Facile Syntheses of Titanium(II), Tin(II), and Vanadium(II) Porphyrin Complexes through Homogeneous Reduction. Reactivity of *trans*-(TTP)TiL$_2$ (L = THF, *t*-BuNC)

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Facile syntheses of the *meso*-tetra-*p*-tolylporphyrin (TTP) complexes *trans*-(TTP)Ti(THF)$_2$ (**1**), (TTP)Sn (**2**), and *trans*-(TTP)V(THF)$_2$ (**3**) are achieved through homogeneous reduction of high-valent precursors using NaBEt$_3$H. The composition of the new compound *trans*-(TTP)Ti(THF)$_2$ was determined by spectroscopic and chemical characterization. Ligand displacement reactions of *trans*-(TTP)Ti(THF)$_2$ with *t*-BuNC produced a new Ti(II) complex, *trans*-(TTP)Ti(*t*-BuNC)$_2$. The ligand-binding preference of (TTP)Ti^{II}L$_n$ (n = 1, 2) is picoline ∼pyridine > *t*-BuNC > PhC≡CPh > EtC≡CEt > THF.

Introduction

Recent interest in divalent metalloporphyrin complexes arises primarily from their rich redox chemistry. For example, the oxidative addition of CH_3I to Sn(II) porphyrins resulted in the first stable Sn(IV) porphyrin alkyl complexes that have potential biological (e.g. anticancer) activity.[2] Moreover, Sn(II)[3] and Ti(II)[4] porphyrin complexes have been very useful in the development and study of inter-metal oxygen, sulfur, and selenium atom transfer reactions. Despite these findings, extensive research with divalent metalloporphyrin complexes is often hampered by the difficulty in synthesizing these materials. A recent preparative method for (TTP)Sn^{II} [5] only afforded a 20% yield.[2] Moreover, only a few well-defined Ti(II) porphyrin complexes exist,[4b,6] including the alkyne adducts (Por)Ti^{II}(η^2-RC≡CR) (R = Et, Ph) and pyridine-based σ-donor ligand adducts such as *trans*-(TTP)Ti^{II}(Py)$_2$. Furthermore, only two isolated V(II) porphyrin complexes have been reported,[7] both synthesized by heterogeneous reduction of dihalovanadium(IV) porphyrins that are obtained with difficulty from cleaving the robust V=O bond in oxovanadium(IV) porphyrins.[8] In this work, we describe the facile syntheses of divalent Ti, Sn, and V porphyrins utilizing NaBEt$_3$H to homogeneously reduce the readily available *trans*-(TTP)M^{IV}Cl$_2$ (M = Sn,[7] Ti[8]) and (TTP)M^{III}Cl[8] (M = Ti, V) complexes. We also discuss the reactivity of a new compound *trans*-(TTP)Ti(THF)$_2$.

Experimental Section

General Considerations. Toluene, benzene-d_6, and hexanes for glovebox use were distilled from purple solutions of sodium benzophenone ketyl. Dry solvents were subsequently degassed on a vacuum line (10^{-5} Torr) with three successive freeze−pump−thaw cycles. NaBEt$_3$H, 4-tolyl sulfoxide, Ph$_3$CH, and PhC≡CPh were purchased from Aldrich and used without further purification. EtC≡CEt, *t*-BuNC, pyridine, and 4-picoline were purchased from Aldrich and vacuum-distilled for glovebox use. Literature procedures were used to prepare (TTP)SnCl$_2$,[9] (TTP)TiCl$_2$,[10] (TTP)TiCl,[10] (TTP)VCl,[10] and (TTP)Ti(η^2-EtC≡CEt).[6] All manipulations were performed either in a Vacuum Atmospheres glovebox equipped with a Model HE-553-2 Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV−visible data were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. ^{1}H NMR spectra were recorded on a Varian 300-MHz spectrometer, with Ph$_3$CH used as an internal reference for some quantitative analyses. IR spectra were recorded from Nujol mulls on NaCl plates on a Bio-Rad Digilab FTS-7 spectrometer. GC-MS analyses were performed on a Finnigan TSQ 700 mass spectrometer coupled to a Varian GC 3400 chromatograph using a 30-m DB5 column. Elemental analyses were obtained from Desert Analytics, Tucson, AZ, or at ISU on a Perkin-Elmer CHN Elemental Analyzer.

