

# Synthesis and Characterization of (Aminotroponiminato)titanium(IV) Dialkyl Complexes: Control of Reactivity by Ligand Design

Dietrich P. Steinhuebel and Stephen J. Lippard\*

Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139

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**Summary:** The synthesis and structural characterization of titanium(IV) dialkyl complexes ligated by a new tetradentate  $C_2$ -symmetric aminotroponimate ligand are reported. Included are rare examples of thermally stable titanium diethyl and di-*n*-butyl complexes and an  $\eta^2$ -imine complex.

Titanium(IV) dialkyl complexes have been extensively studied for use in catalytic and stoichiometric chemistry. Numerous combinations of ancillary ligands and different alkyl groups have been used in the preparation of these molecules. The instability of compounds having short-chain alkyl ligands with  $\beta$ -hydrogen atoms, however, has rendered difficult their isolation and characterization. Apart from two recently described diisobutyl compounds,<sup>1,2</sup> there are no examples to the best of our knowledge of thermally stable titanium(IV) dialkyl complexes containing noncyclic alkyl ligands with  $\beta$ -hydrogen atoms.<sup>3,4</sup> Here we describe the synthesis of a family of thermally stable compounds in this class made accessible with the aid of a new  $C_2$ -symmetric aminotroponimate ligand. This chemistry has also allowed us to access a stable titanium(IV)  $\eta^2$ -imine derivative.

Early studies in titanocene chemistry revealed that complexes such as  $Cp_2TiR_2$  ( $R = n\text{-Bu}$ ) rapidly decompose to equimolar mixtures of alkene and alkane, results consistent with  $\beta$ -elimination.<sup>5,6</sup> Decomposition of  $Cp_2Ti(n\text{-Bu})_2$  or  $Cp_2Ti(Et)_2$  in the presence of  $PMe_3$  yielded  $Cp_2Ti(PMe_3)_2$ , and with the use of modified Cp ligands it was possible to isolate the olefin complexes.<sup>7,8</sup> The orientation of the alkyl group with respect to the metal center is a key factor in determining the feasibility of the  $\beta$ -elimination reaction. When the  $Ti-C_\alpha-C_\beta-H$  dihedral angle is  $0^\circ$ , the orientation of the alkyl group is optimal for  $\beta$ -elimination, as demonstrated by the preparation of a thermally stable  $Cp_2Ti(CH_2)_4$  metallocycle.<sup>6</sup>

We were interested in preparing dialkyltitanium(IV) complexes in order to expand the scope of previously described carbonyl coupling chemistry.<sup>9</sup> The ligand originally employed,  $Me_2ATI^-$  ( $ATI = \text{aminotroponimate}$ ), was unsuitable for this purpose since treatment of  $[TiCl_2(Me_2ATI)_2]$  with  $\beta$ -hydrogen-containing alkyl anions afforded either  $[Ti(Me_2ATI)_3]$  or  $[Ti_2Cl_2(Me_2ATI)_4]$ .<sup>10</sup> We therefore linked the two aminotroponimate ligands with a spacer, *trans*-1,2-diaminocyclohexane, to provide more rigid and stable complexes. In this report we present two dramatic results that arise from this change in the geometrical properties of the ATI ligand: (1) the isolation and characterization of thermally stable titanium(IV) diethyl and di-*n*-butyl complexes and (2) the preparation of a titanium  $\eta^2$ -imine complex. The new  $C_2$ -symmetric ligand allows compounds to be isolated and characterized that are unstable in the unlinked  $Me_2ATI^-$  system while retaining their interesting chemical reactivity.

