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The Coordination and Atom Transfer Chemistry of Titanium Porphyrin Complexes

by

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The coordination and atom transfer chemistry of titanium porphyrin complexes

by

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The preparation, characterization, and reactivity of a series of (η^2-alkyne)(meso-tetratolylporphyrinato)titanium(II) complexes are described. Also described are intermetal oxygen atom transfer reactions involving titanium(IV) and titanium(III) porphyrin complexes. The η^2-alkyne complexes, (TTP)Ti(η^2-R-C≡C-R') (where R = R' = Me, Et, Ph; R = Me, R' = Et), are prepared by treatment of (TTP)TiCl2 with $LiAlH_4$ in the presence of the alkyne. The structure of (OEP)Ti(η^2-Ph-C≡C-Ph) (OEP = octaethylporphryin) was determined by a single-crystal X-ray diffraction. The complex crystallizes in a monoclinic space group C2/c with a = 49.369(7) Å, b = 13.734(9) Å, c = 36.042(4) Å, β = 136.622(7)°, V = 16784(9) $Å^3$, Z = 16, R = 0.060, R_w =.062. These compounds undergo simple substitution to displace the alkyne and produce doubly substituted complexes. Where R = R' = Et or Me, the coordinated internal alkyne is displaced by a terminal alkyne, R"-C≡C-H (R" = Ph, H). The structure of (TTP)Ti(4-picoline)$_2$ was determined by single-crystal X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with 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) Å, $Z = 1$, $R = .0517$, $R_w = .0542$. The η^2-alkynes undergo redox reaction with diazo reagents and phosphine chalcogenides. They also abstract a chalcogenide from (TTP)Ti(η^2-Ch$_2$) where Ch = O, S, Se.

Treatment of (TTP)Ti=O with (OEP)Ti-Cl yields intermetal O/Cl exchange. This is formally a one electron redox process mediated by oxygen atom transfer. The equilibrium and forward rate constants at 20 °C were determined to be 1.6 ± 0.4 and $2.4 \pm 0.3 \times 10^2$ $M^{-1}s^{-1}$, respectively. Studies were performed to determine temperature, axial ligand, and solvent dependencies. Also, a zero-electron redox process mediated by atom transfer is observed when (TTP)TiCl$_2$ is treated with (OEP)Ti=O. The equilibrium constant was determined to be 47 ± 13 at 20 °C. The forward rate constant was found to be 5 ± 1 at 20 °C. Rate constants at various temperatures were determined to examine temperature dependence.

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James Alan Hays

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LIST OF ABBREVIATIONS

acac	acetylacetonate
BM	Bohr magnetons
cal	calorie
cm	centimeter
COT	cyclooctatetranyl
Cp	cyclopentadienyl
DNA	deoxyribonucleic acid
EPR	electron paramagnetic resonance
Et	ethyl
eq	equation
HOMO	highest occupied molecular orbital
H_2cat	*o*-catechol
H_2tdt	2,3-toluenedithiol
IR	infrared
LUMO	lowest unoccupied molecular orbital
Me	methyl
meso-DME	mesoporphyrin dimethyl ester dianion
mL	milliliter
mol	mole
nm	nanometer
NMR	nuclear magnetic resonance

OEP	octaethylporphyrinato dianion
Ph	phenyl
POR	general porphyrinato dianion
SCE	saturated calomel electrode
TBAP	tetra-n-butylammonium perchlorate
THF	tetrahydrofuran
TmTP	*meso*-tetra-*m*-tolylporphyrinato dianion
TTP	*meso*-tetra-*p*-tolylporphyrinato dianion
UV-vis	ultraviolet-visible

GENERAL INTRODUCTION

Life is possible on this planet because of chemical reactions within living systems. In all biological systems, there exist molecules which are required if certain processes are to occur. Nucleic acids are the fundamental building blocks of DNA and RNA, which store and transmit the genetic blueprint of the organism. Amino acids are the subunits of proteins, which dictate the shape and the function of proteins. Steroids are used in a variety of systems ranging from hormones to vitamins.

A class of molecules, which are essential to a multitude of biological processes, are metallomacrocycles. The most predominant are iron hemes. The heme group is protoporphyrin IX with an iron atom coordinated to four nitrogens. It is found in hemoglobin and myoglobin which are the O_2 and CO_2 transports units of many systems. Cytochrome P-450, which is a well known heme enzyme, is involved in a variety of systems. It can activate O_2, act as an oxidizing agent in a variety of degradation processes, or detoxify foreign chemicals. The heme group is also found in peroxidases and catalases, which are involved in the oxidation of organic compounds with H_2O_2. Cytochromes also serve as electron carriers in photosynthesis and respiration. The functional group of vitamin B_{12} is a corrin, a modified porphyrin, which is the only known organometallic complex in biological systems and performs a variety of transformations. Chlorophyll consists of a chlorin, a reduced porphyrin, which captures sunlight and uses it to produce simple sugars. Much work has gone into mimicking the above systems using synthetic porphyrins.

