

A Dimeric Aluminum Hydroxide Supported by a New Disiloxide Ligand

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General procedure. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and Glove Box techniques. THF, THF-D₈, diethyl ether, heptanes and pentanes were distilled under argon from alkali metals prior to use. Toluene-D₈, and Benzene-D₆ were dried over activated molecular sieves and stored in the glove box. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 500 IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

3,6-Dichloro-1,1,1,2,7,8,8,8-octamethyl-2,7-bis(trimethylsilyl)-3,6-bis[1',2',2',2'-tetramethyl-1'-trimethylsilyl-disilanyl]-1,2,3,6,7,8-hexasila-octane (1). In a Schlenk flask with magnetic stirrer were placed rapidly KOBu^t (4.3 g, 38.0 mmol) and MeSi(SiMe₃)₃ (10 g, 38.0 mol). The flask was evaporated and refilled with argon three times and THF (250 mL) was added. After being stirred overnight, the solvent was replaced by pentanes (200 mL) and the resulting suspension was cooled to -78°C. Then, Cl₃Si-CH₂-CH₂-SiCl₃ (2.97 g, 9.99 mol) was added, stirring was continued for 30 min at -78°C and the mixture was allowed to warm up to room temperature within 2 hours. The reaction mixture was filtered, and the solution was concentrated and dried under vacuum (10⁻² mbar, 150°C) to remove all volatiles. Crystallization of the oily residue from heptanes in a freezer afforded 6.1 g (70%) of the title compound. – M.p. 129-130°C. - ¹H-NMR (CDCl₃, 250 MHz): δ = 1.38 (s, CH₂, 4H), 0.27 (s, SiCH₃, 12 H), 0.21

(2s, Si(CH₃)₃, 72 H) ppm. - ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 15.9 (CH₂), 1.1, 0.8 (Si(CH₃)₃), -9.9 (SiCH₃) ppm. - ²⁹Si-NMR (CDCl₃, 59.6 MHz): δ = 35.5 (SiCl), -11.6, -12.6 (Si(CH₃)₃), 75.7 (SiCH₃) ppm. - MS (CI, m/z in %): 878 (9) [M⁺-Cl], 723 (96) [M⁺-Si(SiMe₃)₂Me], 441 (100) [ClSi[Si(SiMe₃)₂Me]₂⁺]. - Anal. calc. for C₃₀H₈₈Cl₂Si₁₄ (913.13): C, 39.46; H, 9.71; Cl, 7.77. Found: C, 39.33; H, 9.57; Cl, 7.69%.

3,6-Dihydroxy-1,1,1,2,7,8,8,8-octamethyl-2,7-bis(trimethylsilyl)-3,6-bis[1',2',2',2'-tetramethyl-1'-trimethylsilyl-disilanyl]-1,2,3,6,7,8-hexasila-octane (2). Compound **1** (2.0 g, 2.19 mmol) was dissolved in diethyl ether (40 mL) and an aqueous solution of NH₄(NH₂COO) (1 M, 4.4 mL, 4.38 mmol) and water (20 mL) were added. After being stirred vigorously at room temperature for 2 days, the organic layer was separated, dried with MgSO₄, filtered and evaporated to leave the title compound as a white solid. Analytical pure samples can be obtained by recrystallization from heptanes. – Yield 1.9 g (99%). - M.p. 110-111°C. - ¹H-NMR (C₆D₆, 250 MHz): δ = 1.52 (s, CH₂, 4 H), 1.39 (s, OH, 2 H), 0.41 (s, SiCH₃, 12 H), 0.34, 0.33 (2s, Si(CH₃)₃, 2 × 36 H) ppm. - ¹³C-NMR (C₆D₆, 75.5 MHz): δ = 15.3 (CH₂), 1.2, 1.1 (Si(CH₃)₃), -10.0 (SiCH₃) ppm. - ²⁹Si-NMR (C₆D₆, 59.6 MHz): δ = 30.3 (SiOH), -12.3, -11.6 (Si(CH₃)₃), -81.9 (SiCH₃) ppm. - MS (CI, m/z in %): 875 (89) [M⁺+1], 859 (100) [M⁺-Me], 685 (66) [M⁺-Si(SiMe₃)₂Me]. - Anal. calc. for C₃₀H₉₀O₂Si₁₄ (876.24): C, 41.12; H 10.35. Found: C, 40.92; H 10.38%. - IR (nujol): ν_{OH} = 3666 cm⁻¹ (non-assoc.).

