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Aluminum Derivatives of *N*-Isopropyl-2-(isopropylamino)troponimine

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The reaction of *N*-isopropyl-2-(isopropylamino)troponimine, [(*i*-Pr)$_2$ATI]H, with Me$_3$N·AlH$_3$ or AlMe$_3$ gave [(*i*-Pr)$_2$ATI]AlH$_2$ or [(*i*-Pr)$_2$ATI]AlMe$_2$ in quantitative yield. The solution ^{1}H and ^{13}C NMR spectroscopic data suggest very symmetric structures for these molecules. The aluminum derivatives are monomeric in the solid state. Their crystal structures show planar, symmetric ring systems. The Al−N bond distances for [(*i*-Pr)$_2$ATI]AlH$_2$ and [(*i*-Pr)$_2$ATI]AlMe$_2$ are 1.882(3), 1.886(4), and 1.915(1) Å, respectively. A high yield method for the synthesis of [(*i*-Pr)$_2$ATI]H is also reported. The X-ray crystal data of [(*i*-Pr)$_2$ATI]H revealed a planar ring but with two different C$_{\text{ring}}$−N distances. Crystal data with Mo Kα (λ = 0.710 73 Å) at 193 K: [(*i*-Pr)$_2$ATI]H, C$_{13}$H$_{20}$N$_2$, $a = b = 15.469(1)$ Å, $c = 9.099(2)$ Å, $V = 1885.9(4)$ Å^3, trigonal, space group $P\bar{3}$, $Z = 6$, $R = 0.0464$; [(*i*-Pr)$_2$ATI]AlH$_2$, C$_{13}$H$_{21}$AlN$_2$, $a = 16.681(4)$ Å, $b = 9.739(2)$ Å, $c = 18.730(5)$ Å, $\beta = 109.14(2)°$, $V = 2874.4(14)$ Å^3, monoclinic, space group $P2_1/c$, $Z = 8$, $R = 0.0536$; [(*i*-Pr)$_2$ATI]AlMe$_2$, C$_{15}$H$_{25}$AlN$_2$, $a = 9.824(1)$ Å, $b = 17.022(1)$ Å, $c = 9.661(1)$ Å, $V = 1615.6(3)$ Å^3, orthorhombic, space group $Pbcn$, $Z = 4$, $R = 0.0383$.

Introduction

Organoaluminum compounds have been explored widely owing to their importance in a variety of applications, including organic syntheses and industrial catalytic processes.[1,2] They have also been utilized as precursors in chemical vapor deposition (CVD) processes. For example, stable aluminum compounds involving nitrogen substituents or neutral nitrogen donors are useful in the preparation of aluminum nitride or AlN-containing materials.[3−10] As a result, there is considerable interest in the structures, properties and transformations of molecules containing Al−N bonds.[11−20]

The products derived from reactions between primary and secondary amines with organoaluminum reagents, (R$_2$AlNR'$_2$)$_n$ or (RAlNR')$_n$, generally tend to form various aggregates such as dimers, trimers, tetramers, or oligomers.[21−27] Structurally characterized monomeric species (e.g., R$_2$AlNR'$_2$) are rare.[28,29] In general, such species are obtained by using sterically demanding substituents on the aluminum and/or nitrogen atoms. An alternative strategy to avoid aggregation is to use chelating ligand systems, which are capable of stabilizing an electrophilic aluminum center through intramolecular coordination. Several different classes of ligands (e.g., ethylenediamine, diazabutadiene, amino alkyl or amino aryl groups) have been used for this purpose.[2,30−33]

Our interest in low-valent and low-coordinate main group species have led us to explore the possibility of preparing stable complexes using a diisopropyl version of a 2-aminotroponimine ligand, [(*i*-Pr)$_2$ATI]$^-$.[34] This ligand [ATI]$^-$, which has a delocalized 10π electron system (Scheme 1), is believed to be much more resistant to electrophiles and nucleophiles than the widely used 1,4-diazabutadiene (DAD) ligand (Scheme 1).[35−38] The importance of DAD has been demonstrated by the synthesis

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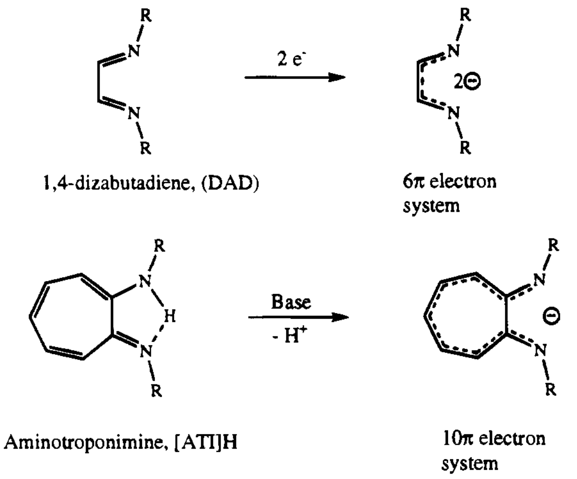
Scheme 1



