# *N*-Methyl-2-(methylamino)troponiminate Complexes of Tin(II), Gallium(III), and Indium(III). Syntheses of $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$ Using the Tin(II) Reagent $[(Me)_2ATI]_2Sn$

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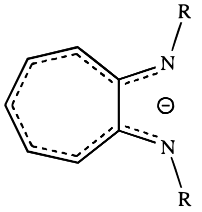
*Received June 7, 1996*[⊗]

The *N*-methyl-2-(methylamino)troponimine $[(Me)_2ATI]H$ reacts with bis[bis(trimethylsilyl)amido]tin(II) to yield $[(Me)_2ATI]_2Sn$ in excellent yield. The treatment of $[(Me)_2ATI]_2Sn$ with GaI and InCl led to the bis(ligand)-gallium(III) and -indium(III) compounds $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$. These metal complexes were characterized by elemental analysis, $^1H$ and $^{13}C$ NMR spectroscopy, and X-ray crystallography. All three metal adducts show fluxional behavior in solution at room temperature. $[(Me)_2ATI]_2Sn$ exhibits a pseudo trigonal bipyramidal structure in the solid state. The gallium and indium atoms in $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$ adopt trigonal bipyramidal geometry around the metal center with the halide occupying an equatorial site. A convenient, high-yield route to $[(Me)_2ATI]H$ is also reported. Crystal data with Mo Kα ($\lambda = 0.710\ 73$ Å) at 183 K: $[(Me)_2ATI]_2Sn$, $C_{18}H_{22}N_4Sn$, $a = 8.4347(11)$ Å, $b = 10.5564(13)$ Å, $c = 11.5527(11)$ Å, $\alpha = 66.931(8)°$, $\beta = 73.579(9)°$, $\gamma = 67.437(7)°$, $V = 863.3(2)$ Å$^3$, triclinic, space group $P\bar{1}$, $Z = 2$, $R = 0.0224$; $[(Me)_2ATI]_2GaI$, $C_{18}H_{22}GaIN_4$, $a = 12.947(2)$ Å, $b = 9.5834(9)$ Å, $c = 16.0132(12)$ Å, $\beta = 107.418(8)°$, $V = 1895.8(3)$ Å$^3$, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.0214$; $[(Me)_2ATI]_2InCl$, $C_{18}H_{22}ClInN_4$, $a = 24.337(3)$ Å, $b = 8.004(2)$ Å, $c = 19.339(3)$ Å, $\beta = 101.537(13)°$, $V = 3691.1(11)$ Å$^3$, monoclinic, space group $C2/c$, $Z = 8$, $R = 0.0224$.

## Introduction

One of our current research interests is the synthesis and reactivity of metal adducts derived from *N*-alkyl-2-(alkylamino)-troponiminate ($[(R)_2ATI]^-$) ligands.[1,2] We are particularly interested in using this ligand system to stabilize low-valent and low-coordinate main group species. Previous studies involving aminotroponiminate ligands have largely been limited to the middle and late transition metal elements.[3−13] Recently, we reported a convenient route to the synthesis of the diisopropyl version of this ligand and described its use in the preparation of novel species such as $[(i\text{-}Pr)_2ATI]AlH_2$ and $\{[(i\text{-}Pr)_2ATI]Sn\}^+$.[1,14] In order to evaluate the effects of steric bulk of the *N*-alkyl substituent, we have decided to investigate the chemistry of the *N*-methylated analog $[(Me)_2ATI]^-$. Such sterically less demanding systems would be ideal for the preparation of metal adducts bearing more than one *N*-alkyl-2-(alkylamino)troponiminate ligands $[(R)_2ATI]_nM$ ($n \geq 2$).



**Aminotroponiminate**, $[(R)_2ATI]^-$

In this paper we wish to report the syntheses and characterization of the first aminotroponiminate derivatives of gallium and indium, $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$. Furthermore, in contrast to the more common synthetic methods used in the preparation of gallium(III)[15−18] and indium(III)[18−20] complexes (e.g., metathesis reactions involving group 13 metal halides and alkali metal reagents or alkane elimination processes), the work described in this article concerns an oxidative ligand transfer process involving a tin(II) reagent ($[(Me)_2ATI]_2Sn$) and a M(I) halide (M = Ga, In).

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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S0020-1669(96)00680-5 CCC: $12.00

## Experimental Section

All operations were carried out under an atmosphere of purified nitrogen using 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.[21] Glassware was oven-dried at 150 °C overnight. Bis[bis(trimethylsilyl)amido]tin(II),[22] GaI,[23] and 2-(tosyloxy)tropone[24] were prepared according to the previously reported methods. Methylamine, $Et_3O{\cdot}BF_4$ and InCl were obtained from commercial sources and used as received. The $^1H$ and $^{13}C$ NMR spectra were recorded in $C_6D_6$ at 25 °C on a Bruker MSL-300 spectrometer ($^1H$, 300.15 MHz. $^{13}C$, 75.47 MHz) or Nicolet NT-200 spectrometer ($^1H$, 200.06 MHz. $^{13}C$, 50.31 MHz). Chemical shifts for $^1H$ NMR spectra are relative to internal $Me_4Si$. The $^{13}C$ NMR spectra were run with $^1H$ decoupling, and the chemical shifts are reported in ppm vs $Me_4Si$ ($C_6D_6$ at 128.0 ppm). Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analysis were performed at The University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer.