[CH₂{Me(Me₃Si)₂Si}₂SiO]₂AlMe×THF (3). Compound **2** (0.4 g, 0.46 mmol) was dissolved in THF (15 mL) and cooled to -78°C. A 2 M solution of AlMe₃ (0.24 ml, 0.48 mmol) in n-heptane was slowly added, the mixture was stirred for 10 min at -78°C and allowed to warm to room temperature. Crystallization of a concentrated n-pentane solution in a freezer afforded the title compound as colorless crystals. Yield g 0.23 g (51%); Mp. 157-159°C. - ¹H-NMR (C₆D₆, 500 MHz): δ = 3.76 (m, THF, 4 H),

1.67 (br, CH₂, 4 H), 1.18 (m, THF, 4 H), 0.53, 0.42 (2s, SiCH₃, 2 × 6 H), 0.42, 0.42, 0.38, 0.36 (4s, Si(CH₃)₃, 4 × 18 H), -0.58 (s, AlCH₃, 3 H) ppm. - ¹³C-NMR (C₆D₆, 75.5 MHz): δ = 70.9 (THF CH₂CH₂O), 24.4 (THF CH₂CH₂O), 22.7 (CH₂), 1.3, 1.4, 1.5, 1.6 (Si(CH₃)₃), -8.5 (SiCH₃), -12.2 (AlCH₃) ppm. ²⁹Si-NMR (C₆D₆, 59.6 MHz): δ = 16.3 (SiOAl), -11.8, -11.9, -12.3 -12.4 (Si(CH₃)₃), -85.2, -85.9 (SiCH₃) ppm. - Anal. calc. for C₃₅H₉₉O₃Si₁₄Al (988.34): C, 42.53; H 10.10. Found: C, 42.27; H 10.16%.

[CH₂{Me(Me₃Si)₂Si}₂SiO]₂AlOH (4). In a glove box, compound **3** (0.1 g, 0.1 mmol) was placed in a glass vial with a plastic screw cap and dissolved in dry heptanes (3 mL). After storage of the vial outside the glove box for ca. two days, colorless single crystals began to precipitate from the solution, which were collected, washed with dry hexanes and dried under vacuum. – Yield 0.030 g (32%); Mp. 190°C (dec.). - ¹H-NMR (THF-D₈, 500 MHz, 323 K): δ = 1.43 (br, CH₂, 4 H), 0.86 (s, OH, 2 H), 0.30, 0.28, 0.24, 0.22, 0.21 (5s, CH₃, 84 H) ppm. - ¹³C-NMR (THF-D₈, 75.5 MHz, 323 K): δ = 22.7 (CH₂), 2.2, 2.0, 1.6, 1.4 (Si(CH₃)₃), -8.5 (br, SiCH₃) ppm. - IR (nujol): ν_{OH} = 3683 cm⁻¹ (non-assoc.). - Anal. calc. for C₆₀H₁₇₈Al₂O₆Si₂₈ (1836.40 g/mol): C, 39.24; H 9.77. Found: C, 39.09; H 9.71%.

