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

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Treatment of (TTP)$TiCl_2$ (**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)$Ti(NPh_2)_2$ (**5**) is prepared in an analogous fashion employing $LiNPh_2$. The disubstituted complexes **2**, **3**, and **5** react cleanly with (TTP)$TiCl_2$ to afford the ligand exchange products (TTP)Ti(OR)Cl [R = Ph (**6**), Me (**7**)] and (TTP)$Ti(NPh_2)$Cl (**8**), respectively. The monosubstituted complexes **6**−**8** are also obtained by treatment of **1** with 1 equiv of the appropriate NaOR or $LiNPh_2$ reagent. Treatment of **5** with excess phenol produces the bis(phenoxide) derivative **2** and 2 equiv of $HNPh_2$. The imido derivatives (TTP)Ti═NR [R = *t*-Bu (**9**), Ph (**10**), C_6H_4-*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 H_2N-*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(η^2-EtC≡CEt) in refluxing toluene. Finally, (TTP)Ti═NTMS (**12**) is obtained by oxidation of (TTP)Ti(η^2-EtC≡CEt) with N_3TMS.

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.[2] For example, group 4 imido complexes can engage in aliphatic and aromatic C−H bond activation processes[3] as well as numerous 2 + 2 cycloaddition reactions with unsaturated organic substrates.[3d] Additionally, group 4 imido complexes have found use in the catalytic hydroamination[3d] of alkynes and the synthesis of various nitrogen heterocycles.[4]

Recently, we reported the synthesis of a variety of imido−titanium *meso*-tetratolylporphyrinato complexes of the type (TTP)Ti═NR (R = Ph, tolyl, cyclohexyl).[5] Our interest in these systems stems from our observation that isoelectronic (POR)Ti═O complexes undergo facile intermetal oxygen atom transfer.[6] In addition, (POR)Ti═O complexes serve as precatalysts for the epoxidation of alkenes.[7] In this report, we summarize the preparation and properties of a variety of imido−titanium-porphyrin complexes and discuss their reactivity. Additionally, we report the synthesis and reactivity of new alkoxide and amide derivatives of titanium-porphyrin. These new complexes extend the class of group 4 porphyrin complexes possessing hard π-donor ligands.[8]

Experimental Section

General. All manipulations were performed under an inert atmosphere of nitrogen using a Vacuum Atmospheres glovebox equipped with a Model MO40-1 Dri-Train gas purifier. The glovebox atmosphere was continuously monitored with an Illinois Instrument Model 2550 trace oxygen analyzer. The concentration of O_2 in the glovebox was kept at less than 5 ppm at all times. All solvents were rigorously degassed and dried prior to use. Benzene-d_6, toluene, and hexane were freshly distilled from purple solutions of sodium benzophenone and brought into the drybox without exposure to air. (TTP)$TiCl_2$ (**1**) was prepared according to published procedures[9] and recrystallized from CH_2Cl_2/hexane prior to use. Phenol was purchased from Aldrich and used as received. Methanol was purchased from Fisher, dried with CaH_2, and vacuum transferred prior to use. NaOR (R = Ph, Me, *t*-Bu) reagents were prepared by treating the appropriate alcohol with sodium in hexanes. Diphenylamine was purchased from Fisher and was recrystallized from hexanes prior to use. $LiNPh_2$ was prepared by reaction of the free amine with *n*-butyl lithium in hexanes. The lithium amide salts, LiNHPh, $LiNHC_6H_4$-*p*-Me, and $LiNHC_6H_{11}$ were prepared as previously described.[5] LiNH-*t*-Bu was prepared by the reaction of H_2N-*t*-Bu with *n*-butylithium in hexanes and was recrystallized from hexanes at −20 °C. All amines used above were purchased from Aldrich and were purified by literature methods.[10] N_3TMS was purchased from Aldrich and used as received.

^{1}H NMR data were recorded at 20.0 °C on either a Varian VXR (300 MHz) or a Bruker DXR (400 MHz) spectrometer. Chemical shifts are referenced to proton solvent impurities (δ 7.15, C_6D_5H). UV−vis data were recorded on a HP8452A diode array spectrophotometer. Elemental analyses (C, H, N) were performed by Atlantic Microlab of Norcross, Georgia. All samples were handled under nitrogen and WO_3 was used as a combustion aid. MS-CI studies were performed on a Finnigan TSQ 700 at 70 eV in the negative ion mode using ammonia as the ionization gas.

(TTP)Ti(OPh)$_2$ (2). (TTP)$TiCl_2$ (200 mg, 0.254 mmol) and NaOPh (62 mg, 0.53 mmol) were stirred in toluene (ca. 10 mL) to afford a

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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)Ti(OPh)$_2$ (123 mg, 0.137 mmol, 54% yield) as a semicrystalline, analytically pure, deep blue solid. UV−vis (toluene): 330, 338, 382, 424 (Soret), 484, 488, 608, 654 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.02 (s, 8H, β-H), 8.01 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 7.26 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 2.38 (s, 12H, −C_6H_4*Me*), 5.83 (overlapping d and t, 6H, *m*-*p*-C_6H_5), 2.67 (m, 2H, *o*-C_6H_5). Anal. Calcd for $C_{60}H_{45}N_4O_2Ti$: C, 79.81; H, 5.13; N, 6.20. Found: C, 80.58; H, 5.44; N, 6.06.