**Synthesis of 2-(Methylamino)tropone.** Methylamine (aqueous 40%, 6.2 mL) was added to a slurry of 2-(tosyloxy)tropone (5.0 g, 18 mmol) in $CH_2Cl_2$ (30 mL) at room temperature. The color of the mixture slowly became yellow. This solution was stirred overnight at room temperature. Then the methylene chloride layer was separated from the mixture, washed with water, and concentrated under reduced pressure to obtain a yellow solid (2 g, 82%). Mp: 75−76 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 3.0 (s, 3H, $J = 4.9$ Hz, $NCH_3$), 6.47 (d, 1H, $J = 9.4$ Hz), 6.63 (t, $J = 9.24$ Hz, 1H), 7.11−7.25 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 29.49 ($CH_3$), 108.24 ($C_6$), 122.02 ($C_2$), 128.40 ($C_4$), 136.24 ($C_5$), 137.25 ($C_4$), 158.48 ($C_7$), 176.68 ($C_1$). Anal. Calcd for $C_8H_9NO$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.69; H, 6.49; N, 10.5.

**Synthesis of *N*-Methyl-2-(methylamino)troponimine, $[(Me)_2ATI]H$.** $Et_3O{\cdot}BF_4$ (3.1 g, 16.3 mmol, 1.1 equiv) in methylene chloride (15 mL) was slowly added to a methylene chloride (20 mL) solution of 2-(methylamino)tropone (2.0 g, 14.8 mmol). After 1 h of stirring, methylamine (aqueous 40%, 10 mL) was added to the brownish yellow solution. This mixture was stirred for 2 h, and the organic layer was isolated and washed with water. The removal of volatile materials under reduced pressure gave $[(Me)_2ATI]H$ as a brownish yellow solid in quantitative yield. Mp: 60−62 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 3.03 (s, 6H, $NCH_3$), 6.10 (t, 1H, $J = 9.3$ Hz, $H_5$), 6.21 (d, 2H, $J = 10.9$ Hz, $H_{3,7}$), 6.73 (t, 2H, $J = 10.0$ Hz, $H_{4,6}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 33.18 ($CH_3$), 109.90 ($C_5$), 117.86 ($C_{3,7}$), 133.16 ($C_{4,6}$), 154.41 ($C_{2,8}$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.77 (s, 6H, $NCH_3$), 6.09 (d, 2H, $J = 11.0$ Hz, $H_{3,7}$), 6.09 (t, 1H, $J = 8.9$ Hz, $H_5$), 6.63 (t, 2H, $J = 9.9$ Hz, $H_{4,6}$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 33.11 ($NCH_3$), 109.84 ($C_5$), 117.67 ($C_{3,7}$), 133.16 ($C_{4,6}$), 154.76 ($C_{2,8}$). MS (EI, 70 eV): *m/z* 148.

**Synthesis of $[(Me)_2ATI]_2Sn$.** Bis[bis(trimethylsilyl)amido]tin(II) (2.639 g, 6 mmol) and $[(Me)_2ATI]H$ (1.78 g, 12 mmol) were mixed in toluene (50 mL) at room temperature. Immediately, the color of the solution became reddish yellow. The reaction mixture was stirred for 3 h, and the resulting cloudy reddish-yellow solution was filtered through Celite. The filtrate was concentrated to obtain $[(Me)_2ATI]_2Sn$ as a red solid in 90% yield. The X-ray quality crystal was grown from toluene−hexane at −25 °C. Mp: dec over 120 °C. $^1H$ NMR ($C_6D_6$): $\delta$ 2.77 (s, 12H, $CH_3$), 6.10 (d, 4H, $J = 10.2$ Hz, $H_{3,7}$), 6.17 (t, 2H, $J = 9.21$ Hz, $H_5$), 6.82 (t, 4H, $J = 9.86$ Hz, $H_{4,6}$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 35.12 ($CH_3$), 112.39 ($C_5$), 116.74 ($C_{3,7}$), 135.09 ($C_{4,6}$), 162.44 ($C_{2,8}$). Anal. Calcd for $C_{18}H_{22}N_4Sn$: C, 52.34; H, 5.37; N, 13.56. Found: C, 51.76; H, 4.72; N, 12.91.

**Synthesis of $[(Me)_2ATI]_2GaI$.** $[(Me)_2ATI]_2Sn$ (100 mg, 0.24 mmol) and GaI (48 mg, 0.24 mmol) were mixed in toluene at room temperature. The color of the mixture became dark yellow. The reaction mixture was stirred overnight. The resulting solution was then filtered through Celite; the filtrate was collected and concentrated under reduced pressure to yield $[(Me)_2ATI]_2GaI$ as a yellow solid (110 mg). It was recrystallized from methylene chloride−hexane. The X-ray quality crystals of $[(Me)_2ATI]_2GaI$ were grown from toluene at room temperature. Mp: became opaque at 95 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 3.10 (s, 12H, $CH_3$), 6.57 (t, 2H, $J = 9.2$ Hz, $H_5$) 6.74 (d, 4H, $J = 11.3$ Hz, $H_{3,7}$), 7.24 (t, 4H, $J = 9.64$ Hz, $H_{4,6}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 34.98 ($CH_3$), 113.56 ($C_5$), 119.96 ($C_{3,7}$), 136.40 ($C_{4,6}$), 157.91 ($C_{2,8}$). Anal. Calcd for $C_{18}H_{22}N_4GaI$: C, 44.03; H, 4.52; N, 11.41. Found: C, 43.77; H, 4.17; N, 11.07.