Porphyrins are not the exclusive realm of biological systems. Metalloporphyrins, specifically those of vanadium and nickel, are found in shale oil deposits and hydrodemetallation of these species on catalytic surfaces is an ongoing area of research. Also work is progressing in the organometallic chemistry of metalloporphyrins and catalytic systems using metalloporphyrins. Most of this work has mainly dealt with the iron and nickel triads.

For the most part, the chemistry of titanium chemistry is lacking in scope. All of the published research deals with titanium in either the +3 or +4 oxidation states, and reactivity of the low valent complexes, those in the +3 oxidation state, towards O_2. The goal of this research project was to search for new oxidation states, such as synthesizing a stable titanium(II), and broaden the reactivity studies, such as examining atom transfer chemistry.

An Explanation of the Dissertation Organization

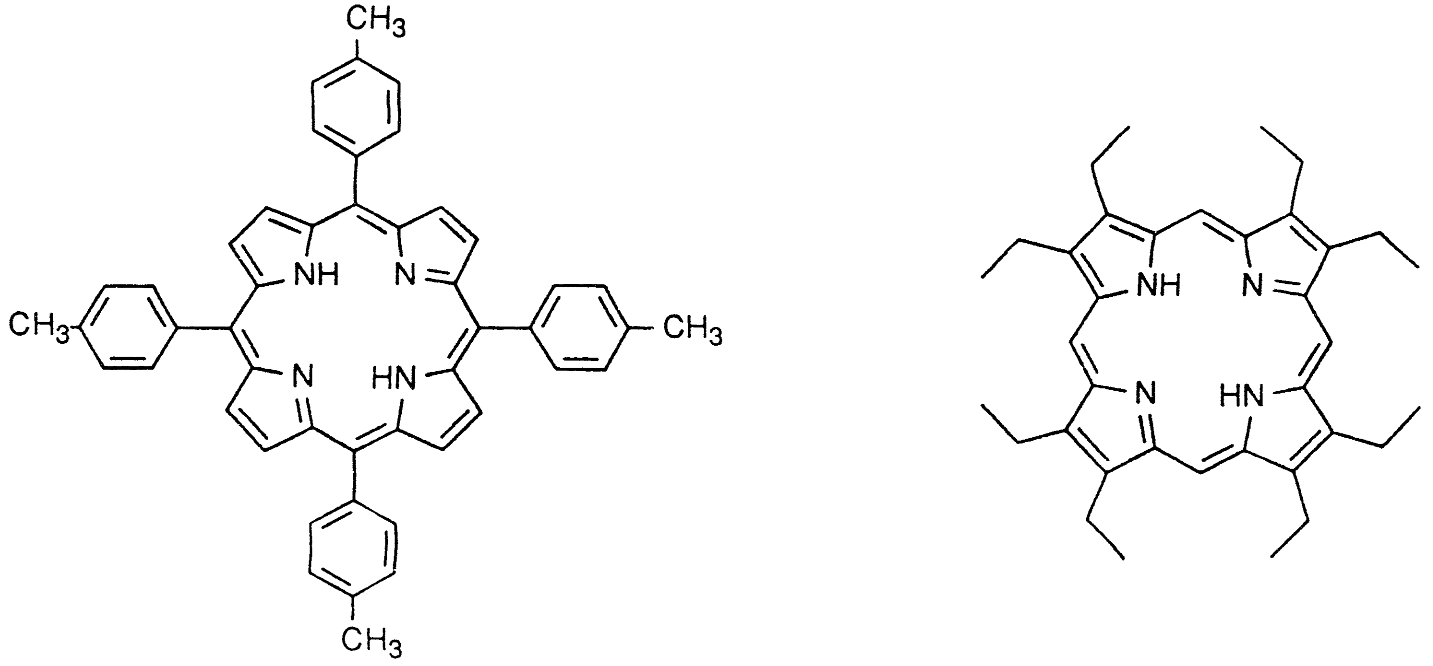
This dissertation is organized as a collection of separate papers. Paper 1 and part of paper 3 have been published in *Organometallics* **1991**, *10*, 2102 and *Inorg. Chem.* **1990**, *29*, 3916, respectively. Paper 2 and 4 is in the process of being submitted for publication. Paper 4 has been accepted for publication by *Inorganic Chemistry*. The organization of the dissertation is as follows. The four papers are proceeded by a general introduction and literature review and followed by a general summary of all results as they apply to the problems addressed and references for the literature review. Each paper has its own introduction and references. Appendices, where appropiate, are placed at the end of the papers.

What is a Porphyrin?

