

Electronic supplementary information

Experimental Section

General: All manipulations were carried out under dry argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. NMR spectra were recorded in benzene- d_6 at ambient probe temperature on a Bruker Avance I (^1H 400.13, ^{13}C 100.6 MHz, ^{15}N 40.54 MHz) or Avance III spectrometer (^1H , 400.03; ^{13}C , 100.59) and referenced internally to residual solvent resonances (chemical shift data in δ) or CH_3NO_2 (^{15}N). ^{13}C NMR spectra were all proton-decoupled. The chemical shifts were assigned on the basis of homo- and heteronuclear 2D NMR experiments (COSY, HSQC, HMBC, ROESY) and the labels in brackets refer to the labels used in the crystal structure determination (Fig. 1). In the case of hydrogen atoms the label of the associated carbon or nitrogen atoms was chosen instead. Elemental analysis was determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR-spectra were recorded as Nujol mull between CsI plates on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra on a Varian mass spectrometer. The sesquihydrazide **1** was synthesized according to a literature procedure (W. Uhl, T. Abel, A. Hepp, S. Grimme and M. Steinmetz, *Eur. J. Inorg. Chem.* 2008, 543 – 551).

Synthesis of compound 2

A solution of dry CH_3OH (0.027 g, 0.034 mL, 0.84 mmol) in toluene (5 mL) was added at room temperature dropwise to a solution of $\text{Al}[(\text{NH-NHMe})_2\text{AlMe}_2]_3$ (**1**, 0.78 g, 1.67 mmol) in toluene (15 mL). The mixture was then heated under reflux conditions for three days. The solvent was removed *in vacuo*, the solid residue was treated with diisopropyl ether (10 mL), the solvent was decanted. The remaining colourless solid was recrystallised from diethyl ether (5 mL) at $-28\text{ }^\circ\text{C}$ to give colourless crystals of compound **2** (0.18 g, 39%). Melting point (de-

comp.): 182 °C. ¹H NMR (400.03 MHz, C₆D₆, 298 K): δ 3.06 (s, OMe, C10, 3H), 2.92 (s, NH, N6, 1H), 2.79 (s, NH, N4, 1H), 2.63 (s, NMe, C701, 3H), 2.50 (s, NMe, C501, 3H), 2.21 (s, NMe, C301, 3H), 2.13 (s, NMe, C101, 3H), 1.97 (s, NH, N2, 1H), -0.35 (s, AlMe, C51, 3H), -0.43 (s, AlMe, C31, 3H), -0.44 (s, AlMe, C72, 3H), -0.45 (s, AlMe, C52, 3H), -0.51 (s, AlMe, C7, 3H), -0.52 (s, AlMe, C11 and C61, 6H), -0.59 (s, AlMe, C12, 3H), -0.61 (s, AlMe, C21), -0.64 (s, AlMe, C62, 3H), -0.69 (s, AlMe, C41, 3H). ¹³C NMR (100.59 MHz, C₆D₆, 298 K): δ 48.7 (OMe, C10), 42.9 (NMe, C701), 40.9 (NMe, C501), 40.3 (NMe, C301), 39.7 (NMe, C101), -3.4 (br, AlMe, C31), -3.8 (br, AlMe, C51), -6.3 (br, AlMe, C7), -7.6 (br, AlMe, C11 and C62), -7.8 (br, AlMe, C72), -8.7 (br, AlMe, C52), -11.4 (br, AlMe, C41 and C61), -11.8 (br, AlMe, C12), -15.9 (br, AlMe, C21). ¹⁵N NMR (40.54 MHz, C₆D₆, 298 K): δ -506 (N6), -507 (N2), -509 (N4), -533 (N7), -544 (N5), -545 (N1), -547 (N3), N8 not unambiguously determined. IR-spectroscopy (cm⁻¹): 3275 w, 3260 m, 3229 w ν(NH); 2924 vs, 2851 vs (paraffin); 1578 vs, 1558 s δ(NH); 1462 vs, 1377 s (paraffin); 1339 w, 1319 w δ(CH₃); 1207 vs, 1157 w, 1045 s, 976 w, 903 w, 898 s, 826 m, 799 vw, 772 m ν(C-N), ν(C-O); 721 m (paraffin); 691 s, 683 s, 613 vw, 583 w, 556 w, 529 w, 509 w, 482 w, 436 w 413 w ν(AlC), ν(Al-N), ν(Al-O). MS (EI, 20 eV, 333 K): *m/z* (%): 560 (2) [M⁺], 545 (59) [M⁺ – Me], 529 (50) [M⁺ – OMe], 488 (17) [M⁺ – AlMe₃], 472 (100) [M⁺ – Me₂AlOMe], 457 (88) [M⁺ – Me – Me₂AlOMe]. Anal calcd for C₁₆H₅₁Al₇N₈O (560.6), %: C 34.3; H 9.2; N 20.0. Found, %: C 33.6; H 9.0; N 18.9.

X-ray Crystallography

Crystals suitable for X-ray crystallography were obtained by recrystallisation from diethyl ether. Intensity data was collected on a Bruker APEX II diffractometer with monochromated Mo K_α radiation. The collection method involved ω-scans. Data reduction was carried out using the program *SAINTE* [SAINTE+; Version 6.02 (includes XPREP and SADABS), Bruker

AXS INC., Madison, Wisconsin, USA, 1999; b) G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996]. The crystal structures were solved by direct methods using *SHELXTL*[(a) *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison, WI, 1990; b) G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Structures; Universität Göttingen, Germany, 1997]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using *SHELXTL*. Hydrogen atoms (except those bound to nitrogen) were positioned geometrically and allowed to ride on their respective parent atoms.

Crystal data for compound 2

$C_{16}H_{51}Al_7N_8O$, $M_r = 560.51$, colourless blocks, 0.25 x 0.15 x 0.11 mm, monoclinic space group $P2_1/n$, $a = 10.2584(3)$, $b = 29.8067(9)$, $c = 10.6366(3)$ Å, $\beta = 102.940(1)^\circ$, $V = 3.1698(2)$ nm³, $Z = 4$, $\rho_{\text{calc.}} = 1.175$ g cm⁻³, $\mu = 0.253$ mm⁻¹, $F(000) = 1208$, $T = 153(2)$ K, $R_1 = 0.0394$, $wR_2 = 0.1090$, 8885 independent reflections [$2\theta \leq 59.20^\circ$; $R(\text{int}) = 0.0383$], 6996 reflections $I > 2\sigma(I)$, 317 parameters.