***trans*-(TTP)Ti(THF)$_2$, 1. Method A.** To a rapidly stirred deep red-purple solution of (TTP)TiCl (154.2 mg, 0.21 mmol) in toluene (ca. 10 mL) was added allylmagnesium chloride (2 M solution in THF, 400 μL, 0.80 mmol, 3.8 equiv) dropwise. The solution rapidly turned deep brown-black upon allylmagnesium chloride addition. After 18 h, the solvent was removed under reduced pressure to provide a deep brown oil. This oil was extracted with toluene, and the extract was filtered through Celite. The solvent was removed under reduced pressure from the resultant purple filtrate to provide a black oil. The oil was triturated with hexanes (ca. 8 mL), and the solvent was removed to provide *trans*-(TTP)Ti(THF)$_2$ (119.8 mg, 0.139 mmol, 66.3%) as a black microcrystalline solid. The compound may be crystallized by slow diffusion of hexanes into concentrated toluene solutions of *trans*-(TTP)Ti(THF)$_2$. ^{1}H NMR (C$_6$D$_6$, ppm): 17.65 (br s, 8H, THF), 7.80 (br s, 8H, THF), 6.25 (d, 8H, −C$_6$*H*$_4$Me), 5.00 (d, 8H, −C$_6$*H*$_4$Me), 1.58 (s, 12H, −C$_6$H$_4$*Me*), −4.93 (br s, 8H, β-H). UV−vis (toluene, nm): 396, 426 (Soret), 448, 554.

***trans*-(TTP)Ti(THF)$_2$, 1. Method B, from (TTP)TiCl.** NaBEt$_3$H (0.25 mL of 1.0 M solution in THF) was added to a solution of 142.3

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mg (0.19 mmol) of (TTP)TiCl in ca. 10 mL of THF. After the mixture was stirred vigorously for 4 h, the THF was removed under reduced pressure, leaving a nearly black solid. This solid was dissolved in a minimal amount of boiling THF (ca. 50 mL), and the solution was filtered through a sintered frit. The filtrate was refrigerated at −30 °C for 4 days. The product (92 mg, 0.11 mmol, 56%) was isolated by filtration as nearly black microcrystalline solids, washed with cold THF, and dried in vacuo at room temperature. The ^{1}H NMR (C_6D_6) spectrum was identical to that from method A. UV−vis (THF, nm): 318, 386, 424 (Soret), 552. IR (Nujol on NaCl plates, cm^{-1}): 869 (m), ν(C−O) of bound THF; 1024 (m), ν(C−C) of bound THF. Anal. Calcd (found) for $C_{56}H_{52}N_4O_2Ti$: C, 78.13 (75.18); H, 6.09 (6.16); N, 6.51 (5.27). Combustion analyses were tried several times on different batches. Analytically pure samples could not be obtained due to the extreme air and thermal sensitivity of this compound.

***trans*-(TTP)Ti(THF)$_2$, 1. Method C, from (TTP)TiCl$_2$.** The procedure was similar to the above except that (TTP)$TiCl_2$ (60.5 mg, 0.077 mmol) and 0.16 mL of 1 M $NaBEt_3H$ in THF were employed and that the mixture was stirred for 12 h. The product (23 mg, 32%) was shown to be identical to samples prepared by methods A and B by ^{1}H NMR.

(TTP)Sn, 2. $NaBEt_3H$ (0.15 mL of 1.0 M solution in toluene) was added to a solution of 64.3 mg (0.075 mmol) of (TTP)$SnCl_2$ in ca. 10 mL of toluene. After the mixture was stirred vigorously for 4 h, it was filtered through a sintered frit. The solvent was removed from the filtrate under reduced pressure. The residues were redissoved in ca. 2 mL of toluene, the solution was layered with ca. 4 mL of hexanes, and the layered mixture was refrigerated at −30 °C overnight. The product (45 mg, 0.057 mmol, 76%) was isolated by filtration and dried in vacuo at room temperature. ^{1}H NMR (C_6D_6, ppm): 9.19 (s, 8H, β-H), 8.08 (br d, 8H, $-C_6H_4$Me), 7.25 (d, 8H, $-C_6H_4$Me), 2.40 (s, 12H, $-C_6H_4$*Me*); identical with the reported data.[2]