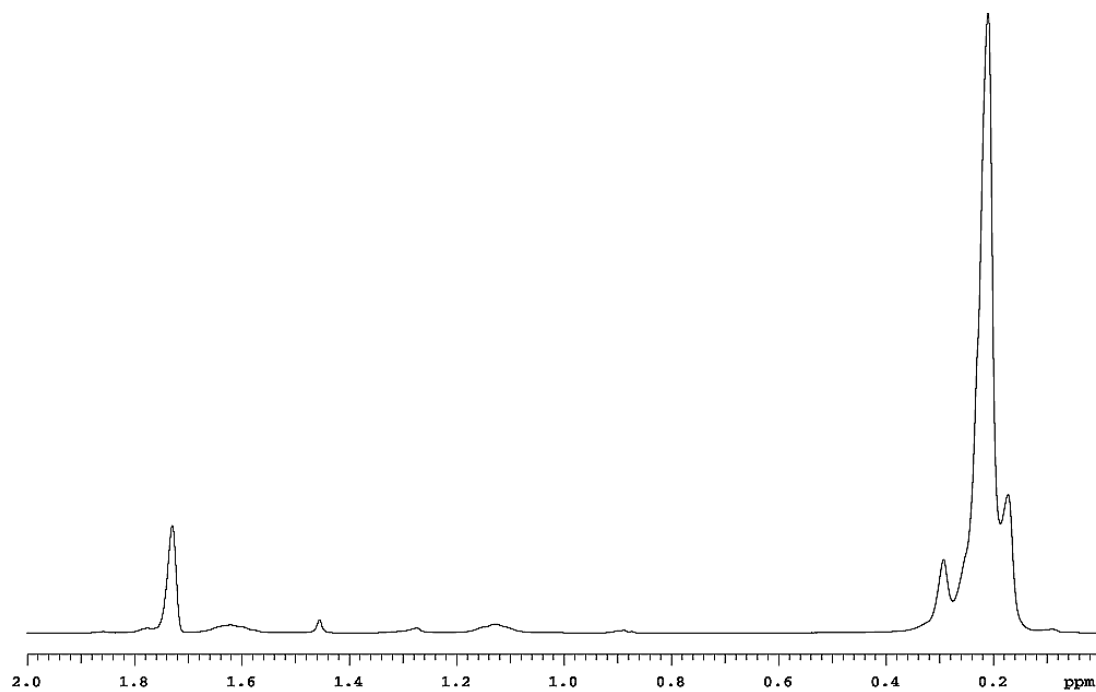


Figure 1. ¹H-NMR spectrum of **4** in THF-D₈ at 253 K.

