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Synthesis of Dimeric Iminoalanes by Oxidative Addition of Azides to $(Cp^*Al)_4$: Structural Characterization of $(Cp^*AlNSi^tBu_3)_2$ ($Cp^* = C_5Me_5$)

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Summary: The reaction of $(Cp^*Al)_4$ *with organic azides offers an alternative synthetic route for the formation of iminoalanes with a low degree of oligomerization. This method was used to prepare the dimeric iminoalanes* $(Cp^*AlNSi^iPr_3)_2$ *(**1**),* $(Cp^*AlNSiPh_3)_2$ *(**2**), and* $(Cp^*AlNSi^tBu_3)_2$ *(**3**). The crystal structure of **3** was determined by X-ray diffraction study.*

Introduction

Compounds containing aluminum and nitrogen have attracted a great deal of interest due to their potential as single-source precursors for AlN. We are especially interested in the synthesis and structural characterization of iminoalanes $(RAlNR')_x$, which were generally synthesized by alkane elimination from $(RHAlNHR')_x$ compounds.[1−3] This method often leads to the formation of heterocubanes ($x = 4$)[4−8] or compounds of higher degree of oligomerization ($x = 5−16$).[1,9] However, Power et al. obtained an iminoalane of lower degree of oligomerization with the composition of $(MeAlN\text{-}2,6\text{-}^iPr_2C_6H_3)_3$.[10] Recently, we reported a new synthetic route for the formation of iminoalanes. $(Cp^*Al)_4$,[11] synthesized by reduction of Cp^*AlCl_2[12] with potassium, reacts with Me_3SiN_3 by an oxidative addition to give a dimeric iminoalane.[13] This is the first compound having a degree of oligomerization of two. More recently, Shapiro and co-workers reported the synthesis of another dimeric iminoalane by alkane elimination.[14] Considering the six-membered Al_3N_3 ring synthesized by Power et al., which can formally be described as being "quasi-aromatic" due to its six π-electrons, dimeric iminoalanes, which have four π-electrons, could formally be described as "antiaromatic".

We were interested in examining the possibility of controlling the degree of oligomerization by the steric bulk of the azide reactant. Herein, we report the reactions of $(Cp^*Al)_4$ using $^iPr_3SiN_3$, Ph_3SiN_3, and $^tBu_3SiN_3$.

Results and Discussion

The oxidative addition of $^iPr_3SiN_3$, Ph_3SiN_3, and $^tBu_3SiN_3$ to $(Cp^*Al)_4$ with elimination of nitrogen at temperatures between 50 and 75 °C affords the dimeric iminoalanes $(Cp^*AlNSi^iPr_3)_2$ (**1**), $(Cp^*AlNSiPh_3)_2$ (**2**), and $(Cp^*AlNSi^tBu_3)_2$ (**3**), respectively, in nearly quantitative yield.

$$(Cp^*Al)_4 + 4R_3SiN_3 \xrightarrow[-4N_2]{} 2(Cp^*AlNSiR_3)_2$$

$$R = {}^iPr\ (\mathbf{1}),\ Ph\ (\mathbf{2}),\ {}^tBu\ (\mathbf{3})$$

The compounds are soluble in common organic solvents. All compounds have been characterized by melting point, elemental analysis (C, H, N), IR, ^1H and ^{13}C NMR, and mass spectroscopy. The mass spectra in all cases show the molecular ions (*m/z* 666 (**1**), 871 (**2**), and 750 (**3**)). The ^1H NMR spectrum of compound **1** indicates that the Cp* ligand is η^5-bonded to the aluminum since only one signal for the protons of the methyl groups is found. In contrast to these findings, there are three different signals in the ^1H NMR spectra of compounds **2** and **3**, indicating that the Cp* ligand is σ-bonded to the aluminum in these compounds. The solid-state structure of **3** is in accordance with this assumption.

