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Alkoxido, Amido, and Imido Derivatives of Titanium(IV) Tetratolylporphyrin

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Tetratolylporphyrin

Abstract
Treatment of (TTP)TiCl2 (1) [TTP = meso-5,10,15,20-tetra-p-tolylporphyrinato dianion] with excess NaOR (R = Ph, Me, t-Bu) affords the bis(alkoxide) derivatives (TTP)Ti(OR)2 [R = Ph (2), Me (3), t-Bu (4)] in moderate yield. The corresponding amido derivative (TTP)Ti(NPh2)2(5) is prepared in an analogous fashion employing LiNPh2. The disubstituted complexes 2, 3, and 5 react cleanly with (TTP)TiCl2 to afford the ligand exchange products (TTP)Ti(OR)Cl [R = Ph (6), Me (7)] and (TTP)Ti(NPh2)Cl (8), respectively. The monosubstituted complexes 6–8 are also obtained by treatment of 1 with 1 equiv of the appropriate NaOR or LiNPh2 reagent. Treatment of 5 with excess phenol produces the bis(phenoxide) derivative 2 and 2 equiv of HNPh2. The imido derivatives (TTP)TiNR [R = t-Bu (9), Ph (10), C6H4-p-Me (11)] are prepared by the treatment of 1 with excess LiNHR. The t-Bu derivative (9) is also obtained by reaction of 1 with excess H2N-t-Bu at elevated temperatures. The phenyl imido complex (10) may be produced by the reaction of 0.5 equiv of PhNNPh with (TTP)Ti(η2-EtC⋮CEt) in refluxing toluene. Finally, (TTP)TiNTMS (12) is obtained by oxidation of (TTP)Ti(η2-EtC⋮CEt) with N3TMS.

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Alkoxido, Amido, and Imido Derivatives of Titanium(IV) Tetratolylporphyrin

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Treatment of (TTP)TiCl₂ (1) [TTP = meso-5,10,15,20-tetra-p-tolylporphynato dianion] with excess NaOR (R = Ph, Me, t-Bu) affords the bis(alkoxide) derivatives (TTP)Ti(OR)₂ (2) in moderate yield. The corresponding amido derivative (TTP)Ti(NPh₂) (5) is prepared in an analogous fashion employing LiNPh₂. The disubstituted complexes 2, 3, and 5 react cleanly with (TTP)TiCl₂ to afford the ligand exchange products (TTP)Ti(OR)Cl [R = Ph (6), Me (7)] and (TTP)Ti(NPh₂)Cl (8), respectively. The monosubstituted complexes 6–8 are also obtained by treatment of 1 with 1 equiv of the appropriate NaOR or LiNPh₂ reagent. Treatment of 5 with excess phenol produces the bis(phenoxy) derivative 2 and 2 equiv of HNPh₂. The imido derivatives (TTP)Ti=NR [R = t-Bu (9), Ph (10), C₆H₄-p-Me (11)] are prepared by the treatment of 1 with excess LiNHR. The t-Bu derivative (9) is also obtained by reaction of 1 with excess H₂N-t-Bu at elevated temperatures. The phenyl imido complex (10) may be produced by the reaction of 0.5 equiv of PhN=NPh with (TTP)Ti(η²–EnC≡C≡E) in refluxing toluene. Finally, (TTP)Ti=NTMS (12) is obtained by oxidation of (TTP)Ti(η²–EnC≡C≡E) with N₃TMS.

Introduction

The highly reactive nature of the metal–nitrogen bond in many group 4 imido complexes has lead to a rapidly growing area of research. For example, group 4 imido complexes can engage in aliphatic and aromatic C–H bond activation processes as well as numerous 2 + 2 cycloaddition reactions with unsaturated organic substrates. Additionally, group 4 imido complexes have found use in the catalytic hydroamination of alkenes and the synthesis of various nitrogen heterocycles. The highly reactive nature of the metal–nitrogen bond in many group 4 imido complexes has lead to a rapidly growing area of research. For example, group 4 imido complexes can engage in aliphatic and aromatic C–H bond activation processes as well as numerous 2 + 2 cycloaddition reactions with unsaturated organic substrates. Additionally, group 4 imido complexes have found use in the catalytic hydroamination of alkenes and the synthesis of various nitrogen heterocycles.


