Synthesis, Characterization, Substitution, and Atom-Transfer Reactions of (η²-Alkyne)(tetratolylporphyrinato)titanium(II). X-ray Structure of *trans*-Bis(4-picoline)(tetratolylporphyrinato)titanium(II)

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A general preparative method for (tetratolylporphyrinato)titanium(II) η^2-acetylene complexes, (TTP)Ti(η^2-RC≡CR'), (R = R' = CH₃, CH₂CH₃, C₆H₅; R = CH₃, R' = CH₂CH₃) is described. Displacement of 2-butyne from (TTP)Ti(η^2-MeC≡CMe) with terminal acetylenes allows the preparation of (TTP)Ti(η^2-HC≡CH) and (TTP)Ti(η^2-PhC≡CH). The π complexes undergo simple substitution reactions with pyridine (py) and 4-picoline (pic) to afford the bis(ligand) complexes *trans*-(TTP)Ti(py)₂ and *trans*-(TTP)Ti(pic)₂. The structure of the bis(picoline) complex, C₆₆H₅₆N₄Ti, was determined by single-crystal X-ray diffraction (triclinic, $P\bar{1}$, a = 9.764(2) Å, b = 10.899(2) Å, c = 13.530(2) Å, α = 92.18(2)°, β = 98.10(2)°, γ = 114.14(2)°, V = 1293.6(4) Å³, Z = 1, R = 5.2%, and R_w = 5.4%). Crystallographic symmetry requires that the Ti atom resides in the center of the 24 atom porphyrin plane. The Ti–N_pic distance is 2.223(3) Å, and the average Ti–N_pyrrole distance is 2.047(8) Å. The two picoline ligands are coplanar, and the dihedral angle formed by the plane of the picoline rings and the Ti–N₁ vector is 43°. When (η^2-PhC≡CPh)Ti(TTP) is treated with di-*p*-tolyldiazomethane, a diazo adduct (TTP)Ti=NN=C(C₆H₄CH₃)₂ is formed. Atom transfer occurs when (η^2-PhC≡CPh)Ti(TTP) is treated with X=PPh₃ (X = S, Se), resulting in a two-electron oxidized product, (TTP)Ti=X, PPh₃, and free PhC≡CPh. Treatment of (TTP)Ti(η^2-PhC≡CPh) with elemental sulfur or selenium produces the perchalcogenido complexes (TTP)Ti(S₂) and (TTP)Ti(Se₂). The chalcogenide ligand complexes (TTP)Ti=S and (TTP)Ti=Se were also electrochemically characterized for comparison with related derivatives of (P)Ti(S₂) and (P)Ti(Se₂). Each compound undergoes two reversible one-electron reductions which are located at $E_{1/2}$ = –1.07 ± 0.01 and 1.47 ± 0.01 V in CH₂Cl₂ containing 0.1 M tetra-*n*-butylammonium perchlorate. They also undergo two oxidations, the first of which is irreversible, consistent with an electrode reaction involving the axial ligand rather than the porphyrin macrocycle. A comparison of potentials for oxidation of (TTP)Ti=X and (TPP)Ti(η₂-X₂) indicates a stronger titanium–chalcogen bond in the case of the terminal selenide and sulfide derivatives as compared to the metal–chalcogen bond in the η^2-X₂ complexes.

Introduction

The great interest in titanium chemistry has been driven largely by the key role of titanium complexes in the Ziegler–Natta process.[2] Despite the importance of titanium, the chemistry of low-valent titanium is still lacking in scope. Nonetheless, efforts devoted toward developing this area are likely to reap significant rewards as exemplified by the ability of Ti(II) to activate small molecules such as CO,[3] CO₂,[4] N₂,[5] and H₂.[6] To date, only a few types of Ti(II) complexes have been developed. By far, the largest

group is comprised of bis(cyclopentadienyl) complexes (Cp₂TiL₂).[7] The next largest class consists of bis-chelate complexes, (η^2-L⌒L)₂TiX₂, where the chelate ligand can be (dimethylphosphino)ethane,[8] dimethoxyethane, tetramethylethylenediamine,[9] or 2,2'-bipyridine[10] and X is halide, alkoxide, or alkyl. Less well-studied are the η^6-C₆H₆ complexes, (η^6-C₆H₆)Ti(AlX₄)₂, where X = halide,[11] and the η^8-cyclooctatetraene (COT⁻²) complexes, (η^8-COT)Ti(η^4-COT).[12] We have recently added a new category involving macrocycle ligands, (porphyrinato)titanium(II) complexes.[13] Previously, Marchon, Guilard, and co-workers implicated titanium(II) porphyrin species as transient intermediates in the photodecomposition of peroxotitanium(IV) porphyrin complexes.[14] Observation or isolation of the putative titanium(II) complex was not achieved.

Titanium porphyrin complexes have been known for several years but were limited to titanium in the +3[15] and +4[16] oxidation states. Furthermore, the chemistry of these complexes was primarily examined with regard to reactions with O₂ and oxygen-or sulfur-containing reagents. As part of our continuing studies

⊛ Abstract published in *Advance ACS Abstracts*, September 1, 1993.

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on early transition metal porphyrin chemistry,[17] we recently reported the synthesis and characterization of the first acetylene complexes of titanium porphyrins, (TTP)Ti(η^2-Ph-C≡C-Ph) (1) and (OEP)Ti(η^2-Ph-C≡C-Ph) (2).[13,18] Spectroscopic and structural data for these complexes are consistent with a formalism in which titanium is in the +II oxidation state and is stabilized by a four-electron donor acetylene ligand.[13] The reactivity studies described here are in accord with this formalism.

Experimental Section

General Methods. All manipulations of reagents and products were carried out under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. All solvents were rigorously dried and degassed. Benzene-d_6, toluene, hexane, pyridine, and 4-methylpyridine were freshly distilled from purple solutions of sodium/benzophenone. CDCl$_3$ was stored over P$_2$O$_5$ and freshly distilled when needed. Alkynes (3-hexyne, 2-butyne, 2-pentyne) were dried over Na prior to distillation. Phenylacetylene was dried over 4-Å molecular sieves and distilled under reduced pressure. Acetylene was used as received from Matheson. ^{1}H NMR spectra were recorded on a Nicolet 300-MHz or a Varian VXR 300-MHz spectrometer, UV–vis spectra were obtained on an HP 8452A diode array spectrophotometer, and parent ion masses were determined on a Finnigan 5000 mass spectrometer using electron impact ionization. Elemental analyses were obtained from Oneida Research Services, Whitesboro, NY, or Desert Analytics, Tuscon, AZ. Ti(TTP)Cl$_2$ was prepared using a modified literature procedure.[15d,19] Ti(TTP)(η^2-PhC≡CPh) was prepared as previously reported.[13] All other reagents were obtained commercially and used as received.

Electrochemistry. Cyclic voltammograms were performed using a conventional three-electrode configuration. A platinum or a glassy carbon button served as the working electrode, and a platinum wire was used as the counter electrode. A saturated calomel electrode (SCE), separated from the bulk of the cell by a fritted glass disk, was used as the reference electrode. The ferrocene/ferrocenium couple was used as an internal standard. Current voltage curves were recorded on an IBM 225 voltammetric analyzer connected to a Houston Instruments Model 2000 X-Y recorder. All the cyclic voltammetric experiments were run in a drybox (Vacuum Atmospheres) that contained less than 1 ppm of oxygen. The solvent used for electrochemistry was CH$_2$Cl$_2$ which was dried over CaH$_2$ and distilled under N$_2$ atmosphere before use. Tetra-n-butylammonium perchlorate (TBAP), at a concentration of 0.1 M, was used as the supporting electrolyte.