***trans*-(TTP)V(THF)$_2$, 3.** This compound was prepared in the same manner as method B for **1**, using 423 mg (0.53 mmol) of (TTP)VCl, 0.6 mL of 1 M $NaBEt_3H$ in THF, and 120 mL of THF for extraction and a 12-h reaction time. The isolated yield of black-purple crystals was 243 mg (0.28 mmol, 53%). ^{1}H NMR (C_6D_6, ppm): 1.37 (br s, $-C_6H_4$*Me*). UV−vis (THF, nm): 368, 425 (Soret), 525. IR (Nujol on NaCl plates, cm^{-1}): 879 (m), ν(C−O) of bound THF; 1037 (m), ν(C−C) of bound THF. Anal. Calcd (found) for $C_{56}H_{52}N_4O_2V$: C, 77.85 (77.23); H, 6.08 (5.41); N, 6.48 (4.92).

***trans*-(TTP)Ti(*t*-BuNC)$_2$, 8. Method A, from *trans*-(TTP)Ti(THF)$_2$.** *t*-BuNC (15 mg, 0.18 mmol) was dissolved in ca. 10 mL of toluene, and 35 mg (0.041 mmol) of *trans*-(TTP)Ti(THF)$_2$ was added. The mixture was vigorously stirred at ambient temperature for 3 h, after which the toluene was removed under reduced pressure. The solid was dissolved in a minimal amount of toluene (ca. 7 mL), and the solution was refrigerated at −30 °C for 24 h. The purple crystalline product (11.2 mg, 0.013 mmol, 32%) was isolated by filtration, washed with cold pentane, and dried in vacuo at room temperature. ^{1}H NMR (C_6D_6, ppm): 7.35 (br d, 8H, $-C_6H_4$Me), 5.48 (br s, 18H, *t*-Bu), 3.95 (br d, 8H, $-C_6H_4$Me), 2.43 (s, 12H, $-C_6H_4$*Me*). (β-H gives no identifiable signal.) UV−vis (toluene, nm): 426 (Soret), 554, 594. IR (Nujol on NaCl plates, cm^{-1}): 2177 (m), υ(C≡N) of bound *t*-BuNC. Anal. Calcd (found) for $C_{58}H_{54}N_6Ti(C_7H_8)_{0.5}$: C, 79.51 (79.42); H, 6.29 (6.21); N, 9.05 (9.08). One-half equivalent of toluene was observed by ^{1}H NMR in the sample submitted for combustion analysis.

***trans*-(TTP)Ti(*t*-BuNC)$_2$, 8. Method B, from (TTP)Ti(η^2-EtC≡CEt).** A minimal amount of toluene (3 mL) was used to dissolve (TTP)Ti(η^2-EtC≡CEt) (53 mg, 0.066 mmol). *t*-BuNC (25 mg, 0.3 mmol) was added, and the mixture was stirred for 4 h. During this time, a black precipitate formed. The product was isolated by filtration and dried in vacuo (32 mg, 0.036 mmol, 55%).

(TTP)Ti(η^2-EtC≡CEt) from (TTP)TiCl. $NaBEt_3H$ (0.62 mL of 1.0 M solution in toluene) was added to a solution of 330 mg (0.44 mmol) of (TTP)TiCl and 94 μL (0.83 mmol) of 3-hexyne in ca. 18 mL of toluene. After the mixture was stirred vigorously at ambient temperature for 8 h, it was filtered through a sintered frit, and the solvent was removed from the filtrate under reduced pressure. The residues were redissoved in ca. 4 mL of toluene, the solution was layered with ca. 6 mL of hexanes, and the layered mixture was refrigerated at −30 °C over a period of 6 days. The product (182 mg, 0.23 mmol, 52%) was isolated in two crops. ^{1}H NMR (C_6D_6, ppm): 9.05 (s, 8H, β-H), 8.23 (d, 4H, $-C_6H_4$Me), 7.98 (d, 4H, $-C_6H_4$Me), 7.28 (m, 8H, $-C_6H_4$-Me), 2.39 (s, 12H, $-C_6H_4$*Me*), −0.12 (q, 4H, -CH_2CH$_3$), −0.87 (t, 6H, -CH$_2$CH_3); identical with the reported data.[3b]