light brown solution which became an opaque deep brown color after several minutes. After 4 h, the solution was filtered. Removal of solvent from the filtrate under reduced pressure afforded (TTP)TiOPh (123 mg, 0.137 mmol, 54% yield) as a semicrystalline, analytically pure, deep blue solid. UV–vis (toluene): 330, 383, 424 (Soret), 484, 488, 608, 654 nm. 1H NMR (CD3, 300 MHz): 9.02 (s, 8H, β-H), 8.01 (d, 8H, JHH = 7.8 Hz, -C6HMe), 7.26 (d, 8H, JHH = 7.8 Hz, -C6HMe), 2.38 (s, 12H, -CH2Me), 5.83 (overlapping d and t, 6H, m-Ph), 2.67 (m, 2H, -C6H5). Anal. Calcd for C46H36N2O2Ti: C, 80.36; H, 5.28; N, 8.52. Found: C, 80.29; H, 5.47; N, 8.20.

UV–vis (toluene): (TTP)TiCl2 (101 mg, 0.132 mmol) and LiNPh (10 mg, 0.08 mmol) were dissolved in toluene (ca. 15 mL). The solution gradually darkened to a nearly black color of the solution progressively darkens to a nearly black solution after 4 h, the solution was filtered and the solvent was removed from the filtrate under reduced pressure to afford (TTP)TiNPh2Cl (27 mg, 0.029 mmol, 43% yield) as a deep blue solid. Due to minor differences in stoichiometry, compound is consistently contaminated with (TTP)TiCl or (TTP)TiNPh2 (ca. 5%). Even with several recrystallizations, these impurities could not be removed and hence preclude elemental analysis.

UV–vis (toluene): 327, 428 (Soret), 554 nm. 1H NMR (CD3, 300 MHz): 8.98 (s, 8H, β-H), 8.05 (d, 4H, JHH = 7.8, -C6HMe), 7.88 (d, 4H, JHH = 7.8, -C6HMe), 7.44 (m, 8H, -C6HMe), 2.49 (s, 12H, -CH2Me), 3.12 (t, 2H, JHH = 7.2, p-H), 5.96 (t, 4H, JHH = 7.2, m-H), 2.83 (d, 4H, JHH = 7.2, o-H). MS (Cl) Calcd (found) m/e: [TTP]1751 (751), [TTP]1751Cl1751H1751. Anal. Calcd for C72H56N6Ti: C, 79.78; H, 5.76; N, 8.87. Found: C, 79.78; H, 5.76; N, 8.87.

Reaction of (TTP)TiCl with t-BuOH. An anaerobic CD3 (0.7 mL) solution of (TTP)TiCl (20 mg, 0.026 mmol) and t-BuOH (14 µL, 0.15 mmol) was sealed in an NMR tube under N2. The mixture was monitored by 1H NMR until no further reaction was observed. The only new species observed in solution were (TTP)Ti(t-BuCl) (80%) and (TTP)Ti=O (7%). Unreacted (TTP)TiCl was also present. 1H NMR signals for (TTP)Ti(t-BuCl) (300 MHz): 9.06 (s, 8H, 8.13 (d, 4H, JHH = 7.8, -C6HMe), 7.92 (d, 4H, JHH = 7.8, -C6HMe), 7.29 (m, 8H, -C6HMe), 2.38 (s, 12H, -CH2Me), -2.25 (s, 9H, t-Bu).
deep purple crystals formed. The crystals were collected by filtration and dried in vacuo to afford analytically pure (TTP)Ti=NTMS (40 mg, 0.050 mmol, 38% yield). UV−vis (toluene): δ 428 (Soret), 550 nm. 1H NMR (CD2Cl2, 300 MHz): 9.25 (s, 8H, β-H), 8.31 (d, 3JH−H = 9.0 Hz, 4H, −C6H4Me), 8.00 (d, 3JH−H = 9.0 Hz, 4H, −C6H4Me), 7.32 (m, 8H, −C6H4Me), 2.42 (s, 12H, −C6H2−CH3), −2.04 (s, 9H, Si(CH3)3).