Solid-State Structure of 3. Crystals of compound **3** suitable for an X-ray diffraction study were obtained by slow evaporation of a solution of **3** in toluene. Compound **3** is dimeric, with 1.5 molecules in the asymmetric unit. Both dimers have nearly identical geometries. Figure 1 shows the structure of one independent dimer. Bond lengths and angles are listed in Table 1. The Cp* rings are σ-bonded to the aluminum atoms, and the Al−C bond lengths (2.025−2.033 Å) are in the range of known Al−C distances.[15] The Al−N

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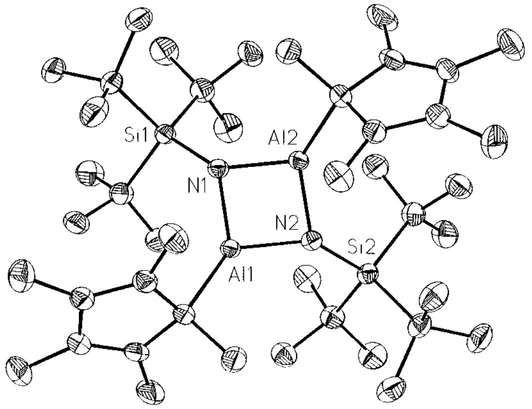

Figure 1. Molecular structure of **3** giving the numbering scheme used in Table 1. (Anisotropic displacement ellipsoids are drawn at the 50% probability level.)

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

N(1)−Si(1)	1.730(2)	N(1)−Al(2)	1.836(2)
N(1)−Al(1)	1.840(2)	Al(1)−N(2)	1.842(2)
Al(1)−C(70)	2.034(3)	N(2)−Si(2)	1.731(2)
N(2)−Al(2)	1.835(2)	Al(2)−C(80)	2.025(3)
Si(1)−N(1)−Al(2)	138.56(13)	Si(1)−N(1)−Al(1)	129.88(12)
Al(2)−N(1)−Al(1)	85.18(10)	N(1)−Al(1)−N(2)	92.86(10)
N(1)−Al(1)−C(70)	131.41(11)	N(2)−Al(1)−C(70)	125.89(11)
Si(2)−N(2)−Al(2)	129.29(12)	Si(2)−N(2)−Al(1)	138.93(13)
Al(2)−N(2)−Al(1)	85.17(10)	N(2)−Al(2)−N(1)	93.20(10)
N(2)−Al(2)−C(80)	130.74(11)	N(1)−Al(2)−C(80)	125.28(11)

bond lengths range from 1.835(2) to 1.842(2) Å and are longer than those in the other known dimeric iminoalanes.[13,14] The iminoalane prepared with Me_3SiN_3 shows an almost planar four-membered ring.[13] Also, the nitrogen atoms are nearly planar (sum of angles 359.2−358.1°). In compound **3** the two AlNAl triangles of the four-membered ring deviate from planarity by 19.5 and 19.1°, respectively. Here the nitrogen atoms deviate significantly from planarity (sum of angles 353.4 and 353.7°). This deviation from planarity is due to the steric demand of the bulky Si^tBu_3 groups. The N−Si distances (1.729−1.731 Å) are in the usual range of N−Si bond lengths.[16]

Experimental Section

General Comments. All manipulations were performed using general high-vacuum, glovebox, and Schlenk techniques. All solvents (including C_6D_6) were dried, distilled under nitrogen, and degassed prior to use. IR spectra were recorded on a Bio-Rad Digilab FTS-7, mass spectra on a Varian MAT CH5, and NMR spectra on a Bruker AM 250, respectively. Chemical shifts are reported in ppm and referenced to TMS. Melting points (uncorrected) were obtained in sealed capillaries on a HWS-SG 3000. Elemental analyses were determined by the analytical laboratory of the University of Göttingen. $^iPr_3SiCl$ and Ph_3SiCl were available form Aldrich; $^tBu_3SiCl$[17] and $(Cp^*Al)_4$[11] were prepared by literature methods. The azides have been described in the literature[18] and were prepared by the following, alternative general method.

The silyl chloride (20 mmol) and NaN_3 (200 mmol) were heated in refluxing dimethoxyethane (DME) (60 mL) for 12 h. The mixture was filtered and the solvent evaporated *in vacuo* (50 mbar). In the case of $^iPr_3SiN_3$ and $^tBu_3SiN_3$ the residues were distilled at 15 mbar to give the azides in 70−75% yield. Ph_3SiN_3 was crystallized from pentane at 25 °C to give a 65% yield of the corresponding azide.

Synthesis of $(Cp^*AlNSiR_3)_2$ (1−3). To a suspension of $(Cp^*Al)_4$ (1.00 mmol, 0.64 g) in toluene (50 mL) was added the trialkylsilyl (or triaryl) azide (4.00 mmol; 0.80 g of $^iPr_3SiN_3$, 1.21 g of Ph_3SiN_3, and 0.97 g of $^tBu_3SiN_3$) using a syringe (in the case of the triphenylsilyl azide a solution of the azide in toluene (10 mL) was used). The suspension was heated slowly to 70 °C. Starting at 50 °C, the formation of gas was observed. After 30 min, the reaction was finished. The solvent was distilled *in vacuo* and the residue was dried for 12 h in high *vacuo*. All the compounds are obtained in nearly quantitative yield (>90%). Crystals of $(Cp^*AlNSi^tBu_3)_2$ are obtained by evaporating the solvent from the solution of the reaction slowly within 3 days.

