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# Synthetic and Structural Studies of Titanium Aminotroponiminate Complexes

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The synthesis and characterization of a series of Ti(III) and Ti(IV) aminotroponiminate complexes are described. Six-coordinate [TiMe$_2$(Me$_2$ATI)$_2$] and [TiPh$_2$(Me$_2$ATI)$_2$] were synthesized and structurally characterized, where Me$_2$ATI is *N,N′*-dimethylaminotroponiminate. The mono-alkyl complexes [TiClR(Me$_2$ATI)$_2$], R = Me, CH$_2$SiMe$_3$, were prepared, and treatment of the former, generated in situ, with PhMgCl yielded the alkyl−aryl complex [TiMePh(Me$_2$ATI)$_2$]. The solid state structures of most of these complexes were determined and reveal slightly distorted, trigonal-prismatic coordination geometries. Attempts to prepare alkyl complexes containing $\beta$-hydrogen atoms resulted instead in the isolation of [Ti(Me$_2$ATI)$_3$] or [Ti$_2$Cl$_2$(Me$_2$ATI)$_4$], depending on the alkyl reagent and stoichiometry. Because of the modest steric requirements of the $\{$Ti(Me$_2$ATI)$_2\}^{2+}$ fragment, five-coordinate Ti(IV) complexes were only generated with a bulky $\sigma$-2$\pi$ donor ligand, [Ti(N-(2,6)-*i*-Pr$_2$C$_6$H$_3$)(Me$_2$ATI)$_2$] being a specific example. Attempts to prepare the isoelectronic oxo analogue afforded only dimeric [Ti$_2$O$_2$(Me$_2$ATI)$_4$]. Comparison of the metrical parameters for these complexes with those in the literature containing aryloxide and benzamidinate ligands indicate that the $\{$Ti(Me$_2$ATI)$_2\}^{2+}$ fragment is quite electron releasing.

## Introduction

Inorganic chemistry continues to be enriched by the introduction of novel ligand systems. In addition to offering new compositions, such ligands provide a means for controlling metal center reactivity. In the case of early transition metals, noncyclopentadienyl compounds have been widely explored in an attempt to improve upon existing metallocene-based olefin polymerization catalysts. Various anionic nitrogen and oxygen donor ligands of different denticity have been examined, with most of the work having focused on Zr and Hf chemistry.[1−4] There are only scattered reports of titanium compounds with these types of ligands, most of which have attempted to stabilize metal−ligand multiply bonded species or Ti(III) derivatives.[5−10]

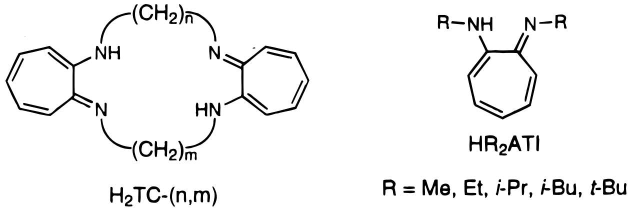

**Figure 1.** Drawings of the H$_2$TC-(*n,m*) and HR$_2$ATI ligands.

Our laboratory has had a longstanding interest in the tropocoronand ligand family H$_2$TC-(*n,m*) as a means of controlling metal ion reactivity by varying the length of the linker chains, *n* and *m* (Figure 1).[11] Previously we reported the chemistry of Zr and Hf tropocoronand complexes.[12,13] More recent efforts have focused on three-component carbonyl coupling reactions, with the use of titanium aminotroponiminate (ATI) compounds.[14] The ATI ligand class was attractive since its members are significantly easier to prepare than the tropocoronand macrocycles, and the steric properties of HR$_2$ATI (Figure 1) can be readily manipulated by varying the R groups. Investigations of early transition metal chemistry with aminotroponiminate ligands are few, the only reports to our knowledge involving [M(R$_2$ATI)$_3$] complexes, M = V, Cr, and (*i*-Pr)$_2$ATI complexes with Zr, Hf, and related lanthanide metals.[15−19]

The reaction chemistry of dialkyl titanium aminotroponiminate complexes has benefitted from the steric and solubility properties of the Me$_2$ATI ligand. In this article, we describe our investigations of the coordination chemistry of titanium *N,N′*-dimethylaminotroponiminate complexes. The results contribute significantly to the literature on complexes with ancillary ligands other than cyclopentadienyl. From comparisons with other work, we can gauge the donating capability and steric

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properties of aminotroponiminate titanium systems. The ultimate goal is to use this knowledge in order to control the reactivity of such complexes.

## Experimental Section

**Materials and Methods.** Hexane and benzene were distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from sodium and halogenated solvents were distilled from calcium hydride under nitrogen. Diethyl ether was passed through a column of activated alumina and pentane was passed through a column of Ridox catalyst and alumina and then collected under vacuum. $C_6D_6$ and $CD_2Cl_2$ were degassed three times and stored over molecular sieves. $CDCl_3$ was distilled from $KHCO_3$, degassed three times, and stored over molecular sieves. [$TiCl_2(NMe_2)_2$][20] was prepared by slowly adding a toluene solution of $TiCl_4$ to $Ti(NMe_2)_4$ dissolved in toluene. After stirring for 3 h, the solution was evaporated and washed with cold toluene and pentane to afford [$TiCl_2(NMe_2)_2$] as a brown-red powder in 85% yield. The reagents $HMe_2ATI$,[21] Li(NH-(2,6)-*i*-$Pr_2C_6H_3$),[22] and $TiCl_3(THF)_3$[23] were prepared as reported in the literature. All Grignard reagents, *n*-BuLi, and trimethylsilyl triflate were purchased from Aldrich and used as received. Experiments were either performed in a nitrogen-filled glovebox or with conventional Schlenk line techniques under argon. Evans method magnetic susceptibility measurements were made as described in the literature.[24] NMR spectra were recorded on a Bruker AC 250, Varian Unity, or Mercury 300 spectrometer at ambient probe temperature, 283 K, and referenced to the internal $^1H$ and $^{13}C$ solvent peaks. Infrared spectra were recorded as pressed KBr disks with a BioRad FTS-135 FTIR spectrometer. EPR spectra were recorded in toluene solution on a Bruker model 300 ESP X-band spectrometer operating at 9.47 GHz and running WinEPR software. Low temperatures were maintained with a liquid He Oxford Instruments EPR 900 cryostat.

**[$TiCl_2(Me_2ATI)_2$] (1).** To a rapidly stirred slurry of $TiCl_2(NMe_2)_2$ (2.17 g, 10.49 mmol) in 150 mL of benzene/toluene (3:1) was added a benzene solution of $HMe_2ATI$ (3.21 g, 21.7 mmol). The slurry immediately turned purple and after 30 min it was almost black. The thick suspension was vigorously stirred for an additional 4 h, and then the fluffy purple product was collected on a frit. The solid was washed with pentane until the washings were colorless and dried under vacuum to yield the product (4.25 g, 95%). This material was used without further purification. $^1H$ NMR ($C_6D_6$, 250 MHz): $\delta$ 6.62 (4H, t, $J$ = 9.3 Hz), 6.13 (2H, t, $J$ = 9.4 Hz), 6.0 (4H, d, $J$ = 11.3 Hz), 3.38 (12H, s). $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ 7.17 (4H, t, $J$ = 10.1 Hz), 6.55 (6H, m), 3.48 (12H, s).