Results

Synthesis and Properties of Bis(alkoxide) Complexes. The titanium(IV) tetratolylporphyrinato complex (TTP)TiCl2 (1) reacts readily with sodium phenoxide in toluene to afford the blue, bis(phenoxide) complex (TTP)Ti(OPh)2 (2) in moderate yield (eq 1). The bis(alkoxide) complexes (TTP)Ti(OMe)2 (3)

\[(TTP)TiCl_2 + NaOR \rightarrow (TTP)Ti(OR)_2 + 2NaCl \quad (1)\]

and (TTP)Ti(O-t-Bu)2 (4) are obtained in an analogous fashion. Complexes 2 and 3 have also been prepared by the reaction of 1 with 2 equiv of the free alcohols in the presence of piperidine, which serves to scavenge the HCl byproduct. The 1H NMR spectra of these complexes are consistent with the alkoxide ligands being arranged in a trans geometry. In particular, the spectra of these complexes are consistent with the alkoxide ligands in (TTP)TiCl2. Instead an equilibrium is established for monoalkoxide formation as represented in eq 3. In a mixture of 2.7 PHOH and (TTP)TiCl2 in C6D6, the equilibrium lies far to the left. No monophenoxide complex is detected by 1H NMR. When 6.7 equiv of MeOH is added to (TTP)TiCl2 in C6D6, the equilibrium ratio of (TTP)Ti(OMe)Cl to (TTP)TiCl2 is 0.37:1. With the more basic tert-butanol (5.8 equiv), the resulting ratio of (TTP)Ti(O-t-Bu)Cl to (TTP)TiCl2 is 6.2:1. Addition of an exogenous base drives the reaction completely to bis(alkoxide) formation. Thus, injection of 3 equiv of piperidine into an equilibrated NMR tube containing (TTP)-TiCl2 and tert-butanol in C6D6 resulted in quantitative formation of (TTP)Ti(O-t-Bu)2.

Preparation of Bis(amido) Complexes. Treatment of freshly prepared (TTP)TiCl2 with ≥2 equiv of LiNPh2 in hexanes results in the formation of the bis(amido) complex (TTP)Ti(NPh2)2 (5) in modest yield (eq 4). This reaction is very sensitive to solvent choice. In our hands, 5 could not be produced in pure fashion employing toluene, benzene, THF, or CH2Cl2 as a solvent. In these solvents, intractable paramagnetic (presumably Ti(III)) species are formed. Another difficulty in preparing 5 is its extreme moisture-sensitivity. Complex 5 decomposes instantaneously in air to afford (TTP)Ti=O and free HNPh2. Our attempts to prepare other bis(amido) complexes have met with no success. Thus, the reaction of 1 with LiNPh2, LiNTMS2, LiN(C6H11)2, TMSN2, or lithium tetrahydro-quinolinolide, under similar conditions employed to produce 5, leads only to intractable, paramagnetic products. Finally, treatment of 5 with other secondary amines, such as HNEt2, piperidine, t-BuNH2, or 1,2,3,4-tetrahydroquinolinolide, did not result in the production of any new bis(amido) transamination products. These observations parallel those described for the alkoxide/alkanol system. The equilibrium favors the complex bound to the least basic secondary amide.

Like the bis(alkoxide) complexes discussed above, the diphénylamido ligands in 5 are disposed in a trans fashion. Thus, 5 displays pseudo D2h symmetry in the ambient temperature 1H NMR spectrum. In C6D6, the resonances for the phenyl groups of the NPh2 ligands are shifted upfield [δ 6.17 (Hδ), δ 6.05 (Hδ), and δ 2.86 (Hδ)] relative to the free amine, again due to their proximity to the porphyrin ring current.