(TTP)Ti(η^2-EtC≡CEt), 1a. EtC≡CEt (0.100 mL, 0.924 mmol) was added to a solution of 126.4 mg (0.160 mmol) of (TTP)TiCl$_2$ and 254 mg (6.69 mmol) of LiAlH$_4$ in approximately 20 mL of toluene. After stirring of the solution vigorously for 5 h, the remaining aluminum salts were removed by filtration. The solvent was removed from the filtrate under reduced pressure, the residues were redissolved in a minimum of toluene, and the solution was layered with hexane and cooled to –20 °C overnight. The product (71.7 mg, 60.6%) was isolated by filtration as purple crystals, washed with hexane, and dried *in vacuo* at 50 °C. NMR (C$_6$D$_6$): δ 9.05 (s, 8H, β-H), 8.23 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.98 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.28 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH_3), –0.12 (q, 7.4 Hz, 4H, -CH_2CH$_3$), –0.87 (t, 7.5 Hz, 6H, -CH$_2$CH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 225.9 (C≡C). UV–vis (toluene): 414 (Soret), 594 nm. Anal. Calcd (found) for C$_{54}$H$_{46}$N$_4$Ti: C, 81.19 (80.41); H, 5.80 (5.58); N, 7.01 (7.00).

(TTP)Ti(η^2-MeC≡CMe), 1b. This compound was produced and isolated in the same manner as above using 162 mg (0.206 mmol) of (TTP)TiCl$_2$, 358 mg (9.43 mmol) of LiAlH$_4$, 0.100 mL (1.40 mmol) of 2-butyne, and 15 mL of toluene. The isolated yield of purple crystals was 100 mg (65%). ^{1}H NMR (C$_6$D$_6$): δ 9.06 (s, 8H, β-H), 8.18 (d, 7.6 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.99 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.27 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH_3), –0.54 (s, 6H, -CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 221.9 (C≡C). UV–vis (toluene): 414 (Soret), 554 nm.

(TTP)Ti(η^2-MeC≡CEt), 1c. This compound was produced and isolated in the same manner as above using 70 mg (0.089 mmol) of (TTP)TiCl$_2$, 226 mg (6.1 mmol) of LiAlH$_4$, 0.2 mL (2.1 mmol) of 2-pentyne, and 10 mL of toluene. The isolated yield of purple crystals was 43 mg (62%). ^{1}H NMR (C$_6$D$_6$): δ 9.06 (s, 8H, β-H), 8.21 (d, 7.2 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.98 (d, 7.2 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.26 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH_3), –0.20 (q, 7.5 Hz, 2H -CH_2CH$_3$), –0.46 (s, 6H, -CH$_3$), –0.87 (t, 7.5 Hz, 3H, -CH$_2$CH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 225.2 (C≡CEt), 222.3 (MeC≡C). UV–vis (toluene): 414 (Soret), 592 nm. Anal. Calcd (found) for C$_{53}$H$_{44}$N$_4$Ti: C, 81.19 (81.00); H, 5.65 (5.66); N, 7.14 (7.47).

(TTP)Ti(p-CH$_3$C$_5$H$_4$N)$_2$, 2a. A 3-mL volume of 4-picoline was added to 42.1 mg (0.0470 mmol) of (TTP)Ti(η^2-PhC≡CPh) (N.B.: other η^2-acetylene complexes can be used here also) in 15 mL of toluene, the solution was allowed to stir for 5 h, and the solvent was removed under reduced pressure. The resulting solid was redissolved in a minimum of toluene, and the solution was layered with hexane and placed in a refrigerator (–20 °C) overnight. The product (29.3 mg, 69.0%) was isolated as dark purple-brown crystals after filtration, washing with hexane, and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$): δ 23.59 (br s, 4H, NC$_5$H$_4$CH$_3$), 13.45 (br s, 4H, NC$_5$H$_4$CH$_3$), 7.47 (s, 6H, NC$_5$H$_4$CH_3), 6.19 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 4.39 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 1.56 (s, 12H, *meso*-C$_6$H$_4$CH_3), –10.31 (br s, 8H, β-H). UV–vis (toluene): 426 (Soret), 552 nm. Anal. Calcd (found) for C$_{60}$H$_{50}$N$_6$Ti: C, 79.81 (79.32); H, 5.58 (5.79).

(TTP)Ti(C$_5$H$_5$N)$_2$, 2b. Using the same reaction conditions and workup as for the bis(picoline) complex, (TTP)Ti(C$_5$H$_5$N)$_2$ was prepared from 75 mg (0.08 mmol) of (TTP)Ti(η^2-PhC≡CPh) and 1 mL of pyridine to yield 56 mg (76%) of product. ^{1}H NMR (C$_6$D$_6$): 22.87 (br s, 4H, o-py), 13.78 (br s, 4H, m-py), 6.27 (d, 8H, 6.9 Hz, *meso*-C$_6$H$_4$CH$_3$), 4.31 (d, 8H, 7.2 Hz, *meso*-C$_6$H$_4$CH$_3$), 1.62 (s, 12H, *meso*-C$_6$H$_4$CH_3), –11.91 (br s, 8H, β-H). UV–vis (toluene): 412 (Soret), 556 nm.

(TTP)Ti(η^2-PhC≡CH), 1e. Phenylacetylene (0.2 mL, 1.82 mmol) and 54 mg (0.070 mmol) of (TTP)Ti(η^2-MeC≡CMe) were dissolved in 10 mL of toluene, and the solution was stirred for 4 h. After evaporation of the solution to dryness under reduced pressure, the residues were redissolved in toluene, and the new solution was layered with hexane. The resulting purple crystals were filtered out, washed with cold hexane, and dried in vacuo to yield 28 mg (49%) of product. ^{1}H NMR (C$_6$D$_6$): δ 9.08 (s, 8H, β-H), 8.04 (d, 7.2 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.98 (d, 7.2 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.27 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.46 (m, 3H, *m-, p*-C$_6$H$_5$), 5.73 (s, 1H, ≡CH), 4.58 (m, 2H, o-C$_6$H$_5$), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 226.0 (PhC≡CH), 211.3 (PhC≡CH). UV–vis (toluene): 416 (Soret), 554 nm. Anal. Calcd (found) for C$_{56}$H$_{42}$N$_4$Ti: C, 81.54 (81.30); H, 5.87 (5.34); N, 6.79 (6.15).

(TTP)Ti(η^2-HC≡CH), 1f. A medium-walled 5-mm NMR tube attached to a 14/20 ground glass joint was loaded with 3.6 mg (4.67 μmol) of (TTP)Ti(η^2-MeC≡CMe) and evacuated to 10^{-5} Torr. After C$_6$D$_6$ (0.51 mL) was added by vacuum transfer, the tube was backfilled with acetylene, and flame sealed. ^{1}H NMR (C$_6$D$_6$): δ 9.09 (s, 8H, β-H),

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8.12 (d, 7.8 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.97 (d, 7.4 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.21 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH$_3$), 5.81 (s, 2H, η^2-HC≡CH). ^{13}C NMR (C$_6$D$_6$): δ 216.0 (dd, $^1J_{CH}$ = 174.8 Hz, $^2J_{CH}$ = 1.96 Hz, C≡C).

