Facile Syntheses of Titanium(II), Tin(II), and Vanadium(II) Porphyrin Complexes through Homogeneous Reduction. Reactivity of trans-(TTP)TiL₂ (L = THF, t-BuNC)

Xiaotai Wang, Steve D. Gray, Jinyuan Chen, and L. Keith Woo*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received July 31, 1997

Facile syntheses of the meso-tetra-p-tolyloporphyrin (TTP) complexes trans-(TTP)Ti(THF)₂, (TTP)Sn(2), and trans-(TTP)V(THF)₂ are achieved through homogeneous reduction of high-valent precursors using NaBEt₃H. 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(â-BuNC)₂. The ligand-binding preference of (TTP)Ti⁺⁺L₉ (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 CH₃Cl to Sn(II) porphyrins resulted in the first stable Sn(IV) porphyrin alkyl complexes that have potential biological (e.g. anticancer) activity. Moreover, Sn(II) and Ti(II) 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)SnII only afforded a 20% yield. Moreover, only a few well-defined Ti(II) porphyrin complexes exist, including the alkyl adducts (Por)Ti[â](η²-RC≡CR) (R = Et, Ph) and pyridine-based σ-donor ligand adducts such as (TTP)Ti[â](Py)₂. Furthermore, only two isolated V(II) porphyrin complexes have been reported, both synthesized by heterogeneous reduction of dihalovanadium(IV) porphyrins. In this work, we describe the facile syntheses of divalent Ti, Sn, and V porphyrins utilizing NaBEt₃H to homogeneously reduce the readily available trans-(TTP)MIIICl₂ (M = Sn, Ti) and (TTP)MIIIC₆F₅ (M = Ti, V) complexes. We also discuss the reactivity of a new compound trans-(TTP)Ti(THF)₂.

Experimental Section

General Considerations. Toluene, benzene-d₆, and hexanes for glovebox use were distilled from purple solutions of sodium benzophenone-ketyl. Dry solvents were subsequently degassed on a vacuum line (10⁻³ Torr) with three successive freeze–pump–thaw cycles. NaBEt₃H, 4-tolyl sulfoxide, Ph₃CH, and PhC≡CPh were purchased from Aldrich and used without further purification. EtC≡CPh, pyridine, and 4-picoline were purchased from Aldrich and vacuum-distilled for glovebox use. Literature procedures were used to prepare (TTP)SnCl₂, (TTP)TiCl₃, (TTP)TiCl, and (TTP)VCl₃. All manipulations were performed in a Finnigan TQ 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, 20 mL, 0.127 mmol, 10 equiv) dropwise. The solution rapidly turned brown, and 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 solid was removed to provide trans-(TTP)Ti(THF)₂ (119.5 mg, 0.139 mmol, 66.2%) 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. 1H NMR spectra were recorded on a Varian 300-MHz spectrometer, with Ph₃CH 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 TQ 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.
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 filter. 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 1H NMR (CD30, ppm): 318, 386, 424 (Soret), 552. IR (Nujol on NaCl plates, cm$^{-1}$): 896 (m), ν(−C=O) of bound THF; 1024 (m), ν(C−C) of bound THF. Anal. Calcd (found) for C56H52N4O2Ti: C, 78.13 (75.18); H, 6.09 (6.16); N, 6.51 (5.27).

**trans-(TTP)Ti(THF)$_2$.** 1. Method C, from (TTP)TiCl. The procedure was similar to the above except that (TTP)TiCl (60.5 mg, 0.077 mmol) and 0.16 mL of 1 M NaBEt$_3$H 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 1H NMR.

(TTP)Sn. 2. NaBEt$_3$H (0.15 mL of 1 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 filter. The solvent was removed from the filtrate under reduced pressure. The residues were redissolved 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 for 1 h, the sample was monitored by 1H NMR. The spectrum indicated the formation of (TTP)Ti(THF)$_2$. The formation of the 4-tolyl sulfide was further indicated by GC-MS molecular peak (m/e = 214).

**Reaction of trans-(TTP)Ti(THF)$_2$ with 4-Trimethylsilylmethylchloride.** trans-(TTP)Ti(THF)$_2$ (0.65 mL of 4.0 M solution in THF, 2.56 mmol) was added to a solution of 33.5 mL (0.47 mmol) of TMSCl and 9.4 mL (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 filter, and the solvent was removed from the filtrate under reduced pressure. The residues were redissolved 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. 1H NMR (CD$_3$0, ppm): 9.05 (s, 8H, β-H), 8.23 (d, 4H, −CHMe$_2$), 7.98 (d, 4H, −CHMe$_2$), 7.28 (m, 8H, −CH$_2$Me), 2.39 (s, 12H, −CH$_2$Me), −0.12 (q, 4H, −CH$_2$CH$_3$), −0.87 (t, 6H, −CH$_2$CH$_3$); identical with the reported data.