**[$Ti(OTf)_2(Me_2ATI)_2$] (2).** To a rapidly stirred slurry of [$TiCl_2(Me_2ATI)_2$] (173 mg, 0.419 mmol) in 25 mL of dichloromethane was added neat trimethylsilyl triflate (176 $\mu$L, 0.838 mmol). The purple slurry turned brilliant blue-purple and was stirred for 5 h. The solution was filtered and the solvent removed. The purple residue was dissolved in warm $CH_2Cl_2$ and filtered. After cooling, pentane was layered on the filtrate. Storage at −30 °C yielded purple blocks (190 mg, 70%) suitable for X-ray crystallography. $^1H$ NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 7.55 (4H, q, $J$ = 10.8 Hz), 7.00 (2H, t, $J$ = 10.3 Hz), 6.87 (4H, d, $J$ = 11.2 Hz), 3.49 (12H, s). FTIR (KBr, $cm^{-1}$) 3200, 3000, 2885, 1586, 1458, 1407, 1352, 1273, 1241, 1166, 1101, 1032, 916, 885, 843, 758, 744, 714, 692, 632, 592, 569, 520, 509, 482, 472. Anal. Calcd for $TiC_{20}H_{22}N_4O_6F_6S_2$: C, 37.51; H, 3.46; N, 8.75. Found: C, 37.97; H, 3.38; N, 8.99.

**[$TiMe_2(Me_2ATI)_2$] (3).** A suspension of [$TiCl_2(Me_2ATI)_2$] (862 mg, 2.09 mmol) in 100 mL of diethyl ether was cooled to −30 °C. Methylmagnesium chloride (3 M in THF, 1.46 mL, 4.38 mmol) was added dropwise to the solution which immediately turned reddish purple. After complete addition, the solution was a brilliant red color. The slurry was stirred for 30 min and then filtered through Celite. The solvent was evaporated to yield a red solid, which was dissolved in a minimum amount of toluene, filtered, and carefully layered with pentane. This solution was stored at −30 °C for 24 h during which time more pentane was added. The deep red crystalline mass was isolated on a frit, washed with cold pentane, and dried to yield analytically pure product (471 mg, 61%). Crystals suitable for X-ray crystallography were obtained in an analogous fashion. $^1H$ NMR ($C_6D_6$, 250 MHz): $\delta$ 6.97 (4H, d, $J$ = 10.3 Hz), 6.52 (4H, d, $J$ = 11.2 Hz), 6.42 (2H, t, $J$ = 9.4 Hz), 3.09 (12H, s), 1.45 (6H, s). $^{13}C\{^1H\}$ ($C_6D_6$, 250 MHz): $\delta$ 164.6, 135.2, 120.7, 111.4, 64.8, 40.1. Anal. Calcd for $TiC_{20}H_{28}N_4$: C, 64.51; H, 7.58; N, 15.05. Found: C, 64.46; H, 7.58; N, 14.89.

**[$TiPh_2(Me_2ATI)_2$] (4).** A suspension of [$TiCl_2(Me_2ATI)_2$] (204 mg, 0.494 mmol) in diethyl ether was cooled to −30 °C. To this suspension, in dim room light, was added phenylmagnesium bromide (3 M in ether, 329 $\mu$L, 0.987 mmol), and the color of the resulting homogeneous solution changed to deep red. After a few minutes, the product began to precipitate and stirring was continued for 15 min. The red solid was isolated on a frit, washed with pentane, and dried. This solid was then dissolved in benzene and filtered, and the solvent was removed. The residue was then collected with pentane, washed, and dried to yield the product as a dull red powder (194 mg, 70%). Plates suitable for X-ray crystallography were obtained by vapor diffusion of pentane into a saturated dichloromethane solution at −30 °C. $^1H$ NMR ($C_6D_6$, 250 MHz): $\delta$ 7.51 (4H, d, $J$ = 7.7 Hz), 7.07 (6H, m), 6.94 (4H, t, $J$ = 11.2 Hz), 6.51 (4H, d, $J$ = 11.2 Hz), 6.42 (2H, t, $J$ = 9.3 Hz) 2.88 (12H, s). Anal. Calcd for $TiC_{30}H_{32}N_4$: C, 72.57; H, 6.50; N, 11.28. Found: C, 72.59; H, 6.35; N, 10.42.

**[$TiCl(CH_2SiMe_3)(Me_2ATI)_2$] (5).** A suspension of [$TiCl_2(Me_2ATI)_2$] (292 mg, 0.707 mmol) in $CH_2Cl_2$ was treated with $Me_3SiCH_2MgCl$ (1 M in $Et_2O$, 707 $\mu$L, 0.707 mmol) at −30 °C. The red-purple solution was stirred for 2 h, treated with dioxane (1−2 mL), and filtered. The solvent was removed, and the red-brown solid was washed with pentane and dried to yield **5** (280 mg, 85%). Vapor diffusion of pentane into a saturated toluene solution at −30 °C yielded red blocks suitable for X-ray work and elemental analysis. $^1H$ NMR ($C_6D_6$, 250 MHz): $\delta$ 6.81 (4H, d, $J$ = 10.5 Hz), 6.27 (6H, m), 3.20 (12H, s), 2.33 (2H, s), 0.14 (9H, s). $^{13}C\{^1H\}$ ($C_6D_6$, 75.4 MHz): $\delta$ 164.4, 135.7, 122.4, 112.5, 92.4, 42.2, 3.5. Anal. Calcd for $TiC_{22}H_{33}N_4SiCl$: C, 56.83; H, 7.15; N, 12.05. Found: C, 56.23; H, 6.97; N, 11.54.

**[$TiMePh(Me_2ATI)_2$] (6).** A solution of [$TiClMe(Me_2ATI)_2$], 0.034 M in 15 mL of $CH_2Cl_2$, generated by treating **1** with MeMgCl (1 equiv) in $CH_2Cl_2$, was allowed to react with PhMgBr (3 M in $Et_2O$, 168 $\mu$L, 0.504 mmol) at −30 °C in dim room light. The red solution was stirred for 30 min and then filtered to yield a red powder (120 mg, 55%) that was dried. The solid was extracted with $CH_2Cl_2$, treated with dioxane (1−2 mL), and filtered. The solvent was removed and the red residue washed with pentane. Crystallization by vapor diffusion of pentane into a toluene solution at −30 °C yielded red blocks suitable for X-ray work. $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 7.46 (2H, d, $J$ = 7.6 Hz), 7.14 (3H, m), 7.00 (4H, t, $J$ = 11.3 Hz), 6.59 (4H, d, $J$ = 11.2 Hz), 6.46 (2H, t, $J$ = 9.3 Hz), 2.95 (12H, s), 1.49 (3H, s). Anal. Calcd for $TiC_{25}H_{30}N_4$: C, 69.12; H, 6.96; N, 12.90. Found: C, 69.74; H, 7.07; N, 12.75.

**[$Ti(Me_2ATI)_3$] (7).** *n*-Butyllithium (1.6 M in hexanes, 987 $\mu$L, 1.58 mmol) was added to a stirred solution of $HMe_2ATI$ (234 mg, 1.58 mmol) in THF. After the orange-yellow solution was stirred for 30 min, it was added dropwise to a slurry of $TiCl_3(THF)_3$ (195 mg, 0.526 mmol) in THF. The dark brown solution was stirred overnight and then filtered. The solvent was removed and the brown solid dissolved in hot benzene (10−15 mL), filtered, and layered with pentane to yield large, dark brown blocks (180 mg, 70%) suitable for X-ray crystallography. UV−vis (THF) nm ($M^{-1}$ $cm^{-1}$): 822 (1399), 565 (1049), 480 (9860), 462 (10070), 432 (8180). EPR (toluene, 14.4 K): $g$ = 1.95, 1.99. Anal. Calcd for $TiC_{27}H_{33}N_6$: C, 66.25; H, 6.80; N, 17.17. Found: C, 65.92; H, 6.12; N, 17.14.