(TTP)Ti(OMe)$_2$ (3). (TTP)TiCl$_2$ (158 mg, 0.20 mmol) and NaOMe (122, 2.25 mmol) were slurried in toluene and the resultant brown solution was rapidly stirred. After 5 h, the solution was filtered and the solvent was removed from the dark brown filtrate to afford blue (TTP)Ti(OMe)$_2$ (100 mg, 0.129 mmol, 66% yield). Despite numerous efforts to obtain analytically pure compound, **3** consistently contains a trace (ca. 5%) of (TTP)Ti═O impurity which precluded elemental analysis. UV−vis (toluene): 426 (Soret), 552 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.07 (s, 8H, β-H), 8.07 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4-Me), 7.26 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 2.39 (s, 12H, −C_6H_4*Me*), −0.83 (s, 6H, OCH_3). MS (CI) Calcd (found) *m/e*: [M$^-$] 778 (778).

(TTP)Ti(O-*t*-Bu)$_2$ (4). (TTP)TiCl$_2$ (44 mg, 0.056 mmol) and NaO-*t*-Bu (26 mg, 0.28 mmol) were slurried in toluene and the resultant brown solution was rapidly stirred at ambient temperature. After 5 h, the solution was filtered and the solvent was removed from the dark brown filtrate to afford blue (TTP)Ti(O-*t*-Bu)$_2$ (32 mg, 0.037 mmol, 67% yield). Despite numerous efforts to obtain an analytically pure compound, **4** consistently contained traces (ca. 5%) of impurities which precluded elemental analysis. UV−vis (toluene): 450 (Soret), 584, 622 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.05 (s, 8H, β-H), 8.23 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 7.31 (d, 8H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 2.40 (s, 12H, −C_6H_4*Me*), −2.18 (s, 18H, O-*t*-Bu).

(TTP)Ti(NPh$_2$)$_2$ (5). (TTP)TiCl$_2$ (326 mg, 0.413 mmol) and LiNPh$_2$ (150 mg, 0.0859 mmol) were slurried in hexanes (ca. 20 mL). The solution slowly changed from light brown to chocolate brown. After 5 h, the solution was filtered to collect a dark brown solid. This solid was placed on a clean fritted filter and extracted with CH_2Cl_2 (3 × 3 mL). Removal of solvent from the resultant filtrate afforded (TTP)-Ti(NPh$_2$)$_2$ (251 mg, 0.238 mmol, 58% yield) as a semicrystalline, blue solid. UV−vis (toluene): 426 (Soret), 552 nm. ^{1}H NMR (C_6D_6, 400 MHz): 8.83 (s, 8H, β-H), 8.09 (d, 8H, $^3J_{H-H}$ = 7.6 Hz, −C_6H_4Me), 7.37 (d, 8H, $^3J_{H-H}$ = 7.6 Hz, −C_6H_4Me), 6.17 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, C_6H_5), 6.05 (d, 4H, $^3J_{H-H}$ = 7.2 Hz, C_6H_5), 2.86 (d, 4H, $^3J_{H-H}$ = 7.2 Hz, C_6H_5), 2.44 (s, 12H, −C_6H_4*Me*). Anal. Calcd for $C_{72}H_{56}N_6Ti$: C, 82.11; H, 5.36; N, 7.98. Found: C, 81.58; H, 5.98; N, 7.56.

(TTP)Ti(OPh)Cl (6). (TTP)TiCl$_2$ (45 mg, 0.058 mmol) and LiOPh (6 mg, 0.06 mmol) were stirred in toluene (ca. 10 mL). The initial dark brown color of the solution progressively darkens to a nearly black color. After 15 h, the solution was filtered and solids on the frit were extracted with toluene. The solvent was removed from the combined filtrates under reduced pressure to yield (TTP)Ti(OPh)Cl (31 mg, 0.37 mmol, 64% yield) as a deep blue solid. UV−vis (toluene): 352, 404, 426 (Soret), 552 nm. ^{1}H NMR (C_6D_6, 400 MHz): 9.04 (s, 8H, β-H), 7.94 (d, 8H, $^3J_{H-H}$ = 7.6 Hz, −C_6H_4Me), 7.24 (m, 8H, −C_6H_4Me), 5.77 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, −OC_6H_5), 5.69 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, −OC_6H_5), 2.72 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, −OC_6H_5), 2.37 (s, 12H, −C_6H_4*Me*). MS (CI) Calcd (found) *m/e*: [(TTP)TiOPh$^-$] 767 (767); [(TTP)TiCl$^-$] 751 (751).