Reaction of *trans*-(TTP)Ti(THF)$_2$ with Air. An NMR tube containing a C_6D_6 solution of *trans*-(TTP)Ti(THF)$_2$ (1.2 mg, 1.4×10^{-4} mmol) was exposed to air for 20 min, and the sample was subsequently monitored by ^{1}H NMR. The spectrum shows the presence of three species: (TTP)Ti═O, (TTP)Ti(O_2), and THF in a ratio of 1.06:1.00:4.27. Within experimental error, the reaction was quantitative and the ratio of total observed Ti:THF of 1.00:2.07 supports the composition of (TTP)Ti(THF)$_2$.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with 4-Tolyl Sulfoxide. *trans*-(TTP)Ti(THF)$_2$ (1.9 mg, 2.2×10^{-3} mmol), 4-tolyl sulfoxide (1.1 mg, 4.8×10^{-3} mmol), and Ph_3CH (1.3 mg, 5.3×10^{-3} mmol, internal standard) were transferred to a 10-mL beaker. About 1 mL of C_6D_6 was added to the beaker. The mixture was agitated for 5 min and then transferred to an NMR tube and sealed under nitrogen. This sample was monitored by ^{1}H NMR, and the spectrum showed three products: (TTP)Ti═O (2.0×10^{-3} mmol), 4-tolyl sulfide (2.0×10^{-3} mmol), and THF (4.2×10^{-3} mmol). Within experimental error, the reaction was quantitative and its mass balance supports the composition of (TTP)Ti(THF)$_2$. The formation of the 4-tolyl sulfide was further confirmed by its GC-MS molecular peak (m/e = 214).

Reaction of *trans*-(TTP)Ti(*t*-BuNC)$_2$ with 4-Tolyl Sulfoxide. This experiment was conducted in the same maner as the above, using 1.0 mg (1.13×10^{-3} mmol) of *trans*-(TTP)Ti(*t*-BuNC)$_2$, 1.7 mg (7.4×10^{-3} mmol) of 4-tolyl sulfoxide, and 3.7 mg (1.5×10^{-2} mmol) of Ph_3CH. The ^{1}H NMR spectrum showed three products: (TTP)Ti═O (1.1×10^{-3} mmol, 97%), 4-tolyl sulfide (9.7×10^{-4} mmol, 86%), and free *t*-BuNC (2.15×10^{-3} mmol, 95%). Within experimental error, this reaction was quantitative.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with EtC≡CEt. To a vial containing a C_6D_6 solution of *trans*-(TTP)Ti(THF)$_2$ (1.4 mg, 1.63×10^{-3} mmol) and Ph_3CH (3.1 mg, 1.27×10^{-2} mmol) was added 0.5 μL (4.4×10^{-3} mmol) of 3-hexyne. The mixture was agitated for 5 min and transferred to an NMR tube. After standing at ambient temperature for 2 h, the sample was monitored by ^{1}H NMR. The spectrum indicated the formation of (TTP)Ti(η^2-EtC≡CEt) (9.2×10^{-4} mmol, 56%) with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with PhC≡CPh. To a vial containing a C_6D_6 solution of *trans*-(TTP)Ti(THF)$_2$ (1.5 mg, 1.74×10^{-3} mmol) and Ph_3CH (2.4 mg, 9.8×10^{-3} mmol) was added 0.8 mg (4.5×10^{-3} mmol) of PhC≡CPh. The mixture was agitated for 5 min and transferred to an NMR tube. After standing at ambient temperature for 1.5 h, the sample was monitored by ^{1}H NMR. The spectrum indicated the formation of (TTP)Ti(η^2-PhC≡CPh) (1.6×10^{-3} mmol, 92%) with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with Pyridine. To a vial containing a C_6D_6 solution of *trans*-(TTP)Ti(THF)$_2$ (1.0 mg, 1.2×10^{-3} mmol) and Ph_3CH (2.7 mg, 1.1×10^{-2} mmol) was added 0.4 μL (5.0×10^{-3} mmol) of pyridine. The mixture was agitated for 5 min and transferred to an NMR tube. After standing at ambient temperature for 1 h, the sample was monitored by ^{1}H NMR. The spectrum indicated the formation of (TTP)Ti(Py)$_2$ (6.7×10^{-4} mmol, 56%) with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with 4-Picoline. To a vial containing a C_6D_6 solution of *trans*-(TTP)Ti(THF)$_2$ (1.4 mg, 1.6×10^{-3} mmol) and Ph_3CH (3.3 mg, 1.4×10^{-2} mmol) was added 0.5 μL (5.1×10^{-3} mmol) of 4-picoline (Pic). The mixture was agitated for 5 min and transferred to an NMR tube. After standing at ambient temperature for 1 h, the sample was monitored by ^{1}H NMR. The spectrum indicated the formation of (TTP)Ti(Pic)$_2$ (1.2×10^{-3} mmol, 75%) with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of (TTP)Ti(η^2-EtC≡CEt) with THF. To an NMR tube containing a C_6D_6 solution (0.65 mL) of (TTP)Ti(η^2-EtC≡CEt) (1.1 mg, 1.36×10^{-3} mmol) and Ph_3CH (2.6 mg, 1.06×10^{-2} mmol) was added 0.9 μL (1.1×10^{-2} mmol) of THF. ^{1}H NMR spectra taken at 45 min and 13 h of reaction indicated that an equilibrium was reached