**[$Ti_2Cl_2(Me_2ATI)_4$] (8).** A suspension of [$TiCl_2(Me_2ATI)_2$] (75 mg, 0.182 mmol) in diethyl ether was cooled to −30 °C. Isobutylmagnesium chloride (2 M in diethyl ether, 91 $\mu$L, 0.182 mmol) was added, and the red-brown solution was stirred for 5 min and then recooled to −30 °C for 15 min. The solution was quickly filtered and then stored at −30 °C to yield brown blocks (25 mg, 36%) suitable for X-ray crystallography. The sample for elemental analysis was crystallized by

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vapor diffusion of pentane into a toluene solution at −30 °C. UV−vis (THF) nm ($M^{-1}$ $cm^{-1}$): 461 (10600), 432 (8385). Evans method: ($C_6D_6$, 293 K) $\mu_{eff} = 2.5\ \mu_B$. EPR (toluene, rt): $g = 1.937$. Anal. Calcd for $Ti_2C_{36}H_{44}N_8Cl_2$: C, 57.23; H, 5.87; N, 14.83. Found: C, 57.37; H, 5.80; N, 14.86.

**[Ti(N-(2,6)-(*i*-Pr)$_2$C$_6$H$_3$)(Me$_2$ATI)$_2$] (9).** Solid Li(NH-(2,6)-(*i*-Pr)$_2$C$_6$H$_3$) (208 mg, 1.13 mmol) was added to a benzene suspension of [TiCl$_2$(Me$_2$ATI)$_2$] (234 mg, 0.57 mmol). The dark red solution was stirred overnight and filtered, and then the solvent was removed. The resulting solid was washed thoroughly with pentane and dried. The residue was dissolved in hot toluene and, after cooling, the solution was layered with pentane and stored at −30 °C to yield 200 mg (68%) of dark red blocks after washing with cold pentane and drying. Crystals suitable for X-ray crystallography were obtained in a similar manner. $^1$H NMR ($C_6D_6$, 250 MHz): $\delta$ 7.06 (2H, d, $J = 7.5$ Hz), 6.88 (5H, m), 6.39 (4H, d, $J = 11.3$ Hz), 6.29 (2H, t, $J = 9.2$ Hz), 4.05 (2H, sept, $J = 6.9$ Hz), 3.18 (12H, s), 1.30 (12H, d, $J = 6.9$ Hz). $^{13}$C{$^1$H} ($C_6D_6$, 75.4 MHz): $\delta$ 165.4, 158.5, 141.9, 135.5, 122.4, 121.2, 119.8, 113.1, 38.9, 29.4, 24.3. Anal. Calcd for $TiC_{30}H_{39}N_5$: C, 69.62; H, 7.60; N, 13.53. Found: C, 69.67; H, 7.77; N, 13.68.

**[Ti$_2$O$_2$(Me$_2$ATI)$_4$] (10).** A benzene solution of [TiMe$_2$(Me$_2$ATI)$_2$] (86 mg, 0.231 mmol) was treated with degassed water (4 $\mu$L, 0.3 mmol). The light red solution was stirred for 12 h during which time a dull red powder precipitated from the solution. This material was collected, washed with pentane, and dried (22 mg, 26%). Vapor diffusion of pentane into a saturated benzene solution at room temperature yielded long red-orange needles suitable for X-ray crystallography. $^1$H NMR ($CDCl_3$, 250 MHz): $\delta$ 6.94 (8H, m), 6.36 (8H, d, $J = 11.1$ Hz), 6.27 (4H, t, $J = 9.3$ Hz), 3.29 (12H, s), 2.88 (12H, s). $^{13}$C{$^1$H} ($CDCl_3$, 75.4 MHz): $\delta$ 165.4, 163.3, 135.2, 134.9, 118.7, 112.1, 109.9, 43.9, 38.6. FTIR (KBr, $cm^{-1}$) 3200, 3000, 2868, 1592, 1517, 1451, 1432, 1339, 1384, 1346, 1268, 1228, 1146, 1100, 1042, 981, 888, 871, 823, 719, 638, 598, 500, 484. Anal. Calcd for $Ti_2C_{36}H_{44}N_8O_2$: C, 60.34; H, 6.19; N, 15.64. Found: C, 60.68; H, 6.23; N, 15.49.

**Collection and Reduction of X-ray Data.** All crystals were covered with Paratone-N (Exxon) and then removed from the drybox for examination. Suitable single crystals were attached to the tips of quartz fibers and transferred to a Bruker CCD X-ray diffraction system with graphite-monochromatized Mo $K_\alpha$ radiation ($\lambda = 0.71073$ Å) controlled by a pentium-based PC running the SMART software package. The temperature of the crystal was maintained with a Bruker LT-2A nitrogen cryostat. Procedures for data collection and reduction have been previously reported.[25] Space groups were determined by examining systematic absences and confirmed by the successful solution and refinement of the structures. The structures were solved by using either the direct methods program SIR-92,[26] XS or Patterson methods and then refined by full matrix least squares and Fourier techniques with SHELXTL-PLUS.[27] In general all non-hydrogen atoms were refined anisotropically; hydrogen atoms were either located from the difference maps and refined isotropically or, for compound **8**, assigned idealized positions and given a thermal parameter 1.2 times the thermal parameter of the carbon atom to which each was attached. Absorption corrections were performed with the SADABS program.[28] Compound **10** crystallizes with two lattice benzene molecules, the carbon atoms of which were refined anisotropically and hydrogen atoms were added. A summary of X-ray crystallographic data for **2**−**10** is shown in Table 1. Labeled ORTEP plots of all structures representing 50% thermal ellipsoids are shown in Figures 2 and 3. Full crystallographic information and bond distances and angles can be found in Tables S1−S36.

**Table 1.** Summary of X-ray Crystallographic Data

| complex | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10·2C$_6$H$_6$** |
|---|---|---|---|---|---|---|---|---|---|
| formula | $C_{20}H_{22}F_6N_4O_6S_2Ti$ | $C_{20}H_{28}N_4Ti$ | $C_{30}H_{32}N_4Ti$ | $C_{22}H_{33}ClN_4SiTi$ | $C_{25}H_{30}N_4Ti$ | $C_{27}H_{33}N_6Ti$ | $C_{36}H_{44}Cl_2N_8Ti_2$ | $C_{30}H_{39}N_5Ti$ | $C_{48}H_{56}N_8O_2Ti_2$ |
| fw | 640.44 | 372.36 | 496.50 | 464.96 | 434.43 | 489.49 | 755.49 | 517.56 | 872.81 |
| space group | *Pbcn* | $P2_1/n$ | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ | *Pbcn* | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| *a*, Å | 13.031(4) | 12.1157(5) | 36.43(2) | 8.7649(2) | 8.109(2) | 13.106(2) | 12.134(5) | 10.149(1) | 12.458(5) |
| *b*, Å | 10.062(1) | 14.7560(6) | 8.538(4) | 8.8170(2) | 10.981(3) | 11.386(2) | 12.761(4) | 19.831(3) | 13.087(5) |
| *c*, Å | 20.040(4) | 12.1415(5) | 16.821(6) | 16.5938(5) | 13.547(4) | 17.082(4) | 13.154(4) | 14.193(2) | 16.018(5) |
| $\alpha$, deg |  |  |  | 96.090(1) | 94.93(2) |  | 111.70(3) |  | 100.405(5) |
| $\beta$, deg |  | 117.53(1) | 103.477(17) | 104.407(1) | 103.31(2) |  | 104.28(4) | 104.37(1) | 104.522(5) |
| $\gamma$, deg |  |  |  | 99.062(1) | 105.87(3) |  | 93.54(5) |  | 113.489(5) |
| *V*, Å$^3$ | 2627.5(10) | 1924.9(1) | 5088(4) | 1212.31(5) | 1114.9(5) | 2549.2(8) | 1807.3(11) | 2767.2(6) | 2199.8(14) |
| *Z* | 4 | 4 | 8 | 2 | 2 | 4 | 2 | 4 | 2 |
| $\rho_{calcd}$, g/cm$^3$ | 1.619 | 1.285 | 1.296 | 1.274 | 1.294 | 1.275 | 1.388 | 1.242 | 1.318 |
| *T*, °C | −85 | −85 | −85 | −85 | −85 | −85 | −85 | −85 | −85 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 0.571 | 0.454 | 0.362 | 0.528 | 0.403 | 0.362 | 0.628 | 0.336 | 0.412 |
| 2$\theta$ limits, deg | 4.06−56.54 | 3.92−56.5 | 4.60−56.58 | 4.74−56.44 | 3.12−56.52 | 4.74−56.56 | 3.48−56.56 | 3.60−56.56 | 2.76−56.52 |
| total no. of data | 14127 | 11617 | 14565 | 7276 | 6839 | 15086 | 11463 | 16197 | 13249 |
| no. of unique data | 3093 | 4433 | 5836 | 5135 | 4777 | 3057 | 7994 | 6301 | 9291 |
| observed data$^a$ | 2074 | 3755 | 3343 | 3818 | 3750 | 2176 | 5104 | 5081 | 5932 |
| no. of parameters | 221 | 338 | 444 | 394 | 391 | 221 | 433 | 481 | 765 |
| R$^b$ | 0.0658 | 0.0313 | 0.0676 | 0.0443 | 0.0432 | 0.0378 | 0.0540 | 0.0372 | 0.0569 |
| *w*R$^{2\ c}$ | 0.1120 | 0.0821 | 0.1012 | 0.0994 | 0.0837 | 0.0958 | 0.1425 | 0.0872 | 0.1139 |
| max, min peaks, e/Å$^3$ | 0.518, −0.398 | 0.267, −0.404 | 0.307, −0.333 | 0.374, −0.455 | 0.287, −0.426 | 0.245, −0.299 | 0.500, −0.530 | 0.213, −0.377 | 0.355, −0.538 |