(TTP)Ti(OMe)Cl (7). (TTP)TiCl$_2$ (56 mg, 0.72 mmol) and LiOMe (3 mg, 0.08 mmol) were dissolved in toluene (ca. 10 mL) to give a deep brown solution. After 4 h, the nearly black solution was filtered. The solid left on the frit was extracted with toluene and CH_2Cl_2. Removal of the solvent from the resultant filtrate under reduced pressure afforded (TTP)Ti(OMe)Cl (20 mg, 36% yield) as a deep blue, microcrystalline solid which is slightly contaminated with (TTP)TiCl$_2$ (ca. 5%), presumably due to stoichiometry deficiencies. UV−vis (toluene): 376, 426 (Soret), 502 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.08 (s, 8H, β-H), 8.07 (d, 4H, $^3J_{H-H}$ = 7.8, −C_6H_4Me), 7.90 (d, 4H, $^3J_{H-H}$ = 7.8, −C_6H_4Me), 7.26 (d, 4H, $^3J_{H-H}$ = 8.1, −C_6H_4Me), 7.21 (d, 4H, $^3J_{H-H}$ = 8.1, −C_6H_4Me), 2.38 (s, 12H, −C_6H_4Me), −0.79 (s, 3H, −OMe). MS(CI) Calcd (found) *m/e*: [(TTP)TiClO$^-$], 767 (767); [(TTP)TiCl$^-$], 751 (751).

Reaction of (TTP)TiCl$_2$ with *t*-BuOH. An anaerobic C_6D_6 (0.7 mL) solution of (TTP)TiCl$_2$ (20 mg, 0.026 mmol) and *t*-BuOH (14 μL, 0.15 mmol) was sealed in an NMR tube under N_2. The mixture was monitored by ^{1}H NMR until no further reaction was observed. The only new species observed in solution were (TTP)Ti(O-*t*-Bu)Cl (80%) and (TTP)Ti═O (7%). Unreacted (TTP)TiCl$_2$ (13%) and *t*-BuOH were also present. ^{1}H NMR signals for (TTP)Ti(O-*t*-Bu)Cl (300 MHz): 9.06 (s, 8H), 8.13 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 7.92 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, −C_6H_4Me), 7.29 (m, 8H, −C_6H_4Me), 2.38 (s, 12H, −C_6H_4*Me*), −2.25 (s, 9H, *t*-Bu).

(TTP)Ti(NPh$_2$)Cl (8). In a general procedure, approximately 1 equiv of LiNPh$_2$ was added to (TTP)TiCl$_2$. For example, (TTP)TiCl$_2$ (53 mg, 0.067 mmol) and LiNPh$_2$ (13 mg, 0.073 mmol) were stirred in hexanes (ca. 10 mL). The initial light brown solution gradually darkened to deep brown solution. After 4 h, the solution was filtered and the solvent was removed from the filtrate under reduced pressure to afford (TTP)Ti(NPh$_2$)Cl (27 mg, 0.029 mmol, 43% yield) as a deep blue solid. Due to minor differences in stoichiometry, compound **8** is consistently contaminated with (TTP)TiCl$_2$ or (TTP)Ti(NPh$_2$)$_2$ (ca. 5%). Even with several recrystallizations, these impurities could not be removed and hence preclude elemental analysis. UV−vis (toluene): 372, 428 (Soret), 554 nm. ^{1}H NMR (C_6D_6, 300 MHz): 8.98 (s, 8H, β-H), 8.05 (d, 4H, $^3J_{H-H}$ = 7.8, −C_6H_4Me), 7.88 (d, 4H, $^3J_{H-H}$ = 7.8, −C_6H_4Me), 7.44 (m, 8H, −C_6H_4Me), 2.41 (s, 12H, −C_6H_4Me), 6.12 (t, 2H, $^3J_{H-H}$ = 7.2, *p*-H), 5.96 (t, 4H, $^3J_{H-H}$ = 7.2, *m*-H), 2.83 (d, 4H, $^3J_{H-H}$ = 7.2, *o*-H). MS (CI) Calcd (found) *m/e*: [(TTP)TiCl$^-$], 751 (751); [(TTP)Ti(NPh$_2$)Cl-H$^-$], 918 (918).

(TTP)Ti═N-*t*-Bu (9). (TTP)TiCl$_2$ (101 mg, 0.13 mmol) and LiNH-*t*-Bu (21 mg, 0.27 mmol) were dissolved in toluene (ca. 10 mL) to afford a deep red solution. After 5 min, the solution was filtered and the resultant deep red filtrate was taken to dryness under reduced pressure to afford (TTP)Ti═N-*t*-Bu (95 mg, 0.12 mmol, 94% yield) as a semicrystalline, purple solid. Analytically pure samples could be obtained by recrystallization from toluene/hexane solution at −20 °C. UV−vis (toluene): 424 (Soret), 548 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.24 (s, 8H, β-H), 8.32 (d, $^3J_{H-H}$ = 7.65 Hz, 4H, −C_6H_4Me), 8.04 (d, $^3J_{H-H}$ = 7.05 Hz, 4H, −C_6H_4Me), 7.34 (d, J = 5.70 Hz, −C_6H_4Me), 7.30 (d, J = 5.70 Hz, −C_6H_4Me), 2.42 (s, 12H, −C_6H_4-CH_3), −1.58 (s, 9H, *t*-Bu). Anal. Calcd for $C_{52}H_{45}N_5Ti$: C, 79.28; H, 5.76; N, 8.89. Found: C, 79.34; H, 5.76; N, 8.75.