$(Cp^*AlNSi^iPr_3)_2$ (1). IR (Nujol): 1466, 1304, 1261, 1094, 1043, 1016, 969, 918, 883, 805, 741, 706, 634, 593, 504 cm^{-1}. ^1H NMR (250 MHz, C_6D_6): 0.95 (m, 3H, ^iPr), 1.24 (d, 18H, ^iPr), 1.95 (s, 15H, Cp*). ^{13}C NMR (63 MHz, C_6D_6): 12.7 (Cp*), 17.2 (^iPr), 20.6 (^iPr), 120 (Cp*). Mass spectrum (EI, 70 eV): *m/z* 666 (M^+). Anal. Calcd for $C_{38}H_{72}Al_2N_2Si_2$: C, 68.5; H, 10.8; N, 4.2. Found: C, 67.5; H, 10.6; N, 3.9. Mp: 173 °C.

$(Cp^*AlNSiPh_3)_2$ (2). IR (Nujol): 1429, 1306, 1261, 1188, 1106, 1055, 1026, 948, 778, 737, 728, 704, 679, 626, 516 cm^{-1}. ^1H NMR (250 MHz, C_6D_6): 1.61 (s, 12H, Cp*), 1.76 (s, 12H, Cp*), 2.15 (s, 6H, Cp*), 7.21 (m, 30H, aromatic). ^{13}C NMR (100 MHz, C_6D_6): 10.6 (Cp*), 118.2 (Cp*), 128−140 (m, Cp*, Ph). Mass spectrum (EI, 70 eV): *m/z* 871 (M − H). Anal. Calcd for $C_{56}H_{60}Al_2N_2Si_2$: C, 77.2; H, 6.9; N, 3.2. Found: C, 76.0; H, 6.7; N, 3.2. Mp: 151 °C.

$(Cp^*AlNSi^tBu_3)_2$ (3). IR (Nujol): 1467, 1379, 1366, 1214, 1123, 1001, 919, 914, 818, 788, 728, 694, 669, 613, 489, 464 cm^{-1}. ^1H NMR (250 MHz, C_6D_6): 1.07 (s, 12H, Cp*), 1.16 (s, 54H, ^tBu), 1.91 (s, 12H, Cp*), 2.10 (s, 6H, Cp*). ^{13}C NMR (63 MHz, C_6D_6): 15.1 (Cp*), 22.7 (^tBu), 32.1 (^tBu), 122.4 (Cp*). Mass spectrum (EI, 70 eV): *m/z* 750 (M^+). Anal. Calcd for $C_{44}H_{84}Al_2N_2Si_2$: C, 70.5; H, 11.2; N, 3.7. Found: C, 69.4; H, 10.9; N, 3.5. Mp: 246 °C.

X-ray Structure Determination of 3. Data were collected at −120 °C on a Stoe-Siemens-AED diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods.[19] All non-hydrogen atoms were refined anisotropically.[20] For the hydrogen atoms the riding model was used. The structure was refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (0.0574P)^2 + 3.7765P$ with $P = (F_o^2 + 2F_o^2)/3$. The R values are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$.

There are 1.5 toluene molecules in the asymmetric unit. The half one is disordered over the inversion center. They are refined with distance restraints. Crystal data for **3**: $C_{44}H_{84}Al_2N_2Si_2 \cdot C_7H_8$, M_r = 843.41, *monoclinic*, space group *P*2/*c*, a = 23.432(11) Å, b = 17.364(9) Å, c = 21.004(10) Å, β = 113.76(3)°, V = 7822(7) $Å^3$, Z = 6, ρ(calcd) = 1.074 Mg m^{-3}, μ = 0.135 mm^{-1}, $F(000)$ = 2796, crystal size (mm) 0.3 × 0.5 × 0.5, 16 164 reflections collected, 10 223 unique reflections (R_{int} = 0.0524), 10 221 reflections and 35 restraints used for the refinement of 846 parameters, S = 1.021, $R1$ = 0.046 for $I > 2\sigma(I)$, $wR2$ = 0.120 for all data, maximum/minimum residual density 0.324/−0.239 e $Å^{-3}$.

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Supporting Information Available: For **3**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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