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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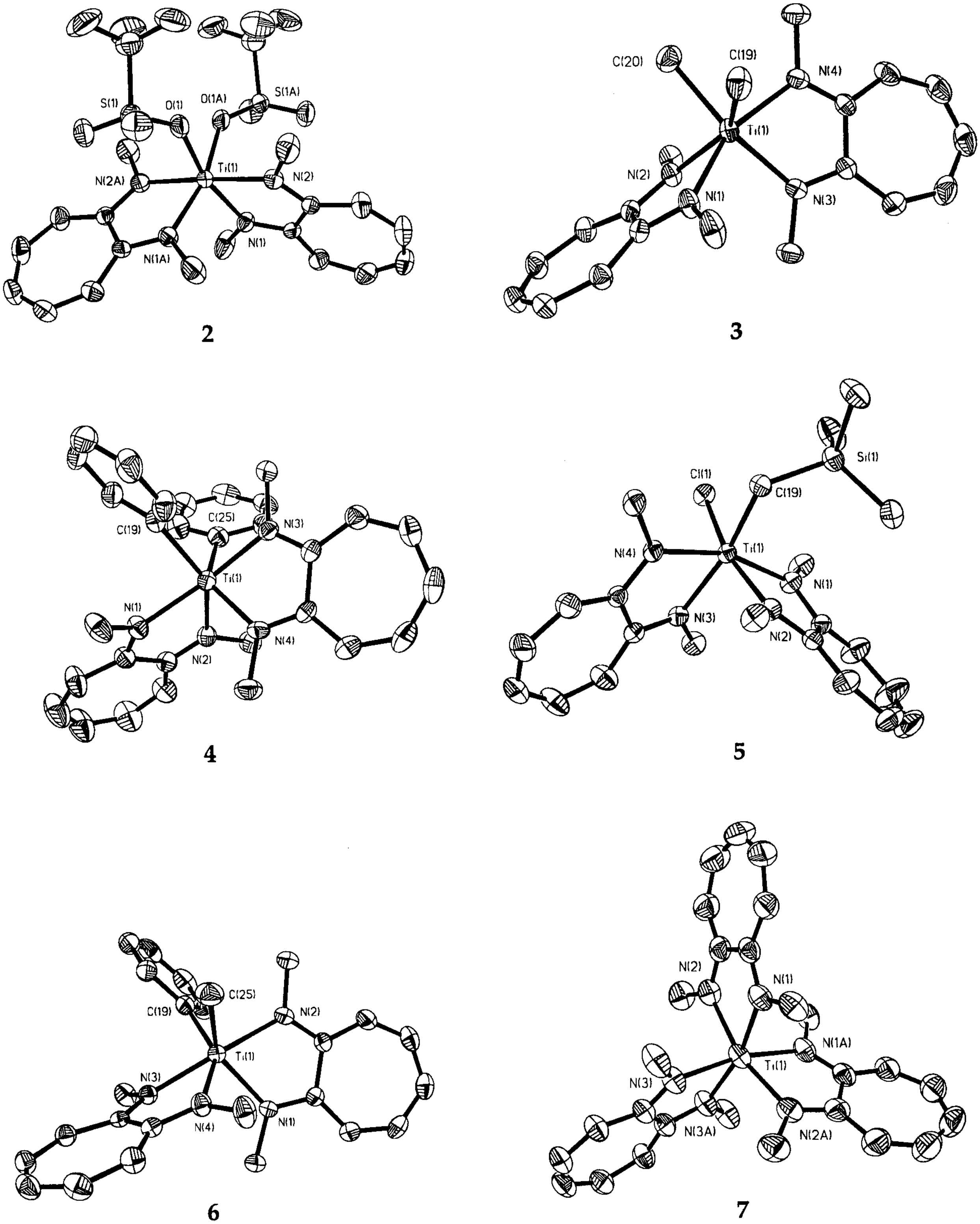


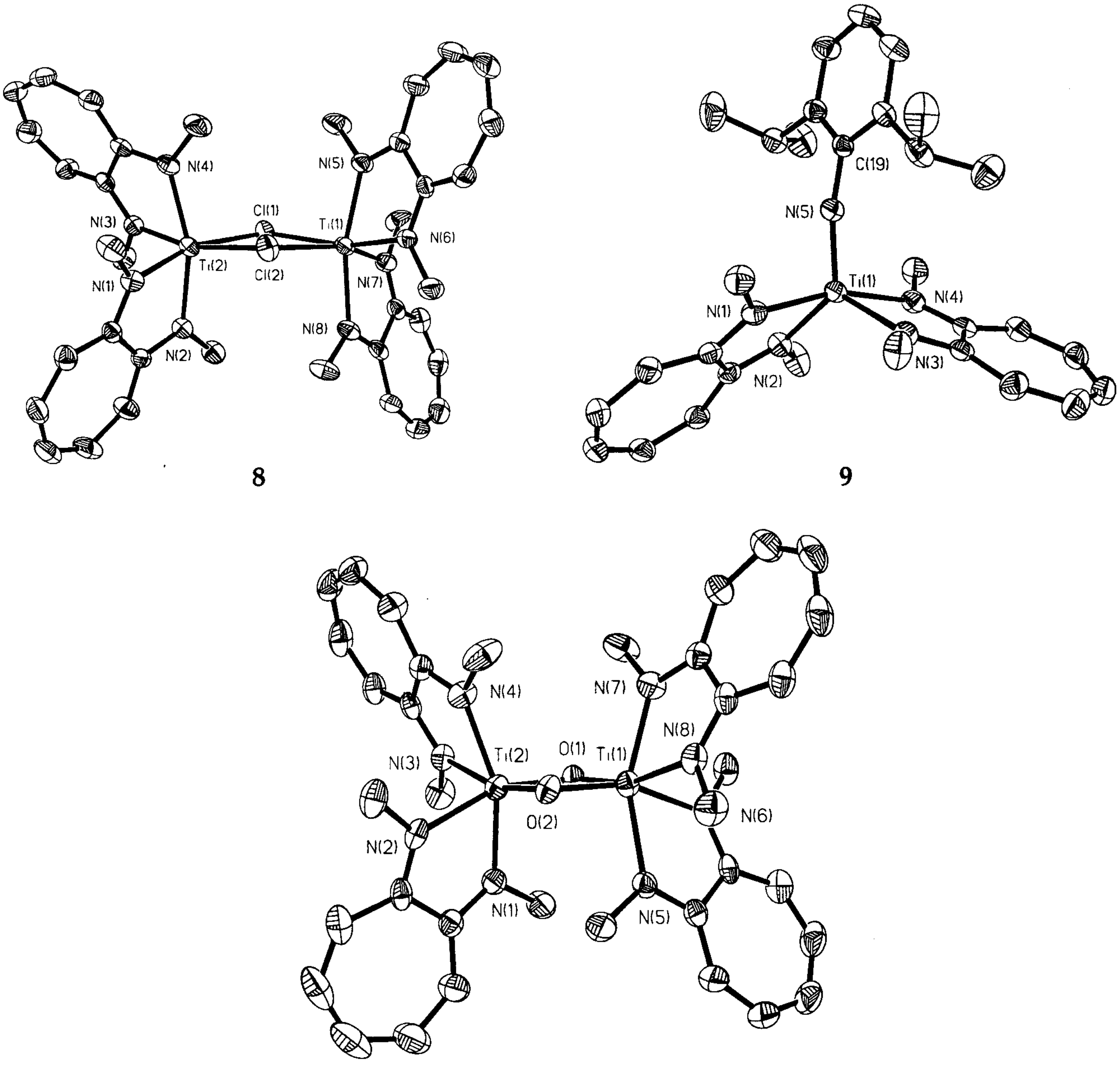
**Figure 2.** ORTEP diagrams of [Ti(OTf)$_2$(Me$_2$ATI)$_2$] (**2**), [TiMe$_2$(Me$_2$ATI)$_2$] (**3**), [TiPh$_2$(Me$_2$ATI)$_2$] (**4**), [TiCl(CH$_2$SiMe$_3$)(Me$_2$ATI)$_2$] (**5**), [Ti(Me)(Ph)(Me$_2$ATI)$_2$] (**6**), and [Ti(Me$_2$ATI)$_3$] (**7**) showing 50% thermal ellipsoids and selected atom labels.