(TTP)Ti=NN=C(C$_6$H$_4$CH$_3$)$_2$. A solution of (TTP)Ti(η^2-PhC≡CPh) (56.7 mg, 0.063 mmol) and di-*p*-tolyldiazomethane (16.9 mg, 0.076 mmol) in toluene (15 mL) was stirred under N$_2$ for 3 h. After removal of the solvent under reduced pressure, the residues were redissolved in a minimum of toluene, layered with hexane, and cooled to –20 °C for 7 h. Purple microcrystals were isolated by filtration, washing with hexane, and drying in *vacuo* at 50 °C. ^{1}H NMR (C$_6$D$_6$): δ 9.11 (s, 8H, β-H), 8.16 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.95 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.34 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.28 (d, 7.5 Hz, 4H, *meso*-C$_6$H$_4$CH$_3$), 6.59 (d, 8.1 Hz, 2H, N$_2$C(C$_6$H$_4$CH$_3$)$_2$), 6.09 (m, 4H, N$_2$C(C$_6$H$_4$CH$_3$)$_2$), 5.01 (d, 8.1 Hz, 4H, N$_2$C(C$_6$H$_4$CH$_3$)$_2$), 2.43 (s, 12H, *meso*-C$_6$H$_4$CH$_3$), 2.24 (s, 3H, N$_2$C(C$_6$H$_4$CH$_3$)$_2$), 1.55 (s, 3H, N$_2$C(C$_6$H$_4$CH$_3$)$_2$). UV–vis (toluene) 426 (Soret), 550 nm. Anal. Calcd (found) for C$_{63}$H$_{50}$N$_6$Ti: C, 80.58 (80.06); H, 5.37 (5.38); N, 8.95 (8.54).

Hydrolysis of (TTP)Ti=NN=C(C$_6$H$_4$CH$_3$)$_2$. An NMR tube containing a C$_6$D$_6$ solution of (TTP)Ti=NN=C(C$_6$H$_4$CH$_3$)$_2$ and sealed under N$_2$ with a rubber septum was injected with 1 μL of degassed water. The ^{1}H NMR spectrum clearly showed the complete conversion of the diazo adduct to (TTP)Ti=O and the hydrazone. Signals for (TTP)-Ti=O: δ 9.24 (s, 8H, β-H), 7.99 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 7.28 (d, 8H, *meso*-C$_6$H$_5$CH$_3$), 7.28 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.42 (s, 12H, *meso*-C$_6$H$_5$CH$_3$). Signals for H$_2$NN=C(C$_6$H$_4$CH$_3$)$_2$: δ 7.02 (m, H$_2$NN=C(C$_6$H$_4$CH$_3$)$_2$), 2.00 (s, 2H, H$_2$NN=C(C$_6$H$_4$CH$_3$)$_2$), 2.07 (s, 6H, H$_2$NN=C(C$_6$H$_4$CH$_3$)$_2$).

(TTP)Ti=S, 4. A solution of 56.0 mg (0.0621 mmol) of (TTP)Ti(η^2-PhC≡CPh) and 20 mg (0.072 mmol) of Ph$_3$P=S in 10 ml of toluene was heated to 50–60 °C for 11 h. The solution was then evaporated to dryness. The maroon solid was redissolved in a minimum of toluene, and the solution was layered with hexane and cooled to –20 °C overnight. The product (31 mg, 66%) was filtered out, washed with hexane, and dried *in vacuo*, giving maroon crystals. ^{1}H NMR (C$_6$D$_6$): δ 9.29 (s, 8H, β-H), 8.14 (d, 4H, –C$_6$H$_4$Me), 7.95 (d, 4H, –C$_6$H$_4$Me), 7.30 (m, –C$_6$H$_4$Me), 2.41 (s, 12H, –CH$_3$). IR (mull): 572 cm^{-1} (Ti=S). MS calcd (found) for C$_{48}$H$_{36}$TiS (*m/e*): 748.8 (748.7). Anal. Calcd (found) for C$_{48}$H$_{36}$N$_4$TiS: C, 77.00 (77.24); H, 4.85 (5.00); N, 7.48 (7.19).

(TTP)Ti=Se, 5. This compound was prepared in a manner similar to that for (TTP)Ti=S using 56 mg (0.063 mmol) of (TTP)Ti(η^2-PhC≡CPh), 22 mg (0.064 mmol) of Ph$_3$P=Se, and 20 mL of toluene. Dark purple crystals (36 mg, 73%) were isolated. ^{1}H NMR (C$_6$D$_6$): δ 9.30 (s, 8H, β-H), 8.18 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.95 (d, 4H, *meso*-C$_6$H$_5$CH$_3$), 7.28 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.42 (s, 12H, *meso*-C$_6$H$_5$CH$_3$). UV–vis (toluene): 432 (Soret), 554 nm. IR (KBr): 465 cm^{-1} (Ti=Se). MS Calcd (found) C$_{48}$H$_{36}$N$_4$TiSe: 796.7 (796.6). Anal. Calcd (found) for C$_{48}$H$_{36}$N$_4$TiSe: C, 72.46 (72.87); H, 4.56 (4.84); N, 7.04 (6.48).

(TTP)Ti(η^2-S$_2$), 6. Method 1. A solution of 32.6 mg (0.036 mmol) of (TTP)Ti(η^2-PhC≡CPh) and 23.5 mg (0.092 mmol) of sulfur in 10 mL of toluene was heated to 50–60 °C for 11 h. The solution was cooled to ambient temperature and filtered to remove excess sulfur. After the filtrate was evaporated to dryness under reduced pressure, the residues were dissolved in a minimum of toluene and the solution was layered with hexane and cooled to –20 °C for 16 h. The product was isolated as purple crystals (23.8 mg, 84%) after filtration, washing with hexane, and drying in vacuo.

Method 2. A 10-mL toluene solution of (TTP)Ti=S (20.4 mg, 0.027 mmol) and 27.7 mg (0.108 mmol) of S$_8$ were heated to 50–60 °C for 12 h. Workup of the reaction mixture using the procedure described in method 1 produced 20.1 mg (95%) of purple crystals. ^{1}H NMR (C$_6$D$_6$): δ 9.11 (s, 8H, β-H), 8.12 (d, 8.1 Hz, 4H, –C$_6$H$_4$Me), 7.92 (d, 6.9 Hz, 4H, –C$_6$H$_4$Me), 7.26 (m, 8H, –C$_6$H$_4$Me), 2.38 (s, 12H, CH$_3$). UV–vis (toluene): 380, 432 (Soret), 548 nm.

(TTP)Ti(η^2-Se$_2$), 7. Method 1. A solution of 33.5 mg (0.044 mmol) of (TTP)Ti(η^2-MeC≡CMe) and 39.6 mg (0.50 mmol) of gray selenium in 10 mL of toluene was heated to 50–60 °C for 11 h. The solution was cooled to ambient temperature and filtered to remove excess selenium. After the filtrate was evaporated to dryness under reduced pressure, the residues were dissolved in a minimum of toluene and the solution was layered with hexane and cooled to –20 °C for 16 h. The product was isolated as purple crystals (23.3 mg, 58%) after filtration, washing with hexane, and drying in vacuo.

Method 2. A 10-mL toluene solution of (TTP)Ti=Se (11.6 mg, 0.015 mmol) and 12.3 mg (0.16 mmol) of gray selenium were heated to 50–60 °C for 12 h. Workup of the reaction mixture using the procedure described

Table I. Structue Determination Summary

empirical formula	C$_{66}$H$_{56}$N$_6$Ti
color; habit	brown; prism
cryst size (mm)	0.40 × 0.10 × 0.10
crystal system	triclinic
space group	P$\bar{1}$
cell dimens	
a (Å)	9.764(2)
b (Å)	10.899(2)
c (Å)	13.530(2)
α (deg)	92.18(2)
β (deg)	98.10(2)
γ (deg)	114.14(2)
V (Å^3)	1293.6(4)
	1
fw	981.1
d(calc) (Mg/m^3)	1.259
abs coeff (mm^{-1})	1.771
F(000)	516
diffractometer used	Siemens P4/RA
radiation (λ, Å)	CuKα (1.54178)
temp (K)	213
monochromator	highly oriented graphite cryst
scan range	5.0–115.0°
scan type	2θ–θ
no. of reflcns collcd	4759
no. of independent reflcns	3490 (R$_{int}$ = 5.46%)
no. of obsd reflcns	2736 (F > 4.0σ(F))
hydrogen atoms	riding model, fixed isotropic
no. of params refined	332
final R indices (obsd data) (%)	R = 5.17, R$_w$ = 5.42
goodness-of-fit	2.64
data-to-param ratio	8.2:1
largest diff peak (e Å^{-3})	0.27
largest diff hole (e Å^{-3})	–0.38

in method 1 produced 10.1 mg (79%) of purple crystals. ^{1}H NMR (C$_6$D$_6$): δ 9.08 (s, 8H, β-H), 8.15 (d, 7.2 Hz, 4H, –C$_6$H$_4$Me), 7.89 (d, 6.6 Hz, 4H, –C$_6$H$_4$Me), 7.26 (m, 8H, –C$_6$H$_4$Me), 2.39 (s, 12H, CH$_3$). UV–vis (toluene): 389, 437 (Soret), 550 nm.