at 20 °C, with (TTP)Ti(η^2-EtC≡CEt) and THF producing *trans*-(TTP)-Ti(THF)$_2$ and EtC≡CEt. K_{eq} was found to be 3.8.

Reaction of *trans*-(TTP)Ti(*t*-BuNC)$_2$ with Pyridine. To a vial containing a C_6D_6 solution of *trans*-(TTP)Ti(*t*-BuNC)$_2$ (0.36 mg, 4.1×10^{-4} mmol) and Ph_3CH (3.0 mg, 1.23×10^{-2} mmol) was added 0.3 μL (3.7×10^{-3} mmol) of pyridine. The mixture was agitated for 5 min and transferred to an NMR tube. After standing at ambient temperature for 2 h, the sample was monitored by ^{1}H NMR. The spectrum indicated the formation of (TTP)Ti(Py)$_2$ (4.1×10^{-4} mmol) and free *t*-BuNC (8.0×10^{-4} mmol) with no *trans*-(TTP)Ti(*t*-BuNC)$_2$ left. Within experimental error, this reaction was quantitative and its mass balance supports the composition of (TTP)Ti(*t*-BuNC)$_2$.

Results

Syntheses of Ti(II), Sn(II), and V(II) Porphyrin Complexes. In examining the reactivity of chlorotitanium porphyrin complexes with carbanions, we found that the treatment of (TTP)TiCl with allyl Grignard reagent in THF produced a new compound which could be identified as a bis-THF complex, *trans*-(TTP)Ti(THF)$_2$ (**1**, reaction 1), through spectroscopic and

$$\text{(TTP)TiCl} \xrightarrow[\text{toluene}]{\text{CH}_2{=}\text{CHCH}_2\text{MgCl}} \underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} + \text{C}_6\text{H}_{10} + \text{MgCl}_2 \quad (1)$$

chemical characterization. The organic product from this reaction was identified as the allyl radical dimer, C_6H_{10}, by mass spectrometry through observation of the minor parent ion peak ($m/e = 82$) and the intense daughter ion peak at $m/e = 67$. Although paramagnetic, *trans*-(TTP)Ti(THF)$_2$ (**1**) exhibits an ^{1}H NMR spectrum with relatively sharp resonances, which is interpretable and comparable with that of the known compound *trans*-(TTP)Ti(Py)$_2$. The tolyl ortho and meta protons of **1** appear as two doublets at 6.25 (8H) and 5.00 (8H) ppm, suggesting a pseudo-D_{4h} symmetry and a *trans* geometry for this THF adduct. The resonances of the THF protons (7.80 [8H], 17.67 [8H] ppm) are broad and paramagnetically shifted to low field. The electronic absorption spectrum of **1** in THF contains an intense Soret band at 424 nm with additional bands at 318, 386, and 552 nm, which is characteristic of metalloporphyrin complexes. In the IR spectrum of *trans*-(TTP)Ti(THF)$_2$, two new bands at 869 (m) and 1024 (m) cm^{-1} are assigned to the C−O and C−C stretches of THF, respectively.