The desired ligand was prepared by treating *trans*-(*R,R*)-1,2-diaminocyclohexane with a suitably activated aminomethyltropolone in  $CH_2Cl_2$ .<sup>11</sup> The new  $C_2$ -symmetric ligand  $[H_2\{(MeATI)_2Cy\}]$  (**1**) was isolated as an analytically pure yellow solid on a 2–3 g scale in 44% yield. Reaction of **1** with  $[TiCl_2(NMe_2)_2]$ <sup>12</sup> in benzene gave  $[TiCl_2\{(MeATI)_2Cy\}]$  (**2**) as a dark green solid in 82% yield (Scheme 1). Dark purple THF solutions of  $[TiCl_2\{(MeATI)_2Cy\}]$  reacted cleanly with 2 equiv of  $MeMgCl$  to afford  $[TiMe_2\{(MeATI)_2Cy\}]$  (**3**) in 69% yield after crystallization. The X-ray structure of **3** reveals a  $C_2$ -symmetric aminotroponimate ligand that is nearly planar.<sup>13</sup> The Ti–C distances of 2.141(2) and 2.167(2)

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(11) See the Supporting Information for experimental procedures and spectral and analytical data for all compounds.

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(13) Crystal structure analysis of **3**:  $C_{24}H_{32}N_4Ti$ ,  $M_r = 424.44$ , monoclinic, space group  $P2_1$ ,  $a = 11.6235(6)$  Å,  $b = 8.8621(5)$  Å,  $c = 12.2011(7)$  Å,  $\beta = 116.8300(10)^\circ$ ,  $V = 1121.52(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 452$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ),  $\mu(\text{Mo K}\alpha) = 0.398$  mm<sup>-1</sup>;  $T = 188$  K, crystal dimensions 0.35 mm  $\times$  0.3 mm  $\times$  0.2 mm. The structure was solved by direct methods using XS and then refined by full-matrix least squares and Fourier techniques using SHELXTL-PLUS. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in difference Fourier maps and refined isotropically. The 3890 observed reflections ( $I > 2\sigma(I)$ ) were collected on a Bruker CCD-detector-based diffractometer ( $1.87^\circ < \theta < 28.22^\circ$ ), corrected for absorption by using the SADABS program, and refined to a conventional R1 value of 0.0259 (wR2 = 0.0632). Crystallographic data for all structures, including bond distances and angles in addition to positional and thermal parameters (excluding structure factors), can be found in the Supporting Information.

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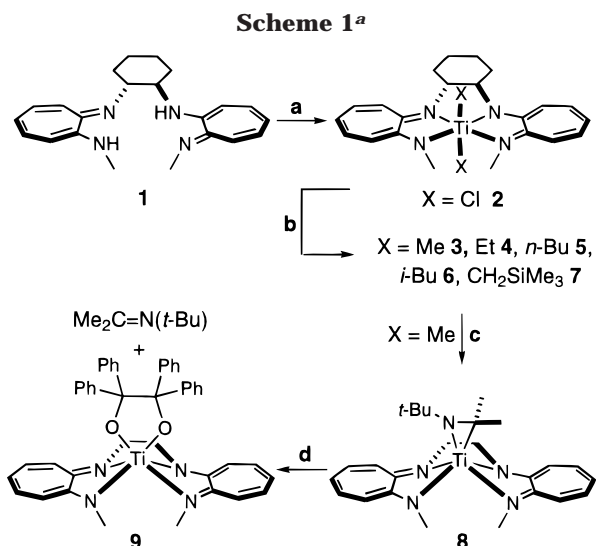
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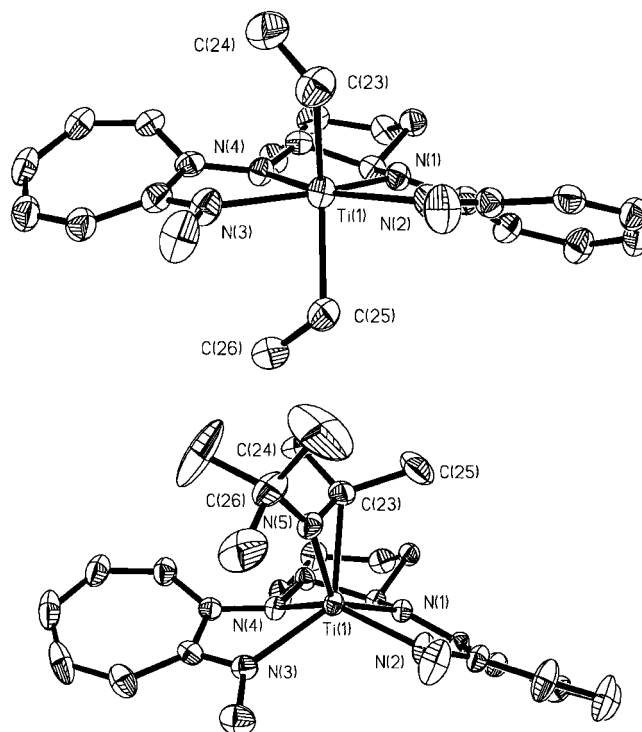
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<sup>a</sup> Reagents: (a) TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>; (b) 2 RMgCl; (c) *t*-BuNC; (d) 2 Ph<sub>2</sub>CO.