Porphyrins are a macrocyclic system incorporating four pyrrole groups bridged in the two and five positions by methine units. The methine bridges are designated as the meso position and the two non-bridged carbon positions of the pyrroles are the β-pyrrole positions. A variety of functional groups can be placed on these positions. For those interested, books by Dolphin[1] and Smith[2] contain a variety of synthetic procedures for porphyrins. The porphyrin macrocycle is thermally stable and can be sublimed at approximately 350 °C. A porphyrin has 11 conjugated double bonds, obeying Hückel's 4n + 2 rule, so is considered aromatic. Porphyrins are semi-rigid, planar molecules with an inner hole diameter of 4 Å. Virtually all transition metals and many metalloids in a wide range of oxidation states (0 to +6) can be coordinated by the four pyrrole nitrogen atoms.

In this work, two porphyrins were used exclusively, meso-tetratolylporphyrin (TTP) and octaethylporphyrin (OEP). Figure 1a shows meso-tetra-p-tolylporphyrin. This molecule has tolyl groups situated at each of the meso positions and hydrogens at the β-pyrrole positions. Octaethylporphyrin (Figure 1b) has hydrogens at the meso positions and ethyl groups at the β-pyrrole positions. These porphyrins are convenient for the study of metalloporphyrin chemistry. They are easily synthesized or are commercially available, and are soluble in a variety of organic solvents.

Porphyrins are excellent spectroscopic tags for UV-vis and ^{1}H NMR spectroscopies. Due to the aromaticity of the porphyrin ligand, strong absorptions are observed in the near UV and visible regions of the electromagnetic spectrum. The HOMO-LUMO separations are small enough so that the π-π^* transitions occur in this region. A typical UV-vis spectrum exhibits an intense absorption band between 350 and 500 nm known as the Soret band. Soret bands have molar absorptivities on the order of 10^5 $M^{-1}cm^{-1}$. Several less intense bands, known as Q-bands,



a

b

Figure 1. a. *meso*-tetra-*p*-tolylporphyrin. b. octaethylporphyrin

are observed between 450 and 700 nm with molar absorptivities on the order of 10^3 to 10^4 $M^{-1}cm^{-1}$. Coordination of a metal by the porphyrin ligand can be quickly determined by inspection of the Q-bands. For free-base porphyrin, four absorption bands are observed, where as upon metallation, the number of bands decrease to two or three. Also the position of the absorption bands can be dependent upon the oxidation state of the coordinated atom as well as the presence of any coordinating ligands. Proton NMR spectroscopy can reveal much about the molecular symmetry of the porphyrin complexes. When the four-fold symmetry of *meso*-tetratolylporphyrin is maintained on the NMR timescale, the ^1H NMR spectrum exhibits single resonances for the β-pyrrole protons and the methyl protons of the tolyl group. When the porphyrin exhibits mirror symmetry through the horizontal plane of the porphyrin ring, the *o* and *m* protons of the tolyl ring appear as doublets. If the mirror symmetry is absent, such as having two different ligand environments on opposite sides of the porphyrin plane, then the *o*, *o'* and *m*, *m'* protons of the tolyl group are magnetically inequivalent and 4 doublets are observed. However, fast rotation on the NMR timescale of the tolyl group around the meso-carbon can give the appearance of higher symmetry. Due to the fact that porphyrins are aromatic, ring current effects can effectively shield/deshield nuclei. This facilitates the detection of ligands coordinated to the central atom by NMR methods.

Review of Titanium Porphyrin Literature

The first titanium metalloporphyrin, (meso-DME)Ti=O, was synthesized in 1967 by Tsutui *et al.* as shown in reaction 1.[3,4] In the following years, several papers were

$$H_2(meso\text{-}DME) + TiPh_2 \rightarrow (meso\text{-}DME)Ti{=}O \qquad 1$$

published on the synthesis of (POR)Ti=O complexes using a variety of metallating systems.[5,6,7] These methods are outlined in Table I. In the IR spectrum, the Ti-O double bond stretch was observed between 1050 and 950 cm^{-1}. The UV-vis spectra were "normal", consisting of a Soret band between 400 and 430 nm and Q-bands between 450 and 650 nm, depending upon the porphyrin examined. These complexes are diamagnetic and NMR spectroscopy was useful in elucidating the structure. Single-crystal X-ray structures were obtained for (OEP)Ti=O[8], (TPP)Ti=O,[9] and (Me_2OEP)Ti=O.[10] In these cases, the metal was in an almost perfect square pyramidal structure defined by the four nitrogen atoms and the oxygen atom. The average titanium-oxygen distance was 1.618(5) Å and is typical of a Ti-O double bond. The average titanium-nitrogen distance was 2.206(8) Å, and the titanium atom sits approximately 0.54 Å out of the mean nitrogen plane.