**Table 1.** Crystal Data and Data Collection and Refinement Details

| | $[(Me)_2ATI]_2Sn$ | $[(Me)_2ATI]_2GaI$ | $[(Me)_2ATI]_2InCl$ |
|---|---|---|---|
| formula | $C_{18}H_{22}N_4Sn$ | $C_{18}H_{22}GaIN_4$ | $C_{18}H_{22}ClInN_4$ |
| fw | 413.09 | 491.02 | 444.67 |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/c$ | $C2/c$ |
| $a$, Å | 8.4347(11) | 12.947(2) | 24.337(3) |
| $b$, Å | 10.5564(13) | 9.5834(9) | 8.004(2) |
| $c$, Å | 11.5527(14) | 16.0132(12) | 19.339(3) |
| α, deg | 66.931(8) | 90 | 90 |
| $\beta$, deg | 73.579(9) | 107.418(8) | 101.537(13) |
| $\gamma$, deg | 67.437(7) | 90 | 90 |
| $V$, Å$^3$ | 863.3(2) | 1895.8(3) | 3691.1(11) |
| Z | 2 | 4 | 8 |
| $T$, K | 183 | 183 | 183 |
| $\lambda$(Mo Kα), Å | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho$(calc), g/cm$^3$ | 1.589 | 1.720 | 1.600 |
| abs coeff, mm$^{-1}$ | 1.485 | 3.087 | 1.432 |
| R1, wR2 [$I > 2\sigma(I)$],[a] % | 2.24, 5.75 | 2.14, 4.93 | 2.24, 5.61 |
| R1, wR2 [all data],[a] % | 2.50, 5.89 | 2.52, 5.20 | 2.55, 5.77 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

**Synthesis of $[(Me)_2ATI]_2InCl$.** $[(Me)_2ATI]_2Sn$ (260 mg, 0.63 mmol) and InCl (100 mg, 0.66 mmol) were mixed in toluene at room temperature. The color of the solution became greenish yellow. The reaction mixture was stirred overnight. Resulting dark yellow solution was filtered through Celite, and the filtrate was concentrated under reduced pressure to obtain $[(Me)_2ATI]_2InCl$ as a yellow solid (250 mg, 89%). The X-ray quality crystals were grown from toluene. Mp: slowly changed to brown at 110 °C. $^1H$ NMR ($C_6D_6$): $\delta$ 2.90 (s, 12H, $CH_3$), 6.28 (t, $J = 9.0$ Hz, 2H, $H_5$) 6.32 (d, 4H, $J = 11.5$ Hz, $H_{3,7}$), 6.87 (t, 4H, $J = 10.4$ Hz, $H_{4,6}$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 36.30 ($CH_3$), 113.36 ($C_5$), 118.74 ($C_{3,7}$), 135.75 ($C_{4,6}$), 159.87 ($C_{2,8}$). $^1H$ NMR ($CDCl_3$): $\delta$ 3.15 (s, 12H, $CH_3$), 6.45 (t, $J = 9.1$ Hz, 2H, $H_5$) 6.65 (d, $J = 11.3$ Hz, 4H, $H_{3,7}$), 7.16 (t, $J = 9.9$ Hz, 4H, $H_{4,6}$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 36.50 ($CH_3$), 112.98 ($C_5$), 118.67 ($C_{3,7}$), 135.65 ($C_{4,6}$), 159.54 ($C_{2,8}$). Anal. Calcd for $C_{18}H_{22}N_4InCl$: C, 48.62; H, 4.99; N, 12.6. Found: C, 49.19; H, 4.82; N, 11.70.

**X-ray Structure Determination.** 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.[25] Data collections were carried out at −90 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The unit cell parameters of $[(Me)_2ATI]_2Sn$, $[(Me)_2ATI]_2GaI$, and $[(Me)_2ATI]_2InCl$ were determined by least-squares refinement of 30, 30, and 20 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, polarization, and absorption (using $\psi$ scans) effects. All three structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement on $F^2$ and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions. Software programs and the sources of scattering factors are contained in the SHELXTL PC (version 5) software package provided by Siemens

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**Table 2.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ $\times$ $10^3$)