Like the bis(alkoxide) derivatives, the bis(amido) complex undergoes rapid ligand redistribution upon treatment with 1 equiv of (TTP)TiCl2 to afford the monoamido complex (TTP)Ti(NPh2)Cl (6) (eq 5). Again, this reaction appears to be entirely irreversible. Complex 6 can be prepared independently from treatment of 1 with 1 equiv of LiNPh2.

\[(TTP)TiCl_2 + 2HOR \leftrightarrow (TTP)Ti(OR)_2 + [H_2OR]^+ + Cl^- \quad (3)\]

\[(TTP)TiCl_2 + 2LiNPh_2 \rightarrow (TTP)Ti(NPh_2)_2 + 2LiCl \quad (4)\]

\[(TTP)TiCl_2 \rightarrow (TTP)Ti(OR)_2 + H_2OR \quad (5)\]

As is typical for early transition metal amido complexes, 5 undergoes rapid alcoholysis with phenol to afford (TTP)Ti(OPh)2 (2) (eq 6). Not surprisingly, this reaction is irreversible.
Complex 2 does not react with HNPh₂ to any observable extent. This behavior is attributed to the acidity of phenol relative to diphenylamine. Correspondingly, water rapidly converts (TTP)-Ti(NPh₂)Cl, a model complex for (TTP)-Ti(NPh₂)Cl, to the oxo complex, (TTP)Ti=O.

\[
(TTP)\text{Ti(NPh₂)Cl} + 2\text{H₂O} \rightarrow (TTP)\text{Ti(OH)₂} + 2\text{HNPh₂}
\]

(6)

**Preparation of Imido Complexes. From Ti(IV) Species via α-Hydrogen Abstraction.** Treatment of (TTP)TiCl₂ with 2 equiv of LiNH-t-Bu in toluene results in the formation of the imido derivative (TTP)Ti=NH-t-Bu (9) (eq 7). This reaction is

\[
(TTP)\text{TiCl₂} + 2\text{LiNHBu} \rightarrow \frac{1}{2}(TTP)\text{Ti=NH-t-Bu} + \text{H₂N-t-Bu} + 2\text{LiCl}
\]

(7)

\[\text{[R = t-Bu (9), Ph (10), p-tolyl (11)]}\]

extremely clean and proceeds quantitatively in C₆D₆ to afford 9 along with 1 equiv of tert-butylamine (¹H NMR, Ph₆CH internal standard). The ¹H NMR spectrum (C₆D₆) of 9 reveals four doublets assignable to the H₆, H₆', H₅, and H₅' resonances of the [TTP]³⁻ ligand, indicating the expected lack of a mirror plane of symmetry coincident with the porphyrin plane. The protons of the t-Bu group are shifted strongly upfield (δ = -1.54 ppm), which as discussed above, is diagnostic for axially bound ligands in porphyrin systems. Analogous preparations have been employed to synthesize the series (TTP)Ti=NEt₃ (eq 8), (TTP)Ti=NEt₂ (eq 9), and (TTP)Ti=NEt (eq 10) all of which are obtained in high yield (eq 7). Attempts to prepare the parent imido complex by treatment of 1 with LiNH₂ have, thus far, proved unsuccessful.

As noted above, with the secondary lithium amide, LiNPh₂, we can prepare the monosubstituted amido complex (TTP)Ti(NPh₂)Cl. However, with primary lithium amides this is not possible. For example, treatment of 1 with 1 equiv of LiNH-t-Bu failed to produce any (TTP)Ti(NH-t-Bu)Cl. Instead, this reaction led to the formation of a half equivalent of (TTP)Ti(NH₂-t-Bu) (9) and left an equimolar amount of unreacted 1 (eq 8). The reaction of (TTP)Ti(NPh₂)Cl, a model complex for (TTP)-Ti(NH₂)Cl, with 1 equiv of LiNH-t-Bu did not allow the isolation or observation of the mixed amido complex (TTP)-Ti(NPh₂)(NH₂-t-Bu). Instead, the only spectroscopically observable products at early times (~10 min) were (TTP)Ti=NE-t-Bu, the bis(amido) complex (TTP)Ti(NPh₂)₂, formed in an approximate 1:1 ratio along with free H₂N-t-Bu (eq 9). The bis(amido) complex apparently forms from displaced NPh₂, which undergoes metathesis with unreacted (TTP)Ti(NPh₂)Cl. After long reaction times (>10 h), the final products were (TTP)-Ti=NE-t-Bu and free HNPh₂ from the subsequent reaction between (TTP)Ti(NPh₂)₂ and H₂N-t-Bu. This latter process was confirmed independently. Treatment of (TTP)Ti(NPh₂)₂ with excess H₂N-t-Bu quantitatively produced (TTP)Ti=NE-t-Bu and HNPh₂ (eq 10).