and isolation of many main group and transition metal complexes, especially low-coordinate and low-valent group 14 compounds (e.g., stable carbenes, silylenes).[38-42] On the other hand, studies on the 2-aminotroponimine ligand (including those of the related tropocoronand) have been mostly limited to the first row elements of transition metal complexes such as manganese, iron, cobalt, nickel, copper and zinc.[35,43-54] The limited use of this 2-aminotroponimine ligand may be a result of the difficulties in its synthesis, which involves a somewhat laborious, multistep synthetic procedure (*cf.* diazabutadiene can be prepared easily from the condensation of primary amines with α-diketones).[35,43,55-57] In this paper, we describe a convenient route to the synthesis of *N*-alkyl-2-(alkylamino)-troponimine and its utility in main group chemistry, as well as the synthesis and characterization of aluminum derivatives, $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use.[58] Glassware was oven-dried at 150 °C overnight. Tropolone,[59] 2-(tosyloxy)tropone,[60] $\text{AlH}_3\cdot\text{NMe}_3$[61] were synthesized according to the literature procedures. Trimethylaluminum (2.0 M) in heptane and isopropylamine were purchased from Aldrich Chemical Co., and the triethyloxonium tetrafluoroborate was purchased from Lancaster Synthesis, and used as received. ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 at 25 °C on Nicolet NT-200 spectrometer (^{1}H, 200.06 MHz; ^{13}C, 50.31 MHz), unless otherwise noted. Chemical shifts for ^{1}H NMR spectra are relative to internal Me_4Si. ^{13}C NMR spectra were run with ^{1}H decoupling, and the chemical shifts are reported in parts per million vs Me_4Si (CDCl_3 at 77 ppm and C_6D_6 at 128 ppm). Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer, using thin films obtained from hexane solutions on KBr disk. Melting points were measured on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed using Perkin-Elmer 2400 CHN analyzer (UTA) or at Texas Analytical Laboratories, Inc., Houston, TX.

2-(Isopropylamino)tropone. Finely powdered 2-(tosyloxy)tropone (5.0 g, 18 mmol; prepared from tropolone)[60] was slowly added at 0 °C to isopropylamine (*ca.* 20 mL) over a period of 10 min. After the addition, the resulting yellow solution was allowed to stir for 2 h at 0 °C. During this period, the solid slowly dissolved in the isopropylamine solution. The mixture was allowed to warm to room temperature and stirred overnight. The excess isopropylamine was removed by distillation. The resulting yellow residue was dried under vacuum, extracted into diethyl ether, and filtered through a thin bed of Celite. The filtrate was concentrated under reduced pressure to obtain 2-(isopropylamino)-tropone as a yellow solid (2.83 g, 94%). It can be recrystallized from hexanes at −20 °C; mp 44−45 °C. ^{1}H NMR (CDCl_3): δ 1.33 (d, 6H, $(\text{C}H_3)_2\text{CH}$, $J = 6.22$ Hz), 3.82 (septet, 1H, $(\text{CH}_3)_2\text{C}H$, $J = 6.97$ Hz), 6.53−6.69 (m, 2H), 7.11−7.28 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.92 ($C\text{H}_3$), 43.71 ($C\text{H}$), 108.65 (C_7), 121.66 (C_3), 128.17 (C_5), 136.11 (C_6), 137.01 (C_4), 154.58 (C_2−N), 176.52 (C_8=O). IR (cm^{-1}): 3290 (N−H). Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.30; H, 8.19; N, 8.29.

***N*-Isopropyl-2-(isopropylamino)troponimine ($[(i\text{-Pr})_2\text{ATI}]\text{H}$).** $\text{Et}_3\text{O}\cdot\text{BF}_4$ (3.53 g, 18.6 mmol) in 20 mL of methylene chloride was slowly added to a methylene chloride (20 mL) solution of 2-(isopropylamino)tropone (3.00 g, 18.4 mmol) under nitrogen. After stirring for 3 h, ca. 20 mL of isopropylamine was slowly added to the resulting reddish yellow solution. Immediately, the color of the solution became yellow. The reaction mixture was stirred for a further 2 h, and the volatiles were removed under vacuum. The residue was extracted into hexane, filtered through Celite, and concentrated under vacuum to obtain $[(i\text{-Pr})_2\text{ATI}]\text{H}$ as a yellow solid (3.07 g, 82%). X-ray quality crystals were grown from *n*-pentane at −20 °C; mp 57−60 °C. ^{1}H NMR (CDCl_3): δ 1.23 (d, 6H, $(\text{C}H_3)_2\text{CH}$, $J = 6.26$ Hz), 3.74 (septet, 2H, $(\text{CH}_3)_2\text{C}H$), 6.06 (t, 1H, H_5, $J = 9.22$ Hz), 6.26 (d, 2H, $H_{3,7}$, $J = 10.99$ Hz), 6.68 (dd, 2H, $H_{4,6}$, $J = 9.11, 9.63$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 22.87 ($C\text{H}_3$), 45.72 ($C\text{H}$), 109.73 (C_5), 116.98 ($C_{3,7}$), 132.45 ($C_{4,6}$), 151.41 ($C_{2,8}$). ^{1}H NMR (C_6D_6): δ 1.09 (d, 6H, $(\text{C}H_3)_2\text{CH}$, $J = 5.85$ Hz), 3.60 (septet, 2H, $(\text{CH}_3)_2\text{C}H$), 6.10 (t, 1H, H_5, $J = 8.15$ Hz), 6.22 (d, 2H, $H_{3,7}$, $J = 11.05$ Hz), 6.64 (dd, 2H, $H_{4,6}$, $J = 9.51, 9.47$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 23.02 ($C\text{H}_3$), 46.00 ($C\text{H}$), 110.32 (C_5), 117.55 ($C_{3,7}$), 133.05 ($C_{4,6}$), 151.98 ($C_{2,8}$). IR (cm^{-1}): 3180 (N−H). Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.49; H, 10.09; N, 13.25.