| atom | *x* | *y* | *z* | *U*(eq)[a] | atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|---|---|---|---|---|
| [(Me)$_2$ATI]$_2$Sn | | | | | | | | | |
| Sn | 1961(1) | 9221(1) | 3925(1) | 27(1) | N(12) | 4045(3) | 7957(2) | 2774(2) | 28(1) |
| N(1) | 2003(3) | 11223(2) | 2149(2) | 29(1) | C(13) | 4237(3) | 6579(3) | 2976(2) | 25(1) |
| C(2) | 908(3) | 11682(3) | 1351(2) | 26(1) | C(14) | 5442(4) | 5824(3) | 2156(3) | 34(1) |
| C(3) | 827(4) | 12960(3) | 281(3) | 33(1) | C(15) | 6001(4) | 4383(3) | 2202(3) | 39(1) |
| C(4) | −134(4) | 13630(3) | −701(3) | 39(1) | C(16) | 5563(4) | 3215(3) | 3130(3) | 42(1) |
| C(5) | −1357(4) | 13251(3) | −956(3) | 42(1) | C(17) | 4327(4) | 3268(3) | 4214(3) | 40(1) |
| C(6) | −1908(4) | 12055(3) | −212(3) | 43(1) | C(18) | 3260(4) | 4432(3) | 4616(3) | 34(1) |
| C(7) | −1445(4) | 11010(3) | 921(3) | 37(1) | C(19) | 3089(3) | 5935(3) | 4109(2) | 26(1) |
| C(8) | −251(3) | 10786(3) | 1695(2) | 26(1) | N(20) | 1932(3) | 6870(2) | 4658(2) | 29(1) |
| N(9) | −86(3) | 9724(2) | 2807(2) | 28(1) | C(21) | 5262(4) | 8629(3) | 1775(3) | 39(1) |
| C(10) | 3109(4) | 12071(3) | 2004(3) | 43(1) | C(22) | 817(4) | 6381(3) | 5857(3) | 39(1) |
| C(11) | −1293(4) | 8869(3) | 3295(3) | 37(1) | | | | | |
| [(Me)$_2$ATI]$_2$GaI | | | | | | | | | |
| I | 1095(1) | 6160(1) | 2214(1) | 30(1) | C(11) | 2529(3) | 7399(4) | 5460(2) | 35(1) |
| Ga | 2614(1) | 5944(1) | 3802(1) | 19(1) | N(12) | 4102(2) | 5624(3) | 3798(2) | 21(1) |
| N(1) | 2132(2) | 4025(2) | 3939(2) | 20(1) | C(13) | 4650(2) | 6753(3) | 3680(2) | 22(1) |
| C(2) | 1693(2) | 3842(3) | 4581(2) | 20(1) | C(14) | 5713(2) | 6662(4) | 3622(2) | 30(1) |
| C(3) | 1210(2) | 2559(3) | 4697(2) | 28(1) | C(15) | 6443(3) | 7675(4) | 3538(2) | 36(1) |
| C(4) | 715(3) | 2134(4) | 5313(2) | 33(1) | C(16) | 6340(3) | 9103(4) | 3467(2) | 40(1) |
| C(5) | 527(2) | 2856(4) | 5999(2) | 32(1) | C(17) | 5427(3) | 9856(4) | 3446(2) | 41(1) |
| C(6) | 802(2) | 4222(4) | 6220(2) | 32(1) | C(18) | 4435(3) | 9418(4) | 3502(2) | 36(1) |
| C(7) | 1349(2) | 5179(3) | 5857(2) | 27(1) | C(19) | 4040(2) | 8077(3) | 3624(2) | 26(1) |
| C(8) | 1774(2) | 5081(3) | 5144(2) | 21(1) | N(20) | 3059(2) | 7904(3) | 3695(2) | 28(1) |
| N(9) | 2294(2) | 6155(2) | 4914(2) | 22(1) | C(21) | 4628(3) | 4262(3) | 3931(2) | 29(1) |
| C(10) | 2072(3) | 2924(3) | 3292(2) | 31(1) | C(22) | 2326(3) | 9091(4) | 3622(3) | 44(1) |
| [(Me)$_2$ATI]$_2$InCl | | | | | | | | | |
| In | 3727(1) | 1381(1) | 5831(1) | 24(1) | C(11) | 5048(2) | 1109(5) | 6244(2) | 48(1) |
| Cl | 3135(1) | −953(1) | 5373(1) | 35(1) | N(12) | 3377(1) | 3299(3) | 6389(1) | 28(1) |
| N(1) | 3672(1) | 2579(3) | 4815(1) | 26(1) | C(13) | 3292(1) | 2913(4) | 7031(2) | 25(1) |
| C(2) | 4146(1) | 2893(4) | 4602(2) | 29(1) | C(14) | 2950(1) | 3925(4) | 7369(2) | 33(1) |
| C(3) | 4145(2) | 3684(4) | 3946(2) | 39(1) | C(15) | 2795(2) | 3813(4) | 8022(2) | 37(1) |
| C(4) | 4570(2) | 4201(5) | 3618(2) | 49(1) | C(16) | 2953(1) | 2703(5) | 8566(2) | 35(1) |
| C(5) | 5146(2) | 4060(5) | 3832(3) | 57(1) | C(17) | 3308(1) | 1351(4) | 8557(2) | 33(1) |
| C(6) | 5416(2) | 3306(5) | 4440(3) | 55(1) | C(18) | 3557(1) | 760(4) | 8024(2) | 29(1) |
| C(7) | 5213(2) | 2554(5) | 4982(2) | 45(1) | C(19) | 3565(1) | 1331(4) | 7335(2) | 26(1) |
| C(8) | 4662(1) | 2353(4) | 5106(2) | 31(1) | N(20) | 3830(1) | 487(3) | 6911(1) | 29(1) |
| N(9) | 4576(1) | 1641(3) | 5697(2) | 32(1) | C(21) | 3170(1) | 4885(4) | 6056(2) | 33(1) |
| C(10) | 3131(1) | 2985(5) | 4362(2) | 38(1) | C(22) | 4061(2) | −1174(4) | 7122(2) | 40(1) |

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

Analytical X-ray Instruments, Inc.[26] Some details of data collection and refinements are given in Table 1. The atomic positional parameters are listed in Table 2, and selected bond distances and angles are given in Table 3. Further details of the crystal structures are presented in the Supporting Information.

## Results and Discussion

**Syntheses of [(Me)$_2$ATI]H and Its Tin(II) Derivative.** The synthesis of *N*-methyl-2-(methylamino)troponimine, [(Me)$_2$ATI]H, has been reported previously,[3,27] However, the starting material used in that method is not readily accessible. The procedure described in this paper involves the use of 2-(tosyloxy)tropone, MeNH$_2$, and Et$_3$O·BF$_4$. The overall procedure is very similar to that described for the synthesis of closely related *N*-isopropyl-2-(isopropylamino)troponimine.[1] [(Me)$_2$ATI]H was isolated in an excellent yield. It was purified by recrystallization from CH$_2$Cl$_2$−hexane at −20 °C.