(TTP)Ti═NPh (10). (TTP)TiCl$_2$ (104 mg, 0.132 mmol) and LiNHPh (50 mg, 0.51 mmol) were dissolved in toluene (ca. 15 mL). The solution gradually turned a deep red color. After 30 min, the solution was filtered to remove a black solid and the resultant ruby filtrate was taken to dryness under reduced pressure. This afforded (TTP)Ti═NPh (94 mg, 0.12 mmol, 88% yield) as a purple solid. Analytically pure samples could be obtained by recrystallization from toluene/hexanes at −20 °C. UV−vis (toluene): 426 (Soret), 548 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.21 (s, 8H, β-H), 8.14 (d, 4H, −C_6H_4-CH_3), 8.03 (d, 4H, −$C_6H_4CH_3$), 7.30 (d, 8H, −$C_6H_4CH_3$), 5.72 (m, 3H, *m-*, *p-H*), 3.85 (d, 2H, *o-H*), 2.41 (s, 12H, −$C_6H_4CH_3$). MS(EI) Calcd (found) (*m/e*): 806 (807), [M]$^+$. Anal. Calcd for $C_{54}H_{41}N_5Ti$: C, 80.29; H, 5.12; N, 8.67. Found: C, 79.26; H, 5.48; N, 8.28.

(TTP)Ti═NC$_6$H$_4$-*p*-Me (11). (TTP)TiCl$_2$ (82 mg, 0.104 mmol) and LiNHC$_6$H$_4$Me (45 mg, 0.40 mmol) were dissolved in toluene (ca. 15 mL) to produce a red solution. After 4 h, the solution was filtered and the resultant deep red filtrate was taken to dryness under reduced pressure to afford (TTP)Ti═NC$_6$H$_4$-*p*-Me (74 mg, 0.09 mmol, 87% yield) as a purple-red solid. Analytically pure samples could be obtained by recrystallization from toluene/hexanes at −20 °C. UV−vis (toluene): 426 (Soret), 548 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.21 (s, 8H, β-H), 8.15 (d, 4H, −$C_6H_4CH_3$), 8.04 (d, 4H, −$C_6H_4CH_3$), 7.30 (d, 8H, −$C_6H_4CH_3$), 5.53 (d, 2H, *m-H*), 3.81 (d, 2H, *o-H*), 2.41 (s, 12H, −$C_6H_4CH_3$), 1.29 (s, 3H, −CH_3). Anal. Calcd for $C_{55}H_{43}N_5Ti$: C, 80.36; H, 5.28; N, 8.52. Found: C, 80.29; H, 5.47; N, 8.20.

(TTP)Ti═NTMS (12). (TTP)Ti(η^2-EtC≡CEt) (105 mg, 0.132 mmol) was dissolved in toluene (ca. 10 mL), and neat N_3TMS (ca. 0.5 mL, ca. 4.0 mmol) was added to the rapidly stirred solution. Evolution of gas was observed, and after 16 h, the solution was taken to dryness under reduced pressure to afford a dark oil. The oil was dissolved in a minimum of toluene (ca. 2 mL), and the solution was layered with hexanes (ca. 6 mL). After cooling the solution at −20 °C for 14 h,

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): 428 (Soret), 550 nm. ^{1}H NMR (C_6D_6, 300 MHz): 9.25 (s, 8H, β-H), 8.31 (d, $^3J_{H-H}$ = 9.0 Hz, 4H, $-C_6H_4$Me), 8.00 (d, $^3J_{H-H}$ = 9.0 Hz, 4H, $-C_6H_4$Me), 7.32 (m, 8H, $-C_6H_4$Me), 2.42 (s, 12H, $-C_6H_4-CH_3$), −2.04 (s, 9H, SiCH_3). Anal. Calcd for: $C_{51}H_{45}N_5SiTi$: C, 76.20; H, 5.64; N, 8.71. Found: C, 76.04; H, 5.99; N, 8.04.

