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An Unusual Hydride-Bridged Aluminum Complex with a Square-Planar Tetraaluminum Core Stabilized by 2,5-Bis((Dimethylamino)methyl)pyrrole Ligands

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Summary: The novel hydride-bridged tetranuclear aluminum complex $\{AlH_2[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_3\}_2$ (**2**) *and the related deuterium complex* $\{AlD_2[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlD_3\}_2$ (**2-D**) *have been synthesized by reaction of* $AlCl_2[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]$ (**1**) *with 2 equiv of* $LiAlH_4$ *or* $LiAlD_4$*. The crystal structure of complex* **2-D** *reveals an unusual structure in which the aluminum atoms are in a square-planar arrangement. Reaction of* **2** *with 2 equiv of* H_2O *in diethyl ether affords the aluminum dihydride complex* $[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_2$ (**3**).

Metal hydrides[1] play an important role in catalytic reactions due to their highly reactive metal−hydrogen bonds. Among the metal hydrides, aluminum hydrides are well-known and the topic has been reviewed.[2] Hydride ions bound to aluminum atoms have been observed in either terminal or bridging positions in accord with varied auxiliary ligands in mononuclear,[3] dinuclear,[4] or trinuclear[5] aluminum hydride complexes. However, a hydride-bridged tetranuclear[6] aluminum complex has not been reported thus far. Currently, we are interested in using the tridentate substituted pyrrole[7] $[C_4H_3N(CH_2NMe_2)_2\text{-}2,5]$ as an auxiliary ligand in early-transition-metal[8] or group 13 metal complexes.[9] We now report the synthesis and structural characterization of a novel, hydride-bridged, tetranuclear aluminum complex, which contains bis((dimethylamino)-

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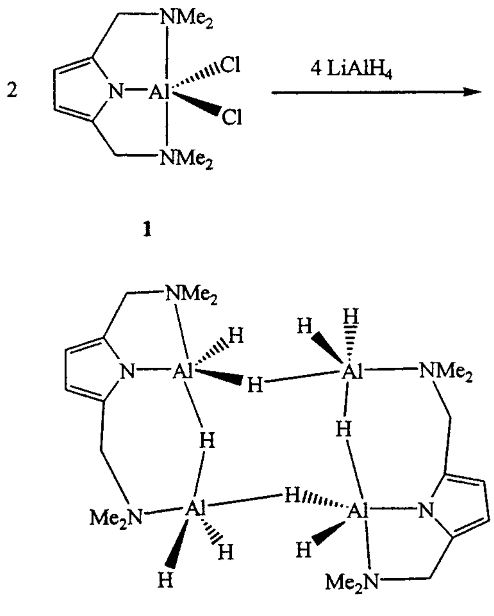
methyl)pyrrole as a ligand. The reaction of compound **1**[9] with 2 equiv of $LiAlH_4$ in diethyl ether at 0 °C generates compound **2**[10] in 84% yield (eq 1).



1

(1)

2

Compound **2** is highly air and moisture sensitive. However, it is stable for months if stored in a well-greased Schlenk flask in an inert-atmosphere glovebox. **2** is slightly soluble in diethyl ether and very soluble in methylene chloride. The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows resonances for the $[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]$ ligand at δ 6.00, 3.65, and 2.50. However, the Al−H and Al−H−Al hydride signals were not observed even at −60 °C in $CDCl_3$ using a 600 MHz NMR spectrometer. We suggest that rapid exchanging of the bridging hydride ligand with a low activation energy broadens the ^{1}H NMR signals. However, the solid-state IR spectrum supports the existence of Al−H terminal and Al−H−Al bridge bonds in compound **2**, as evidenced by the absorptions at 1826 and 1766 cm^{-1}. To confirm the structure of compound **2**, $LiAlD_4$ was used (instead of $LiAlH_4$) to yield compound **2-D**,[11] in which the terminal and bridging hydrides of **2** were replaced with deuterium atoms. The ^{1}H and ^{13}C NMR spectra of **2** and **2-D** exhibit the same resonance pattern with chemical shifts of very close magnitude. The Al−D stretching frequency of **2-D** is shifted to 1285 and 1332 cm^{-1} due to the isotope effects, which are calculated at 1249 and 1291 cm^{-1}.