The treatment of bis[bis(trimethylsilyl)amido]tin(II)[22] with 2 equiv of [(Me)$_2$ATI]H provides a facile high-yield route to [(Me)$_2$ATI]$_2$Sn (Scheme 1). [(Me)$_2$ATI]$_2$Sn is soluble in aromatic hydrocarbon and halocarbon solvents. It was characterized by $^1$H and $^{13}$C NMR spectroscopy and elemental analysis. The three sets of multiplets observed in the aromatic region of the $^1$H NMR spectrum can be assigned to H$_{3,7}$, H$_{4,6}$, and H$_5$. Methyl groups appear as singlets in both the $^1$H and $^{13}$C NMR spectra. The $^{13}$C NMR signal corresponding to the C$_{2,8}$ of [(Me)$_2$ATI]$_2$Sn appears at a position (162.44 ppm) significantly downfield from that of the free ligand [(Me)$_2$ATI]H (154.76 ppm).

The structure of [(Me)$_2$ATI]$_2$Sn was confirmed by X-ray diffraction (Figure 1). It shows a monomeric structure with a pseudo trigonal bipyramidal arrangement at the Sn center. The steroechemically active lone pair on Sn(II) presumably occupies an equatorial site. This geometry is fairly common for 4-coordinate Sn(II) complexes. However, in some instances, pseudo square pyramidal geometry for 4-coordinate Sn(II) has also been observed (e.g., in tetraaza macrocyclic systems).[28,29] The relatively simple $^1$H and $^{13}$C NMR spectra of [(Me)$_2$ATI]$_2$Sn (e.g., equivalent Me groups) suggest that this molecule may be fluxional in solution at room temperature.

Nitrogen atoms of each bidentate [(Me)$_2$ATI]$^-$ ligand in [(Me)$_2$ATI]$_2$Sn occupy an axial and an equatorial site with axial and equatorial N−Sn−N angles of 144.85(8) and 94.41(8)°, respectively. The Sn−N$_{ax}$ bond distances of 2.301(2) and 2.295(2) Å are slightly longer than the two Sn−N$_{eq}$ bond distances (2.215(2) and 2.225(2) Å). Interestingly, the differ-

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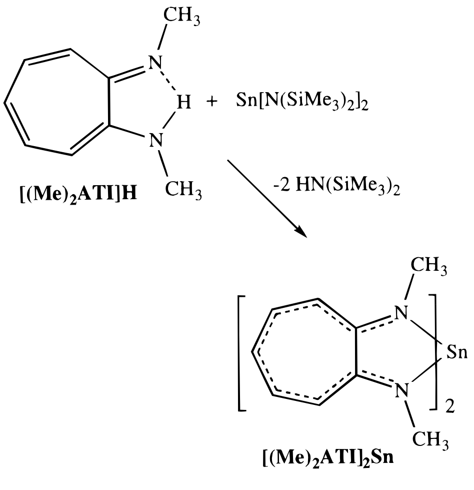
**Table 3.** Selected Bond Distances (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| $[(Me)_2ATI]_2Sn$ | | | |
| Sn−N(12) | 2.215(2) | Sn−N(20) | 2.295(2) |
| Sn−N(9) | 2.225(2) | Sn−N(1) | 2.301(2) |
| N(1)−C(2) | 1.313(3) | C(8)−N(9) | 1.334(3) |
| N(1)−C(10) | 1.461(4) | N(9)−C(11) | 1.467(3) |
| N(12)−C(13) | 1.331(3) | C(19)−N(20) | 1.315(3) |
| N(12)−C(21) | 1.462(3) | N(20)−C(22) | 1.465(3) |
| C(2)−C(8) | 1.484(4) | C(13)−C(19) | 1.485(3) |
| N(12)−Sn−N(9) | 94.41(8) | N(12)−Sn−N(20) | 69.72(8) |
| N(9)−Sn−N(20) | 86.65(8) | N(12)−Sn−N(1) | 86.46(8) |
| N(9)−Sn−N(1) | 69.29(8) | N(20)−Sn−N(1) | 144.85(8) |
| $[(Me)_2ATI]_2GaI$ | | | |
| Ga−N(12) | 1.953(2) | Ga−N(9) | 1.955(2) |
| Ga−N(1) | 1.975(2) | Ga−N(20) | 1.987(3) |
| N(1)−C(2) | 1.327(4) | N(1)−C(10) | 1.466(4) |
| C(8)−N(9) | 1.340(4) | N(9)−C(11) | 1.456(4) |
| N(12)−C(13) | 1.337(4) | N(12)−C(21) | 1.458(4) |
| C(19)−N(20) | 1.319(4) | N(20)−C(22) | 1.464(4) |
| C(2)−C(8) | 1.475(4) | C(13)−C(19) | 1.483(4) |
| I-Ga | 2.7178(5) | | |
| N(12)−Ga−N(9) | 119.81(10) | N(12)−Ga−N(1) | 101.50(10) |
| N(9)−Ga−N(1) | 80.49(9) | N(12)−Ga−N(20) | 80.57(10) |
| N(9)−Ga−N(20) | 97.27(10) | N(1)−Ga−N(20) | 177.50(10) |
| N(12)−Ga−I | 116.57(7) | N(9)−Ga−I | 123.58(7) |
| N(1)−Ga−I | 90.63(7) | N(20)−Ga−I | 89.69(8) |
| $[(Me)_2ATI]_2InCl$ | | | |
| In−N(9) | 2.143(3) | In−N(12) | 2.147(3) |
| In−N(1) | 2.167(2) | In−N(20) | 2.174(2) |
| N(1)−C(2) | 1.325(4) | N(1)−C(10) | 1.464(4) |
| N(9)−C(11) | 1.460(4) | N(9)−C(8) | 1.330(4) |
| N(12)−C(13) | 1.337(4) | N(12)−C(21) | 1.466(4) |
| C(19)−N(20) | 1.325(4) | N(20)−C(22) | 1.469(4) |
| C(2)−C(8) | 1.491(5) | C(13)−C(19) | 1.495(4) |
| In−Cl | 2.4174(9) | | |
| N(9)−In−N(12) | 118.69(10) | N(9)−In−N(1) | 74.58(10) |
| N(12)−In−N(1) | 100.36(10) | N(9)−In−N(20) | 102.67(10) |
| N(12)−In−N(20) | 74.61(10) | N(1)−In−N(20) | 172.46(10) |
| N(9)−In−Cl | 123.30(8) | N(12)−In−Cl | 118.00(7) |
| N(1)−In−Cl | 94.87(7) | N(20)−In−Cl | 92.48(7) |