Results

Synthesis and Properties of Bis(alkoxide) Complexes. The titanium(IV) tetratolylporphyrinato complex (TTP)$TiCl_2$ (**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**)

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

$$[R = Ph\ (\mathbf{2}),\ Me\ (\mathbf{3}),\ t\text{-}Bu\ (\mathbf{4})]$$

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 ^{1}H NMR spectra of these complexes are consistent with the alkoxide ligands being arranged in a trans geometry. In particular, the H_o and H_m protons of the tolyl groups of the $[TTP]^{2-}$ ligand appear as two sharp sets of doublets. These data indicate that the molecule possesses a mirror plane through the center of the porphyrin and an approximate D_{4h} symmetry. In the ambient temperature ^{1}H NMR spectrum of **2** in C_6D_6, the protons of the phenoxide ligands appear at 2.67 ppm (H_o) and 5.83 ppm (H_m and H_p). The large upfield shift of these protons is representative of ligands above the porphyrin plane. Similarly, a strong upfield shift is observed for the Me groups of the methoxide ligands in **3**.

In the solid state, complex **2** is inert and remains unchanged for more than 4 months in air. The bis(phenoxide) is also stable to hydrolysis in solution with excess water for more than 1 week. In contrast, exposure of a solution of the bis(methoxide) to air results in instantaneous and quantitative conversion to the oxo complex (TTP)Ti=O. Treatment of (TTP)$Ti(OR)_2$ (R = Me, *t*-Bu) with excess phenol cleanly produces (TTP)$Ti(OPh)_2$ and ROH. In general, the spontaneous reaction involves the most basic ligand becoming protonated. Thus, treatment of (TTP)-$Ti(OPh)_2$ with 7.6 equiv MeOH produces only 0.3 equiv of (TTP)Ti(OPh)(OMe) and 0.1 equiv of (TTP)$Ti(OMe)_2$.

In solution **2** has been found to engage readily in intermetal ligand exchange reactions. Thus, treatment of **2** with 1 equiv of (TTP)$TiCl_2$ in toluene rapidly (ca. 10 min) and quantitatively affords a new product, **6**, in high yield. The ^{1}H NMR spectrum of **6** displays an aa′mm′ pattern for the porphyrin tolyl protons. Thus, the porphyrin plane does not serve as a mirror plane of symmetry in this new molecule. In addition, the porphyrin tolyl ligands are not freely rotating about the $C_{meso}-C_{ipso}$ bond on the NMR timescale. Accordingly, this new complex is formulated as (TTP)Ti(OPh)Cl (**6**) (eq 2). Complex **6** is also prepared

$$(TTP)TiCl_2\ (\mathbf{1}) + (TTP)Ti(OPh)_2\ (\mathbf{2}) \rightarrow 2(TTP)Ti(OPh)Cl\ (\mathbf{6}) \quad (2)$$

by the reaction of (TTP)$TiCl_2$ with 1 equiv of NaOPh in toluene. The monomethoxide complex, (TTP)Ti(OMe)Cl has also been synthesized by both of these routes. Interestingly, the intermetal ligand redistribution reaction described in eq 2, unlike previously reported exchanges for (TTP)Ti(IV) complexes, appears to be driven to completion. The reverse process, disproportionation of (TTP)Ti(OPh)Cl (**6**) to (TTP)$TiCl_2$ and (TTP)$Ti(OPh)_2$, has not been observed by either variable temperature ^{1}H NMR experiments or UV−vis studies.

Alcohols are not sufficiently basic to displace both chloro ligands in (TTP)$TiCl_2$. Instead an equilibrium is established for monoalkoxide formation as represented in eq 3. In a mixture

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

of 2.7 PhOH and (TTP)$TiCl_2$ in C_6D_6, the equilibrium lies far to the left. No monophenoxide complex is detected by ^{1}H NMR. When 6.7 equiv of MeOH is added to (TTP)$TiCl_2$ in C_6D_6, the equilibrium ratio of (TTP)Ti(OMe)Cl to (TTP)$TiCl_2$ 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)$TiCl_2$ 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)-$TiCl_2$ and *tert*-butanol in C_6D_6 resulted in quantitative formation of (TTP)Ti(O-*t*-Bu)$_2$.

Preparation of Bis(amido) Complexes. Treatment of freshly prepared (TTP)$TiCl_2$ with ≥2 equiv of $LiNPh_2$ in hexanes results in the formation of the bis(amido) complex (TTP)$Ti(NPh_2)_2$ (**5**) in modest yield (eq 4). This reaction is

$$(TTP)TiCl_2 + 2LiNPh_2 \rightarrow (TTP)Ti(NPh_2)_2\ (\mathbf{5}) + 2LiCl \quad (4)$$

very sensitive to solvent choice. In our hands, **5** *could not be produced in pure fashion* employing toluene, benzene, THF, or CH_2Cl_2 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 $HNPh_2$. Our attempts to prepare other bis(amido) complexes have met with no success. Thus, the reaction of **1** with $LiNEt_2$, $LiNTMS_2$, $LiN(C_6H_{11})_2$, $TMSNEt_2$, or lithium tetrahydroquinolide, under similar conditions employed to produce **5**, leads only to intractable, paramagnetic products. Finally, treatment of **5** with other secondary amines, such as $HNEt_2$, piperidine, *t*-$BuNH_2$, or 1,2,3,4-tetrahydroquinoline, did not result in the production of any new bis(amido) transamination products. These observations parallel those described for the alkoxide/alcohol system. The equilibrium favors the complex bound to the least basic secondary amide.