**Reaction of trans-(TTP)Ti(THF)$_2$ with Air.** An NMR tube containing a CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.2 mg, 1.4 × 10$^{-4}$ mmol) was exposed to air for 20 min, and the sample was subsequently monitored by 1H NMR. The spectrum shows the presence of three species: (TTP)Ti=O, (TTP)Ti(O), and THF in a ratio of 1.06: 1.00: 2.47. 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(O).

**Reaction of trans-(TTP)Ti(THF)$_2$ with 4-Toly1 Sulfide.** trans-(TTP)Ti(THF)$_2$ (1.2 mg, 2.2 × 10$^{-4}$ mmol), 4-tolyl sulfoxide (1.1 mg, 4× 10$^{-5}$ mmol), and Ph$_3$CH (1.3 mg, 5.3 × 10$^{-5}$ mmol, internal standard) were transferred to a 10-mL beaker. About 1 mL of CD$_3$0 was added to the beaker. The mixture was agitated for 5 min and then transferred to an NMR tube and sealed under nitrogen. This sample was monitored by 1H NMR, and the spectrum showed three products: (TTP)Ti=O (2.0 × 10$^{-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(O).

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 Sulfide.** This experiment was conducted in the same manner 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$^{-4}$ mmol) of 4-tolyl sulfide, and 3.7 mg (1.5 × 10$^{-2}$ mmol) of Ph$_3$CH. The 1H NMR spectrum showed three products: (TTP)Ti=O (1.1 × 10$^{-3}$ mmol, 97%), 4-tolyl sulfide (9.7 × 10$^{-3}$ 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 CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.4 mg, 1.63 × 10$^{-4}$ mmol) and Ph$_3$CH (3.1 mg, 1.27 × 10$^{-2}$ mmol) was added 0.5 µL (4.4 × 10$^{-3}$ mmol) of 3-butyne. 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 1H 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 CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.5 mg, 1.74 × 10$^{-4}$ mmol) and Ph$_3$CH (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 1H 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 CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.0 mg, 1.2 × 10$^{-3}$ mmol) and Ph$_3$CH (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 1.5 h, the sample was monitored by 1H NMR. The spectrum indicated the formation of (TTP)Ti(η$_2$-PhC=CPh) (1.6 × 10$^{-3}$ mmol, 75%) with no trans-(TTP)Ti(THF)$_2$ left.

**Reaction of trans-(TTP)Ti(THF)$_2$ with 4-Picoline.** To a vial containing a CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.4 mg, 1.6 × 10$^{-3}$ mmol) and Ph$_3$CH (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 1H NMR. The spectrum indicated the formation of (TTP)Ti(η$_2$-4-Pic) (6.7 × 10$^{-4}$ mmol, 56%) with no trans-(TTP)Ti(THF)$_2$ left.

**Reaction of trans-(TTP)Ti(THF)$_2$ with THF.** To a vial containing a CD$_3$0 solution of trans-(TTP)Ti(THF)$_2$ (1.1 mg, 1.36 × 10$^{-3}$ mmol) and Ph$_3$CH (2.6 mg, 1.06 × 10$^{-2}$ mmol) was added 0.9 µL (1.1 × 10$^{-3}$ mmol) of THF. 1H NMR spectra taken at 45 min and 13 h of reaction indicated that an equilibrium was reached.
at 20 °C, with (TTP)(TiCl\textsuperscript{η}-EtC≡C=Et) and THF producing trans-(TTP)-Ti(THF)\textsubscript{2} and EtC≡C=Et. K\textsubscript{C} was found to be 3.8.

**Reaction of trans-(TTP)(t-BuNC)\textsubscript{2} with Pyridine.** To a vial containing a C\textsubscript{6}D\textsubscript{6} solution of trans-(TTP)(Ti(t-BuNC)\textsubscript{2}) (0.36 mg, 4.1 \times 10^{-4} mmol) and Ph\textsubscript{2}CH (3.0 mg, 1.23 \times 10^{-2} mmol) was added 0.3 μL (3.7 \times 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 \textsuperscript{1}H NMR. The spectrum indicated the formation of (TTP)(Ti(Ph)\textsubscript{2}) (4.1 \times 10^{-4} mmol) and free t-BuNC (8.0 \times 10^{-4} mmol) with no trans-(TTP)(t-BuNC)\textsubscript{2} left. Within experimental error, this result was quantitatively and its mass balance supports the composition of (TTP)(Ti(t-BuNC)\textsubscript{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)\textsubscript{2} (1, reaction 1), through spectroscopic and chemical characterization. The organic product from this reaction was identified as the allyl radical dimer, C\textsubscript{6}H\textsubscript{10}, by mass spectrometry. The electronic absorption spectrum of (TTP)Ti(THF)\textsubscript{2}, trans-(TTP)Ti(THF)\textsubscript{2} + C\textsubscript{6}H\textsubscript{10} + MgCl\textsubscript{2} (1)

\[\text{(TTP)TiCl}_{\text{t}} \rightarrow \text{trans-(TTP)Ti(THF)}_{\text{t}} + C_{6}H_{10} + MgCl_{2}\]