**Scheme 1**



**$[(Me)_2ATI]H$**

**$[(Me)_2ATI]_2Sn$**

ence (0.078 Å) is notably small compared to the case of various other pseudo trigonal bipyramidal systems of Sn(II) (see Table 4).

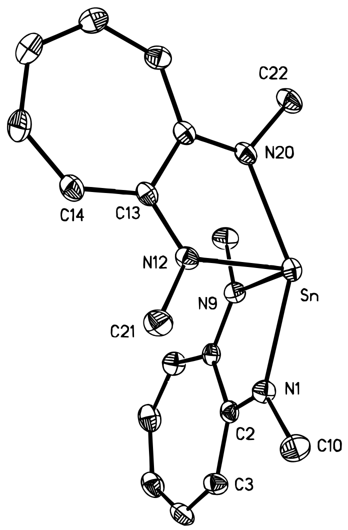


**Figure 1.** Structure and atom-numbering scheme for $[(Me)_2ATI]_2Sn$ (thermal ellipsoids at 30% level). Hydrogens have been omitted for clarity.

The Sn−N distances of $[(Me)_2ATI]_2Sn$ (average 2.298(5), 2.220(5) Å) are longer than those in 2-coordinate species such as $Sn[N(SiMe_3)_2]_2$ (2.096(1), 2.088 Å) or $\{[(i\text{-}Pr)_2ATI]Sn\}^+$ (2.142(3), 2.153(3) Å) and 3-coordinate $[(i\text{-}Pr)_2ATI]SnCl$ (2.164(5) Å).[14,34] They are closer to the distances found in $[2,6\text{-}i\text{-}Pr_2C_6H_3NSn]_4$ (2.23(2), 2.34 (2) Å)[35] or $[(Me)_2ATI]SnMe_3$ (2.173(4), 2.281(4) Å).[36] For comparison, the average axial and equatorial Sn−N bond distances of 4-coordinate $[B(Pz)_4]_2Sn$ (where Pz = pyrazolyl) and $[Ph_2P(NSiMe_3)_2]_2Sn$ are 2.480(3), 2.258(3) Å and 2.491(6), 2.233(5) Å, respectively.[30,31]

The heterobicyclic $C_7N_2Sn$ ring systems in $[(Me)_2ATI]_2Sn$ are essentially planar. The N−Sn−N ring angles (69.72(8), 69.29(8)°) are more acute than those of $[(i\text{-}Pr)_2ATI]_2SnCl$ (73.9(2)°), $[(i\text{-}Pr)_2ATI]Li(thf)_2$ (81.5(2)°), and $[(i\text{-}Pr)_2ATI]AlMe_2$ (83.3(1)°).[1,2,14] Larger angles in the lithium and aluminum derivatives may be a consequence of their smaller sizes (and therefore, shorter metal−N bond distances). The N−Sn−N ring angle of $[(Me)_2ATI]_2Sn$ is much wider than that of $[Ph_2P(NSiMe_3)_2]_2Sn$ (65.7(2)°).[30] However, in contrast to $[(Me)_2ATI]_2Sn$, which has five-membered $C_2N_2Sn$ ring systems, the iminophosphinate $[Ph_2P(NSiMe_3)_2]_2Sn$ has four-membered $PN_2Sn$ rings.

Interestingly, a long Sn···Sn interaction (3.769 Å) was observed between the tin atoms of neighboring $[(Me)_2ATI]_2Sn$ molecules. Contacts of similar magnitude have been observed between the anionic 3-coordinate tin(II) atoms of $SnCl_3^-$ (3.60−3.80 Å).[37] Although, this intermolecular Sn···Sn separation in $[(Me)_2ATI]_2Sn$ is shorter than the sum of van der Waals radii of two tin atoms (4.34 Å),[28] it is significantly longer than the typical Sn−Sn single-bond distance (2.75 Å),[28,38] suggesting only a very weak nonbonding interaction.