Preparation of $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$. A hexane solution of $[(i\text{-Pr})_2\text{ATI}]\text{H}$ (0.330 g, 1.62 mmol) was added slowly to $\text{AlH}_3\cdot\text{NMe}_3$ (0.145g, 1.63 mmol) in hexane at 0 °C. After addition, the mixture was allowed

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Table 1. Crystal Data and Summary of Data Collection and Refinement

	$[(i\text{-Pr})_2\text{ATI}]\text{H}$	$[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$	$[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$
formula	$C_{13}H_{20}N_2$	$C_{13}H_{21}AlN_2$	$C_{15}H_{25}AlN_2$
fw	204.3	232.3	260.4
color, habit	yellow, hexagonal rods	yellow blocks	yellow blocks
size, mm	0.30 × 0.32 × 0.60	0.31 × 0.53 × 0.69	0.30 × 0.47 × 0.55
cryst syst	trigonal	monoclinic	orthorhombic
space group	$P3$	$P2_1/c$	$Pbcn$
a, Å	15.469 (1)	16.681 (4)	9.824 (1)
b, Å	15.469 (1)	9.739 (2)	17.022 (1)
c, Å	9.099 (2)	18.730 (5)	9.661 (1)
α, deg	90	90	90
β, deg	90	109.14 (2)	90
γ, deg	120	90	90
vol, Å^3	1885.9 (4)	2874.4 (14)	1615.6 (3)
Z	6	8	4
T, K	193	193	193
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
density (calc), mg/m^3	1.079	1.074	1.070
absorpn coeff, mm^{-1}	0.064	0.120	0.113
scan type	$\theta-2\theta$	$\theta-2\theta$	ω
2θ max, deg	45	45	50
no. collecd reflecns	2333	4769	1927
no. indepen reflecns	1623	3734	1423
no. obs. reflecns ($F > 4\sigma(F)$)	1197	2621	1423
R, R_w,[a] %	4.64, 4.88	5.36, 5.36	3.83, 4.33

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

to warm to room temperature and stirred overnight. The volatiles were removed under vacuum to produce $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ as a yellow solid in quantitative yield. The product can be crystallized from hexanes at −25 °C; mp 53−55 °C. ^{1}H NMR (C_6D_6): δ 1.08 (br, 2H, Al*H*$_2$), 1.27 (d, 6H, C*H*$_3$, $J = 6.44$ Hz), 3.45 (septet, 2H, C*H*, $J = 6.41$ Hz), 6.22 (t, 1H, H_5, $J = 8.78$ Hz), 6.28 (d, 2H, $H_{3,7}$, $J = 11.2$ Hz), 6.74 (t, 2H, $H_{4,6}$, $J = 10.0$ Hz). ^{13}C{H} NMR (C_6D_6): δ 22.28 (*C*H$_3$), 47.64 (*C*H), 114.29 (C_5), 119.62 ($C_{3,7}$), 136.70 ($C_{4,6}$), 161.48 ($C_{2,8}$). IR (cm^{-1}): 1770, 1800. Anal. Calcd for $C_{13}H_{21}N_2Al$: C, 67.21; H, 9.21; N, 12.06. Found: C, 67.08; H, 9.07; N, 12.14.