Table I. Synthetic routes to oxotitanium porphyrin complexes

Metallating system	Temperature (°C)	Reference
$(acac)_2Ti=O$ / phenol	180 - 240	5, 6
$TiPh_2$ / mesitylene	200	3, 4
$TiCl_4$ / solvent[a]	115 - 191	7

[a] Toluene, benzonitrile, dimethylformamide

Due to the relative inertness and high bond energy of the Ti=O^{+2} unit, no reaction chemistry of titanium porphyrin complexes was reported until the mid seventies. The first notable reaction of the titanyl porphyrin was with hydrogen peroxide or benzoyl peroxide to form the peroxo derivative, (POR)Ti(η^2-O_2) as shown in equation 2 and 3.[11,12] The complexes exhibit

$$(POR)Ti{=}O \;+\; H_2O_2 \;\rightarrow\; (POR)Ti(\eta^2\text{-}O_2) \;+\; H_2O \qquad 2$$

$$(POR)Ti{=}O \; + \; PhOOH \; \rightarrow \; (POR)Ti(\eta^2\text{-}O_2) \; + \; PhOH \qquad 3$$

characteristic IR stretches for the side-on bound O_2^{-2} unit at approximately 895 (ν(O-O)), 645 (ν(Ti-O)), and 600 cm^{-1} (ν(Ti-O)). A single-crystal X-ray structure was reported for (OEP)Ti(η^2-O_2).[11] In this complex, the titanium atom was hexacoordinated with the peroxo unit bound side-on to the metal. The titanium-oxygen distances were 1.927(4) Å and 1.822(4) Å and the oxygen-oxygen bond was 1.445(5) Å. The titanium atom was displaced out of the mean plane of the four nitrogen atoms by 0.657(6) Å. The peroxo unit eclipses two of the nitrogen atoms in the crystal structure. This orientation was not caused by packing but was due to electronic factors. Theoretical studies showed that the metal d_{xz} orbital interacts strongly with the π_g^* orbitals of the peroxo unit resultingin the eclipsed configuration.[13,14] The complexes are diamagnetic and exhibit fluxional behavior, suggesting that exchange between two equivalent sites was occurring. This observation plus the molecular structure confirmed that the structure was the same in both the solution and solid states. The method of addition of the peroxo unit was also examined.[15] Using a porphyrin that was blocked on the back side to prevent a S_N2 type reaction mechanism and labelling studies using ^{18}O, the results indicated that retention of configuration of the molecule occurred during the reaction and the integrity of the oxygen-oxygen bond of the peroxo unit was maintained. Photodeoxygenation of these peroxo species was reported as part of ongoing studies at the time.[16] When (TmTP)Ti(η^2-O_2) was photolyzed, O_2 and (TmTP)Ti=O were formed in the stoichiometry outlined in equation 4. Labelling studies with ^{18}O produced

$$2\;(TmTP)Ti(\eta^2\text{-}O_2) \;\xrightarrow{h\nu}\; 2\;(TmTP)Ti{=}O \; + \; O_2 \qquad 4$$

only (TmTP)Ti=^{18}O and $^{18}O_2$ suggesting the products were derived only from the original reactant. Also a 1:1 mixture of (TmTP)Ti$^{16}O_2$ and (TmTP)Ti$^{18}O_2$ produced only $^{16}O_2$ and $^{18}O_2$. The authors proposed the following mechanism (eq. 5 and 6) where the peroxo unit, in a net two electron

$$(TmTP)Ti(O_2) \xrightarrow{h\nu} [(TmTP)Ti(II)] + O_2 \qquad 5$$

$$(TmTP)Ti(O_2) + [(TmTP)Ti(II)] \rightarrow 2\ (TmTP)Ti{-}O \qquad 6$$

process, produces dioxygen and a reduced titanium(II) complex. The titanium(II) species could then abstract an oxygen atom from another peroxo complex giving two (TmTP)Ti=O products. Attempts to isolate the proposed titanium(II) complex, either by photochemical or chemical means, failed.

Neither the titanyl nor the peroxo complexes were found to be good precursors to low-valent titanium porphyrin complexes. At approximately the same time that the peroxo derivatives were being explored, the dihalide species were also being synthesized.[17] Upon treatment of (TPP)Ti=O with HX (X = F, Cl, Br), (TPP)TiX$_2$ was formed as outlined in eq. 7. The reaction

$$(TPP)Ti{-}O + 2\ HX \rightleftharpoons (TPP)TiX_2 + H_2O \qquad 7$$

was observed to be in equilibrium, as shown, but could be driven in the forward direction with excess hydrogen halide to produce clean dihalide complexes. In the ^{1}H NMR spectrum of (TPP)TiX$_2$, only two resonances for the phenyl hydrogens were observed, leading to the conclusion that the halides occupy trans coordination sites. The UV-vis spectrum of the dihalide complexes exhibit a "split" Soret at approximately 380 and 430 nm and two Q-bands between 500 and 600 nm. Single-crystal X-ray structures for (TPP)TiBr$_2$[18] and (TPP)TiF$_2$[19] confirmed the trans configuration of the halides.