**Syntheses of Gallium and Indium Derivatives.** Syntheses of gallium and indium compounds have been the focus of many

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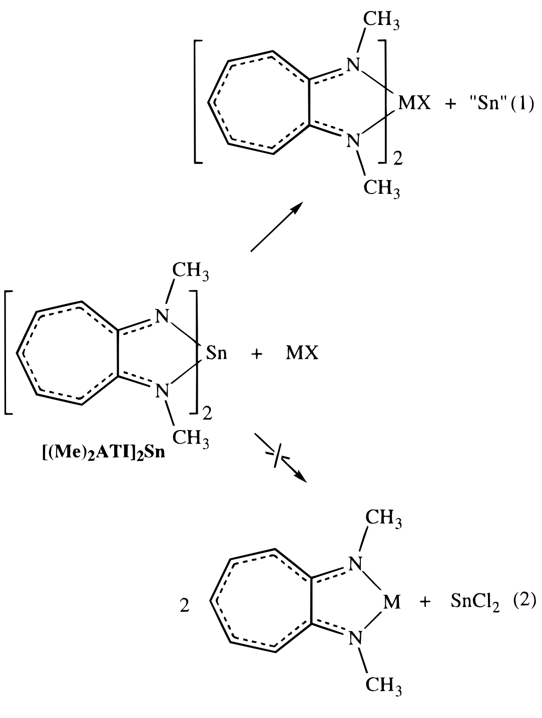
**Table 4.** Selected Bond Distances (Å) for 4-Coordinate, Pseudo Trigonal Bipyramidal Tin(II) Complexes

| compound | Sn−X$_{ax}$ | Sn−X$_{eq}$ | Δ(ax−eq) | ref |
|---|---|---|---|---|
| [(Me)$_2$ATI]$_2$Sn | 2.301(2), 2.295(2) | 2.215(2), 2.225(2) | 0.078 | this work |
| [Ph$_2$P(NSiMe$_3$)$_2$]$_2$Sn | 2.511(6), 2.471(6) | 2.227(5), 2.239(5) | 0.258 | 30 |
| [B(Pz)$_4$]$_2$Sn | 2.625(4), 2.336(4) | 2.268(3), 2.248(3) | 0.222 | 31 |
| [MeOCS$_2$]$_2$Sn | 2.813(3), 2.802(4) | 2.603(3), 2.644(3) | 0.184 | 32 |
| [PhCOCHCOMe]$_2$Sn | 4.63(1) | 4.18(1) | 0.45 | 33 |

**Scheme 2**



M = Ga or In, X = I or Cl

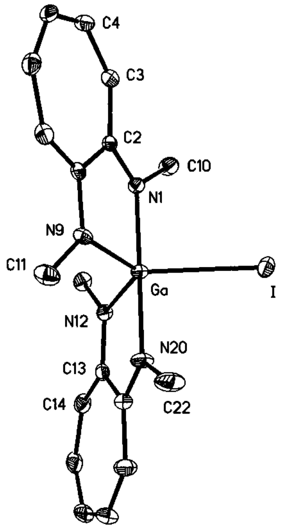


**Figure 2.** Structure and atom-numbering scheme for [(Me)$_2$ATI]$_2$GaI (thermal ellipsoids at 30% level). Hydrogens have been omitted for clarity.

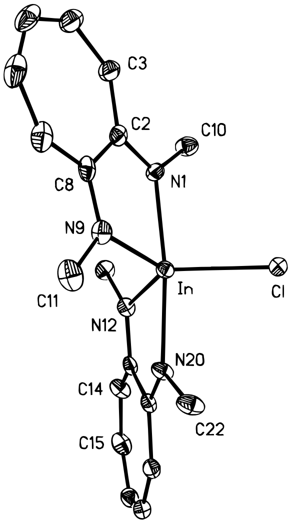


**Figure 3.** Structure and atom-numbering scheme for [(Me)$_2$ATI]$_2$InCl (thermal ellipsoids at 30% level). Hydrogens have been omitted for clarity.

research groups. However, the majority of currently available synthetic routes to these Ga(III) and In(III) compounds involve (i) the salt elimination reactions which use alkali or alkaline earth metal reagents or (ii) alkane or hydrogen elimination reactions utilizing group 13 metal alkyls or hydrides. The approach we used involves an interesting combination of starting materials, a Sn(II) reagent and a low-valent Ga or In halide.

The reaction of [(Me)$_2$ATI]$_2$Sn with GaI or InCl in toluene afforded the gallium or indium compound [(Me)$_2$ATI]$_2$GaI or [(Me)$_2$ATI]$_2$InCl (eq 1 in Scheme 2) along with a dark gray/black precipitate (presumably the Sn metal). These group 13 metal adducts were isolated in high yield. Interestingly, the ligand exchange reaction leading to the low-valent compounds [(Me)$_2$ATI]M (M = Ga, In; eq 2 in Scheme 2) did not work as first contemplated. The reaction between [(Me)$_2$ATI]$_2$Sn and GaI or InCl in 1:2 ratio led also to the same final product. Minor contaminant, [(Me)$_2$ATI]H, was observed during the synthesis of [(Me)$_2$ATI]$_2$GaI. However, [(Me)$_2$ATI]$_2$GaI can be purified easily by recrystallization using toluene at room temperature (or methylene chloride/hexane at −25 °C). [(Me)$_2$ATI]$_2$GaI and [(Me)$_2$ATI]$_2$InCl were soluble in ether or chlorocarbon solvents. However, unlike [(Me)$_2$ATI]$_2$Sn, they show significantly less solubility in aromatic solvents such as toluene. [(Me)$_2$ATI]$_2$GaI and [(Me)$_2$ATI]$_2$InCl were characterized by $^1$H and $^{13}$C NMR spectroscopy and elemental analyses.

The orange crystals of [(Me)$_2$ATI]$_2$GaI and [(Me)$_2$ATI]$_2$InCl were obtained from toluene at room temperature. They were characterized by X-ray crystallography. Solid state packing diagrams show well-separated molecules with no unusual intermolecular contacts. The ORTEP diagrams of [(Me)$_2$ATI]$_2$GaI and [(Me)$_2$ATI]$_2$InCl are given in Figures 2 and 3, respectively.