Preparation of $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$. This compound was prepared in a manner similar to that for $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$, using 2.0 M trimethylaluminum (1.0 mL) and $[(i\text{-Pr})_2\text{ATI}]\text{H}$ (0.408g, 2 mmol). The yellow product, $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$, was isolated in quantitative yield; mp 89−91 °C. ^{1}H NMR (C_6D_6): δ −0.23 (s, 6H, AlC*H*$_3$), 1.20 (d, 6H, C*H*$_3$, $J = 6.5$ Hz), 3.53 (septet, 2H, C*H*, $J = 6.5$ Hz), 6.22 (t, 1H, H_5, $J = 9.1$ Hz), 6.32 (d, 2H, $H_{3,7}$, $J = 11.4$ Hz), 6.77 (dd, 2H, $H_{4,6}$, $J = 9.61$, 9.4 Hz). ^{13}C{H} NMR (C_6D_6): δ −4.18 (b, Al*C*H$_3$), 22.57 (*C*H$_3$), 47.54 (*C*H), 113.49 (C_5), 119.0 ($C_{3,7}$), 136.47 ($C_{4,6}$), 161.14 ($C_{2,8}$). Anal. Calcd for $C_{15}H_{25}N_2Al$: C, 69.20; H, 9.68; N, 10.36. Found: C, 69.13; H, 9.62; N, 10.68.

X-ray Structure Determination. Crystals of $[(i\text{-Pr})_2\text{ATI}]\text{H}$ were obtained from *n*-pentane at −20 °C and $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ from hexanes at −25 °C. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream.[62] Data collections were carried out at −80 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite monchromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters of $[(i\text{-Pr})_2\text{ATI}]\text{H}$, $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$, and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ were determined by least-squares refinement of 27, 36, and 27 reflections, respectively. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects (an empirical absorption correction was also applied for $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$). All the software programs and the sources of scattering factors are contained in the SHELXTL PC (version 4.2) software package provided by Siemens Analytical X-ray Instruments, Inc.[63] Some details of data collection and refinements are given in Table 1. The atomic parameters are listed in Table 2. Selected bond distances and angles are given in Table 3. Further details of the crystal structures are available in the supplementary material.

(a) $[(i\text{-Pr})_2\text{ATI}]\text{H}$. The structure was solved by direct methods in the trigonal $P\bar{3}$ space group (No. 147). All the non-hydrogen atoms were refined anisotropically. The hydrogen on the N was located from a difference map and refined isotropically. All the other hydrogens were included in calculated positions with C−H = 0.96 Å and fixed U_H.

(b) $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$. The structure was solved by direct methods in the monoclinic $P2_1/c$ space group (No. 14). The asymmetric unit contains two well-separated $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ molecules. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to Al(1) and Al(2) were located from a difference map, and the coordinates and isotropic thermal parameters of each were allowed to refine freely. All the other hydrogen atoms were included in the refinement at calculated positions using a riding model and refined (with the exception of H on the isopropyl group; refined with fixed U_H) isotropically.

(c) $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$. This molecule crystallizes in the orthorhombic $Pbcn$ space group (No. 60) with a crystallographically imposed 2-fold axis containing Al and C(5). The structure was solved by direct methods, and all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the Me groups attached to Al were located from a difference map and refined with isotropic thermal parameters. All the other hydrogen atoms were included in the refinement at calculated positions using a riding model (with C−H = 0.96 Å) and refined isotropically.

Results and Discussion

The *N*-isopropyl-2-(isopropylamino)troponimine, $[(i\text{-Pr})_2\text{ATI}]\text{H}$, was synthesized by a two step procedure, which involves minimal workup, and isolated in excellent overall yield. The first step involves the direct nucleophilic displacement of the tosyl group on the 2-(tosyloxy)tropone using excess isopropylamine. The 2-(isopropylamino)tropone was isolated in 94% yield. The second step involves the ethylation of 2-(isopropylamino)tropone with $Et_3O{\cdot}BF_4$ followed by the treatment with excess isopropylamine to obtain analytically pure $[(i\text{-Pr})_2\text{ATI}]\text{H}$ as a bright yellow solid. This ligand is very soluble in most organic solvents, including saturated hydrocarbons such as *n*-pentane or hexanes, and has a relatively low melting point

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(62) Hope, H. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; p 257.

(63) *Siemens SHELXTL (PC Version 4.2)*; Siemens Industrial Automation, Inc.: Madison, WI.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