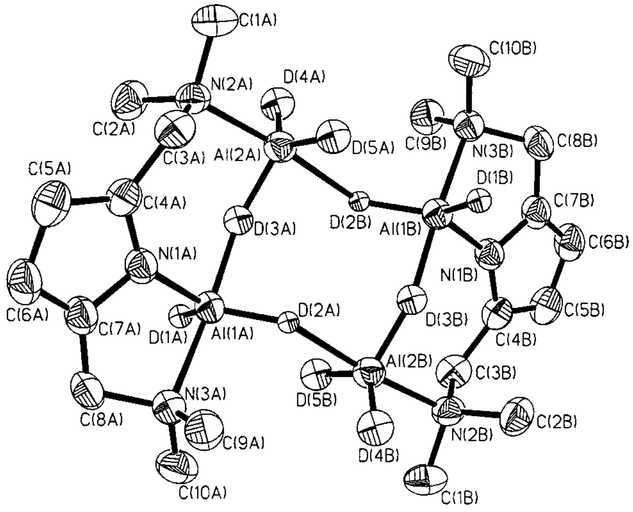


Figure 1. ORTEP plot of compound **2-D** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Al(1B)−D(2B) = 1.564(11), Al(1B)−D(3B) = 1.834(12), Al(1B)−D(1B) = 1.563(12), Al(2B)−D(2A) = 2.056(12), Al(2B)−D(4B) = 1.552(13), Al(2B)−D(5B) = 1.481(14); N(3B)−Al(1B)−D(3B) = 175.1(4), N(2B)−Al(2B)−D(2A) = 175.2(3).

Crystals of **2-D** suitable for crystallographic studies[12] were obtained from a diethyl ether/methylene chloride solvent mixture at −20 °C. The ORTEP plot and selected bond distances and angles of **2-D** are given in Figure 1. The electron density of deuterium atoms was found and refined isotropically. **2-D** exhibits a deuterium-bridged, square-planar, tetranuclear aluminum core with an eight-membered $(Al{-}D)_4$ ring. Further, the four aluminum atoms adopt trigonal-bipyramidal structures with dimethylamino and deuterium atoms taking the axial positions. The long distances of Al(1B)−Al(2A) and Al(1B)−Al(2B) at 3.31 and 3.35 Å, respectively, suggest little, if any, Al−Al interaction, and the four aluminum atoms construct a square plane. Interestingly, two types of bridging deuterium atoms are present in the eight-membered-ring core, with D(3A) and D(3B) adopting a approximately symmetrical mode with bond distances of Al(2A)−D(3A) and Al(1A)−D(3A) (likewise, Al(2B)−D(3B) and Al(1B)−D(3B)) at 1.614(12) and 1.834(12) Å, respectively. Conversely, the D(2A) and D(2B) atoms adopt an asymmetrical mode with the bond distances of Al(2B)−D(2A) and Al(1A)−D(2A) (likewise, Al(2A)−D(2B) and Al(1B)−D(2B)) at 2.056(12) and 1.564(11) Å, respectively. To our knowledge, compound **2-D** is the first example of a tetranuclear aluminum compound bridged with hydrogen or deuterium atoms.

The aluminum hydride complex **2** exhibits strong Lewis acidity, as evidenced by its moisture sensitivity. Preliminary results show that the reaction of **2** with 2 equiv of H_2O in diethyl ether affords the aluminum

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(10) **$\{AlH_2[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_3\}_2$ (2)**. A 100 mL Schlenk flask containing $AlCl_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$ (**1**;[9] 2.0 g, 7.1 mmol) was cooled to 0 °C, and 20 mL of diethyl ether was added. To the ether solution was added $LiAlH_4$ (0.542 g, 14.3 mmol) in 20 mL of diethyl ether dropwise with stirring. The reaction mixture was stirred at room temperature for 12 h after the addition was completed. The resulting suspension was filtered through Celite, and the residue was extracted with 15 mL of dichloromethane in three portions and filtered through Celite again. The combined filtrate was vacuum-dried to yield 1.43 g of white solid in 84% yield. ^{1}H NMR ($CDCl_3$): δ 6.00 (s, br, 4H, C_4H_2N), 3.75 (s, 8H, CH_2NMe_2), 2.50 (s, 24H, NMe_2). ^{13}C NMR ($CDCl_3$): 129.7 (s, C_{ipso}), 104.5 (d, J_{CH} = 167 Hz, CH), 103.8 (d, J_{CH} = 167 Hz, CH), 59.3 (t, J_{CH} = 139 Hz, CH_2), 46.9 (q, J_{CH} = 137 Hz, CH_3). IR (KBr) for Al−H: 1826, 1766 cm^{-1}. Anal. Calcd for $C_{20}H_{46}Al_4N_6$: C, 50.20; H, 9.69; N, 17.57. Found: C, 48.98, H, 9.27; N, 17.24.

(11) The same procedure as for **2** has been used, except $LiAlD_4$ was used instead of $LiAlH_4$.

(12) Crystallographic data for **2-D**: $C_{20}H_{36}Al_4D_{10}N_6$, M_r = 488.61, orthorhombic, space group *Pbca*, a = 10.3560(6) Å, b = 12.1443(8) Å, c = 22.0752(15) Å, V = 2776.3(3), Z = 4, T = 293(2) K, μ = 1.403 mm^{-1}, Mo Kα radiation, graphite monochromator. The data were processed using SADABS, and calculations were carried out with SHELXTL. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. All deuterium atoms were found and refined isotropically. The final R index for $I > 2\sigma(I)$ on 3197 independent reflections was R1 = 0.0307.