## Results and Discussion

**Preparation and Characterization of [TiCl$_2$(Me$_2$ATI)$_2$] and [Ti(OTf)$_2$(Me$_2$ATI)$_2$].** A convenient entry into titanium aminotroponiminate chemistry was obtained through the reaction of HMe$_2$ATI with TiCl$_2$(NMe$_2$)$_2$ (eq 1). This chemistry afforded [TiCl$_2$(Me$_2$ATI)$_2$] (**1**) as a purple powder in nearly quantitative yield on a 1−2 g scale. The $^1$H NMR spectrum of this complex is consistent with $C_2$ symmetry. The poor solubility of **1** has

$$\mathrm{TiCl_2(NMe_2)_2 + 2\,HMe_2ATI \xrightarrow{C_6H_6} \underset{\mathbf{1}}{TiCl_2(Me_2ATI)_2}} \quad (1)$$

prevented its full characterization. A more tractable derivative was obtained by treatment of **1** with 2 equiv of Me$_3$SiOTf in CH$_2$Cl$_2$ to yield purple, crystalline [Ti(OTf)$_2$(Me$_2$ATI)$_2$] (**2**) in 80% yield (Figure 4). Compound **2** is also $C_2$-symmetric in solution and contains strong bands in the infrared spectrum at



**8**

**9**

**10**

**Figure 3.** ORTEP diagrams of $[Ti_2Cl_2(Me_2ATI)_4]$ (**8**), $[Ti(N\text{-}(2,6)\text{-}i\text{-}Pr_2C_6H_3)(Me_2ATI)_2]$ (**9**), and $[Ti_2O_2(Me_2ATI)_4]$ (**10**) showing 50% thermal ellipsoids and selected atom labels.

1352, 1032, and 632 cm$^{-1}$, consistent with the presence of a triflate group. The structure of **2** determined by X-ray crystallography reveals nearly octahedral coordination geometry with two monodentate triflate ligands (Figure 2). The three trans-angles, N(1a)−Ti−O(1a), N(2)−Ti−N(2a), and N(1)−Ti−O(1) are 163.9(1)°, 176.7(2)°, and 163.9(1)°, respectively. The Ti−O bond distance of 2.046(2) Å is in the range of other structurally characterized titanium triflate complexes.[29]

**Preparation and Characterization of $[TiMe_2(Me_2ATI)_2]$ and $[TiPh_2(Me_2ATI)_2]$.** The chloride ligands of **1** can be substituted by either methyl or phenyl groups. Reaction with the appropriate Grignard reagent gave dark red, crystalline $[TiMe_2(Me_2ATI)_2]$ (**3**) or $[TiPh_2(Me_2ATI)_2]$ (**4**) after workup (Figure 4). Compound **3** is best isolated after filtration of the ether solution, evaporation, and crystallization from toluene. Compound **4** can be obtained as a crude, thermally sensitive powder in reasonable yield. Recrystallization of **4** is challenging due to its moderate solubility and instability in solution. These factors account for the modest isolated yield of 30−40%. Both **3** and **4** display NMR spectra consistent with $C_2$-symmetric molecules. The structure of **3** has been determined by X-ray crystallography and displays cis stereochemistry. The complex can be described as distorted trigonal prismatic (Figure 2).[30] Complex **3** contains Ti−C bond distances of 2.145(2) and 2.166(2) Å, and the C−Ti−C angle is 86.29(7)°. The solid-state structure of **4** is very similar to that of **3** and the Ti−C bond distances of 2.170(3) and 2.185(3) Å are longer than those observed in **3** (Figure 2). The sterically more demanding phenyl group has also increased the C−Ti−C angle to 96.7(1)°. The

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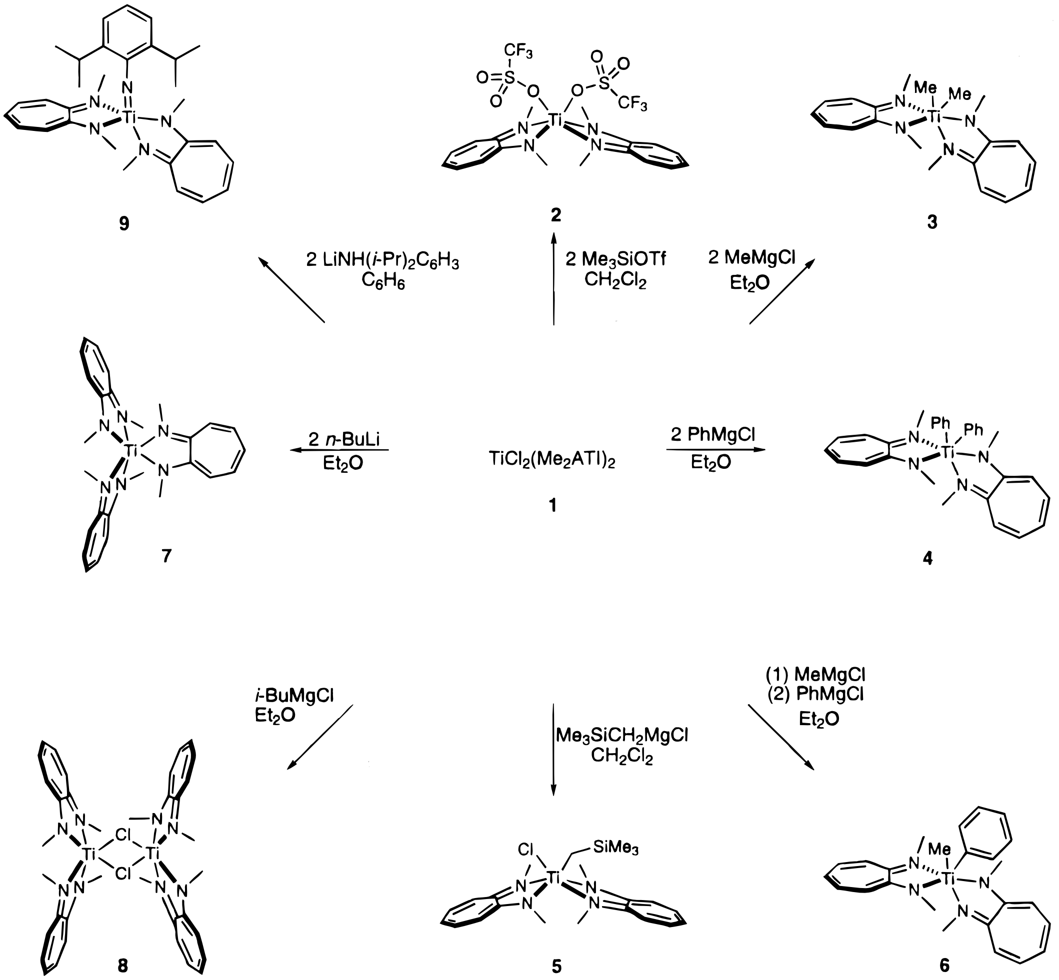