atom	*x*	*y*	*z*	*U*(eq)^a
		[(*i*-Pr)$_2$ATI]H		
N(1)	1674(2)	4714(2)	2335(2)	38(1)
N(9)	2077(1)	3336(2)	2426(2)	40(1)
C(2)	1908(2)	4509(2)	1009(3)	35(1)
C(3)	1961(2)	5065(2)	−231(3)	44(1)
C(4)	2191(2)	4987(2)	−1705(2)	54(1)
C(5)	2424(2)	4331(2)	−2345(3)	56(2)
C(6)	2503(2)	3570(2)	−1638(3)	56(2)
C(7)	2383(2)	3295(1)	−192(3)	48(1)
C(8)	2133(2)	3675(2)	1084(3)	37(1)
C(10)	1436(2)	5490(2)	2678(3)	40(1)
C(11)	374(2)	5186(2)	2227(3)	51(1)
C(12)	1585(2)	5705(2)	4315(3)	54(2)
C(13)	2295(2)	2534(2)	2760(3)	47(1)
C(14)	1373(2)	1521(2)	2507(4)	77(2)
C(15)	2632(2)	2652(2)	4357(3)	57(2)
		[(*i*-Pr)$_2$ATI]AlH$_2$		
Al(1)	8618(1)	1984(1)	1012(1)	44(1)
Al(2)	5183(1)	7100(2)	1021(1)	48(1)
N(1)	9148(2)	725(3)	1785(2)	39(1)
N(9)	8134(2)	2691(4)	1714(2)	44(1)
N(16)	6242(2)	7823(4)	1635(2)	49(1)
N(24)	5329(2)	5881(4)	1840(2)	42(1)
C(2)	8975(2)	910(4)	2426(2)	37(2)
C(3)	9322(3)	63(5)	3067(2)	45(2)
C(4)	9251(3)	103(5)	3783(3)	56(2)
C(5)	8795(3)	960(6)	4083(3)	61(2)
C(6)	8294(3)	2022(6)	3718(3)	63(2)
C(7)	8121(3)	2508(5)	2989(3)	52(2)
C(8)	8392(2)	2066(4)	2387(2)	39(2)
C(10)	9681(3)	−418(5)	1688(3)	54(2)
C(11)	9176(3)	−1742(5)	1514(3)	73(2)
C(12)	10044(3)	-38(7)	1064(3)	84(3)
C(13)	7554(3)	3884(5)	1552(3)	57(2)
C(14)	7055(3)	3938(6)	732(3)	86(3)
C(15)	8034(3)	5161(6)	1821(3)	81(3)
C(17)	6553(3)	7235(4)	2320(2)	43(2)
C(18)	7298(3)	7720(5)	2869(3)	53(2)
C(19)	7752(3)	7231(6)	3581(3)	62(2)
C(20)	614(3)	6130(5)	3978(3)	62(2)
C(21)	6933(3)	5254(5)	3744(3)	54(2)
C(22)	6255(3)	5223(5)	3071(2)	44(2)
C(23)	6037(3)	6073(4)	2426(2)	39(2)
C(25)	6673(3)	8984(5)	1394(3)	65(2)
C(26)	6385(4)	10294(6)	1634(3)	85(3)
C(27)	6486(4)	8929(7)	559(3)	103(4)
C(28)	4743(3)	4732(5)	1822(3)	61(2)
C(29)	3889(3)	5077(8)	1268(3)	118(4)
C(30)	5088(4)	3400(6)	1620(3)	85(3)
		[(*i*-Pr)$_2$ATI]AlMe$_2$		
Al	0	3622(1)	2500	27(1)
N(1)	874(1)	2781(1)	1528(1)	28(1)
C(2)	505(2)	2059(1)	1921(2)	27(1)
C(3)	1031(2)	1375(1)	1307(2)	37(1)
C(4)	828(2)	578(1)	1555(2)	45(1)
C(5)	0	212(2)	2500	50(1)
C(6)	1821(2)	2892(1)	347(2)	35(1)
C(7)	1074(2)	2799(1)	−1017(2)	52(1)
C(8)	2486(2)	3697(1)	451(2)	47(1)
C(9)	−1205(2)	4247(1)	1301(2)	45(1)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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

	[(*i*-Pr)$_2$ATI]H		
N(1)−C(2)	1.342 (3)	N(9)−C(8)	1.314 (3)
C(2)−C(3)	1.396 (4)	C(2)−C(8)	1.498 (5)
C(3)−C(4)	1.408 (4)	C(4)−C(5)	1.366 (5)
C(5)−C(6)	1.399 (5)	C(6)−C(7)	1.367 (4)
C(7)−C(8)	1.438 (4)		
N(1)−C(2)−C(8)	111.7 (2)	C(3)−C(2)−C(8)	126.9 (3)
C(2)−C(3)−C(4)	131.1 (3)	C(3)−C(4)−C(5)	129.9 (3)
C(4)−C(5)−C(6)	126.6 (3)	C(5)−C(6)−C(7)	130.5 (3)
C(6)−C(7)−C(8)	132.2 (3)	C(2)−C(8)−C(7)	122.8 (2)
N(9)−C(8)−C(2)	112.8 (3)		
	[(*i*-Pr)$_2$ATI]AlH$_2$		
Al(1)−H(1A)	1.461 (37)	Al(2)−H(2A)	1.451 (45)
Al(1)−H(1B)	1.379 (45)	Al(2)−H(2B)	1.466 (42)
Al(1)−N(1)	1.882 (3)	Al(2)−N(16)	1.898 (4)
Al(1)−N(9)	1.886 (4)	Al(2)−N(24)	1.893 (4)
N(1)−C(2)	1.337 (6)	N(16)−C(17)	1.344 (5)
N(9)−C(8)	1.337 (5)	N(24)−C(23)	1.335 (5)
C(2)−C(8)	1.474 (6)	C(17)−C(23)	1.474 (6)
N(1)−Al(1)−N(9)	84.4 (2)	N(16)−Al(2)−N(24)	83.9 (2)
H(1A)−Al(1)−H(1B)	114.6 (24)	H(2A)−Al(2)−H(2B)	118.0 (21)
Al(1)−N(1)−C(2)	114.7 (3)	Al(2)−N(16)−C(17)	114.3 (3)
Al(1)−N(9)−C(8)	114.3 (3)	Al(2)−N(24)−C(23)	115.0 (3)
N(1)−C(2)−C(8)	113.0 (3)	N(16)−C(17)−C(23)	113.3 (3)
N(9)−C(8)−C(2)	113.5 (4)	N(24)−C(23)−C(17)	113.3 (4)
	[(*i*-Pr)$_2$ATI]AlMe$_2$		
Al−N(1)	1.915 (1)	Al−C(9)	1.969 (2)
Al−N(1A)	1.915 (1)	Al−C(9A)	1.969 (2)
N(1)−C(2)	1.337 (2)	C(2)−C(2A)	1.496 (3)
N(1)−Al−C(9)	112.7 (1)	N(1)−Al−N(1A)	83.3 (1)
C(9)−Al−N(1A)	115.0 (1)	N(1)−Al−C(9A)	115.0 (1)
C(9)−Al−C(9A)	114.6 (1)	Al−N(1)−C(2)	115.3 (1)
N(1)−C(2)−C(3)	122.9 (2)	N(1)−C(2)−C(2A)	113.1 (1)