Analogous to the bis(alkoxide) complexes discussed above, the diphenylamido ligands in **5** are disposed in a trans fashion. Thus, **5** displays pseudo D_{4h} symmetry in the ambient temperature ^{1}H NMR spectrum. In C_6D_6, the resonances for phenyl groups of the NPh_2 ligands are shifted upfield [δ 6.17 (H_p), δ 6.05 (H_m), and δ 2.86 (H_o)] 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)$TiCl_2$ to afford the monoamido complex (TTP)-$Ti(NPh_2)Cl$ (**8**) (eq 5). Again, this reaction appears to be entirely irreversible. Complex **8** can be prepared independently from treatment of **1** with 1 equiv of $LiNPh_2$.

$$(TTP)Ti(NPh_2)_2 + (TTP)TiCl_2 \rightarrow 2(TTP)Ti(NPh_2)Cl \quad (5)$$

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 $HNPh_2$ to any observable extent. This behavior is attributed to the acidity of phenol relative to diphenylamine. Correspondingly, water rapidly converts (TTP)-$Ti(NPh_2)_2$ to the oxo complex, (TTP)Ti=O.

$$(TTP)Ti(NPh_2)_2 + 2HOPh \rightarrow (TTP)Ti(OPh)_2 + 2HNPh_2 \quad (6)$$

Preparation of Imido Complexes. From Ti(IV) Species via α-Hydrogen Abstraction. Treatment of $(TTP)TiCl_2$ with 2 equiv of LiNH-*t*-Bu in toluene results in the formation of the imido derivative (TTP)Ti=N-*t*-Bu (**9**) (eq 7). This reaction is

$$(TTP)TiCl_2 + 2LiNHR \rightarrow (TTP)Ti{=}NR + H_2NR + 2LiCl \quad (7)$$

[R = *t*-Bu (**9**), Ph (**10**), *p*-tolyl (**11**)]

extremely clean and proceeds quantitatively in C_6D_6 to afford **9** along with 1 equiv of *tert*-butylamine (^{1}H NMR, Ph_3CH internal standard). The ^{1}H NMR spectrum (C_6D_6) of **9** reveals four doublets assignable to the H_o, H_o', H_m, and H_m' resonances of the $[TTP]^{2-}$ ligand, indicating the expected lack of a mirror plane of symmetry coincidental 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=NR [R = Ph (**10**), *p*-tolyl (**11**)] all of which are obtained in high yield (eq 7). Attempts to prepare the parent imido complex by treatment of **1** with $LiNH_2$ have, thus far, proved unsuccessful.

As noted above, with the secondary lithium amide, $LiNPh_2$, we can prepare the monosubstituted amido complex (TTP)Ti-$(NPh_2)Cl$. 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=N-*t*-Bu (**9**) and left an equimolar amount of unreacted **1** (eq 8). The reaction of $(TTP)Ti(NPh_2)Cl$, a model complex for (TTP)-Ti(NHR)Cl, with 1 equiv of LiNH-*t*-Bu *did not* allow the isolation or observation of the mixed amido complex (TTP)-$Ti(NPh_2)$(NH-*t*-Bu). Instead, the only spectroscopically observable products at early times (∼10 min) were (TTP)Ti=N-*t*-Bu, the bis(amido) complex $(TTP)Ti(NPh_2)_2$, formed in an approximate 1:1 ratio along with free H_2N-*t*-Bu (eq 9). The bis-(amido) complex apparently forms from displaced NPh_2, which undergoes metathesis with unreacted $(TTP)Ti(NPh_2)Cl$. After long reaction times (>10 h), the final products were (TTP)-Ti=N-*t*-Bu and free $HNPh_2$ from the subsequent reaction between $(TTP)Ti(NPh_2)_2$ and H_2N-*t*-Bu. This latter process was confirmed independently. Treatment of $(TTP)Ti(NPh_2)_2$ with excess H_2N-*t*-Bu quantitatively produced (TTP)Ti=N-*t*-Bu and $HNPh_2$ (eq 10).

$$(TTP)TiCl_2 + 1LiNH\text{-}t\text{-}Bu \rightarrow {}^1/_2(TTP)Ti{=}N\text{-}t\text{-}Bu + {}^1/_2(TTP)TiCl_2 + {}^1/_2H_2N\text{-}t\text{-}Bu + LiCl \quad (8)$$

$$(TTP)Ti(NPh_2)Cl + 1LiNH\text{-}t\text{-}Bu \rightarrow (TTP)Ti{=}N\text{-}t\text{-}Bu + (TTP)Ti(NPh_2)_2 + H_2N\text{-}t\text{-}Bu + LiCl \quad (9)$$

$$(TTP)Ti(NPh_2)_2 + H_2N\text{-}t\text{-}Bu \rightarrow (TTP)Ti{=}N\text{-}t\text{-}Bu + 2NHPh_2 \quad (10)$$

It has been previously reported that treatment of $(TTP)TiCl_2$ 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 $[H_3N$-*t*-Bu]Cl byproduct.