X-ray Structure Determination of (TTP)Ti(pic)$_2$. Crystals of (TTP)-Ti(pic)$_2$ were grown from benzene/octane at ambient temperature. A brown prismatic crystal was attached to the tip of a glass fiber and mounted on a Siemens P4/RA diffractometer for data collection at –60 ± 1 °C using Cu Kα radiation (λ = 1.54178 Å). Cell constants were determined from a list of reflections found by a rotation photograph. Pertinent data collection information is given in Table I. Lorentz and polarization corrections were applied. A correction based on a nonlinear decay in the standard reflections of 1.8% was applied to the data. An absorption correction was unnecessary for this study. The agreement factor for the averaging of observed reflections was 1.4% (based on F).
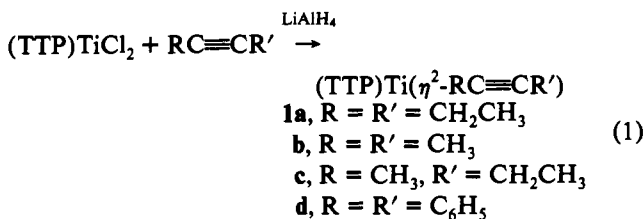
The centric space group P$\bar{1}$ was indicated by intensity statistics.[20] The positions of all non-hydrogen atoms were determined by Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least-squares converged, all hydrogen atoms were placed at calculated positions 0.96 Å from the attached carbon with isotropic temperature factors set at a default value of 0.05 Å^2. One benzene molecule was found in the asymmetric unit.

The X-ray data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. VaxStation 3100 using the SHELXTL PLUS version 4.0 programs.

Results

Synthesis of Ti(II) Acetylene Complexes. We have previously reported that (porphyrinato)titanium(II) η^2-diphenylacetylene complexes can be prepared by the anaerobic reduction of (POR)TiCl$_2$ with lithium aluminum hydride in toluene, in the presence of diphenylacetylene. This is a general procedure for the preparation of a variety of Ti(II) η^2-acetylene complexes. As illustrated in reaction 1, complexes containing 2-butyne, 3-hexyne, 2-pentyne, and diphenylacetylene have been prepared in 40–60% yields. These complexes exhibit ^{1}H NMR spectra which are
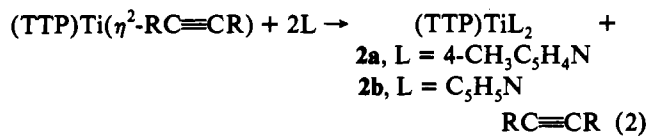
(20) SHELXTL PLUS, Siemens Analytical X-ray Instruments, Inc., Madison, WI.

$$(TTP)TiCl_2 + RC\equiv CR' \xrightarrow{LiAlH_4}$$

$$(TTP)Ti(\eta^2\text{-}RC\equiv CR')$$

1a, R = R' = CH$_2$CH$_3$
b, R = R' = CH$_3$ $\qquad$ (1)
c, R = CH$_3$, R' = CH$_2$CH$_3$
d, R = R' = C$_6$H$_5$

typical of diamagnetic porphyrin complexes. For example, the 2-butyne complex, **1b**, has a β-pyrrole proton singlet at 9.06 ppm and a tolyl-CH$_3$ signal at 2.39 ppm. The η^2-coordinated 2-butyne ligand gives rise to a six-proton singlet at –0.54 ppm. Furthermore, the η^2-acetylene ligands must be rotating rapidly on the NMR time scale because the porphyrin complexes retain 4-fold symmetry on the NMR time scale. Even in the most sterically congested case, (TTP)Ti(η^2-PhC≡CPh), the β-pyrrole proton signal remains as a singlet down to –70 °C. All of the complexes, **1a–d**, are extremely oxygen sensitive in solution and rapidly decompose on exposure to air to produce (TTP)Ti=O and free acetylene.

Reduction of (TTP)TiCl$_2$ in the presence of C$_2$H$_4$ or CO has not afforded Ti(II) complexes of ethylene or carbon monoxide.

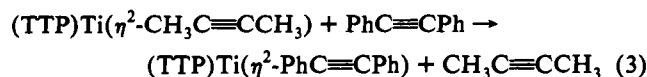**Substitution Reactions of (TTP)Ti(η^2-RC≡CR).** Simple displacement reactions at the metal center are possible for titanium(II) porphyrin complexes. When the the η^2-acetylene complexes, **1a–d**, are treated with pyridine or picoline, loss of the proton signals for **1a-d** in the NMR spectrum is accompanied by appearance of resonances for free acetylene and a new titanium complex (eq 2). These displacement reactions occurs readily at

$$(TTP)Ti(\eta^2\text{-}RC\equiv CR) + 2L \rightarrow \qquad (TTP)TiL_2 \qquad +$$

2a, L = 4-CH$_3$C$_5$H$_4$N
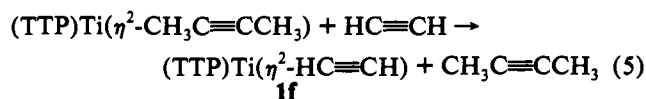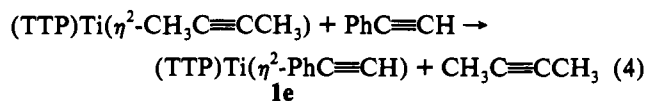**2b**, L = C$_5$H$_5$N

$$RC\equiv CR \quad (2)$$

ambient temperature in less than 1 h. The new substitution products are paramagnetic in solution as indicated by the broad range of proton resonances ($\sim$30 ppm) in the NMR spectra. The paramagnetic behavior in solution is clearly not due to reversible dissociation of a picoline ligand. For example, addition of excess picoline to a C$_6$D$_6$ solution of **2a** results in no change in the magnetic property. Furthermore, ^{1}H NMR saturation transfer experiments on this sample show no evidence for the exchange of free and bound picoline ligands.

Despite the paramagnetism of complexes **2a,b**, sharp NMR signals are still observed and integration of the resonances indicate that two axial ligands are present. Furthermore, the *trans*-geometries of these bis(ligand) complexes, **2a,b**, are clearly evident from the AB multiplet pattern exhibited by the *o*- and *m*-protons of the tolyl substituents. When ca. 1 equiv of picoline is added to the diphenylacetylene complex, **1d**, only a mixture of **1d** and **2a** is observed. No intermediate monopicoline complexes are observed by ^{1}H NMR.