(57−60 °C). Although it is fairly stable toward air and moisture, [(*i*-Pr)$_2$ATI]H should preferably be stored at 0 °C, because it gradually changes color from yellow to dark brown at room temperature.

[(*i*-Pr)$_2$ATI]H has been characterized by ^{1}H and ^{13}C NMR and IR spectroscopies and elemental analysis. The ^{1}H NMR spectrum shows well-defined three sets of multiplets in the aromatic region, which can be assigned to H(3,7), H(4,6), and H(5), indicating the presence of a very symmetric species in solution. The ^{13}C NMR spectrum also shows only four signals corresponding to the ring carbons, C(2,8), C(4,6), C(3,7), and C(5). The carbons attached to the amine and imine groups (C(2,8)) appear at 151.98 ppm in the ^{13}C NMR spectrum. These chemical shift values suggest [(*i*-Pr)$_2$ATI]H to be in a rapid tautomeric equilibrium in solution.[64,65] The presence of N−H in [(*i*-Pr)$_2$ATI]H is clear from the IR spectrum (3180 cm^{-1}). Most of these NMR chemical shift values and the IR data for N−H agree well with the corresponding values observed for similar *N*-alkyl-2-(alkylamino)troponimines (e.g., [{(Ph)(CH$_3$)CH}$_2$ATI]H).[35]

Yellow hexagonal rod shaped crystals of [(*i*-Pr)$_2$ATI]H were obtained from *n*-pentane at −20 °C. The X-ray crystal structure was determined to investigate the relative orientation of the isopropyl substituents on the nitrogens (Figure 1). Selected bond length and angles are listed in Table 3. The solid state structure is not symmetric as expected for the [(*i*-Pr)$_2$ATI]H molecule. The imine N−C distance (1.314(3) Å) is significantly different from the amine N−C bond length (1.342(3) Å). The seven-membered ring and the two nitrogens are nearly planar. These observations are consistent with the X-ray structure of [{(Ph)(CH$_3$)CH}$_2$ATI]H.[66] Interestingly, the isopropyl groups in [(*i*-Pr)$_2$ATI]H orient in a manner which minimizes the steric interaction with the two hydrogens on C(3) and C(7) of the seven-membered ring system.

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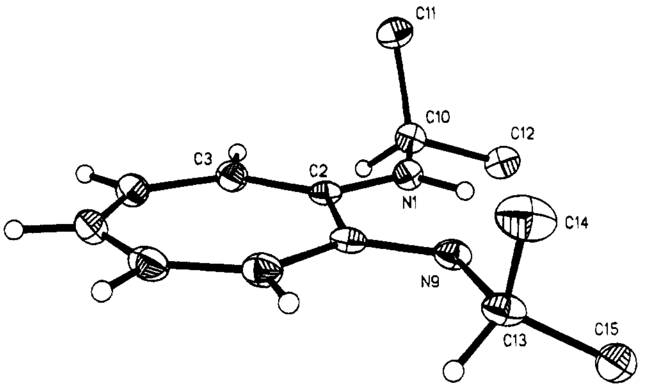
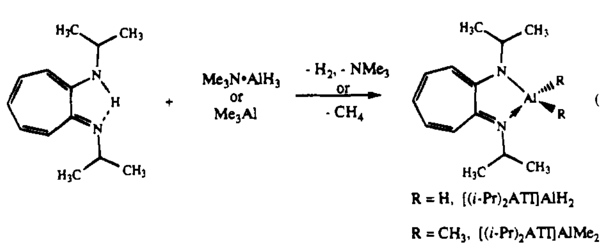


Figure 1. ORTEP drawing of $[(i\text{-Pr})_2\text{ATI}]\text{H}$ with H atoms on methyl groups omitted for clarity.