\[
(TTP)\text{TiCl₂} + \text{LiNH-t-Bu} \rightarrow \frac{1}{2}(TTP)\text{Ti=NE-t-Bu} + \frac{1}{2}(TTP)\text{TiCl₂} + \frac{1}{2}\text{H₂N-t-Bu} + \text{LiCl}
\]

(8)

\[
(TTP)\text{Ti(NPh₂)Cl} + \text{LiNH-t-Bu} \rightarrow \frac{1}{2}(TTP)\text{Ti=NE-t-Bu} + (TTP)\text{Ti(NPh₂)₂} + \frac{1}{2}\text{H₂N-t-Bu} + \text{LiCl}
\]

(9)

\[
(TTP)\text{Ti(NPh₂)₂} + \text{H₂N-t-Bu} \rightarrow \frac{1}{2}(TTP)\text{Ti=NE-t-Bu} + 2\text{HNPh₂}
\]

(10)

It has been previously reported that treatment of (TTP)TiCl₂ with excess aniline does not produce the imido derivative, (TTP)Ti=NPh (10).¹¹ In accord with this earlier report, we have confirmed that the arylimido complexes cannot be synthesized in this manner. Thus, under similar conditions, 1 is unreactive toward p-toluidine. We have found, however, that heating toluene solutions of 1 with excess tert-butylamine produces (TTP)Ti=N-t-Bu (9) in high yield along with [H₂N-t-Bu]Cl byproduct.

**Imido Complexes Via Disproportionation of Ti(III).** We have also found that Ti(IV)=mido complexes can be produced from Ti(III)=precursor complexes. For example, toluene solutions of (TTP)TiCl react instantaneously with LiNH-t-Bu in the presence of PhC==CPh to provide (TTP)Ti=N-t-Bu (9) and the known alkylene adduct, (TTP)Ti(q²-PhC==CPh) (10) in a 1:1 ratio (eq 11). Similarly, reaction of (TTP)TiCl with 1 equiv of LiNH-t-Bu followed by the addition of excess pyridine affords 0.5 equiv of the imido complex 9 along with 0.5 equiv of (TTP)-Ti=py₂ (eq 12). These disproportionation reactions underscore the strong thermodynamic driving force for the formation of these robust Ti(IV)=imido complexes.

\[
(TTP)\text{TiCl₄} + \text{LiNH-t-Bu} + \text{excess PhC==CPh} \rightarrow \frac{1}{2}(TTP)\text{Ti=NE-t-Bu} + \frac{1}{2}(TTP)\text{Ti(q²-PhC==CPh)} + \frac{1}{2}\text{H₂N-t-Bu} + \text{LiCl}
\]

(11)

\[2(TTP)\text{TiCl₄} + \text{LiNH-t-Bu} + \text{excess py} \rightarrow \frac{1}{2}(TTP)\text{Ti=NE-t-Bu} + \frac{1}{2}(TTP)\text{Ti(py)₂} + \frac{1}{2}\text{H₂N-t-Bu} + \text{LiCl}
\]

(12)

**Imido Complexes via Oxidation of Ti(II) Complexes.** Imido complexes are available from the oxidation of Ti(II) complexes with [NR]²⁻ sources. For example, the Ti(II) alkynyl complex (TTP)Ti(q²-CEt) reacts instantaneously with excess N₃TMS in toluene to provide the imido complex (TTP)-Ti=NTMS (12) and 1 equiv of free EtC==Ct (eq 13). Additionally, treatment of (TTP)Ti(q²-CEt) with 0.5 equiv PhN=NPh in refluxing toluene provides (TTP)Ti=NPh (10) as the sole porphyrin product (eq 14). Details of this reaction will be reported elsewhere.

