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Synthesis and Characterization of an Unusually Stable Dialkylaluminum Aldimine Complex: X-ray Crystal Structure of *trans*-[(1,2,3-(*t*-Bu)$_3$-*cyclo*-C$_3$)CH=NAl(*i*-Bu)$_2$]$_2$

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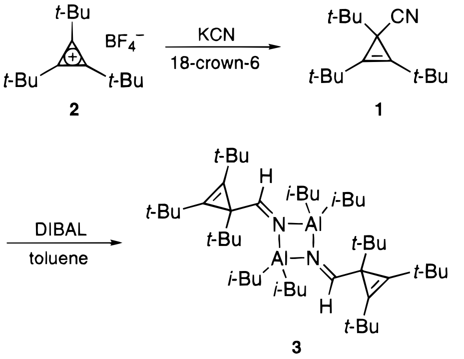
Summary: Treatment of nitrile **1** *with an equimolar amount of DIBAL produces the alane complex [(1,2,3-(t-Bu)$_3$-cyclo-C$_3$)CH=NAl(i-Bu)$_2$]$_2$ (**3**), which reacts sluggishly with protic nucleophiles. The X-ray crystal structure of* **3** *shows unusual geometric distortions in the Al$_2$N$_2$ core and about the imine carbon, as well as in the cyclopropene ring, all of which are attributed to the extreme steric bulk of the hydrocarbon ligands.*

Organoaluminum imine complexes are common intermediates in organic synthesis.[1] They are formed by the reduction of nitriles with dialkylaluminum hydrides[2] and by the thermal rearrangement of trialkylaluminum·nitrile complexes. The resulting aluminum imines can be used for the preparation of a variety of functional groups including aldehydes,[2] ketones,[3] amines,[4] and phosphorus ylides.[5] The proton α to the imine carbon can be removed with a base, and the resulting carbanion can be alkylated with various electrophiles.[6] Organoaluminum imines have also been used in the preparation of aluminum nitride ceramics.[7]

Although aluminum imines, in general, are thermally stable at room temperature and in most cases can be purified by vacuum distillation or crystallization,[3,8] they tend to be highly reactive with water and other protic reagents. Like the majority of organoaluminum compounds, handling of aluminum imines typically requires an inert atmosphere to avoid decomposition of the material.[3,8,9] As such, aluminum imines are seldom isolated and are generally used in situ for subsequent transformations. For the above reasons, reports concerning the structural characterization of aluminum imines, particularly aldimine complexes, are quite rare.[8] This report describes the synthesis, spectroscopic analysis, and single-crystal X-ray structure of an organoaluminum aldimine that, due mainly to steric factors, is remarkably stable to atmospheric conditions.

Scheme 1



Results and Discussion

The synthesis of the title compound is shown in Scheme 1. 3-Cyano-1,2,3-tri-*tert*-butylcyclopropene (**1**) was prepared by a modification of the literature procedure:[10] addition of a catalytic amount of 18-crown-6 to a mixture of tri-*tert*-butylcyclopropenylium tetrafluoroborate[11] (**2**) and potassium cyanide in acetonitrile provided **1** in excellent yield (89%) after radial chromatography. The nitrile group of **1** was easily reduced by the addition of diisobutylaluminum hydride in toluene to give **3** in 63% yield after recrystallization from petroleum ether. Although DIBAL is known to reduce the highly strained double bond of cyclopropenes in some instances,[12] no side products resulting from hydroalumination of the cyclopropene π bond were observed.