The aluminum derivatives, $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ or $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$, were synthesized conveniently from $[(i\text{-Pr})_2\text{ATI}]\text{H}$ and $\text{Me}_3\text{N}\cdot\text{AlH}_3$ or AlMe_3, as illustrated in eq 1. These are yellow solids with fairly high sensitivity toward air and moisture.



(1)

These aluminum complexes were identified by ^{1}H and ^{13}C NMR and IR spectroscopies and elemental analysis. The presence of hydride in $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ was evident from the IR spectrum. The IR bands at 1800 and 1770 cm^{-1} can be assigned to asymmetric and symmetric terminal Al—H stretches.[33] The NMR spectroscopic data suggest the presence of very symmetric structures for both the compounds $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$. The ^{13}C NMR signals due to C(2,8) for $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ (δ 161.48) and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ (δ 161.14) appear at about 9 ppm downfield from the corresponding signal in the free ligand (δ 151.98). The ^{1}H NMR chemical shift of the isopropyl CH_3 of the aluminum complexes, $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ (δ 1.27) and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ (δ 1.20), also show a downfield shift relative to the 1.09 ppm in $[(i\text{-Pr})_2\text{ATI}]\text{H}$.

Structures of the aluminum derivatives have been confirmed by X-ray crystallography (Figures 2 and 3). To our knowledge, these represent the first structurally characterized main group metal derivatives of 2-aminotroponimines. The X-ray quality crystals were grown from hexane at −25 °C. The aluminum hydride compound $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ consists of well-separated monomers. The structure of $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ has two chemically equivalent, but crystallographically independent, molecules in the asymmetric unit, one of which is illustrated in Figure 2. The four-coordinate aluminum center adopts a distorted tetrahedral geometry. In contrast to the free ligand, the alane derivative is symmetric in the solid state, with Al—N distances of 1.882(3) and 1.886(4) Å (molecule 2: 1.898(4) and 1.893(4) Å). The hetero-bicyclic ring system containing the seven-membered ring, two N, and the Al is essentially planar with an average deviation from the plane of 0.02 Å. The N—Al—N angle is 84.4(2)° (molecule 2: 83.9(2)°). The isopropyl groups adopt an orientation which minimizes the steric interaction with the two hydrogens on C(3) and C(7) of the seven-membered ring system, as observed in the free ligand (thus forcing one of the Me groups of each isopropyl group toward the open face of the ligand).[67] The C_{ring}—N distances (average 1.338 Å) fall within the values observed for the free ligand (1.314(3) and 1.342(3) Å).

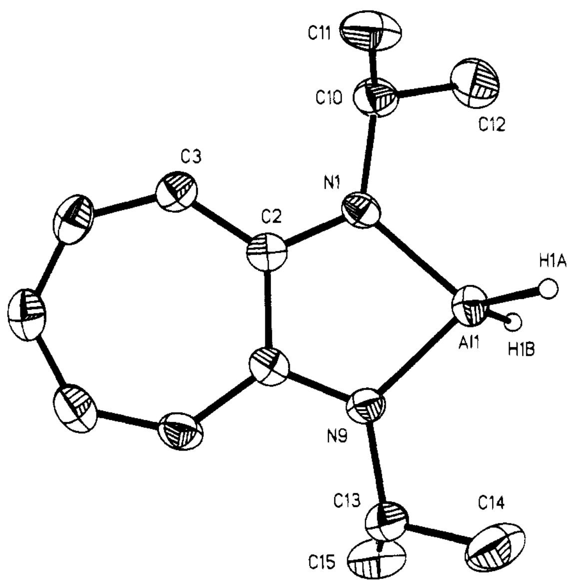


Figure 2. ORTEP drawing of $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ with H atoms on carbons omitted.

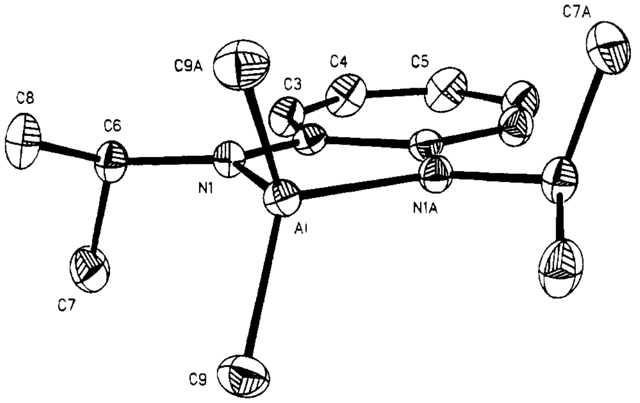


Figure 3. ORTEP drawing of $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ with H atoms omitted.