**Figure 4.** Summary of the reaction chemistry of [TiCl$_2$(Me$_2$ATI)$_2$].

Ti−C bond distance is 2.122(2) Å for the titanium trimethylsilyl substituted benzamidinate complex [TiMe$_2${PhC(NSiMe$_3$)$_2$}$_2$],[31] and the average Ti−C bond lengths of the aryloxide titanium phenyl complex [TiPh$_2$(OAr)$_2$] is 2.088 Å,[32] both shorter than the Ti−C bond lengths in **3** and **4**. The Ti−C bond length of 2.15(1) Å for the salen complex [TiMe$_2$(salen)] is very close to the average Ti−C bond distance of 2.155 Å for **3.**[33] These data suggest that the {Ti(Me$_2$ATI)$_2$}$^{2+}$ fragment is more electron rich than the corresponding aryloxide and benzamidinate fragments and comparable to the salen complex. The {Cp$_2$Ti}$^{2+}$ fragment is even more electron releasing, consistent with its formally higher electron count.[34,35]

Compound **3** is thermally robust in the solid state but less so in solution; it is best stored as a solid at −30 °C. Compound **4**, however, is significantly less thermally stable than **3**, especially in solution. Storage of C$_6$D$_6$ solutions of **4** for greater than 45 min at room temperature, even in the dark, results in decomposition. This decomposition is characterized by a decrease in intensity of all the resonances in the $^1$H NMR spectrum of **4** and the appearance of peaks most likely corresponding to biphenyl. Production of biphenyl from early metal cyclopentadienyl diphenyl complexes has been reported previously, although this reaction typically proceeds under photochemical conditions.[36,37] In contrast to the solution chemistry of [TiMe$_2$(salen)], **3** and **4** display no propensity for the methyl group to migrate to the imine carbon atom.[33]

**Preparation and Characterization of [TiCl(CH$_2$SiMe$_3$)(Me$_2$ATI)$_2$] and [TiMePh(Me$_2$ATI)$_2$].** A titanium alkylchloride complex would be a versatile starting material for the synthesis of mixed alkyl complexes. The reaction of [TiCl$_2$(Me$_2$ATI)$_2$] with 1 equiv of Me$_3$SiCH$_2$MgCl allows isolation of [TiCl(CH$_2$SiMe$_3$)(Me$_2$ATI)$_2$] (**5**), which has been fully characterized, including an X-ray structural determination (Figure 2). The important features in the $^1$H NMR spectrum of **5** are a 2H singlet at 2.33 ppm, a 9H singlet at 0.14 ppm, and a 12H singlet at 3.2 ppm corresponding to the two signals for the trimethylsilyl methyl and aliphatic signals of the Me$_2$ATI ligand, respectively. Compound **5** is probably fluxional in solution at room temperature since it displays $C_2$-symmetric $^1$H and $^{13}$C NMR spectra. The X-ray structure of **5** has been determined and confirms nearly octahedral coordination geometry characterized by the three trans angles N(3)−Ti−C(19), N(1)−Ti−N(4), and N(2)−Ti−Cl of 160.57(9)°, 160.49(8)°, and 165.67(6)° (Figure 2, Table 2). The Ti−C bond length is 2.154(3) Å, whereas the Ti−Cl distance is 2.3287(7) Å. Apparently, one trimethylsilyl methyl group is the steric maximum for the {Ti(Me$_2$ATI)$_2$}$^{2+}$ fragment, since the reaction of 2 equiv of Me$_3$SiCH$_2$MgCl with

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**Table 2.** Selected Bond Distances and Angles[a]