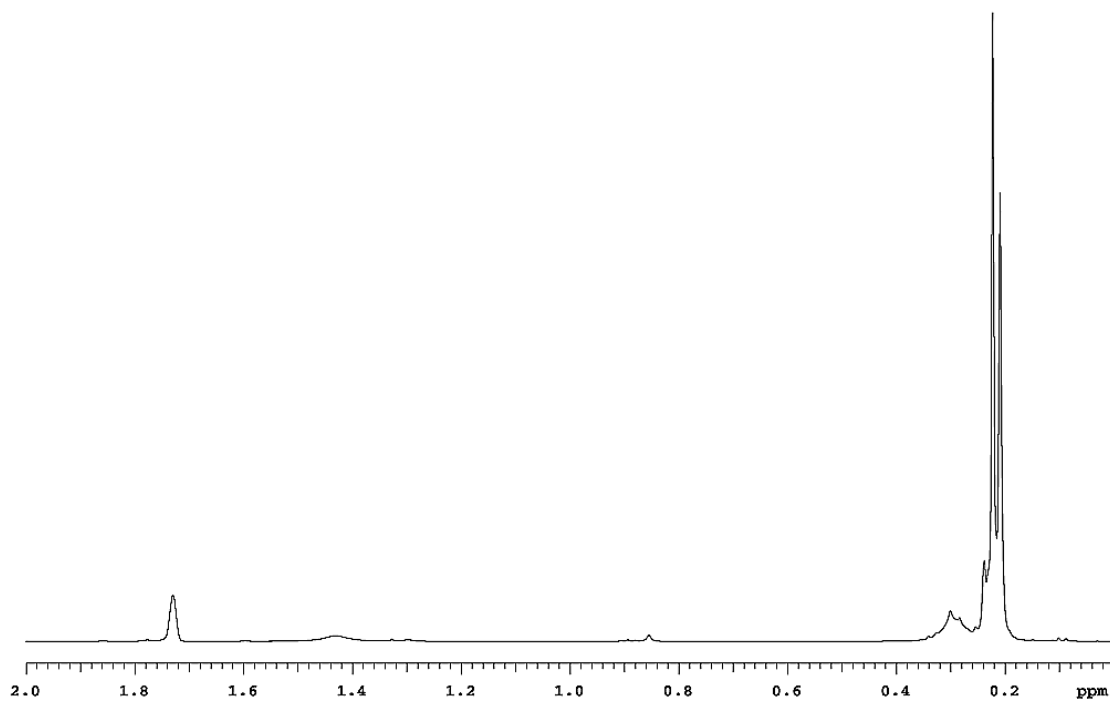


Figure 2. ¹H-NMR spectrum of **4** in THF-D₈ at 323 K.

X-Ray studies

X-ray crystallography: The crystals were fixed with a perfluoropolyether on a tip of a thin glass rod, respectively. Intensity data were then collected at 173(2) K on a Bruker X8 APEX-diffractometer with Mo-K α -radiation ($\lambda = 0.71073$ Å).

Crystal data of 2: Formula C₃₀H₉₀O₂Si₁₄, M = 876.28, space group triclinic, P-1, $a = 10.2513(6)$ Å, $b = 12.3844(7)$ Å, $c = 12.7960(7)$ Å, $\alpha = 83.126(2)^\circ$, $\beta = 73.021(2)^\circ$, $\gamma = 66.837(3)^\circ$, $V = 1428.45(14)$ Å³, $Z = 1$, $\rho_{\text{calc}} = 1.019$ g·cm⁻³, $\mu = 0.336$ mm⁻¹, 29353 measured reflections, 6149 independent reflections ($R_{\text{int}} = 0.045$), 223 parameters, $R1(F) = 0.0472$ for 4607 reflections with $I > 2\sigma(I)$ and $wR2(F^2) = 0.0721$ for all data.

Crystal data of 3: Formula C₃₅H₉₇AlO₃Si₁₄, M = 986.37, space group triclinic, P-1, $a = 12.5376(4)$ Å, $b = 14.6049(4)$ Å, $c = 19.3483(5)$ Å, $\alpha = 100.673(2)^\circ$, $\beta = 92.987(2)^\circ$, $\gamma = 107.535(1)^\circ$, $V = 3297.72(16)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 0.993$ g·cm⁻³, $\mu = 0.311$ mm⁻¹, 90530 measured reflections, 15009 independent reflections ($R_{\text{int}} = 0.0258$), 507 parameters, $R1(F) = 0.0314$ for reflections with $I > 2\sigma(I)$ and $wR2(F^2) = 0.0377$ for all data. The crystal contains pentane near the centre of inversion. However, the atom positions of the solvent could not be properly refined since there is no centre of inversion in pentane. Therefore the hkl was squeezed using the Platon program facilities.

Crystal data of 4: Formula C₆₀H₁₇₈Al₂O₆Si₂₈, M = 1834.49, space group monoclinic, P2₁/n, $a = 12.5114(9)$ Å, $b = 18.1996(10)$ Å, $c = 25.6540(16)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 95.602(2)^\circ$, $V = 5813.6(6)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.048$ g·cm⁻³, $\mu = 0.349$ mm⁻¹, 77499 measured reflections, 11059 independent reflections

($R_{\text{int}} = 0.0653$), 433 parameters, $R1(F) = 0.0694$ for 7045 reflections with $I > 2\sigma(I)$ and $wR2(F^2) = 0.1141$ for all data. There is quite a high residual electron density. However, attempts to allocate the peaks found in the difference map e.g. to disordered atoms failed.