Imido Complexes Via Disproportionation of Ti(III). We have also found that Ti(IV)−imido 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 alkyne adduct, $(TTP)Ti(\eta^2$-PhC≡CPh)[12a] 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)-$Ti(py)_2$ (eq 12). These disproportionation reactions underscore the strong thermodynamic driving force for the formation of these robust Ti(IV)−imido complexes.

$$(TTP)TiCl + LiNH\text{-}t\text{-}Bu + \text{excess } PhC{\infty}CPh \rightarrow {}^1/_2(TTP)Ti{=}N\text{-}t\text{-}Bu + {}^1/_2(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh) + {}^1/_2H_2N\text{-}t\text{-}Bu + LiCl \quad (11)$$

$$2(TTP)TiCl + LiNH\text{-}t\text{-}Bu + \text{excess py} \rightarrow {}^1/_2(TTP)Ti{=}N\text{-}t\text{-}Bu + {}^1/_2(TTP)Ti(py)_2 + {}^1/_2H_2N\text{-}t\text{-}Bu + LiCl \quad (12)$$

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) alkyne complex $(TTP)Ti(\eta^2$-EtC≡CEt) reacts instantaneously with excess N_3TMS in toluene to provide the imido complex (TTP)-Ti=NTMS (**12**) and 1 equiv of free EtC≡CEt (eq 13). Additionally, treatment of $(TTP)Ti(\eta^2$-EtC≡CEt) with 0.5 equiv PhN=NPh in refluxing toluene provides (TTP)Ti=NPh (**10**) as the sole porphyrin product (eq 14).[13] Details of this reaction will be reported elsewhere.[14]

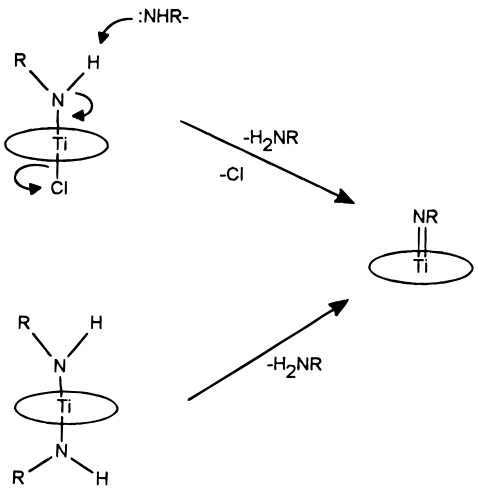
$$(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) + \text{excess } N_3TMS \rightarrow (TTP)Ti{=}NTMS + EtC{\equiv}CEt + N_2 \quad (13)$$

$$(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) + 0.5PhN{=}NPh \rightarrow (TTP)Ti{=}NPh + EtC{\equiv}CEt \quad (14)$$

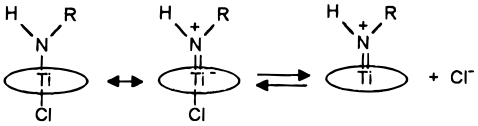
Reactivity of Ti−Imido Complexes. The imido complexes described above show only limited reactivity. As expected, treatment of (TTP)Ti=NR complexes with alcohols such as phenol and methanol results in the clean formation the bis-(alkoxide) complexes **2** and **3**, respectively along with free amine.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

(11) Buchler, J. W.; Pfeifer, S. *Z. Naturforsch., B: Chem. Sci.* **1985**, *40B*, 1362.
(12) (a) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102. (b) Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.
(13) For other examples of azobenzene cleavage leading to imido complexes in Ti chemistry, see: (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.
(14) Gray, S. D.; Woo, L. K. Unpublished results.