The dimethylaluminum analogue, $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$, is structurally very similar to $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$. The only notable difference concerns the slightly longer Al—N bond distance (1.915(1) Å) in the dimethyl analogue, perhaps as a consequence of increased steric demand. The Al—CH_3 separation of (1.969(2) Å) is normal for a molecule involving a 4-coordinate Al center.[20,68]

The Al—N distances of $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ and $[(i\text{-Pr})_2\text{ATI}]\text{AlMe}_2$ are shorter than distances observed for four-coordinate aluminum adducts, such as $\text{Me}_3\text{N}\cdot\text{AlH}_3$ (2.063(8) Å, gas phase)[69] and $\text{Me}_3\text{N}\cdot\text{AlMe}_3$ (2.099(10) Å),[70] or cyclic compounds, like $[\text{Me}_2\text{NAlMe}_2]_2$ (1.958(7) Å),[71] $[\text{Ad(H)NAlMe}_2]_2$ (1.963(2) Å),[25] and $[\text{H}_2\text{NAl(SiMe}_3)_2]_2$ (1.956(2) Å),[72] or five-coordinate aluminum species, e.g., $[\text{H}_2\text{AlCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]_2$

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(67) A different orientation was observed for the $[(i\text{-Pr})_2\text{ATI}]\text{BCl}_2$. In this molecule, the methyl groups of the two isopropyl substituents point away from the open face of the ligand. Dias, H. V. R.; Jin, W.; Bott, S. G. Unpublished results.

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(2.124(2) Å),[16] [H_2Al(*N,N,N′,N″,N″*-pentamethyldiethylenetriamine)]$^+$[AlH_4]$^-$ (2.158(7), 2.01(1) Å).[73] However, the aluminum–nitrogen bond distances in [(*i*-Pr)$_2$ATI]AlH_2 and [(*i*-Pr)$_2$ATI]$AlMe_2$ are longer than the corresponding values in systems which involve bonding between nitrogen and three-coordinate aluminum centers. In general the latter range from 1.78 Å to 1.88 Å; e.g., Al[N($SiMe_3$)$_2$]$_3$ (Al–N = 1.78(2) Å),[28] [(2,6-*i*-$Pr_2C_6H_3$)NAlMe]$_3$ (Al–N = 1.782(4) Å),[24] *t*-Bu_2AlNMes$_2$ (Al–N = 1.823(4) Å), *t*-Bu_2AlN($SiPh_3$)$_2$ (Al–N = 1.880(4), 1.878(4) Å).[29]

The alane hydrogens on [(*i*-Pr)$_2$ATI]AlH_2 were located on the difference map. These Al–H distances (average 1.44 Å) are in good agreement with previously reported values.[14] Interestingly, aluminum hydrides tend to form aggregates even in the presence of relatively sterically demanding substituents. Therefore, the isolation of [(*i*-Pr)$_2$ATI]AlH_2 as a monomer may suggest some stabilization of the aluminum center through interaction with nitrogen π-electrons.

It is interesting to note that, in contrast to the behavior of alane and alkyl aluminum species with 2-aminotroponimine, reaction between $Me_3N{\cdot}AlH_3$ or AlR_3 (R = Et, Me) with DAD (Scheme 1) results in the formation of a hydroalumination product or N- and C-alkylated products.[30,74]

Summary

We have reported a convenient method of synthesizing N-alkyl substituted 2-aminotroponimines from tropolone[75] which allows the synthesis of aluminum derivatives [(*i*-Pr)$_2$ATI]AlH_2 and [(*i*-Pr)$_2$ATI]$AlMe_2$ in quantitative yield. The X-ray crystal structures show that the AlN_2C_7 moieties (containing the aluminum center, two nitrogens, and the seven-membered ring) are planar within experimental error.

Due to the presence of the highly delocalized π-electron system, the planar, 2-aminotroponimine ligand framework is fairly resistant to most nucleophiles and electophiles used in reactions. Therefore, 2-aminotroponimines such as [(*i*-Pr)$_2$ATI]H (or even its precursor, 2-(isopropylamino)tropone) would be very useful as ligands for many applications.[76] We are currently in the process of using this ligand to stabilize low-coordinate and low-valent main group species. The chemistry of 2-aminotroponimine with hard metal ions of d- and f-block elements is also of interest.

Acknowledgment. Financial support received from The Robert A. Welch Foundation and The University of Texas at Arlington (UTA) is gratefully acknowledged. We also thank UTA for providing funds to purchase the Siemens P4 single crystal X-ray diffractometer. The C, H, N analyzer was purchased through a grant from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research.

Supporting Information Available: Tables listing crystal data, complete atomic positional parameters, anisotropic thermal parameters, and bond distances and angles for [(*i*-Pr)$_2$ATI]H, [(*i*-Pr)$_2$ATI]AlH_2, and [(*i*-Pr)$_2$ATI]$AlMe_2$ (13 pages). Ordering information is given on any current masthead page.

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