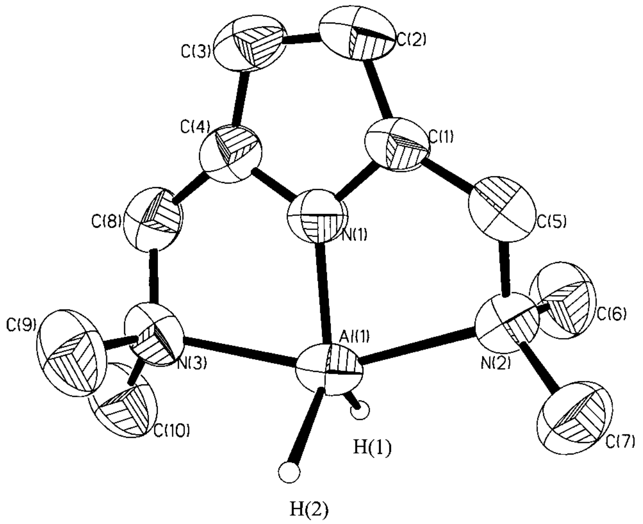
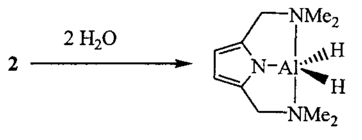


Figure 2. ORTEP plot of complex **3** with the thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Al(1)−N(1) = 1.8381(14), Al(1)−N(2) = 2.2264(15), Al(1)−N(3) = 2.2461(16), Al(1)−H(1) = 1.492(15), Al(1)−H(2) = 1.698(14); N(3)−Al(1)−N(2) = 154.65(6), N(3)−Al(1)−N(1) = 77.30(6), N(1)−Al(1)−N(2) = 77.35(6), N(1)−Al(1)−H(1) = 120.37(56), N(1)−Al(1)−H(2) = 122.17(41), H(1)−Al(1)−H(2) = 117.22(70).

dihydride complex $[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_2$ **3**[13] (eq 2). The ^1H NMR spectrum of **3** in C_6D_6 exhibits symmetrical resonances with the CH_2NMe_2 units at δ 2.17 and 3.32 as two sharp peaks. The hydride resonance of complex **3** was not observed in C_6D_6 at a 200 MHz spectrometer; however, the solid-state IR spectrum again supports the existence of Al−H(terminal), as evidenced by the absorptions at 1778 and 1797 cm^{-1}.



(2)

3

Moreover, the crystal structure of **3**[14] was determined and the ORTEP plot and selected bond distances and angles are given in Figure 2. The structure of **3** is very similar to that of **1**,[9] exhibiting a distorted-trigonal-bipyramidal structure with the two dimethylamino nitrogen atoms occupying axial positions. The Al(1)−H(1) bond distance, 1.492(15) Å, is similar to that of related terminal Al−H bonds; however, the Al(1)−H(2) bond distance, 1.698(14) Å, is somewhat longer than that of expected Al−H bonds.[2f,15] Related reactions of complexes **2** and **3** with small organic molecules are currently under investigation.

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Supporting Information Available: Complete data for the X-ray crystallographic structures of **2-D** and **3**, including tables of crystal data and data collection and refinement details, atomic coordinates, bond distances and angles, and anisotropic and isotropic displacement parameters and ORTEP drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) **$[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_2$ (3).** To a stirred diethyl ether solution of **2** (1.28 g, 2.7 mmol) at −78 °C was added 0.096 g (5.4 mmol) of H_2O via microsyringe. The solution was stirred at room temperature for another 12 h and filtered. The filtrate was vacuum-dried, and the solid was recrystallized from diethyl ether to yield 0.6 g (yield 54%) of product. ^1H NMR (C_6D_6): δ 6.21 (s, 2H, C_4H_2N), 3.32 (s, 4H, CH_2NMe_2), 2.17 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6): δ 131.0 (s, C_{ipso}), 106.0 (d, J_{CH} = 164 Hz, CH), 60.9 (t, J_{CH} = 137 Hz, CH_2), 47.6 (q, J_{CH} = 135 Hz, CH_3). IR (KBr) for Al−H: 1778, 1797 cm^{-1}.

(14) Crystallographic data for **3**: $C_{10}H_{20}AlN_3$, $M_r = 209.27$, monoclinic, space group $P2_1/c$, $a = 11.7262(15)$ Å, $b = 9.0372(12)$ Å, $c = 12.8237(17)$ Å, $\beta = 107.477(3)°$, $V = 1296.2(3)$, $Z = 4$, $T = 293(2)$ K, $\mu = 0.128\ mm^{-1}$, Mo Kα radiation, graphite monochromator. The data were processed using SADABS, and calculations were carried out with SHELXTL. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The final R index for $I > 2\sigma(I)$ on 2962 independent reflections was R1 = 0.0384.

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