Å are in the expected range for these types of complexes.<sup>10</sup> The coordination geometry of **3** is best described as skew trapezoidal bipyramidal in contrast to the *cis*-octahedral geometry of the unlinked [TiMe<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] complex.<sup>14</sup> It appears that linking the two bidentate aminotroponimate ligands with the *trans*-diaminocyclohexane spacer enforces a geometry in which the C–Ti–C angle has increased from 86.29(7)° in [TiMe<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] to 129.77(9)° in **3**.<sup>10</sup>

Treatment of [TiCl<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] with EtMgCl (2 equiv, Et<sub>2</sub>O, –30 °C) generated a red solution that appeared to be stable at room temperature. The NMR properties of the product of this reaction were consistent with [TiEt<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] (**4**). The X-ray structure of [TiEt<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] was determined and is very similar to the solid-state structure of **3** (Figure 1).<sup>15</sup> The ligand adopts an essentially planar geometry, and the C–Ti–C angle is 137.2(2)°. The solid-state geometries of **3** and **4** are similar to that of [TiMe<sub>2</sub>(salen)] except that, in this compound, the C–Ti–C angle is 154.9(6)°. Another important difference between these complexes is the low thermal stability of [TiMe<sub>2</sub>(salen)] compared to that of [Ti(R)<sub>2</sub>{(MeATI)<sub>2</sub>Cy}].<sup>16</sup> Compound **4** is, to our knowledge, the first report of a thermally stable titanium diethyl complex. Treatment of **2** with *i*-BuMgCl, *n*-BuMgCl, or Me<sub>3</sub>SiCH<sub>2</sub>MgCl (2 equiv, Et<sub>2</sub>O) afforded red solutions which yielded [Ti(*n*-Bu)<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] (**5**), [Ti(*i*-Bu)<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] (**6**), and [Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] (**7**), respectively, as thermally robust, red crystalline solids. The NMR properties of each of these molecules were consistent with their formulation as C<sub>2</sub>-symmetric dialkyl complexes. All of these new dialkyl complexes can be heated to 70 °C for at least 1 h without any sign of decomposition. The high thermal stability of dialkyl complexes **4–7** is intriguing, since [TiCl<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] reacts with *n*-BuLi (2 equiv) or *i*-BuMgCl (1 equiv) to afford [Ti(Me<sub>2</sub>ATI)<sub>3</sub>] and [TiCl(Me<sub>2</sub>ATI)<sub>2</sub>],



**Figure 1.** ORTEP diagrams of **4** (top) and **8** (bottom) showing 50% thermal ellipsoids and atom labels. Selected bond distances for **4** and **8**, respectively (Å): Ti–N(1), 2.068(3), 2.114(2); Ti–N(2), 2.120(3), 2.051(2); Ti–N(3), 2.107(3), 2.127(3); Ti–N(4), 2.097(3), 2.095(2). For a more complete listing see the Supporting Information.

respectively.<sup>10</sup> Although [TiCl(CH<sub>2</sub>SiMe<sub>3</sub>)(Me<sub>2</sub>ATI)<sub>2</sub>] can be prepared, attempts to add a second, bulkier alkyl group resulted in reduction.