NMR spectroscopic data were consistent with those reported[8] with regard to the aluminum imine portion of **3**. The imine proton appears as a single peak at 7.89 ppm, and in the ^{13}C spectrum, the imine carbon resonates at 188.58 ppm. The carbon atoms of the cyclopropene π bond resonate in the normal range for tri-

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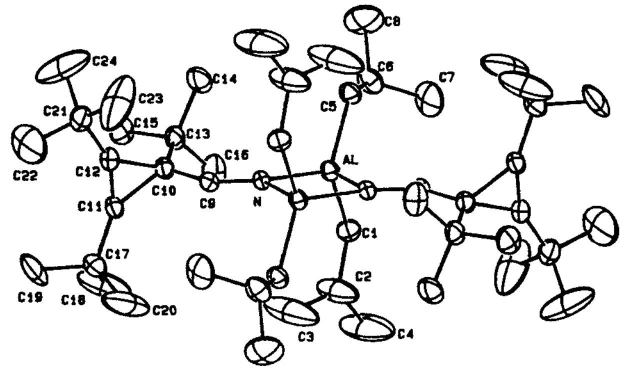

Figure 1. Molecular structure of **3**. The ellipsoids are drawn at the 50% level.

tert-butyl-substituted cyclopropenes at 122.76 ppm.[13,14] Variable-temperature NMR experiments (−50 to 100 °C)[15] showed no change in the imine proton resonance. Previously, isolated organoaluminum imine complexes have been observed to exist as cis:trans dimeric mixtures,[8] with the relative ratio of the trans isomer increasing as the size of the organic group on the imine carbon increased. Seeing no evidence by NMR spectroscopy of a second isomer, we concluded the structure of **3** to be the sterically less-congested trans dimer.

The VT-NMR data did show the isobutyl groups to be dynamic in solution over the 150 °C range.[15] At room temperature, only the methylene protons showed restricted rotation, appearing as an ABX multiplet ($J_{A-B} = 14.3$ Hz, $J_{A-X} = J_{B-X} = 6.7$ Hz). Coalescence to a doublet ($J = 6.6$ Hz) occurred around 80 °C. The methine proton and carbon resonances appeared to remain unchanged. The methyl protons gave a doublet at ambient temperature but split into two doublets below −30 °C. The nonequivalence of the methyls was apparent in the room-temperature ^{13}C NMR spectrum ($\delta = 29.44$, 29.34) but disappeared above 40 °C ($\delta = 29.36$).[15] Homonuclear decoupling of the methine proton at room temperature caused the complex methylene signals to collapse to an AB multiplet ($J = 14.3$ Hz) and the methyl doublet to a singlet.

X-ray crystallography showed a trans geometry for **3**, as illustrated in Figure 1. Colorless single crystals of **3** were grown from chloroform at −25 °C, and data sets were collected at both 120 (LT) and 295 K (HT).[16] Selected bond lengths and bond angles are given in Table 1. Figure 2 clearly shows the four-membered inorganic Al_2N_2 core and the trans orientation of the imine substituents. The centrosymmetric core possesses four interesting features: (1) alternant Al−N bond lengths (1.961(3) vs 1.924(3) Å). This difference (0.037 Å) is somewhat larger than that found in $[(C_6H_3\text{-}2,6\text{-}(Me)_2)CH{=}NAl(i\text{-}Bu)_2]_2$ (**4**; 0.020 Å).[8] (2) The Al−N−C(9) bond angles in **3** vary significantly—150.6(3)° vs 114.9(2)°. The difference in bond angles (35.7°) is quite pronounced compared to **4** (6.7°). (3) The N=C bond of **3** (1.281(4) Å) is markedly longer than the corresponding bond in **4** (1.248(7) Å). (4) The sp^2 bond angle about N−C(9)−C(10) is 135.8(3)°, 9.8° larger than in **4**. The magnitude of the aforementioned geometrical distortions in **3** can be readily attributed to the extreme size of the tri-*tert*-butylcyclopropene fragment. In particular, steric repulsion between the *tert*-butyl group on C(10) and the isobutyl groups forces these moieties apart, resulting in greater bond lengths and bond angles and, thus, precluding cis-isomer formation.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 3[a,b]

