, *Organometallics* **1994**, *13*, 2957–2969; d) H. W. Roesky, M. G. Walawalkar, R. Murugavel, *Acc. Chem. Res.* **2001**, *34*, 201–211, and references therein; e) J. Lewinski, W. Bury, I. Justyniak, J. Lipkowski, *Angew. Chem.* **2006**, *118*, 2938–2941; *Angew. Chem. Int. Ed.* **2006**, *45*, 2872–2875; f) L. B. Jerzykiewicz, J. Utko, P. Sobota, *Organometallics* **2006**, *25*, 4924–4926; g) C. C. Landry, C. J. Harlan, S. G. Bott, A. R. Barron, *Angew. Chem.* **1995**, *107*, 1315–1317; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1201–1202.

[2] a) H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99–149; b) T. L. Feng, P. L. Gurian, M. D. Healy, A. R. Barron, *Inorg. Chem.* **1990**, *29*, 408–411; c) C. J. Harlan, M. R. Mason, A. R. Barron, *Organometallics* **1994**, *13*, 2957–2969; d) Y. Koide, S. G. Bott, A. R. Barron, *Organometallics* **1996**, *15*, 2213–2226; e) M. Galimberti, M. Destro, O. Fusco, F. Piemontesi, I. Camurati, *Macromolecules* **1999**, *32*, 258–263; f) W. Kaminsky, *Catal. Today* **2000**, *62*, 23–34; g) M. Watanabi, C. N. McMahon, C. J. Harlan, A. R. Barron, *Organometallics* **2001**, *20*, 460–467.

[3] a) W. Zheng, N. C. Mosch-Zanetti, H. W. Roesky, M. Noltemeyer, M. Hewitt, H.-G. Schmidt, T. R. Schneider, *Angew. Chem.* **2000**, *112*, 4446 – 4449; *Angew. Chem. Int. Ed.* **2000**, *39*, 4276 – 4279; b) Y. Peng, G. Bai, H. Fan, D. Vidovic, H. W. Roesky, J. Magull, *Inorg. Chem.* **2004**, *43*, 1217 – 1219; c) R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 8387 – 8388.

[4] a) C. Cui, H. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 1885 – 1887; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815 – 1817; b) V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2003**, *125*, 1452 – 1453.

[5] a) G. Bai, H. W. Roesky, J. Li, M. Noltemeyer, H.-G. Schmidt, *Angew. Chem.* **2003**, *115*, 5660 – 5664; *Angew. Chem. Int. Ed.* **2003**, *42*, 5502 – 5506; b) L. G. van Poppel, S. G. Bott, A. R. Barron, *J. Chem. Crystallogr.* **2001**, *31*, 417 – 420; c) C. N. McMahon, A. R. Barron, *J. Chem. Soc. Dalton Trans.* **1998**, 3703 – 3704.

[6] a) Crystal data for **1**: $C_{23}H_{31}AlN_2$ (362.48), monoclinic, space group $P2_1/n$, $a = 7.377(2)$, $b = 24.346(4)$, $c = 12.303(3)$ Å, $\beta = 96.09(3)°$, $V = 2197(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.096$ g cm^{-3}, $F(000) = 784$, $\lambda = 0.71073$ Å, $T = 294(2)$ K, $\mu(Mo_{K\alpha}) = 0.101$ mm^{-1}. Of the 18099 measured reflections, 3999 were independent ($R_{int} = 0.0314$). The final refinements converged at $R_1 = 0.0462$ for $I > 2\sigma(I)$, $wR_2 = 0.1331$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.203/+0.223$ e Å^{-3}. b) Crystal data for **3**·toluene: $C_{60}H_{76}Al_2N_4OS_2$ (987.33), monoclinic, space group $I2/a$, $a = 22.857(5)$, $b = 8.707(2)$, $c = 28.967(5)$ Å, $\beta = 96.22(3)°$, $V = 5731(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.144$ g cm^{-3}, $F(000) = 2120$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 0.165$ mm^{-1}. Of the 14094 measured reflections, 5046 were independent ($R_{int} = 0.0730$). The final refinements converged at $R_1 = 0.0599$ for $I > 2\sigma(I)$, $wR_2 = 0.1650$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.214/+0.389$ e Å^{-3}. c) Crystal data for **4**: $C_{46}H_{60}Al_2N_4O_3$ (770.94), monoclinic, space group $P2_1/n$, $a = 11.248(3)$, $b = 21.112(4)$, $c = 18.346(3)$ Å, $\beta = 93.23(3)°$, $V = 4350(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.177$ g cm^{-3}, $F(000) = 1656$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 0.110$ mm^{-1}. Of the 7990 measured reflections, 7990 were independent ($R_{int} = 0.0478$). The final refinements converged at $R_1 = 0.0528$ for $I > 2\sigma(I)$, $wR_2 = 0.1028$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.302/+0.283$ e Å^{-3}. d) Crystal data for **5**: $C_{46}H_{60}Al_2N_4O_{0.25}S_{2.75}$ (815.10), orthorhombic, space group $Pna2_1$, $a = 20.794(3)$, $b = 9.525(2)$, $c = 23.442(4)$ Å, $V = 4643(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.166$ g cm^{-3}, $F(000) = 1744$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 0.222$ mm^{-1}. Flack parameter was refined to 0.05(12). Of the 13896 measured reflections, 6121 were independent ($R_{int} = 0.0740$). The final refinements converged at $R_1 = 0.0614$ for $I > 2\sigma(I)$, $wR_2 = 0.1299$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.212/+0.276$ e Å^{-3}. Data for the structures of **1** and **3–5** were measured on a Bruker-APEX three-circle diffractometer. Intensity measurements were performed on rapidly cooled crystals ($0.50 \times 0.20 \times 0.17$ mm^3) in the range $3.34° \le 2\theta \le 50.72°$ (**1**), ($0.34 \times 0.21 \times 0.18$ mm^3) in the range $2.82° \le 2\theta \le 50.18°$ (**3**), ($0.18 \times 0.12 \times 0.12$ mm^3) in the range $2.94° \le 2\theta \le 50.86°$ (**4**), and ($0.27 \times 0.25 \times 0.09$ mm^3) in the range $3.48° \le \theta \le 50.08°$ (**5**). The structures were solved by direct methods (SHELXS-97)[8] and refined against all data by full-matrix least squares on F^2.[9] The hydrogen atoms from the OH and SH groups were localized from the difference electron-density map and refined isotropically. The twin law for **4** was determined as a 180° rotation around the real axis [101]. CCDC-630404–630407 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] a) V. Jancik, M. M. Moya-Cabrera, H. W. Roesky, R. Herbst-Irmer, D. Neculai, A. M. Neculai, M. Noltemeyer, H.-G. Schmidt, *Eur. J. Inorg. Chem.* **2004**, 3508 – 3512; b) Y. Peng, H. Fan, V. Jancik, H. W. Roesky, R. Herbst-Irmer, *Angew. Chem.* **2004**, *116*, 6316 – 6318; *Angew. Chem. Int. Ed.* **2004**, *43*, 6190 – 6192; c) H. Zhu, J. Chai, Q. Ma, V. Jancik, H. W. Roesky, H. Fan, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2004**, *126*, 10194 – 10195.

[8] SHELXS-97, Program for Structure Solution: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467 – 473.

[9] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, **1997**.