Two possible decomposition pathways available for  $\beta$ -hydrogen-containing dialkyl complexes are reduction of the titanium halide precursor by the alkylating agent and  $\beta$ -elimination or  $\beta$ -abstraction of a mono- or dialkyl complex. Reduction by the alkyl anion source is the predominate decomposition pathway in the Me<sub>2</sub>ATI<sup>–</sup> systems, since Ti(III) products have been isolated during attempts to alkylate [TiCl<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>]. No products consistent with such a reduction process have been isolated in the [TiR<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] system. Furthermore, the larger C–Ti–C angles of [TiR<sub>2</sub>{(MeATI)<sub>2</sub>Cy}] complexes relative to those of [TiR<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] may render  $\beta$ -abstraction processes more difficult in the former case. Electronic effects may also contribute to the stability of these complexes, but they have not been delineated. Although there are many factors that contribute to the stability of these dialkyl complexes, it is clear that the geometric properties of the {(MeATI)<sub>2</sub>Cy}<sup>2–</sup> ligand play an important role.

Once good synthetic routes to **3–7** were in hand, we wanted to determine whether double alkyl migration or the formation of bis(iminoacyl) complexes would occur upon addition of isocyanides to **3**. Because the C–Ti–C angle in **3** is 129.77(9)°, there was a possibility that the two alkyl groups would add to different isocyanide ligands rather than the same one. The structure of the 1,2-diaminocyclohexane-linked salen complex [Ti(C<sub>2</sub>O<sub>4</sub>)(salchxn)], however, suggested that the analogous ATI ligand might similarly distort to accommodate a double-migration product.<sup>17</sup> When benzene solutions of [TiMe<sub>2</sub>–

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(15) Crystal structure analysis of **4**: C<sub>26</sub>H<sub>36</sub>N<sub>4</sub>Ti, *M<sub>r</sub>* = 452.49, orthorhombic, space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, *a* = 8.3814(13) Å, *b* = 17.059(3) Å, *c* = 34.520(5) Å, *V* = 4935.5(13) Å<sup>3</sup>, *Z* = 8, *F*(000) = 1936, *T* = 188 K, *R*1 = 0.0556 (*wR*2 = 0.1069).

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{(MeATI)<sub>2</sub>Cy} were allowed to react with 1 equiv of *t*-BuNC, a complex was obtained that lacked C<sub>2</sub> symmetry, as revealed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Scheme 1). The *N*-Me groups of the ligand and the two Me substituents bound to titanium afforded four inequivalent resonances and none corresponding to the free imine, Me<sub>2</sub>C=N(*t*-Bu). The spectroscopic data were consistent with the η<sup>2</sup>-imine complex [Ti{η<sup>2</sup>-Me<sub>2</sub>CN(*t*-Bu)}{(MeATI)<sub>2</sub>Cy}] (**8**), formed by double alkyl migration to the isocyanide. This assignment was confirmed by an X-ray structure determination (Figure 1).<sup>18</sup> The metrical parameters of **8** compare well with those of other titanium η<sup>2</sup>-imine complexes.<sup>19</sup> The C–N bond distance of 1.417(4) Å and the Ti–N (1.883(2) Å) and Ti–C bond (2.132(3) Å) lengths are as expected. The structure is best described as square pyramidal, with the four nitrogen atoms of the ligand comprising the base of a square pyramid and the imine ligand occupying the axial position.

The stabilizing effect of the diaminocyclohexane ligand is highlighted by the difference in isocyanide reactivity with analogous Me<sub>2</sub>ATI<sup>−</sup> compounds. [TiMe<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] reacted rapidly with *t*-BuNC to generate dark brown solutions containing the corresponding free imine, together with some starting material and paramagnetic product(s) as determined by NMR spectroscopy. The reduced titanium species formed are unstable and have not been isolated.<sup>10</sup> It is apparent that, with the Me<sub>2</sub>ATI<sup>−</sup> ligand, double alkyl migration occurs but the resulting complex is unstable toward loss of the imine. In contrast, **8** is thermally robust. We attribute the changes in stability of these two η<sup>2</sup>-imine complexes in part to steric factors. Molecular modeling of the putative [Ti{η<sup>2</sup>-Me<sub>2</sub>CN(*t*-Bu)}(Me<sub>2</sub>ATI)<sub>2</sub>] compound reveals steric interactions between the geminal methyl groups of the imine and the *N*-Me groups on the ATI ligand. These steric clashes contribute to the dissociation of the imine.