Al−N	1.924(3)	C(9)−C(10)	1.486(2)
Al−N^i	1.961(3)	C(10)−C(11)	1.545(2)
Al−C(1)	1.976(4)	C(10)−C(12)	1.539(2)
Al−C(5)	1.974(4)	C(11)−C(12)	1.277(2)
N−C(9)	1.281(4)		
Al−N−Al^i	94.4(1)	C(9)−C(10)−C(11)	111.29(12)
Al−N−C(9)	150.6(3)	C(9)−C(10)−C(12)	111.22(13)
Al^i-N−C(9)	114.9(2)	C(9)−C(10)−C(13)	121.78(13)
N−Al−N^i	85.6(1)	C(11)−C(12)−C(10)	65.76(11)
N−Al−C(1)	116.4(2)	C(12)−C(11)−C(10)	65.31(11)
N^i-Al−C(1)	107.1(2)	C(12)−C(10)−C(11)	48.92(10)
N−Al−C(5)	116.3(2)	C(13)−C(10)−C(11)	122.00(13)
N^i-Al−C(5)	108.9(2)	C(13)−C(10)−C(12)	120.47(13)
C(1)−Al−C(5)	117.0(2)	C(12)−C(11)−C(17)	152.3(2)
N−C(9)−C(10)	135.8(3)	C(11)−C(12)−C(21)	152.5(2)

[a] Reference 16. [b] Values in the left column are HT data; the right column is LT data.

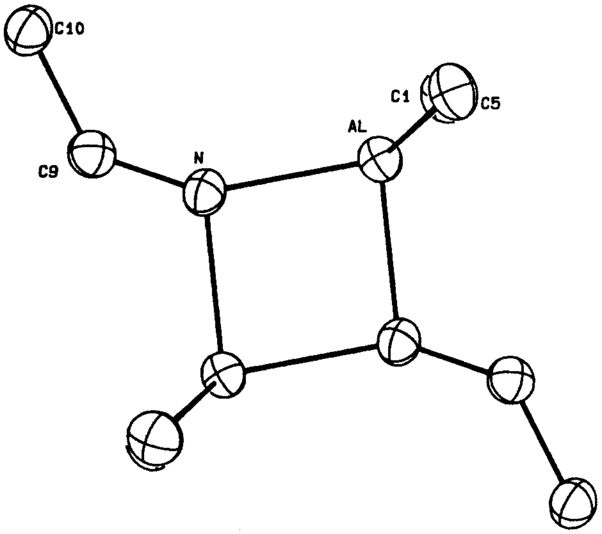

Figure 2. Top view of the Al_2N_2 core in **3**.

Some interesting observations are apparent in the cyclopropene portion of **3** as well. Although the sp^3 bond angles in cyclopropenes are in general very small (ca. 50−52°) due to the constraints of the three-membered ring, the C(12)−C(10)−C(11) bond angle of 48.92(10)° in **3** is in the extreme range even for a cyclopropene.[17] Other tri-*tert*-butylcyclopropenes have sp^3 bond angles ranging from 49.6(1)° [13] to 50.3(2)°.[14] One might expect with the exceptionally small angle that the bond lengths would also be exceptional; however, this is not entirely the case. Whereas the C=C bond length (1.277(2) Å) is typical, the corresponding C−C bond lengths (1.539(2),

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(15) Variable-temperature NMR experiments were performed in toluene-d_8.

(16) To accurately compare bond lengths and bond angles of **3** with other structures in the literature, it was necessary to obtain X-ray data sets at two temperatures. For comparison purposes, all numbers quoted in the text for the Al_2N_2 core are from the 295 K determination (Eugene) and all numbers for the cyclopropene moiety are from the 120 K structure (Essen).