| complex | distances (Å) | | angles (deg) | |
|---|---|---|---|---|
| **2** | Ti−N(1) | 2.006(3) | N(1a)−Ti−O(1a) | 163.9(1) |
| | Ti−N(2) | 2.045(3) | N(2)−Ti−N(2a) | 176.7(2) |
| | Ti−O(1) | 2.046(2) | N(1)−Ti−O(1) | 163.9(1) |
| | | | O(1)−Ti−O(1a) | 83.7(2) |
| **3** | Ti−N(1) | 2.125(1) | N(4)−Ti−N(3) | 72.36(4) |
| | Ti−N(2) | 2.095(1) | C(19)−Ti−N(1) | 83.12(6) |
| | Ti−N(3) | 2.120(1) | C(20)−Ti−N(2) | 79.68(6) |
| | Ti−N(4) | 2.114(1) | C(19)−Ti−C(20) | 86.29(7) |
| | Ti−C(20) | 2.166(2) | N(3)−Ti−C(20) | 147.84(6) |
| | Ti−C(19) | 2.145(2) | N(2)−Ti−N(4) | 123.25(5) |
| **4** | Ti−N(1) | 2.104(3) | N(4)−Ti−N(3) | 72.77(10) |
| | Ti−N(2) | 2.082(3) | N(1)−Ti−C(19) | 80.86(11) |
| | Ti−N(3) | 2.116(3) | N(2)−Ti−C(25) | 78.39(11) |
| | Ti−N(4) | 2.062(2) | C(19)−Ti−C(25) | 96.7(1) |
| | Ti−C(19) | 2.185(3) | N(1)−Ti−N(3) | 151.52(10) |
| | Ti−C(25) | 2.170(3) | C(19)−Ti−N(4) | 119.82(11) |
| **5** | Ti−N(1) | 2.087(2) | N(3)−Ti−C(19) | 160.57(9) |
| | Ti−N(2) | 2.091(2) | N(1)−Ti−N(4) | 160.49(8) |
| | Ti−N(3) | 2.117(2) | N(2)−Ti−Cl(1) | 165.67(6) |
| | Ti−N(4) | 2.098(2) | Cl(1)−Ti−C(19) | 92.04(8) |
| | Ti−Cl(1) | 2.3287(7) | | |
| | Ti−C(19) | 2.154(3) | | |
| **6** | Ti−N(1) | 2.079(2) | N(1)−Ti−N(2) | 72.96(7) |
| | Ti−N(2) | 2.122(2) | N(4)−Ti−C(25) | 79.32(11) |
| | Ti−N(3) | 2.116(2) | N(3)−Ti−C(19) | 81.45(8) |
| | Ti−N(4) | 2.102(2) | C(19)−Ti−C(25) | 93.30(12) |
| | Ti−C(19) | 2.171(2) | N(3)−Ti−N(2) | 154.32(7) |
| | Ti−C(25) | 2.148(3) | C(19)−Ti−N(1) | 119.66(9) |
| **7** | Ti−N(1) | 2.121(1) | N(3)−Ti−N(1a) | 167.26(6) |
| | Ti−N(2) | 2.099(2) | N(2)−Ti−N(2a) | 163.87(8) |
| | Ti−N(3) | 2.110(1) | N(1)−Ti−N(3a) | 167.26(6) |
| **8** | Ti(1)−N(5) | 2.092(3) | N(8)−Ti(1)−N(5) | 165.4(1) |
| | Ti(1)−N(6) | 2.088(3) | Cl(2)−Ti(1)−N(7) | 161.26(9) |
| | Ti(1)−N(7) | 2.081(3) | Cl(1)−Ti(1)−N(6) | 164.75(9) |
| | Ti(1)−N(8) | 2.112(3) | N(3)−Ti(2)−Cl(2) | 165.16(8) |
| | Ti(1)−Cl(1) | 2.550(2) | N(1)−Ti(2)−Cl(1) | 163.52(9) |
| | Ti(1)−Cl(2) | 2.526(1) | N(4)−Ti(2)−N(2) | 161.51(11) |
| | Ti(2)−N(1) | 2.086(3) | Ti(2)−Cl(2)−Ti(1) | 98.29(5) |
| | Ti(2)−N(2) | 2.116(3) | Cl(2)−Ti(2)−Cl(1) | 82.12(5) |
| | Ti(2)−N(3) | 2.094(3) | Cl(2)−Ti(1)−Cl(1) | 80.70(5) |
| | Ti(2)−N(4) | 2.107(3) | Ti(2)−Cl(1)−Ti(1) | 97.97(5) |
| | Ti(2)−Cl(1) | 2.496(1) | Ti(2)−Cl(2)−Ti(1) | 98.29(5) |
| | Ti(2)−Cl(2) | 2.508(1) | | |
| | Ti(1)−Ti(2) | 3.808(2) | | |
| **9** | Ti−N(1) | 2.089(1) | N(4)−Ti−N(1) | 162.10(5) |
| | Ti−N(2) | 2.098(1) | N(2)−Ti−N(3) | 121.93(5) |
| | Ti−N(3) | 2.105(1) | N(3)−Ti−N(5) | 118.37(6) |
| | Ti−N(4) | 2.099(1) | N(5)−Ti−N(2) | 119.51(6) |
| | Ti−N(5) | 1.734(1) | Ti−N(5)−C(19) | 167.1(1) |
| **10** | Ti(1)−N(5) | 2.113(3) | N(7)−Ti(1)−N(5) | 156.7(1) |
| | Ti(1)−N(6) | 2.129(2) | O(2)−Ti(1)−N(6) | 158.8(1) |
| | Ti(1)−N(7) | 2.098(3) | O(1)−Ti(1)−N(8) | 163.0(1) |
| | Ti(1)−N(8) | 2.154(3) | N(3)−Ti(2)−O(2) | 163.2(1) |
| | Ti(1)−O(1) | 1.876(2) | N(2)−Ti(2)−O(1) | 159.4(1) |
| | Ti(1)−O(2) | 1.835(2) | N(4)−Ti(2)−N(1) | 157.8(1) |
| | Ti(2)−N(1) | 2.118(3) | O(1)−Ti(2)−O(2) | 83.18(9) |
| | Ti(2)−N(2) | 2.138(3) | O(1)−Ti(1)−O(2) | 83.41(9) |
| | Ti(2)−N(3) | 2.143(2) | Ti(1)−O(1)−Ti(2) | 96.56(9) |
| | Ti(2)−N(4) | 2.091(3) | Ti(1)−O(2)−Ti(2) | 96.71(9) |
| | Ti(2)−O(1) | 1.841(2) | | |
| | Ti(2)−O(2) | 1.878(2) | | |
| | Ti(1)−Ti(2) | 2.775(1) | | |

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figures 2 and 3.

**1** yields mostly **5** whereas reaction of lithium reagents or excess $Me_3SiCH_2MgCl$ with **1** affords Ti(III) complexes.

Mixing either **1** or **2** with equimolar amounts of **3** produces solutions of either [$TiMeCl(Me_2ATI)_2$] or [$TiMe(OTf)(Me_2ATI)_2$], judging by $^1H$ NMR spectroscopy (eq 2). These two complexes are $C_2$-symmetric in solution and display similar spectra to that of **5**, with 3H singlets at 1.59 or 1.55 ppm,

$$\underset{X = Cl,\ OTf}{TiX_2(Me_2ATI)_2} + TiMe_2(Me_2ATI)_2 \xrightarrow{C_6D_6} \underset{X = Cl,\ OTf}{2TiXMe(Me_2ATI)_2} \quad (2)$$

respectively, for the methyl groups. Generation of [$TiMeCl(Me_2ATI)_2$] in $CH_2Cl_2$ provides a convenient starting material for the preparation of [$TiMeR'(Me_2ATI)_2$] complexes. Treatment of [$TiMeCl(Me_2ATI)_2$], formed in situ, with PhMgCl in diethyl ether provides [$TiMePh(Me_2ATI)_2$] (**6**) after crystallization. Although the yield of crude **6** is good (65%), recrystallization is difficult and the isolated yield is therefore modest. The $^1H$ NMR spectrum of **6** is consistent with a $C_2$-symmetric molecule and comprises a singlet at 1.49 ppm for the methyl group in addition to aromatic resonances. The X-ray crystal structure of **6** has been determined and is very similar to the solid-state structures of **3** and **4** (Figure 2, Table 2). The Ti−C(methyl) and Ti−C(phenyl) bond distances are 2.148(3) and 2.171(2) Å, whereas the C−Ti−C angle is 93.3(1)°, comparable to the values of 86.29(7)° in **3** and 96.7(1)° in **4**. Compound **6** displays thermal stability between that of **3** and **4**; it is best stored at −35 °C as a solid. Interestingly, **6** cannot be prepared by mixing **3** and **4** in $C_6D_6$, as revealed by $^1H$ NMR spectroscopy.

**Preparation and Characterization of [$Ti(Me_2ATI)_3$] and [$Ti_2Cl_2(Me_2ATI)_4$].** Certain aminotroponiminate ligands afford Ti(IV) dialkyl complexes that contain $\beta$-hydrogen atoms.[38] For this reason, reaction of **1** with other Grignard and lithium reagents was investigated. Treatment of **1** with 2 equiv of *n*-BuLi in ether resulted in an immediate color change to brown-black, and no resonances were observed in the $^1H$ NMR spectrum of the reaction mixture. A few brown-black crystals of [$Ti(Me_2ATI)_3$] (**7**) could be isolated, and the X-ray structure revealed nearly octahedral coordination geometry with three trans N−Ti−N angles (N(2a)−Ti−N(2), N(3a)−Ti−N(1), and N(3)−Ti−N(1a)) of 163.87(8)°, 167.26(6)°, 167.26(6)° and Ti−N bond distances of 2.099(2), 2.110(1), and 2.121(1) Å (Figure 2, Table 2). The overall structure is similar to that of other $TiL_3$ (L = bidentate ligand) complexes,[39,40] but it differs slightly from the solid-state structure of [Sc(trop)$_3$], which has a coordination geometry between octahedral and trigonal prismatic.[41] Toluene solutions of **7** at room temperature display an isotropic EPR signal at $g = 1.96$, which resolves into an axial spectrum with $g_{\parallel} = 1.99$ and $g_{\perp} = 1.95$ at 14.4 K. These spectra are consistent with the presence of a symmetric, mononuclear Ti(III) complex and are very similar to those reported in the literature for $TiL_3$ complexes, where L is either a monodentate or bidentate monoanionic ligand.[39,40,42−45] A more efficient, higher yielding route to **7** is the reaction of [$TiCl_3(THF)_3$] with 3 equiv of $LiMe_2ATI$ in THF (eq 3). The preparation of [$Ti(Me_2ATI)_3$] completes the series of $Me_2ATI$ tris-chelate complexes from titanium through cobalt.[18]