The alkynes 2-butyne, 3-hexyne, and 2-pentyne cannot displace η^2-diphenylacetylene from Ti(II) either by heating the reaction mixture to 40 °C in toluene for 24 h or by irradiating with 254-nm light for 24 h. However, diphenylacetylene is capable of displacing 2-butyne from Ti(II) (eq 3). This reaction reaches completion

$$(TTP)Ti(\eta^2\text{-}CH_3C\equiv CCH_3) + PhC\equiv CPh \rightarrow$$

$$(TTP)Ti(\eta^2\text{-}PhC\equiv CPh) + CH_3C\equiv CCH_3 \quad (3)$$

in less than 1 h at ambient temperature. The η^2-coordinated phenylacetylene, **1e**, and acetylene, **1f**, complexes can also be prepared in an analogous manner using (TTP)Ti(η^2-CH$_3$C≡CCH$_3$) as a starting material (eqs 4 and 5). The complexes of terminal acetylenes show a downfield shift for the CH proton of the π-coordinated ligand. For example, in (TTP)Ti(η^2-HC≡CH)

$$(TTP)Ti(\eta^2\text{-}CH_3C\equiv CCH_3) + PhC\equiv CH \rightarrow$$

$$(TTP)Ti(\eta^2\text{-}PhC\equiv CH) + CH_3C\equiv CCH_3 \quad (4)$$
$$\mathbf{1e}$$

$$(TTP)Ti(\eta^2\text{-}CH_3C\equiv CCH_3) + HC\equiv CH \rightarrow$$

$$(TTP)Ti(\eta^2\text{-}HC\equiv CH) + CH_3C\equiv CCH_3 \quad (5)$$
$$\mathbf{1f}$$

the π-acetylene CH signal resonates at 5.81 ppm. This resonance is shifted downfield from that of free acetylene (1.34 ppm). Such a downfield shift is atypical for ligands of a diamagnetic metalloporphyrin complex. In order to rule out the other possible isomer, an ethenylidene complex [(TTP)Ti=C=CH$_2$], a ^{13}C NMR spectrum of **1f** was taken. The ^{13}C NMR spectrum of this complex exhibits a single acetylenic carbon resonance at 216 ppm (dd, $^1J_{CH}$ = 174.8 Hz, $^2J_{CH}$ = 2.0 Hz). The one-bond C–H coupling constant is low in this complex compared to other π-acetylene complexes for which $^1J_{CH}$ = 190–230 Hz.[21] However, it is higher than for typical uncoordinated sp^2-hybridized carbons ($^1J_{CH}$ = 143–160 Hz).[22]

X-ray Structural Determination of (TTP)Ti(pic)$_2$. The molecular structure of the bis(picoline) complex, **2a**, determined by single-crystal X-ray diffraction confirms the *trans*-geometry originally deduced from the ^{1}H NMR spectrum. An ORTEP and atom numbering scheme is shown in Figure 1. Crystallographic data for the structure determination are listed in Table I, and fractional coordinates for the non-hydrogen atoms are in Table II. Selected bond distances and angles are given in Tables III and IV.

The crystallographically imposed symmetry requires that the Ti atom resides in the plane of the porphyrin macrocycle. The metrical parameters of the porphyrinato core are typical of planar metalloporphyrin complexes. The largest out-of-plane deviation from the 24 atom porphyrin core is a 0.12-Å displacement of N(1). The dihedral angle between the tolyl rings and the mean porphyrin core ranges from 57 to 86°. The Ti–N$_{pic}$ bond distance is 2.223(3) Å, and the independent titanium–pyrrole nitrogen distances are 2.041(4) and 2.052(2) Å. The latter bond lengths are slightly shorter than the average 2.094(8)-Å Ti–N distance in the titanium(II) η^2-diphenylacetylene porphyrin complex. The picoline ligand is planar to within 0.01 Å. The two picoline ligands, within a molecule, are mutually eclipsed and make an angle of 43° with the Ti–N$_1$ bond, as illustrated in Figure 2. A few other (bis)pyridine metalloporphyrin complexes have been structurally characterized by single-crystal X-ray diffraction.[23] The complexes Cr(TPP)(py)$_2$,[24] Mo(TTP)(py)$_2$,[25] Fe(TPP)(py)$_2$,[26] and Ru-(OEP)(py)$_2$[27] all show structural features which are similar to those of Ti(TTP)(pic)$_2$.

Magnetic Properties of (TTP)Ti(pic)$_2$. Solid-state SQUID magnetic susceptibility measurements on (TPP)Ti(pic)$_2$ from 6 to 300 K confirm the paramagnetism of the bis(picoline) complex. The magnetic moment of the complex is 1.2 μ_B at 300 K and decreases to 0.58 μ_B at 50 K. This is significantly lower than the expected spin-only value of 2.83 μ_B for two unpaired electrons. Further studies on this unusual aspect are underway.

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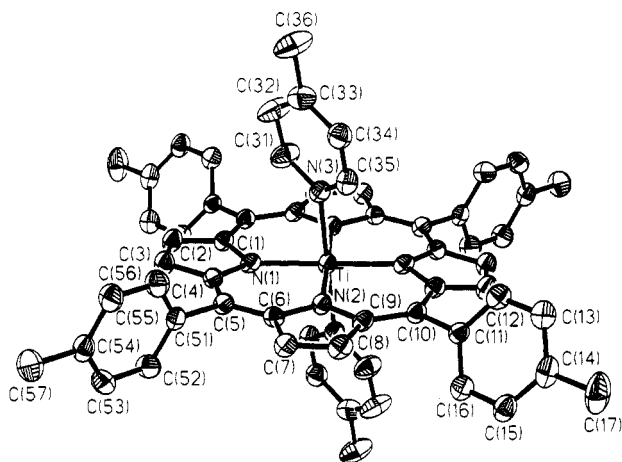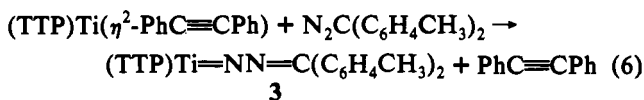(27) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am Chem. Soc.* **1975**, *97*, 277.

Figure 1. Structure and atom-labeling scheme for (TTP)Ti(NC$_5$H$_4$-p-CH$_3$)$_2$. Thermal ellipsoids are drawn at the 30% probability level.

Reaction of (TTP)Ti(η^2-PhC≡CPh) with a Diazo Compound. Treatment of **1d** with di-p-tolyldiazomethane (eq 6) did not yield

$$(TTP)Ti(\eta^2\text{-PhC}\equiv\text{CPh}) + N_2C(C_6H_4CH_3)_2 \rightarrow$$
$$(TTP)Ti=NN=C(C_6H_4CH_3)_2 + PhC\equiv CPh \quad (6)$$
$$\mathbf{3}$$

a carbene complex but instead produced a hydrazido (or a "metalloazine") titanium(IV) complex, **3**. The ^{1}H NMR methyl signals for the axial ligand of **3** occur at 2.24 (3H) and 1.55 (3H) ppm, indicating that the two hydrazido tolyl groups are inequivalent. This data is consistent with either a linear (A) or bent (B) hydrazido ligand.
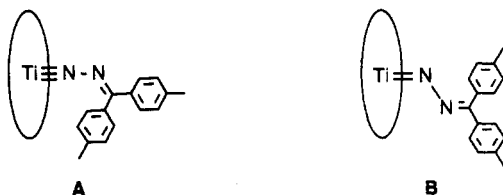
Hydrolysis of the hydrazido complex, **3**, produces (TTP)Ti=O and the hydrazone H$_2$NN=C(C$_6$H$_4$CH$_3$)$_2$, as observed by ^{1}H NMR. This confirms the composition of complex **3**. The formation of hydrazones from the hydrolysis of hydrazido complexes has been previously reported.[28]
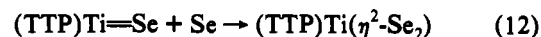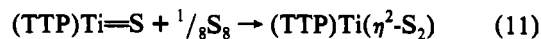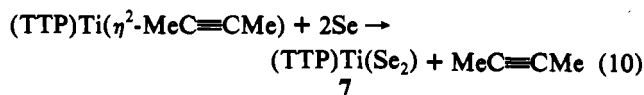
$$(TTP)Ti=NN=C(C_6H_4CH_3)_2 + H_2O \rightarrow$$
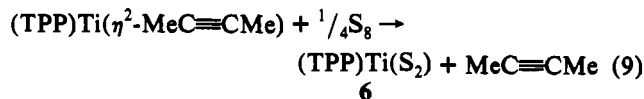$$(TTP)Ti=O + H_2NN=C(C_6H_4CH_3)_2 \quad (7)$$
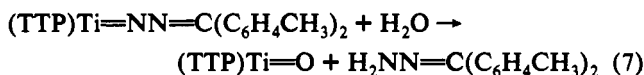
Synthesis of Sulfur and Selenium Complexes. Sulfur and selenium complexes are readily available using the Ti(II) acetylene complexes as starting materials. When (TTP)Ti(η^2-PhC≡CPh) is heated in toluene at 50–60 °C with triphenylphosphine sulfide, Ph$_3$P=S, or triphenylphosphine selenide, Ph$_3$P=Se, formation of the corresponding titanium(IV) complexes (TTP)Ti=S, **4**, and (TTP)Ti=Se, **5**, occurs (eq 8). The resulting byproducts