Subsequently, a more convenient procedure for the production of Ti(II) porphyrin complexes was established with the use of $NaBEt_3H$ as the reducing agent (reactions 2 and 3). This homogeneous reduction process also provides a general method for the synthesis of V(II) and Sn(II) porphyrin complexes as shown in reactions 3 and 4. The ^{1}H NMR data for Sn(TTP)

$$\text{(TTP)TiCl}_2 \xrightarrow[\text{THF}]{\text{NaBEt}_3\text{H}} \underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} \quad (2)$$

$$\text{(TTP)MCl} \xrightarrow[\text{THF}]{\text{NaBEt}_3\text{H}} \underset{\mathbf{1},\ \text{M} = \text{Ti}\quad \mathbf{3},\ \text{M} = \text{V}}{\textit{trans}\text{-(TTP)M(THF)}_2} \quad (3)$$

$$\text{(TTP)SnCl}_2 \xrightarrow[\text{toluene}]{\text{NaBEt}_3\text{H}} \underset{\mathbf{2}}{\text{(TTP)Sn}} \quad (4)$$

(**2**) are the same as reported in the literature.[3] The two previously reported approaches to (TTP)Sn involve metal insertion of Sn(II) (from $SnCl_2$ or SnI_2) into free-base or dianionic porphyrin ligands, both of which require chromatographic separation under inert atmosphere and afford relatively low yields.[3,11] The UV−vis data for *trans*-(TTP)V(THF)$_2$ (**3**) in THF have appeared in the literature, but no isolation and other characterizations were reported.[7b] In this work, the isolated compound **3** has UV−vis data identical with the reported data, having an intense Soret band at 425 nm. Furthermore, it is ^{1}H NMR inactive, except for exhibiting a very broad peak at 1.37 ppm that is assigned to the CH_3 groups of the TTP moiety. The C−O and C−C stretches of bound THF for **3** appear respectively at 879 (m) and 1037 (m) cm^{-1}, comparable with those of the known, structurally characterized *trans*-(OEP)V(THF)$_2$.[7b]

The known compound (TTP)Ti(η^2-EtC≡CEt) may also be prepared conveniently by reducing (TTP)TiCl in the presence of EtC≡CEt in toluene with $NaBEt_3H$. This approach offers an advantage in that the good solubility of (TTP)TiCl in toluene allows for a relatively large-scale synthesis of (TTP)Ti(η^2-EtC≡CEt). A previous synthetic procedure for this compound involved reducing (TTP)TiCl$_2$ in toluene with $LiAlH_4$.[4b] The latter procedure is limited to small quantity preparations because of the low solubility of (TTP)TiCl$_2$ in toluene.

Substitution Chemistry of *trans*-(TTP)Ti(THF)$_2$, 1. Simple displacement reactions at the metal center are possible for **1**. When this THF adduct is treated with 3-hexyne, diphenylacetylene, pyridine, or 4-picoline, loss of the proton signals for **1** in the NMR spectrum is accompanied by appearance of resonances for free THF and the known complexes **4**−**7** (reactions 5 and 6). These substitution reactions occur readily at ambient temperature in less than 2 h.

$$\underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} \xrightarrow[\text{C}_6\text{D}_6]{\text{RC}{\equiv}\text{CR}} \underset{\mathbf{4},\ \text{R} = \text{Et}\quad \mathbf{5},\ \text{R} = \text{Ph}}{\text{(TTP)Ti}(\eta^2\text{-RC}{\equiv}\text{CR})} + 2\text{THF} \quad (5)$$

$$\underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} \xrightarrow[\text{C}_6\text{D}_6]{\text{L}} \underset{\mathbf{6},\ \text{L} = \text{pyridine}\quad \mathbf{7},\ \text{L} = \text{4-picoline}}{\text{(TTP)TiL}_2} + 2\text{THF} \quad (6)$$

Treatment of **1** with *tert*-butyl isocyanide in toluene leads to the isolation of a new complex *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**), as shown in reaction 7. The paramagnetic character of **8** is evident

$$\underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} \xrightarrow[\text{toluene}]{t\text{-BuNC}} \underset{\mathbf{8}}{\textit{trans}\text{-(TTP)Ti}(t\text{-BuNC})_2} + 2\text{THF} \quad (7)$$

as indicated by the broad proton resonances and the missing β-proton signal in the ^{1}H NMR spectrum. Nonetheless, four observed resonances are assignable and support the formulation of *trans*-(TTP)Ti(*t*-BuNC)$_2$. The *trans* geometry is indicated by the two doublets of the TTP tolyl ortho and meta protons at 7.35 and 3.95 ppm, respectively. The *tert*-butyl protons appear at 5.48 ppm (s, 18H), and the tolyl methyl signal is at 2.43 ppm (s, 12H). In addition, the electronic absorption spectrum of **8** in toluene contains an intense Soret band at 426 nm and two Q bands at 554 and 594 nm. The IR spectrum in Nujol shows a diagnostic C≡N stretch at 2177 cm^{-1} (m).