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1.545(2) Å) are slightly elongated compared to most cyclopropenes.[17] To minimize steric interactions between neighboring *tert*-butyls and between the *tert*-butyls and isobutyls, the cyclopropene C−C bonds are stretched by ca. 0.02 Å, similar to what was observed in hexa-*tert*-butyl-3,3′-bicyclopropenyl.[13]

Infrared spectroscopy of **3** shows the standard absorption at 1860 $\mathrm{cm^{-1}}$ for the cyclopropene C═C stretch and the imine C═N stretch at 1604 $\mathrm{cm^{-1}}$. The latter absorption is consistent with the increased length of the imine bond (vide supra), as it appears at slightly lower energy than the range reported for analogous systems (1680−1635 $\mathrm{cm^{-1}}$).[8,18]

The large bulk of the organic fragments in **3** imparts a remarkable stability to the molecule. Although the synthesis shown in Scheme 1 was initially carried out using standard inert atmosphere techniques, the title compound proved to be stable to air, protic solvents, and even strong acids (such as HCl) for short periods of time (see Experimental Section). Hydrolysis in acidic solution took place only after extended periods (>2 h). Reaction of **3** with MeOH in $CDCl_3$ solution proceeded with an approximate half-life of 48 h. NMR analysis showed that crystals of **3** stored in a vial at 5 °C remained unchanged for over 6 months. In contrast, the alane complex derived from the corresponding triphenylcyclopropene hydrolyzed easily upon workup with aqueous NH_4Cl solution.[19] Examination of the crystal structure (Figure 1) of **3** clearly illustrates that the electrophilic imine carbon is shielded from potential nucleophiles. The immense steric congestion virtually shuts down what would normally be an almost instantaneous hydrolysis reaction with protic nucleophiles.

In summary, we have synthesized via standard reduction methods a dialkylaluminum aldimine complex that exhibits unusual stability. The enormous size of the 1,2,3-tri-*tert*-butylcyclopropene moiety and its interaction with the isobutyl substituents produces unique properties in alane **3**, such as low reactivity with nucleophiles, exclusive formation of the trans isomer, and elongated bond lengths that are reflected in both IR and crystallographic data. Experiments utilizing **3** in synthesis will be reported in due course.

Experimental Section

General. Toluene and acetonitrile were distilled from $LiAlH_4$ and CaH_2, respectively. Diisobutylaluminum hydride was purchased from the Aldrich Chemical Co. as a 1.0 M solution in toluene. NMR spectra were acquired on a Varian Unity-INOVA 300 spectrometer at room temperature unless otherwise stated. ^1H and ^{13}C NMR spectra were taken at 299.95 and 75.43 MHz, respectively. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane using the residual chloroform signal (7.26 δ) as an internal standard. Coupling constants are reported in hertz. FT-IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer. Melting points were determined using a Mel-Temp II capillary melting point apparatus equipped with a thermocouple and digital thermometer. Analyses were performed by Desert Analytics.

3-Cyano-1,2,3-tri-*tert*-butylcyclopropene (1). Cyclopropenylium salt **2**[11] (1.04 g, 3.55 mmol), 18-crown-6 (0.100 g, 0.40 mmol), and potassium cyanide (1.96 g, 30.1 mmol) were added to dry acetonitrile (40 mL) under an atmosphere of N_2. The resulting suspension was magnetically stirred at ambient temperature for 7 h. The acetonitrile was removed by rotary evaporation, and the resulting white solids were taken up in Et_2O (50 mL) and water (50 mL). The layers were separated, and the organic phase was washed with brine (30 mL), dried ($MgSO_4$), and then filtered through Celite. Removal of solvent by rotary evaporation gave a colorless oil that was purified by radial thin-layer chromatography (hexanes) to give 0.741 g (89%) of a colorless solid (mp 28.5−30.0 °C). ^1H NMR ($CDCl_3$): δ 1.26 (s, 18H), 1.01 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 118.69, 99.98, 32.83, 31.57, 30.00, 29.64, 28.35. IR (KBr, $\mathrm{cm^{-1}}$): 2209 (C≡N), 1853 (C═C).