$$(TTP)Ti(\eta^2\text{-PhC}\equiv\text{CPh}) + X=PPh_3 \rightarrow$$
$$(TTP)Ti=X + PhC\equiv CPh + PPh_3 \quad (8)$$
$$\mathbf{4}, X = S$$
$$\mathbf{5}, X = Se$$
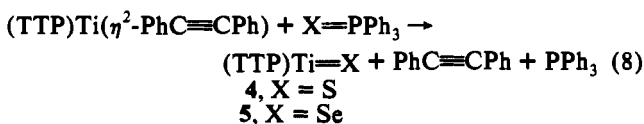
are free diphenylacetylene and triphenylphosphine. However, when the acetylene complex, **1d**, is treated with elemental sulfur (eq 9), the persulfido complex, **6**, is produced. A similar product, **7**, can be prepared with elemental selenium (eq 10). The same

η^2-X$_2$ complexes can be prepared by treating the terminal (TTP)Ti=X complex with elemental chalcogenides (eqs 11 and 12).

$$(TPP)Ti(\eta^2\text{-MeC}\equiv\text{CMe}) + {}^1\!/_4S_8 \rightarrow$$
$$(TPP)Ti(S_2) + MeC\equiv CMe \quad (9)$$
$$\mathbf{6}$$

$$(TPP)Ti(\eta^2\text{-MeC}\equiv\text{CMe}) + 2Se \rightarrow$$
$$(TPP)Ti(Se_2) + MeC\equiv CMe \quad (10)$$
$$\mathbf{7}$$

$$(TTP)Ti=S + {}^1\!/_8S_8 \rightarrow (TTP)Ti(\eta^2\text{-S}_2) \quad (11)$$

$$(TTP)Ti=Se + Se \rightarrow (TTP)Ti(\eta^2\text{-Se}_2) \quad (12)$$

Electrochemistry of (TTP)Ti=S and (TTP)Ti=Se in CH$_2$Cl$_2$. Titanium(IV) porphyrins bearing O^{2-}, η^2-O$_2{}^{2-}$, η^2-S$_2{}^{2-}$, or η^2-Se$_2{}^{2-}$ axial ligands have been characterized in nonaqueous media by electrochemical and spectroelectrochemical techniques.[16c,p] The (TPP)Ti=O derivative undergoes two reversible one-electron oxidations and two reversible one-electron reductions, all four of which involve the porphyrin π ring system.[16c] The disulfur- and diselenium-ligated porphyrin complexes also undergo two reversible one-electron reductions, both of which occur at the conjugated porphyrin macrocycle.[16p] On the other hand, they differ from the titanyl complex in that the perchalcogenido axial ligand rather than the porphyrin macrocycle is involved in the first electrooxidation. The electrochemical behavior of (TTP)-Ti=S and (TTP)Ti=Se is quite similar to that of the η^2-S$_2$ and η^2-Se$_2$ Ti(IV) species in CH$_2$Cl$_2$ containing 0.1 M TBAP and is also similar to that of (P)Sn=S and (P)Sn=Se, where P is one of five different macrocycles.[29]

Figure 3 shows cyclic voltammograms of (TTP)Ti=S and (TTP)Ti=Se in CH$_2$Cl$_2$, 0.1 M TBAP. Both porphyrins undergo two reversible one-electron reductions which occur at $E_{1/2} = -1.07$ or -1.08 V in CH$_2$Cl$_2$ with 0.1 M TBAP. The half-wave potentials are independent of potential scan rate and are within experimental error of the $E_{1/2}$ values reported for reduction of (TTP)Ti(S)$_2$ or (TPP)Ti(Se)$_2$ under the same experimental conditions (see Table V). The electrode reactions of the latter two compounds occur at the porphyrin π ring system as verified by thin-layer spectroelectrochemistry.[16p]

The first electrooxidation of the two (TTP)Ti=X derivatives is irreversible in CH$_2$Cl$_2$, and these reactions occur at $E_{pa} = 0.97$ V (X = S) or 0.83 V (X = Se) for a potential scan rate of 0.1 V/s. This reaction remains irreversible over a scan rate range of 0.050–0.80 V/s, and the peak potential shifts positively with increase in the scan rate. The irreversible nature of the first oxidation and the anodic shift of E_{pa} are self-consistent and suggest that the chalcogen axial ligand itself rather than the porphyrin π ring system is involved in the oxidation processes. A second oxidation is also observed for both compounds at more positive potentials. This reaction is reversible to quasi-reversible and occurs at $E_{1/2} = 1.17$ V. Its current is relatively smaller than that of the first reversible reduction of the same two compounds. The reaction is complicated by the presence of adsorption at the electrode surface and was not further investigated.

The absolute difference in potential between E_{pa} of (TTP)Ti=S and (TTP)Ti=Se is 0.130 V, with the selenide complex being easier to oxidize. This result is consistent with a weaker titanium–selenium bond in (TTP)Ti=Se as compared to that of the titanium–sulfur bond in (TTP)Ti=S. Similar separations in potential have earlier been reported between (TPP)Ti(S)$_2$ and (TPP)Ti(Se)$_2$,[16p] two porphyrins which have been shown to

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Table II. Atomic Coordinates ($\tau 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)^a		x	y	z	U(eq)^a
Ti	0	0	0	26(1)	C(10)	3096(4)	−89(3)	1607(3)	28(2)
N(1)	−1311(3)	1053(3)	26(2)	28(1)	C(11)	4462(4)	−109(3)	2252(3)	27(2)
N(2)	1265(3)	961(3)	1371(2)	27(1)	C(12)	5761(5)	71(4)	1845(3)	36(2)
C(1)	−2488(4)	1002(3)	−720(3)	29(2)	C(13)	7034(4)	−1(4)	2419(3)	37(2)
C(2)	−2887(4)	2082(4)	−490(3)	36(2)	C(14)	7032(5)	−241(4)	3419(3)	39(2)
C(3)	−1968(4)	2807(4)	394(3)	35(2)	C(15)	5758(5)	−393(4)	3829(3)	39(2)
C(4)	−1005(4)	2166(3)	723(3)	27(2)	C(16)	4479(4)	−334(4)	3250(3)	35(2)
C(5)	112(4)	2581(3)	1594(3)	29(2)	C(17)	8418(5)	−299(5)	4024(3)	65(3)
C(51)	250(4)	3783(3)	2251(3)	29(2)	N(3)	1603(3)	1709(3)	−687(2)	32(1)
C(52)	−603(5)	3651(4)	3001(3)	38(2)	C(31)	1110(5)	2381(5)	−1352(3)	49(2)
C(53)	−415(5)	4779(4)	3624(3)	40(2)	C(32)	2075(6)	3533(5)	−1716(3)	59(2)
C(54)	624(5)	6060(4)	3506(3)	36(2)	C(33)	3629(5)	4037(4)	−1408(3)	44(2)
C(55)	1462(5)	6198(4)	2741(3)	42(2)	C(34)	4143(5)	3347(4)	−735(3)	40(2)
C(56)	1267(5)	5073(4)	2113(3)	42(2)	C(35)	3126(5)	2204(4)	−393(3)	37(2)
C(57)	823(5)	7280(4)	4182(3)	53(2)	C(36)	4712(6)	5255(5)	−1816(3)	64(2)
C(6)	1129(4)	2027(3)	1901(3)	27(2)	C(40)	3756(7)	4411(7)	5444(4)	82(3)
C(7)	2277(4)	2488(4)	2797(3)	32(2)	C(41)	4868(9)	3952(6)	5548(4)	78(3)
C(8)	3128(4)	1778(4)	2796(3)	34(2)	C(42)	6115(8)	4547(8)	5113(4)	83(4)
C(9)	2511(4)	805(3)	1908(3)	28(2)					