The dihalides can be easily converted to other titanium(IV) derivatives. Upon treatment of (POR)TiF$_2$ with Cp$_2$TiE$_5$ (E = S, Se), the two fluorides are were displaced producing the sulfur and selenium analogues of peroxo complex, (POR)Ti(η^2-E$_2$) as outlined in reaction 8.[20] The -

$$(POR)TiF_2 \ + \ Cp_2TiE_5 \ \rightarrow \ (POR)Ti(\eta^2\text{-}E_2) \qquad 8$$

UV-vis spectrum exhibit a split Soret and Q-bands similar to their dihalide counterparts. The ^{1}H NMR spectrum are "normal", with the Se compound signals appearing at higher field than the S analogues, due in part to the better electron donating properties of the selenium. A molecular structure was obtained for (TTP)Ti(η^2-S$_2$) by single crystal X-ray experiment. The structure is similar to that of the peroxo derivative with the persulfido ligand coordinated side-on in the eclipsed conformation and the titanium resting 0.658(1) Å out of the mean nitrogen plane.

Recently, the action of protic reagents other than peroxides were found to displace the apical oxygen of the titanyl complex.[21] As shown in equations 9 and 10, treatment of

$$(TPP)Ti{=}O \ + \ H_2cat \ \rightarrow \ (TPP)Ti(cat) \ + \ H_2O \qquad 9$$

$$(TPP)Ti{=}O \ + \ H_2tdt \ \rightarrow \ (TPP)Ti(tdt) \ + \ H_2O \qquad 10$$

(TTP)Ti=O with either *o*-catechol or 3,4-toluenedithiol results in the substitution of the oxo ligand with the corresponding deprotonated dianionic, chelating ligand. It is interesting to note that the catechol derivative is unstable with respect to hydrolysis while the dithiolate is stable. These two complexes exhibit "normal" UV-vis and ^{1}H NMR spectra.

The difluoride complexes also provided an easy synthetic route to low-valent titanium porphyrin complexes. The simplest is (TPP)TiF, which is prepared by Zn/Hg reduction of the difluoride as shown in reaction 11. The compound is a paramagnetic d^1 complex. Well resolved

$$(TPP)TiF_2 \xrightarrow{Zn/Hg} (TPP)Ti\text{-}F \qquad 11$$

signals are observed in the EPR spectrum. The g-factors obtained are in the range exhibited by other known titanium(III) complexes. The UV-vis absorption bands of this complex shift very little from those of titanium(IV) complexes. Addition of a coordinating ligand to (TPP)TiF, such as THF, pyridine, etc., produces changes in both the UV-vis and EPR spectra consistent with the formation of six-coordinate complexes of the type (TPP)Ti(F)(L). A six coordinate complex can be also be formed by treatment of (TTP)TiF with Et_4NF as shown in eq. 12.[22] These

$$(TPP)Ti\text{-}F \ + \ Et_4NF \ \rightarrow \ [Et_4N]^+[(TPP)TiF_2]^- \qquad 12$$

observations suggest that titanium(III) porphyrin complexes have a strong preference to coordinate ligands to the sixth coordination site. The five-coordinate complex was formed only in cases where fluorine abstracting reductants like Zn/Hg were used. When (TTP)Ti-F solutions are exposed to oxygen, they rapidly oxidize resulting in a 1:1 mixture of (TPP)Ti(η^2-O_2) and (TPP)TiF_2 (eq. 13) as deduced by UV-vis spectroscopy and cyclic voltammetry. Autoxidation of

$$2\ (TPP)Ti\text{-}F \ + \ O_2 \ \rightarrow \ (TPP)Ti(\eta^2\text{-}O_2) \ + \ (TPP)TiF_2 \qquad 13$$

(TPP)TiF(L) is somewhat slower, reflecting a kinetic stabilization by the coordinating neutral ligand, which presumably blocks the binding of dioxygen to the backside of the metal. A possible reaction pathway was proposed as shown in eq 14 and 15. Initial attempts to isolate

$$(TPP)TiF \ + \ O_2 \ \rightarrow \ (TPP)Ti^{IV}(F)(O_2) \qquad 14$$

$$(TPP)Ti^{III}F \ + \ (TPP)Ti^{IV}(F)(O_2) \ \rightarrow \ (TPP)TiF_2 \ + \ (TPP)Ti(O_2) \qquad 15$$

the proposed superoxide intermediate in both solution and solid state failed. The high stability of (TPP)Ti(η^2-O_2) and preference for six coordination of the starting material probably are strong driving forces for the reaction. If crystals of (TPP)Ti=O are doped with (TPP)TiF and exposed to oxygen, the proposed superoxide intermediate can be observed as a new EPR signal growing in at the expense of the (TPP)TiF signal. The (TPP)TiF signal could be returned to normal by pumping off the oxygen and introducing an inert atmosphere. This process was repeated many times without any loss of the original (TPP)TiF. The observation of substantial spin density on the porphyrin and only a small spin denisty on the dioxygen ligand suggest a significant contribution of a peroxo-porphyrin cation radical-titanium(IV) resonance form to the electronic configuration of the superoxo complex.