Oxidation Reactions of *trans*-(TTP)TiL$_2$ (L = THF, *t*-BuNC). As a low-valent early transition metal complex, *trans*-(TTP)Ti(THF)$_2$ is prone to oxidation. When exposed to air, it

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reacts with oxygen, producing both the oxo− and peroxo−Ti(IV) species in a 1:1 ratio and releasing 2 equiv of THF/equiv of Ti (reaction 8). The ^{1}H NMR spectrum indicates that reaction

$$\underset{\mathbf{1}}{\textit{trans}\text{-(TTP)Ti(THF)}_2} \xrightarrow[C_6D_6]{\text{air}} \text{(TTP)Ti=O} + \text{(TTP)Ti}(\eta^2\text{-O}_2) + 2\text{THF} \quad (8)$$

8 is quantitative, and its mass balance supports the formulation of (TTP)Ti(THF)$_2$. Treatment of **2** with an excess of 4-tolyl sulfoxide, a weak organic oxidant, results in the formation of (TTP)Ti=O and 4-tolyl sulfide, as well as free THF, as shown in reaction 9. Treatment of *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**) with

$$\textit{trans}\text{-(TTP)TiL}_2 + (\text{MeC}_6\text{H}_5)\text{S(O)}(\text{C}_6\text{H}_5\text{Me}) \xrightarrow{C_6D_6} \text{(TTP)Ti=O} + (\text{MeC}_6\text{H}_5)_2\text{S} + 2\text{L} \quad (9)$$

$$\text{L} = \text{THF, } t\text{-BuNC}$$

4-tolyl sulfoxide affords analogous results. Both oxygen atom transfer reactions occur at ambient temperature and give mass balances that support the compositions of **1** and **8**.

The Relative Binding Stength of Neutral Ligands in (TTP)TiL$_n$ (n = 1, 2). In order to compare the ligand-binding strength in (TTP)TiL$_n$ (n = 1, 2), (TTP)Ti(η^2-EtC≡CEt) in C_6D_6 was treated with an excess of free THF (reaction 10). The

$$\text{(TTP)Ti}(\eta^2\text{-EtC≡CEt}) + 2\text{THF} \overset{C_6D_6}{\rightleftharpoons} \textit{trans}\text{-(TTP)Ti(THF)}_2 + \text{EtC≡CEt} \quad (10)$$

substitution reaction reaches equilibrium within 45 min at 20 °C with a K_{eq} of 3.8. Thus, the (TTP)Ti^{II} fragment has a binding preference for EtC≡CEt over THF. In addition, when (TTP)Ti(η^2-EtC≡CEt) was treated with *t*-BuNC in C_6D_6, EtC≡CEt was completely displaced by 2 equiv of *t*-BuNC, resulting in quantitative formation of *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**). Similarly, it was found that pyridine displaces *t*-BuNC in **8** completely, producing *trans*-(TTP)Ti(Py)$_2$.