The gallium atom in [(Me)$_2$ATI]$_2$GaI adopts a trigonal bipyramidal geometry, with the iodide occupying an equatorial site. As in the tin adduct, the nitrogen atoms of each bidentate ligand occupy an axial and an equatorial site. Compared to the compressed axial N−Sn−N (144.85(8)°) and equatorial N−Sn−N angles (86.65(8)°) in [(Me)$_2$ATI]$_2$Sn, analogous N−Ga−N angles in the gallium adduct shows nearly ideal equatorial and axial (119.81(10) and 177.50(10)°). The axial Ga−N bond distances (1.975(2), 1.987(3) Å) are slightly longer than the equatorial Ga−N bond distances (1.953(2), 1.955(2) Å). They are shorter than the Sn−N separations in [(Me)$_2$ATI]$_2$Sn. The Ga−N bond lengths are on average slightly shorter than the corresponding values in 5-coordinate species such as pseudo square pyramidal Ga(tmtaa)Cl (1.980(4), 1.992(4), 1.987(4), 1.991(4) Å)[29] or pseudo trigonal bipyramidal $[H_2B(Pz)_2]_2GaCl$ (2.180(8), 1.994(8), 1.923(9), 1.94(1) Å).[39] The N−Ga−N angles in the $C_2N_2Ga$ rings are 80.49(9) and 80.57(10)°. They are wider than those in $[(Me)_2ATI]_2Sn$ (69.72(8) and 69.29(8)°) but closer to the angles found in $[(i\text{-}Pr)_2ATI]Li(thf)_2$ (81.5(2)°) and $[(i\text{-}Pr)_2ATI]AlMe_2$ (83.3(1)°). These N−Ga−N ring angles are much smaller than the corresponding angles found in 5- or 6-membered cyclic gallium species such as $[(Bu^tN(CH)_2NBu^t]_2Ga$ (90.4(2), 84.9(2)°)[40] or $[H_2B(Pz)_2]_2GaCl$ (88.5(3), 89.6(4)°).[39]

$[(Me)_2ATI]_2InCl$ shows a very similar structure with the chloride atom occupying an equatorial site. However, the metal−N bond distances in $[(Me)_2ATI]_2InCl$ are longer than those of the gallium complex. This is expected because indium has a larger atomic radius. The structural parameters of $[(Me)_2ATI]_2InCl$ can be compared to the corresponding values in other indium adducts. The In−N bond distances of $[(Me)_2ATI]_2InCl$ (average 2.158 Å) are shorter than those in $[CyNC(Bu^t)NCy]_2InCl$ (average 2.215 Å) (Cy = cyclohexyl).[41] They are considerably shorter than the In−N distances in Lewis acid−base adducts $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]InI_2$ (2.518(8) Å), $[2\text{-}(Me_2NCH_2)C_6H_4]InI_2$ (2.35(1) Å),[42] and $[Me_2N(CH_2)_3]_2InBr$ (average 2.52(1) Å).[43] The In−Cl separation (2.4174(9) Å) is comparable to that in $[CyNC(Bu^t)NCy]_2InCl$ (2.405(1) Å).[41]

The axial and equatorial N−In−N angles in $[(Me)_2ATI]_2InCl$ are 172.46(10) and 118.69(10)°, respectively. The ring N−In−N angles of $[(Me)_2ATI]_2InCl$ (74.58(10) and 74.61(10)°) are smaller compared to those of $[(Me)_2ATI]_2GaI$ but wider than the related angles in $[(Me)_2ATI]_2Sn$. This is consistent with the trend expected on the basis of bond distances (Sn−N (average 2.259 Å) > In−N (average 2.158 Å) > Ga−N (average 1.967 Å)).

$[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$ show similar NMR spectra with only minor difference in the chemical shifts, suggesting closely related structures. As for the tin adduct, the methyl groups are equivalent in the $^1H$ and $^{13}C$ NMR spectra. This perhaps indicates highly fluxional complexes in solution.

## Summary and Conclusion

A convenient route to the synthesis of *N*-methylated aminotroponimine has been described. It was used in the preparation of the Sn(II) complex $[(Me)_2ATI]_2Sn$, which shows a distorted pseudo trigonal bipyramidal geometry at the tin atom in the solid state. The X-ray data also indicate a relatively small difference between the average $Sn-N_{ax}$ and $Sn-N_{eq}$ bond distances. The treatment of $[(Me)_2ATI]_2Sn$ with GaI and InCl led to the bis(ligand)gallium(III) and -indium(III) compounds $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$. To our knowledge, this approach to Ga(III) or In(III) complexes has not been described previously. The metal atoms of $[(Me)_2ATI]_2GaI$ and $[(Me)_2ATI]_2InCl$ adopt trigonal bipyramidal geometry with the halides occupying an equatorial site. These Sn, Ga, and In complexes show fluxional behavior in solution. We are currently exploring the chemistry of tin reagents derived from sterically more demanding aminotroponiminates.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for support of this work. We also acknowledge the University of Texas at Arlington for providing funds to purchase the Siemens P4 single-crystal X-ray diffractometer.

**Supporting Information Available:** Tables of crystallographic data, anisotropic thermal parameters, hydrogen coordinates, and complete bond distances and angles for $[(Me)_2ATI]_2Sn$, $[(Me)_2ATI]_2GaI$, and $[(Me)_2ATI]_2InCl$ (12 pages). Ordering information is given on any current masthead page.

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