The fluoride anion can be displaced by a variety of anionic ligands, such as thiolato,[23] methoxy,[24] and aryls.[25] If (TPP)TiF is treated with $NaSCH_3$ in the presence of methanol the methoxy derivative is isolated as shown in eq 16 and 17.[24] No thiolato derivative was isolated.

$$(TPP)Ti\text{-}F \ + \ NaSCH_3 \ \rightarrow \ [\ (TPP)Ti\text{-}SCH_3\ ] + NaF \qquad 16$$

$$[\ (TPP)Ti\text{-}SCH_3\ ] \ + \ CH_3OH \ \rightarrow \ (TPP)Ti\text{-}OCH_3 \ + \ CH_3SH \qquad 17$$

Once again, little change in the UV-vis spectrum is observed and the complex exhibits an EPR spectrum similar to those of other titanium(III) complexes. A molecular structure of (TPP)Ti(OMe) was obtained by a single crystal X-ray diffraction experiment. Two interesting features were observed. First, the Ti-O bond length was extremely short (1.77(1) Å) compared to other known Ti-O bonds distances (ca. 2.0 Å),[26] being closer to the known titanyl porphyrin complexes (ca. 1.6 Å).[8,9,10] Also, the Ti-O-C bond angle was found to be nearly linear (171(1)°). These observations suggest that the Ti-O interaction has multiple bond character due to donation of electron density from the filled oxygen pπ orbitals to the unfilled d orbitals on the titanium.

Thiolato derivatives can be prepared by treatment of the titanium fluoride with sodium thiolates (R = Ph, CH_2Ph) as shown in eq. 18.[23] These complexes exhibit "normal" UV-vis

$$(TTP)Ti{-}F \;+\; NaSR \;\rightarrow\; (TTP)TiSR \;+\; NaF \qquad 18$$

spectra as well as exhibiting EPR signals similar to those of other titanium(III) complexes. The autoxidation of these complexes was also examined. Upon exposure to oxygen, the only porphyrin product isolated was (TPP)Ti=O. An organic disulfide (PhSSPh) was also identified. The following mechanism was proposed for the autoxidation (eq. 19 - 21). Strikingly different

$$(TPP)TiSR \;+\; O_2 \;\rightarrow\; (TPP)Ti(O_2) \;+\; RS^{\cdot} \qquad 19$$

$$(TPP)TiSR \;+\; (TPP)Ti(O_2) \;\rightarrow\; 2\ (TPP)Ti{=}O \;+\; RS^{\cdot} \qquad 20$$

$$2\ RS^{\cdot} \;\rightarrow\; RSSR \qquad 21$$

behavior of titanium(III) porphyrin complexes towards autoxidation is observed depending upon the type of axial ligand used, pointing to a strong effect of the ligand trans to the coordinated O_2.

The most obvious difference between fluoride and the thiolate lies in the ability of the latter to act as a one-electron reductant. In the thiolato complex both the metal and the axial ligand can donate one electron to the dioxygen molecule to give the peroxo intermediate, which in turn reacts with another (TPP)Ti-SR to give oxo titanium(IV) in a second two-electron step. In contrast, the floride complex can only act as a one-electron reductant and autoxidation proceeds through two successive one-electron steps and stops at the peroxo derivative.

Aryl derivatives can also be derived by treatment of (TPP)TiF with aryl or benzyl Grignard reagents as shown in equation 22.[25] These complexes were characterized by UV-vis and EPR spectroscopies. Addition of various ligands, such as THF, pyridine, etc., leaves the UV-vis spectra unchanged suggesting these complexes prefer to be five-coordinate. This is in contrast to other titanium (III) complexes. The aryl derivative reacts with dioxygen in a manner similat to that of the thiolato complex to produce (TPP)Ti=O and biphenyl in roughly equal molar amounts.

$$(TPP)Ti\text{-}F \;+\; RMgBr \;\rightarrow\; (TTP)Ti\text{-}R \;+\; MgFBr \qquad 22$$

Previously, it was mentioned that the apical oxygen of titanyl porphyrin could be displaced by diprotic ligands. These ligands can also displace the fluorine atom of (TPP)Ti-F of (TPP)Ti(L)F. Treatment of (TPP)Ti(L)F (L = THF or no ligand) with Na_2tdt results in the formation of [(TPP)Ti^{III}(tdt)]Na as shown in equation 23. The titanium(III) tdt complex has a - "normal" UV-vis spectrum closely resembling that of the titanium(IV) analogues. EPR signals are

$$(TPP)Ti(L)F \;+\; Na_2tdt \;\rightarrow\; [(TPP)Ti(tdt)]Na \;+\; NaF \qquad 23$$