where \(C_{6}H_{10}\) is the allyl radical dimer, C\textsubscript{6}H\textsubscript{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)\textsubscript{2} (1) exhibits an \textsuperscript{1}H NMR spectrum with relatively sharp resonances, which is interpretable and comparable with that of the known compound trans-(TTP)Ti(Ph)\textsubscript{2}. The tolyl ortho and meta protons of trans-(TTP)Ti(THF)\textsubscript{2} are shown in reactions 3 and 4. The \textsuperscript{1}H NMR data for Sn(TTP) as indicated by the broad proton resonances and the missing \(\beta\)-proton signal in the \textsuperscript{1}H NMR spectrum. Nonetheless, four observed resonances are assignable and support the formulation of trans-(TTP)(Ti(t-BuNC)\textsubscript{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 \(t\)-butyl isocyanide in toluene leads to the isolation of a new complex trans-(TTP)(t-BuNC)\textsubscript{2} (8), as shown in reaction 7. The paramagnetic character of 8 is evident as indicated by the broad proton resonances and the missing \(\beta\)-proton signal in the \textsuperscript{1}H NMR spectrum. Nonetheless, four observed resonances are assignable and support the formulation of trans-(TTP)(Ti(t-BuNC)\textsubscript{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 \(t\)-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 Sorb band at 425 nm and two Q bands at 554 and 594 nm. The IR spectrum in Nujol shows a diagnostic C≡N stretch at 2177 cm\textsuperscript{-1} (m).

**Oxidation Reactions of trans-(TTP)TiL\textsubscript{2} (L = THF, t-BuNC).** As a low-valent early transition metal complex, trans-(TTP)Ti(THF)\textsubscript{2} is prone to oxidation. When exposed to air, it

\[\text{(TTP)SnCl}_{2} \rightarrow \text{(TTP)Sn}_{\text{t}} \rightarrow \text{(TTP)Sn}_{\text{t}} + C_{6}H_{10} + MgCl_{2}\]

(2) are the same as reported in the literature.\textsuperscript{3} The two previously reported approaches to (TTP)Sn involve metal insertion of Sn(II) (from SnCl\textsubscript{2} or SnL\textsubscript{2}) into free-base or dianionic porphyrin ligands, both of which require chromoto-
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 1H NMR spectrum indicates that reaction

\[
\text{trans-(TTP)Ti(THF)}_2 \quad \text{air} \\
\text{C}_{D_8} \\
\text{(TTP)Ti=O + (TTP)Ti(\eta^2-O_2) + 2THF (8)}
\]

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

\[
\text{trans-(TTP)TiL}_2 + (\text{MeC}_6\text{H}_5)\text{S(O)}(\text{C}_6\text{H}_5\text{Me}) \quad \text{C}_{D_8} \\
\text{(TTP)Ti=O + (MeC}_6\text{H}_5)_2\text{S + 2L (9)}
\]

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 Strength of Neutral Ligands in (TTP)TiLn (n = 1, 2). In order to compare the ligand-binding strength in (TTP)TiLn (n = 1, 2), (TTP)Ti(\eta^2-\text{EtC}=\text{EtC}) in C6D6 was treated with an excess of free THF (reaction 10). The substitution reaction reaches equilibrium within 45 min at 20 °C with a Keq of 3.8. Thus, the (TTP)TiI fragment has a binding preference for EtC=EtC over THF. In addition, when (TTP)-Ti(\eta^2-\text{EtC}=\text{EtC}) was treated with t-BuNC in C6D6, EtC=EtC 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 NaBEt3H to reduce non-porphyrin 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 NaBEt3H. 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(\eta^2-\text{RC}=\text{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\(^{-1}\)). The 1H 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 N2 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 \times 10^{-3} mmol of compound 2 reacts with 4-tolyl sulfoxide to produce 2.0 \times 10^{-3} mmol of (TTP)-Ti=O, 2.0 \times 10^{-3} mmol of 4-tolyl sulfide, and 4.2 \times 10^{-3} mmol of THF, as determined by 1H 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. The C=N stretching frequency for 8 (2177 cm\(^{-1}\)) increases by almost 40 cm\(^{-1}\) relative to that of free t-BuNC (2138 cm\(^{-1}\)). Nonetheless, it is similar to the ν(C=N) values for the two reported, neutral Ti(t-BuNC) complexes: Cp2-Ti(\text{CO})(t-BuNC) (2170 cm\(^{-1}\)) and (η5-indenyl)Ti(\text{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)TiI 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)TiI follows the order

\[
\text{pyridine ~ picoline > RNC > PhC}=\text{CPh > EtC}=\text{EtC > THF.}
\]

Concluding Remarks

The facile preparations of (TTP)Sn and trans-(TTP)M(THF)2 (M = Ti, V) via homogeneous reduction with NaBEt3H 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

addition, the lability of THF in 1 leads to displacement reactions with stronger \( \sigma \)-donor or \( \pi \)-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.

Acknowledgment. Partial support of this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Iowa Soybean Promotion Board.

IC970961N