^{a} Equivalent isotropic U defined as one-third of the trace of orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å)

Ti-N(1)	2.041(4)	C(6)-C(7)	1.445(5)
Ti-N(2)	2.052(2)	C(7)-C(8)	1.348(7)
Ti-N(3)	2.223(3)	C(8)-C(9)	1.452(5)
Ti-N(1A)	2.041(4)	C(9)-C(10)	1.390(6)
Ti-N(2A)	2.052(2)	C(10)-C(11)	1.496(6)
Ti-N(3A)	2.223(3)	C(10)-C(1A)	1.417(5)
N(1)-C(1)	1.399(5)	C(11)-C(12)	1.398(6)
N(1)-C(4)	1.410(5)	C(11)-C(16)	1.380(5)
N(2)-C(6)	1.405(5)	C(12)-C(13)	1.402(6)
N(2)-C(9)	1.403(5)	C(13)-C(14)	1.387(6)
C(1)-C(2)	1.421(7)	C(14)-C(15)	1.385(7)
C(1)-C(10A)	1.417(5)	C(14)-C(17)	1.505(7)
C(2)-C(3)	1.380(5)	C(15)-C(16)	1.403(6)
C(3)-C(4)	1.420(7)	N(3)-C(31)	1.339(6)
C(4)-C(5)	1.406(5)	N(3)-C(35)	1.350(5)
C(5)-C(51)	1.502(6)	C(31)-C(32)	1.385(6)
C(5)-C(6)	1.385(6)	C(32)-C(33)	1.378(7)
C(51)-C(52)	1.378(6)	C(33)-C(34)	1.371(7)
C(51)-C(56)	1.388(5)	C(33)-C(36)	1.502(6)
C(52)-C(53)	1.396(6)	C(34)-C(35)	1.383(5)
C(53)-C(54)	1.380(5)	C(40)-C(41)	1.362(12)
C(54)-C(55)	1.383(6)	C(40)-C(42A)	1.360(11)
C(54)-C(57)	1.513(6)	C(41)-C(42)	1.355(10)
C(55)-C(56)	1.395(6)	C(42)-C(40A)	1.360(11)

Table IV. Bond Angles (deg)

N(1)-Ti-N(2)	91.4(1)	C(53)-C(54)-C(57)	121.1(4)
N(1)-Ti-N(3)	87.4(1)	C(55)-C(54)-C(57)	120.9(3)
N(2)-Ti-N(3)	87.4(1)	C(54)-C(55)-C(56)	120.8(3)
N(1)-Ti-N(1A)	180.0(1)	C(51)-C(56)-C(55)	121.0(4)
N(2)-Ti-N(1A)	88.6(1)	N(2)-C(6)-C(5)	125.7(3)
N(3)-Ti-N(1A)	92.6(1)	N(2)-C(6)-C(7)	108.4(4)
N(1)-Ti-N(2A)	88.6(1)	C(5)-C(6)-C(7)	125.8(4)
N(2)-Ti-(N2A)	180.0(1)	C(6)-C(7)-C(8)	108.5(3)
N(3)-Ti-N(2A)	92.6(1)	C(7)-C(8)-C(9)	107.8(3)
N(1A)-Ti-N(2A)	91.4(1)	N(2)-C(9)-C(8)	108.6(4)
N(1)-Ti-N(3A)	92.6(1)	N(2)-C(9)-C(10)	125.3(3)
N(2)-Ti-N(3A)	92.6(1)	C(8)-C(9)-C(10)	126.0(4)
N(3)-Ti-N(3A)	180.0(1)	C(9)-C(10)-C(11)	118.8(3)
N(1A)-Ti-N(3A)	87.4(1)	C(9)-C(10)-C(1A)	124.6(4)
N(2A)-Ti-N(3A)	87.4(1)	C(11)-C(10)-C(1A)	116.6(4)
Ti-N(1)-C(1)	127.8(2)	C(10)-C(11)-C(12)	120.2(3)
Ti-N(1)-C(4)	125.3(2)	C(10)-C(11)-C(16)	122.0(4)
C(1)-N(1)-C(4)	105.9(3)	C(12)-C(11)-C(16)	117.8(4)
Ti-N(2)-C(6)	125.0(3)	C(11)-C(12)-C(13)	121.5(3)
Ti-N(2)-C(9)	128.1(3)	C(12)-C(13)-C(14)	120.2(4)
C(6)-N(2)-C(9)	106.6(3)	C(13)-C(14)-C(15)	118.4(4)
N(1)-C(1)-C(2)	109.2(3)	C(13)-C(14)-C(17)	119.3(4)
N(1)-C(1)-C(10A)	125.4(4)	C(15)-C(14)-C(17)	122.4(4)
C(2)-C(1)-C(10A)	125.3(4)	C(14)-C(15)-C(16)	121.3(4)
C(1)-C(2)-C(3)	108.2(4)	C(11)-C(16)-C(15)	120.8(4)
C(2)-C(3)-C(4)	107.2(4)	Ti-N(3)-C(31)	121.8(3)
N(1)-C(4)-C(3)	109.5(3)	Ti-N(3)-C(35)	121.8(3)
N(1)-C(4)-C(5)	124.6(4)	C(31)-N(3)-C(35)	116.1(3)
C(3)-C(4)-C(5)	125.9(4)	N(3)-C(31)-C(32)	123.3(4)
C(4)-C(5)-C(51)	116.6(4)	C(31)-C(32)-C(33)	120.3(5)
C(4)-C(5)-C(6)	127.1(4)	C(32)-C(33)-C(34)	116.7(4)
C(51)-C(5)-C(6)	116.2(3)	C(32)-C(33)-C(36)	121.7(4)
C(5)-C(51)-C(52)	121.9(3)	C(34)-C933)-C(36)	121.5(4)
C(5)-C(51)-C(56)	118.1(4)	C(33)-C934)-C(35)	120.5(4)
C(52)-C(51)-C(56)	118.1(4)	N(3)-C(35)-C(34)	123.1(4)
C(51)-C(52)-C(53)	120.8(3)	C(41)-C(40)-C(42A)	119.9(6)
C(52)-C(53)-C(54)	121.3(4)	C(40)-C(41)-C(42)	120.2(6)
C(53)-C(54)-C(55)	119.0(4)	C(41)-C(42)-C(40A)	119.9(8)

undergo oxidation at the chalcogen axial ligand. A similar electrooxidation behavior has also been reported for (P)Sn=S and (P)Sn=Se, where the E_{pa} for the first oxidation of these complexes ranges between 0.63 to 0.85 V (at a scan rate of 0.1 V/s) depending upon the porphyrin macrocycle and the specific axial ligand.[29] Finally, it can be noted that the peak potentials for the first irreversible oxidation of (TTP)Ti=S (0.97 V) and (TPP)Ti(S₂) (0.98 V) are similar to each other and this contrasts with data for (TTP)Ti=Se and (TPP)Ti(Se₂), the former of which is more difficult to oxidize by 60 mV. These results are consistent with a stronger Ti=Se bond in the former complex.