Titanium η<sup>2</sup>-imine complexes are common and have been prepared previously by the reaction of isocyanides with four-coordinate, aryloxy-coordinated titanium dialkyls.<sup>20</sup> Upon treatment with suitable pyridine ligands, these complexes eliminate the imine to yield Ti(II) and Ti(III) complexes.<sup>20,21</sup> The elimination of iminocyclopentenes, produced by the titanocene-induced cyclization of enynes followed by isocyanide insertion, has also been reported.<sup>22,23</sup> The present results provide an

interesting example of how the stability of an η<sup>2</sup> adduct can be improved by altering the geometric requirements of the ligand.

The isolation of the thermally stable η<sup>2</sup>-imine **8** has afforded us the opportunity to explore its reactivity. In principle, **8** could serve as a precursor to new unsymmetrical titanium diamido and amidoalkoxide complexes formed by the insertion of imine and carbonyl compounds, respectively.<sup>24</sup> Reaction of **8** with 2 equiv of benzophenone yields the diolate complex **9** while 1 equiv of benzophenone affords a mixture of **9** and **8**. The inability to stop the reaction after only one molecule of benzophenone has reacted is probably due to the strong driving force to form two titanium–oxygen bonds. The same outcome is observed with [TiMe<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>], *t*-BuNC and Ph<sub>2</sub>CO (2 equiv), which gives [Ti(OCPh<sub>2</sub>-Ph<sub>2</sub>CO)(Me<sub>2</sub>ATI)<sub>2</sub>].<sup>9</sup> This result is consistent with the formation of a transient η<sup>2</sup>-imine complex in the Me<sub>2</sub>ATI<sup>−</sup> chemistry. Compound **8** is unreactive toward other carbonyl compounds and imines under a variety of conditions.

In conclusion, we have prepared a new C<sub>2</sub>-symmetric tetradentate ligand derived from tropolone and *trans*-1,2-diaminocyclohexane. The novel coordination geometries enforced by this ligand have resulted in the isolation of thermally robust titanium dialkyl complexes, including the first example of an isolable titanium diethyl complex. A thermally stable η<sup>2</sup>-imine complex in which the ligand has distorted to support a pseudo-square-pyramidal coordination geometry has also been isolated and characterized. It has not been possible to prepare such complexes when the Me<sub>2</sub>ATI<sup>−</sup> ligand is employed. The C<sub>2</sub>-symmetric ligand reported here can adopt different geometries to stabilize complexes not accessible in the Me<sub>2</sub>ATI<sup>−</sup> system, but the reactivity of these molecules is not completely inhibited. This difference is highlighted by the analogous reactivity of both Me<sub>2</sub>ATI<sup>−</sup> and {(MeATI)<sub>2</sub>Cy}<sup>2−</sup> titanium dimethyl complexes with isocyanides and benzophenone. Further investigations into the reactivity of [TiMe<sub>2</sub>(Me<sub>2</sub>ATI)<sub>2</sub>] with isocyanides will be the subject of a future report.

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**Supporting Information Available:** Text giving experimental procedures for the preparation and characterization of all compounds, in addition to tables giving bond distances and angles and positional and thermal parameters for compounds **3**, **4** and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM9904347

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(18) Crystal structure analysis of **8**: C<sub>25</sub>H<sub>41</sub>N<sub>5</sub>Ti. *M<sub>r</sub>* = 507.57, monoclinic, space group *P*2<sub>1</sub>, *a* = 11.532(4) Å, *b* = 9.561(3) Å, *c* = 12.459(5) Å, β = 96.32(3)°, *V* = 1365.3(8) Å<sup>3</sup>, *Z* = 2, *F*(000) = 544; *T* = 188 K, *R*<sub>1</sub> = 0.0451 (*wR*<sub>2</sub> = 0.1203).

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