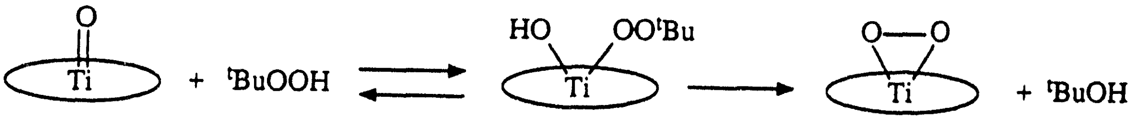
similar to those of other titanium(III) porphyrin complexes. When a solution of [(TPP)Ti(tdt)]Na was exposed to dioxygen, an equimolar mixture of (TPP)Ti=O and (TPP)Ti(tdt) was obtained as shown in equation 24. The stoichiometry of equation 24 requires that half a mole of the tdt

$$2\ [(TPP)Ti(tdt)]^{-} + O_2 \rightarrow (TPP)Ti{=}O + (TPP)Ti(tdt) + \textit{oxidized tdt} \qquad 24$$

ligand is oxidized, although, no oxidized products were observed or isolated. Treatment of (TPP)Ti(L)F with Na_2cat, on the other hand, resulted in unidentifiable titanium(III) complexes. Exposure of the resulting mixture to dioxygen produced a porphyrin radical.

Finally, titanium oxo porphyrins are able to catalytically able to epoxidize alkenes in the presence of an t-butylperoxide.[27,28] The rates and yields of this reaction are much lower, though, compared to other known epoxidation catalysts. The epoxidation was suggested to occur through a cis-hydroxoperoxo intermediate, which goes on to form the catalytically inactive peroxo species as shown in Scheme I.

Scheme I



PAPER 1: LOW-VALENT TITANIUM PORPHYRIN COMPLEXES: SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE FIRST Ti(II) PORPHYRIN COMPLEX, (η^2-DIPHENYLACETYLENE)TITANIUM(OCTAETHYLPORPHYRIN)

INTRODUCTION

Despite the great interest in metalloporphyrins, the chemistry of early transition metal porphyrin complexes remains in an undeveloped state. A primary reason for this stems from the fact that synthesis of these complexes thermodynamically lead to the formation of high-valent oxo complexes.[1] The M=O group in these metalloporphyrins are typically d^0-d^2 and are often extremely difficulty to cleave.[2] We have recently examined the metal-centered redox chemistry of titanium oxo and titanium halide porphyrin complexes.[3] As an extension of our work on titanium porphyrins, we have begun to investigate the chemistry of low-valent Ti porphyrin complexes. To date, Ti(III) is the lowest valent state known to exist in a titanium porphyrin complex.[4] We report here the synthesis and structural characterization of the first Ti(II) porphyrin complexes.

RESULTS AND DISCUSSION

As illustrated in eq. 1, lithium aluminum hydride reduction of toluene solutions of dichloro titanium(IV) porphyrins in the presence of diphenylacetylene produces η^2-alkyne complexes of

$$(\mathrm{POR})\mathrm{TiCl_2} + \mathrm{Ph\text{-}C{\equiv}C\text{-}Ph} \rightarrow (\mathrm{POR})\mathrm{Ti}(\eta^2\text{-}\mathrm{Ph\text{-}C{\equiv}C\text{-}Ph}) \qquad (1)$$