Discussion

The method of using soluble $NaBEt_3H$ to reduce nonporphyrin V(III) or Ti(IV) complexes was reported by Gladysz,[12] Cotton,[13] and Bonnemann.[14] We extended this method to prepare divalent metalloporphyrin complexes **1**−**3** by reducing tri- or tetravalent precursors with stoichiometric amounts of $NaBEt_3H$. This new approach gives good yields under mild reaction conditions. While the compounds (TTP)Sn (**2**) and *trans*-(TTP)V(THF)$_2$ (**3**) previously were reported, the compound *trans*-(TTP)Ti(THF)$_2$ (**1**) is new. This THF adduct of titanium porphyrin can be viewed as containing titanium in the formal +II oxidation state. The two axial THF ligands donate a total of four electrons to titanium d orbitals. This appears to be important in stabilizing the titanium(II) complex as was previously observed for (TTP)Ti(η^2-RC≡CR), in which the acetylene ligand serves as a four-electron donor rather than a two-electron donor. In the IR spectrum of **1**, the C−O and C−C stretches of bound THF are shifted to lower wavenumbers (869 and 1024 cm^{-1}) as compared with those of free THF (910 and 1040 cm^{-1}).[7b] The ^{1}H NMR spectrum of **1** shows strong paramagnetic shifts but is interpretable and consistent with its formulation. Like all other Ti(II) porphyrin complexes, **1** is extremely air-sensitive and is oxidized in air to the oxo and peroxo complexes as shown in reaction 8. In addition, this THF adduct is thermally sensitive. If it is left at ambient temperature under N_2 for a week, partial decomposition of the solid occurs, resulting in uncharacterized products. Consequently combustion analyses did not yield composition results within desired tolerances. As a result, several chemical characterizations were crucial in verifying composition and bulk purity. For example, at ambient temperature, 2.2×10^{-3} mmol of compound **2** reacts with 4-tolyl sulfoxide to produce 2.0×10^{-3} mmol of (TTP)Ti=O, 2.0×10^{-3} mmol of 4-tolyl sulfide, and 4.2×10^{-3} mmol of THF, as determined by ^{1}H NMR. The mass balance, within experimental error, substantiates the composition of **1**. In this two-electron oxygen transfer reaction, it is likely that 4-tolyl sulfoxide first coordinates to the titanium center through oxygen. The next step is the transfer of two electrons from titanium to sulfur mediated by oxygen atom transfer. The scope and mechanism of this new atom transfer reaction will be studied.

As weak σ donors, the THF ligands in **1** are labile and can be displaced by stronger σ-donor ligands like pyridine and 4-picoline, as well as by π-acid ligands such as 3-hexyne and diphenylacetylene. The ligand lability of **1** is utilized to synthesize *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**), a novel Ti(II) porphyrin organometallic complex with a titanium−carbon coordination bond (reaction 7). The characterization of **8** is as described in the preceding section. Unlike the case of metal coordination of CO that results in a lowering of ν(C≡O), the ν(C≡N) in metal isocyanide complexes can shift to both higher or lower wavenumbers.[15] The C≡N stretching frequency for **8** (2177 cm^{-1}) increases by almost 40 cm^{-1} relative to that for free *t*-BuNC (2138 cm^{-1}).[16] Nonetheless, it is similar to the ν(C≡N) values for the two reported, neutral Ti/*t*-BuNC complexes: Cp$_2$Ti(CO)(*t*-BuNC) (2170 cm^{-1}) and (η^5-indenyl)$_2$Ti(CO)(*t*-BuNC) (2173 cm^{-1}).[17] Like *trans*-(TTP)Ti(THF)$_2$ (**1**), *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**) undergoes a quantitative oxygen transfer reaction with 4-tolyl sulfoxide, forming (TTP)Ti=O and 4-tolyl sulfide and releasing *t*-BuNC. Our studies have demonstrated that the (TTP)Ti^{II} fragment can bind a range of neutral ligands (both σ donors and π acceptors) through the titanium center. The binding strengths of these ligands vary significantly. To summarize the results of the controlled displacement reactions described in the preceding section, the relative preference for neutral ligands binding to (TTP)Ti^{II} follows the order

$$\text{pyridine} \sim \text{picoline} > \text{RNC} > \text{PhC≡CPh} > \text{EtC≡CEt} > \text{THF}$$

Concluding Remarks

The facile preparations of (TTP)Sn and *trans*-(TTP)M(THF)$_2$ (M = Ti, V) via homogeneous reduction with $NaBEt_3H$ have been achieved. Spectroscopic and chemical characterizations support the identity of the new compound *trans*-(TTP)Ti(THF)$_2$ (**1**). The strong reducing potential of the Ti(II) center in **1** is demonstrated in reactions with oxygen or 4-tolyl sulfoxide. In

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addition, the lability of THF in **1** leads to displacement reactions with stronger σ-donor or π-acceptor ligands. This property has also been employed to synthesize *trans*-(TTP)Ti(*t*-BuNC)$_2$ (**8**), a novel Ti(II) porphyrin organometallic complex. Further studies of the atom transfer reactions of **1** and of the reactivity of **8** are underway.

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