\[
(TTP)\text{Ti(q²-CEt)} + \text{excess N₃TMS} \rightarrow \text{(TTP)Ti=NTMS} + \text{EtC==Ct} + \text{N₂}
\]

(13)

\[
(TTP)\text{Ti(q²-CEt)} + 0.5\text{PhN=NPh} \rightarrow \text{(TTP)Ti=NPh} + \text{EtC==Ct}
\]

(14)

**Reactivity of Ti=Imido Complexes.** The imido complexes described above show only limited reactivity. As expected, treatment of (TTP)Ti=NR complexes with alcohols such as phenol and methanol results in the clean formation the bis(alkoxide) complexes 2 and 3, respectively along with free amine. Unlike previously reported Ti=imido complexes,¹⁵


The (TTP)Ti fragment serves as a useful template for the study of a wide range of metal–ligand multiple bonds. The series (TTP)Ti=X (X = O, S, Se, NR) is now firmly established.\(^{12}\) In the future, we hope to extend this interesting class of complexes to include other metal–ligand multiply bonded species such as alkylidenes and phosphinidines. In order to design rational syntheses of these complexes, we have attempted to elucidate the mechanism by which the imido ligands are introduced via lithium amides. The formation of imido complexes from (TTP)TiCl does not react with either diphenylacetylene or pyridine to produce (TTP)TiCl\(_2\) and (TTP)Ti(NH-t-Bu) achieve the Ti(III) dimer [(TTP)Ti]\(_2\)(µ-O). In contrast, the imido complexes described above do not react with (TTP)Ti(η\(_5\)-C\(_6\)H\(_5\)) to afford the Ti(III) dimer [(TTP)Ti]\(_2\)(µ-NPh). This difference may be due to the steric problems presented by the imido substituents.

### Discussion

The (TTP)Ti fragment serves as a useful template for the study of a wide range of metal–ligand multiple bonds. The series (TTP)Ti=X (X = O, S, Se, NR) is now firmly established.\(^{12}\) In the future, we hope to extend this interesting class of complexes to include other metal–ligand multiply bonded species such as alkylidenes and phosphinidines. In order to design rational syntheses of these complexes, we have attempted to elucidate the mechanism by which the imido ligands are introduced via lithium amides. The formation of imido complexes from (TTP)TiCl does not react with either diphenylacetylene or pyridine to produce (TTP)TiCl\(_2\) and (TTP)Ti(NH-t-Bu) achieve the Ti(III) dimer [(TTP)Ti]\(_2\)(µ-O). In contrast, the imido complexes described above do not react with (TTP)Ti(η\(_5\)-C\(_6\)H\(_5\)) to afford the Ti(III) dimer [(TTP)Ti]\(_2\)(µ-NPh). This difference may be due to the steric problems presented by the imido substituents.

**Scheme 1**

![Scheme 1](image1)

**Scheme 2**

![Scheme 2](image2)

**Scheme 3**

![Scheme 3](image3)
class of compounds are (TPP)Ti(OMe)\textsuperscript{16} and the \(\eta^2\)-catecholate (TPP)Ti(O\textsubscript{2}C\textsubscript{6}H\textsubscript{4}).\textsuperscript{17} We have shown that the Ti(IV)–bis(alkoxides) can be readily produced. Perhaps surprisingly, given the immense number of Ti–amido complexes known,\textsuperscript{18} we have found that the only isolable bis(amido)–porphyrin complex is (TTP)Ti(NPh\textsubscript{2})\textsubscript{2}. The imido complexes, given the reactivity displayed by the oxo analogue (\textit{vide supra}), are perhaps of the greatest interest. Of particular interest, is the fact that (TTP)-Ti=NR complexes may be isolated starting from Ti-porphyrin complexes in various oxidation states.

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