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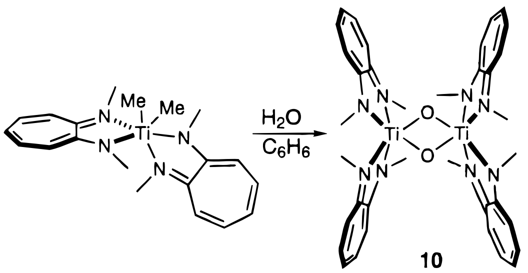
$$\mathrm{TiCl_3(THF)_3 + 3\,LiMe_2ATI \xrightarrow{THF} \underset{\mathbf{7}}{Ti(Me_2ATI)_3}} \qquad (3)$$

A different Grignard reagent, *i*-BuMgCl gives another paramagnetic product in low yield. This material was identified by X-ray crystallography as $[\mathrm{Ti_2Cl_2(Me_2ATI)_4}]$ (**8**) (Figure 3). The X-ray structure of **8** reveals two nearly octahedral Ti(III) centers with long Ti−Cl distances of 2.496(1), 2.508(1), 2.526(1), and 2.550(2) Å and a Ti···Ti separation of 3.808(2) Å (Table 2). The *i*-BuMgCl reagent acts as a single electron reductant in this reaction, and the resulting $\{\mathrm{TiCl(Me_2ATI)_2}\}$ complex dimerizes. The $\{\mathrm{Ti_2Cl_2}\}^{4+}$ motif is common in titanium chemistry and has been supported by several different classes of ligands.[46−50] The Ti···Ti distance can vary in these complexes from almost 4 Å in $[\mathrm{Ti_2Cl_2Cp_4}]$ to 2.9 Å in either $[\mathrm{Ti_2Cl_2(OAr)_4}]$ or a dinuclear cyclohexyl substituted formamidinate complex $[\mathrm{Ti_2Cl_2\{HC(NCy)_2\}_4}]$.[46,47,50] Formation of $[\mathrm{Ti_2Cl_2(Me_2ATI)_4}]$ fulfills the coordinative unsaturation of the $\{\mathrm{TiCl(Me_2ATI)_2}\}$ fragment. The unsaturated character must not be of great consequence since, by increasing the size of the R substituent from Me to *i*-Pr, we were able to isolate monomeric $[\mathrm{TiCl((\textit{i}\text{-}Pr)_2ATI)_2}]$.[51] Similar results, especially with amidinate and cyclopentadienyl ligands, have been reported in the literature.[52,53]

Reaction of $[\mathrm{TiCl_2(Me_2ATI)_2}]$ with allyl, vinyl, neopentyl Grignard, or lithium phenyl acetylide under a variety of conditions resulted in paramagnetic reaction mixtures. In some cases, **6** or **7** could be isolated depending on the number of equivalents of Grignard reagent that were used. Reaction of **1** with 2 equiv of neopentyl Grignard in the presence of excess $\mathrm{PMe_3}$ also gave a paramagnetic reaction mixture. These synthetic studies show that **1** is especially susceptible to reduction by alkylating reagents and that the steric constraints of the $\{\mathrm{Ti(Me_2ATI)_2}\}^{2+}$ fragment only allow formation of monoalkyl complexes, such as $[\mathrm{TiCl(CH_2SiMe_3)(Me_2ATI)_2}]$, having a bulky group.

**Preparation and Characterization of $[\mathrm{Ti(N\text{-}(2,6)\text{-}\textit{i}\text{-}Pr_2C_6H_3)(Me_2ATI)_2}]$.** Since the putative five-coordinate $\{\mathrm{TiCl(Me_2ATI)_2}\}$ species readily dimerizes, we were interested to test whether a five-coordinate Ti(IV) complex might be prepared by using a bulky $\sigma$-$2\pi$ ligand such as a 2,6-*i*-Pr-substituted imide. Reaction of 2 equiv of $\mathrm{Li(NH(2,6)\text{-}\textit{i}\text{-}Pr_2C_6H_3)}$ with **1** afforded a new titanium complex and 1 equiv of arylamine (Figure 4). The $^1$H NMR spectrum of the new complex displayed a 12H doublet at 1.30 ppm and a 2H septet at 4.05 ppm, consistent with a single *i*-Pr group environment. The $^1$H and $^{13}$C signals corresponding to $\mathrm{Me_2ATI}$ were also consistent with $C_2$-symmetry. The structure of **9** was determined by X-ray crystallography, revealing that the bulky aryl-imido ligand had indeed stabilized a five-coordinate complex. The imido ligand occupies the equatorial position of a trigonal bipyramidal coordination polyhedron and the Ti−N bond distance is short, 1.734(1) Å; the Ti−N−C angle is 167.1(1) (Figure 3). The remaining Ti−N bond distances are in the usual range. Titanium aryl imido complexes are common in complexes having multiple nitrogen ligands and many five-coordinate titanium aryl imido analogues have been structurally characterized.[6,22,54−56] Of this group, $[\mathrm{Ti(NPh)Cl_2(tmeda)}]$ has the shortest Ti−N bond length, 1.702(6) Å, whereas the salen complex [TiNAr(salen)] has the longest one, 1.725(2) Å.[57,58] Compound **9** is distinguished in this class by having one of the longer Ti−N bond distances and the smallest Ti−N−C angle. These data reflect the electron-releasing character of the $\{\mathrm{Ti(Me_2ATI)_2}\}^{2+}$ fragment.

**Preparation and Characterization of $[\mathrm{Ti_2O_2(Me_2ATI)_4}]$.** The steric influence of the isopropyl groups in the imido ligand just discussed is further manifest by attempts to prepare the isoelectronic oxo analogue, $\mathrm{TiO(Me_2ATI)_2}$, which instead resulted in isolation of dimeric $[\mathrm{Ti_2O_2(Me_2ATI)_4}]$ (**10**). Compound **10** is best prepared by treating **3** with 1 equiv of water in benzene solution (eq 4), although it can also be obtained in lower yield by the air oxidation of **7** in toluene solution. The $^1$H NMR spectrum of **7** in $\mathrm{CDCl_3}$ comprises two equal intensity singlets for the methyl groups of $\mathrm{Me_2ATI}$, consistent with two distinct methyl environments for the ATI ligand. The X-ray crystal structure of **10** was determined and revealed both titanium centers to have nearly octahedral coordination geometry (Figure 3, Table 2). The Ti−O distances are short, 1.835(2), 1.876(2), 1.841(2), 1.878(2) Å, whereas the Ti−N distances are in their normal range (2.1 Å). The $\{\mathrm{Ti_2O_2}\}^{4+}$ core has also been previously described, and several examples have been structurally characterized.[59−62] The direct comparison of the results to those for **10** is not straightforward because of differences in coordination number and charge. The Ti−O bond distances in **10**, at least when compared to those of $[\mathrm{Ti_2O_2(acac)_4}]$, 1.831(3) Å, 1.824(4) Å, support the idea that the $\mathrm{Me_2ATI}$ ligand is a strong donator of electron density.[61,62]



10

(4)

## Summary and Conclusions

The use of *N*,*N*′-dimethyl-substituted aminotroponiminates

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as ancillary ligands for the preparation of titanium complexes has been demonstrated. A series of dialkyl derivatives and an alkyl−aryl analogue have been prepared and structurally characterized. Trivalent complexes were obtained by using an appropriate $\beta$-hydrogen-containing Grignard or alkyllithium reagent. The steric properies of the $\{Ti(Me_2ATI)\}^{2+}$ fragment are not demanding, so that five-coordinate titanium(IV) complexes were obtained only when a bulky $\sigma$-2$\pi$ ligand was employed. Otherwise, dinuclear complexes formed. Comparisons of structural data for this family of complexes to those in the literature suggest that dialkyl-substituted aminotroponiminate ligands are good donors of electron density; the $\{Ti(Me_2ATI)\}^{2+}$ fragment is electron rich.

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**Supporting Information Available:** Tables and figures reporting bond distances, angles, and positional and thermal parameters for all structurally characterized compounds including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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