Discussion

The acetylene and bis(ligand) complexes of the titanium porphyrins presented here can be viewed as containing titanium in the formal +II oxidation state. The acetylene ligands follow Templeton's criterion for neutral, four-electron donors, in which both π-bonding orbitals interact with titanium d-orbitals. This was initially proposed on the basis of ^{13}C NMR spectroscopic studies. For example, the ^{13}C NMR signals for the acetylene carbons in **1a-d** range from 211 to 226 ppm. The reactions of complexes **1a-d** also support this formalism. The four-electron donor ability of the acetylene ligands appears to be important in stabilizing the titanium(II) complexes. Thus, the analogous CO or ethylene complexes cannot be prepared by either reducing

(TTP)TiCl₂ in the presence of these ligands or by displacement of acetylene from (TTP)Ti(η²-PhC≡CPh). However, the much stronger σ-donor ligands pyridine and 4-picoline are capable of displacing the acetylene ligand and always form the bis(pyridine) or bis(picoline) complexes. For example, no mono(picoline) complexes have been observed even when 1 equiv of 4-picoline is added to (TTP)Ti(η²-PhC≡CPh). Thus, when substitution occurs, the four-electron donor acetylene is replaced by a pair of two-electron ligands.

One four-electron acetylene can be displaced by another four-electron acetylene. Accordingly, when the dialkylacetylene complexes **1a-c** are treated with diphenylacetylene, loss of the dialkylacetylenes is observed and formation of (TTP)Ti(η²-
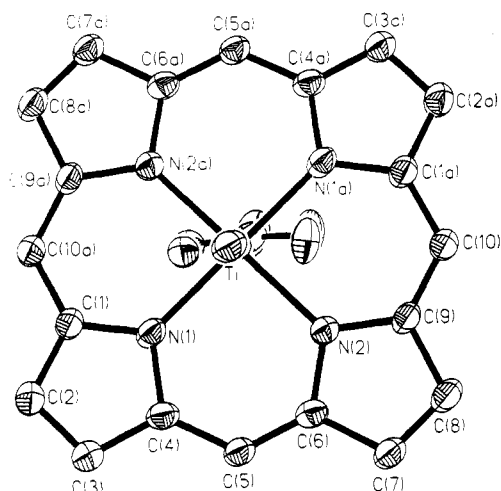
Figure 2. Axial view of (TTP)Ti(NC$_5$H$_4$-p-CH$_3$)$_2$ showing the relationship of the picoline ring to the porphyrin plane.
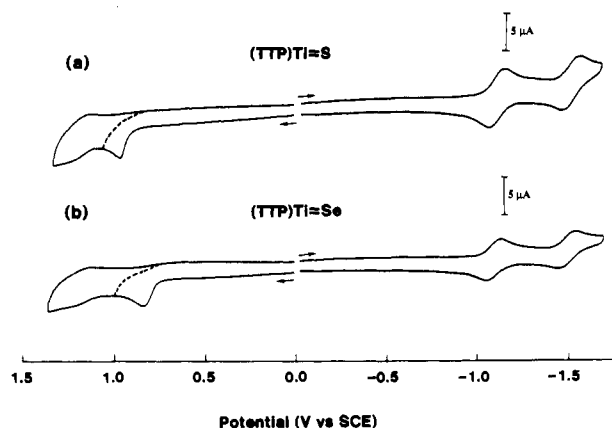
Figure 3. Cyclic voltammograms of (a) (TTP)Ti=S and (b) (TTP)Ti=Se in CH$_2$Cl$_2$, 0.1 M TBAP

Table V. Half-Wave and Peak Potentials (V vs SCE) for the Reduction and Oxidation of Titanium(IV) Porphyrins in CH$_2$Cl$_2$, 0.1 M TBAP

| | oxidn | | redn | | |
porphyrin	2nd	1st	1st	2nd	ref
(TTP)Ti=S	1.17	0.97^a	−1.08	−1.48	b
(TTP)Ti=Se	1.17	0.83^a	−1.07	−1.46	b
(TTP)Ti(S)$_2$		0.98^a	−1.05	−1.40	c
(TPP)Ti(Se)$_2$		0.77^a	−1.06	−1.44	c
(TPP)Ti=O	1.42	1.20	−1.04	−1.43	d

^{a} E_{pa} at a scan rate of 0.1 V/s. ^{b} This work. ^{c} Reference 16p. ^{d} Reference 16c.

PhC≡CPh) occurs. However, the reverse reactions do not occur. For example, addition of 2-butyne to (TTP)Ti(η^2-PhC≡CPh) does not result in the production of the η^2-butyne complex, **1b**. This trend can be rationalized by the π-accepting abilities of the axial ligand as the substituents are changed on the acetylene. Consequently, the stronger π-acid ligand, diphenylacetylene, binds more strongly to the electron-rich Ti d^2 metal center than do the poorer π-accepting dialkylacetylenes.

Because of the ease in which the axial ligands could be displaced from the acetylene complexes, **1a–d**, it seemed likely that the preparation of (TTP)Ti carbene complexes might be possible using diazo reagents as a carbene source. For example, treatment of [Os(TTP)]$_2$ with N$_2$C(C$_6$H$_4$CH$_3$)$_2$ yields (TTP)Os=C(C$_6$H$_4$CH$_3$)$_2$.[30] However, when (TTP)Ti(η^2-PhC≡CPh) is treated with di-p-tolyldiazomethane, loss of N$_2$ and formation of a carbene complex is not observed. Instead, a reaction to produce a hydrazido complex, (TTP)Ti=NN=C(C$_6$H$_4$CH$_3$)$_2$, results. Apparently, the reactivity of the titanium η^2-alkyne complexes is driven by their strong reducing potential. This behavior is also consistent with the Ti(II) formalism proposed here.

Furthermore, (TTP)Ti(η^2-PhC≡CPh) is capable of reducing triphenylphosphine sulfide to the corresponding phosphine. The metalloporphyrin product is a Ti(IV) sulfide complex, (TTP)-Ti=S. In a similar manner, triphenylphosphine selenide is also reduced to triphenylphosphine by (TTP)Ti(η^2-PhC≡CPh) and produces the corresponding Ti(IV) selenide. These chalcogenide complexes are the first terminal sulfide and selenide complexes of titanium porphyrins. The Ti–chalcogenide IR stretching frequencies for these complexes, 572 cm^{-1} (Ti=S) and 465 cm^{-1} (Ti=Se), are comparable to those observed for the V(IV) analogs.[31] When elemental forms of sulfur and selenium are used, η^2-S$_2$ and η^2-Se$_2$ complexes of titanium porphyrins are generated. This reactivity is in contrast to that of (TPP)-V^{II}(THF)$_2$, which forms (TPP)V=S on treatment with elemental sulfur.[16p,q] The titanium η^2-S$_2$ and η^2-Se$_2$ complexes have been prepared previously by Guilard *et al.* by reaction of (TTP)TiF or (TTP)TiF$_2$ with Cp$_2$TiS$_5$ or Cp$_2$TiSe$_5$.[16p] Equations 11 and 12 represent new routes to these perchalcogenido complexes.

Concluding Remarks

The preparation and characterization of novel (η^2-acetylene)- and bis(amine)titanium(II) porphyrin complexes has been accomplished. Spectroscopic and magnetic properties of these complexes as well as their reaction chemistry are consistent with the titanium(II) formalism. The electron-rich titanium center is apparently stabilized by strong π-accepting ligands. Nonetheless, the strong reducing potential of titanium(II) is still manifested in reactions with diazo reagents and phosphine chalcogenides. Further studies of these unique complexes and their potential as versatile starting materials for preparing new titanium compounds are underway.

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