[(1,2,3-(*t*-Bu)$_3$-*cyclo*-C$_3$)CH═NAl(*i*-Bu)$_2$]$_2$ (3). Nitrile **1** (0.680 g, 2.91 mmol) was dissolved in dry toluene (10 mL) under N_2 at 0 °C with magnetic stirring. Diisobutylaluminum hydride (3.0 mL of a 1.0 M solution in toluene, 3.0 mmol) was added over 1 min via syringe. After about 10 min of reaction time, a white precipitate started to appear. Stirring was continued at 0 °C for 30 min and at ambient temperature for an additional 30 min. Et_2O (50 mL) was added followed by 10% HCl (30 mL). The layers were separated, and the Et_2O phase was dried ($MgSO_4$), filtered through Celite, and freed of solvent by rotary evaporation to give 1.019 g (93%) of a spectroscopically pure white powder. The solid was recrystallized from petroleum ether to give 0.688 g (63%) of analytically pure colorless crystals (mp 177−180 °C, sealed tube). ^1H NMR ($CDCl_3$): δ 7.89 (s, 2H), 1.72 (nonet, J = 6.6 Hz, 4H), 1.25 (s, 36H), 1.08 (s, 18H), 0.84 (d, J = 6.6 Hz, 24H), 0.03 (A*B*Xm, J = 14.3, 6.7 Hz, 4H), −0.04 (*A*BXm, J = 14.3, 6.7 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 188.58 (*C*═N), 122.76 (*C*═C), 52.79 (cyclopropyl), 32.95 (−*C*(CH$_3$)$_3$), 31.73 (−*C*(CH$_3$)$_3$), 30.72 (−C(*C*H$_3$)$_3$), 30.50 (−C(*C*H$_3$)$_3$), 28.43 (−CH$_2$CH(*C*H$_3$)$_2$), 28.34 (−CH$_2$CH(*C*H$_3$)$_2$), 26.00 (−CH$_2$*C*H(CH$_3$)$_2$), 23.60 (−*C*H$_2$CH(CH$_3$)$_2$). IR (KBr, $\mathrm{cm^{-1}}$): 1860 (C═C), 1604 (C═N). Anal. Calcd for $C_{48}H_{92}Al_2N_2$: C, 76.74; H, 12.34; N, 3.73. Found: C, 76.88; H, 12.14; N, 3.93.

Crystallography of 3. HT (295 K) Data: Enraf-Nonius CAD-4 diffractometer, a = 10.3655(12) Å, b = 11.2898(27) Å, c = 12.9345(17) Å, V = 1312.7(10) Å^3, α = 97.07(2)°, β = 113.03(1)°, γ = 103.78(2)°, triclinic, space group $P\bar{1}$, Z = 1, ρ_{calc} = 0.950 g cm^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ = 0.806 cm^{-1}, $2\theta_{max}$ = 50°, 4614 independent reflections scanned, 3019 reflections in refinement ($I \geq 1.5\sigma(I)$), structure refinement (C atoms anisotropic, H atoms riding) with TEXSAN v. 5.0, 235 parameters, R = 0.078, R_w = 0.086.

LT (120 K) Data: Nicolet R3m/V diffractometer, a = 10.196(3) Å, b = 11.224(3) Å, c = 12.725(3) Å, V = 1259.1(6) Å^3, α = 97.20(2)°, β = 113.19(2)°, γ = 103.92(2)°, triclinic, space group $P\bar{1}$, Z = 1, ρ_{calc} = 0.991 g cm^{-3}, Mo Kα radiation (λ = 0.71073 Å), μ = 0.088 mm^{-1}, $2\theta_{max}$ = 55°, 5975 reflections collected, 5722 independent reflections ($I \geq 2\sigma(I)$), structure refinement (C atoms anisotropic, H atoms riding) with SHELXTL v. 5.03, 235 parameters, R = 0.0517, R_w = 0.0587.

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Supporting Information Available: X-ray structure of **3**, structure refinement details, and tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes (25 pages). Ordering information is given on any current masthead page.

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