Scheme 1



Scheme 2

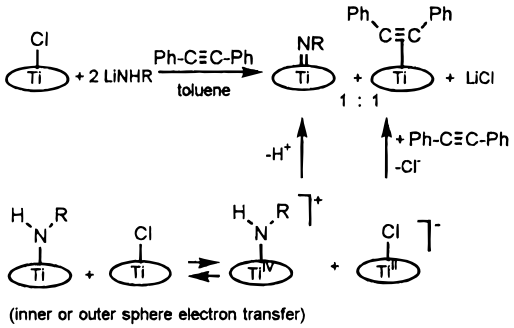


(TTP)Ti═NR complexes do not undergo exchange with primary amines. Thus, treatment of (TTP)Ti═N-*t*-Bu with aniline *does not* afford (TTP)Ti═NPh and free *tert*-butylamine. The reverse reaction of (TTP)Ti═NPh with excess *tert*-butylamine also does not proceed to any observable extent. We have previously shown that the oxo analogue, (TTP)Ti═O rapidly undergoes incomplete oxygen atom transfer with (TTP)Ti(II) species to afford the bridging Ti(III)-oxo dimer $[(TTP)Ti]_2(\mu\text{-O})$. In contrast, the imido complexes described above do not react with (TTP)Ti(η^2-EtC≡CEt) 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 **1** and LiNHR must involve α-hydrogen abstraction. Two possible mechanisms are shown in Scheme 1. A concerted intramolecular elimination from the bis(amido) complex is unlikely given the known trans disposition of the amido ligands in $(TTP)Ti(NPh_2)_2$ (**5**). A concerted bimolecular pathway in which 2 equiv of H_2NR are simultaneously eliminated from 2 mol of $(TTP)Ti(NHR)_2$ is also implausible due to the steric nature of the porphyrin ligands. Intermolecular deprotonation of an imido ligand by a second equivalent of LiNHR is a reasonable alternative. Moreover, the strong π-donor character of the amide ligand may facilitate the dissociation of the trans chloride and/or increase the acidity of the α-proton (Scheme 2). This hypothesis is supported by reaction 8 in which only (TTP)Ti═N-*t*-Bu was formed and no monoamido complex, (TTP)Ti(NH-*t*-Bu)Cl, was observed on treating **1** with 1 equiv of LiNH-*t*-Bu. Additionally, since other amide reagents (e.g., $LiNEt_2$) lead only to reduction of Ti(IV) to Ti(III), deprotonation of a primary amide ligand appears to compete effectively with reduction processes. Moreover, our inability to isolate or observe a monoamido complex is consistent with the high acidity of the N−H proton of the complexed amido ligand.

Scheme 3



The strong π-donor ability of the amido ligand also provides a rationale for reactions 5 and 8. In the ligand disproportionation (eq 5), the amido ligand prefers to be trans to a weaker chloro ligand than trans to a second strong π-donor amido ligand. Correspondingly, treatment of $(TTP)Ti(NPh_2)Cl$ with LiNH-*t*-Bu (eq 9) is likely to produce transiently the mixed amido complex $(TTP)Ti(NPh_2)(NH\text{-}t\text{-}Bu)$. Competing π-donation serves to labilize both ligands. The loss of the *t*-Bu amide is nonproductive. However, dissociation of NPh_2 produces $[(TTP)Ti(NH\text{-}t\text{-}Bu)]^+$ having an acidic α-hydrogen which is rapidly deprotonated to produce (TTP)Ti═N-*t*-Bu.

To the best of our knowledge, the production of imido complexes from Ti(III) sources (reactions 11 and 12) is unprecedented. There are several scenarios one could envision to account for these reactions. It is important to note that (TTP)TiCl does not react with either diphenylacetylene or pyridine to produce $(TTP)TiCl_2$ and (TTP)Ti(η^2-Ph−C≡C-Ph) or $(TTP)Ti(py)_2$. Thus, (TTP)TiCl does not readily disproportionate. If the reaction of (TTP)TiCl with LiNH-*t*-Bu affords initially (TTP)Ti(NH-*t*-Bu), this species could undergo electron transfer (either in an inner- or outer-sphere sense) with a second Ti(III) species to afford either (TTP)Ti(NH-*t*-Bu)X (X = NH-*t*-Bu or Cl) or $[(TTP)Ti(NH\text{-}t\text{-}Bu)]^+$ along with a Ti(II) complex (Scheme 3). The former complex could be deprotonated by an additional equivalent of lithium amide to afford the imido complex while the latter complex is readily trapped by pyridine or diphenylacetylene. However, it is not clear why (TTP)Ti-NH-*t*-Bu would be more prone to disproportionation than (TTP)-TiCl. However, on the basis of the observations above, it appears that α-hydrogen abstraction occurs much more rapidly than reduction for Ti-porphyrin complexes. Thus, we propose that any (TTP)Ti(NH-*t*-Bu) formed in the reaction is rapidly deprotonated to afford the transient Ti(III)−imido complex anion $[(TTP)Ti{=}N\text{-}t\text{-}Bu]^-$. Due to its anionic charge, this Ti(III)−imido complex presumably is more capable of reducing (TTP)-TiCl to Ti(II), which is subsequently trapped by either pyridine or diphenylacteylene.

Conclusions

In this work we have demonstrated that $(TTP)TiCl_2$, which is readily prepared from the reaction of $TiCl_4(THF)_2$ with $Li_2(THF)_2TTP$, serves as a useful precursor for the synthesis of a variety of Ti-porphyrin complexes possessing hard π-donor ligands. Prior to this work, the only reported complexes of this

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class of compounds are (TPP)Ti(OMe)[16] and the η^2-catecholate (TTP)Ti($O_2C_6H_4$).[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,[18] we have found that the only isolable bis(amido)−porphyrin complex is (TTP)Ti(NPh_2)$_2$. The imido complexes, given the reactivity displayed by the oxo analogue (*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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