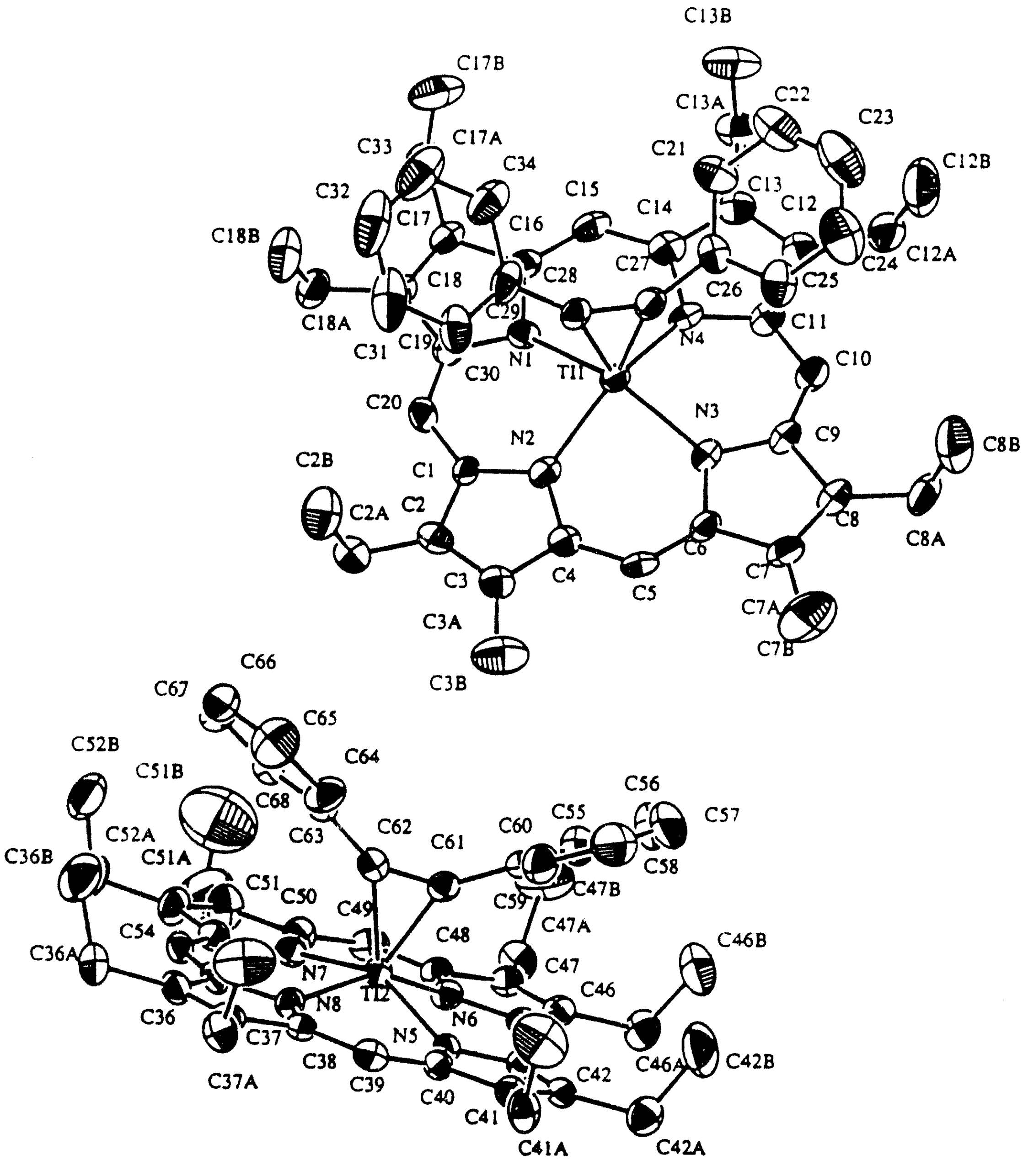
1, POR = OEP
2, POR = TTP

Ti(II). In a typical reaction, 131 mg of (OEP)TiCl$_2$[5] (0.201 mmol), 141 mg of LiAlH$_4$ (3.67 mmol) and 41 mg of Ph-C≡C-Ph (0.23 mmol) were stirred in toluene (40 ml) under N$_2$ at 22 °C. Over twelve hours, the brown solution turned into the ruby-red color of the alkyne adduct, **1**. Filtration of the reaction mixture, concentration of the filtrate to ca. 2 ml, and cooling to -20 °C for 3 d produced 78 mg of purple microcrystals (51% yield) after washing with cold pentane.[6] The TTP[6] analog, **2**, can be prepared in a similar manner.[7]

The alkyne adducts, **1** and **2**, are diamagnetic complexes which exhibit sharp ^{1}H NMR signals. For example, in C$_6$D$_6$ the diphenylacetylene protons of **1** appear as two multiplets at 6.29 (6H, *m*-, *p*-protons) and 4.37 (4H, *o*-protons). The significant upfield shift of these resonances are consistent with a structure in which the C≡C triple bond of the alkyne binds to titanium, holding the phenyl substituents above the porphyrin ring current. The porphyrin *meso*-protons resonate as a singlet at 10.33(4H) ppm. This indicates that rotation of the alkyne ligand about the axis along the Ti-triple bond centroid is rapid on the NMR time scale.

Crystals of the OEP complex, **1**, suitable for single-crystal x-ray diffraction were grown by cooling a toluene solution to -20 °C. Complex **1** crystallizes in the centrosymmetric space group C2/c with two molecules in the asymmetric unit and sixteen molecules per unit cell.[7] The large number of non-hydrogen atoms (110) in the asymmetric unit significantly increased the difficulty and complexity of the structure determination. Direct methods were attempted but were unsuccessful. A new method was therefore tried and proved capable of readily determining the structure. A sharpened Patterson map was calculated and a Patterson superposition procedure was carried out using a vector identified as a probable Ti-Ti vector.[8] From the resulting map, the positions of all the titanium atoms in the cell plus likely positions for the coordinated nitrogens could be readily determined. Due to the size of this structure, those positions alone were ineffective at phasing the observed data. Therefore, using the titanium and nitrogen positions as departure points, the main porphyrin rings were modeled using the PCMODEL molecular mechanics program and the resulting positions were input into the crystallographic least squares refinement procedure. Refinement proceeded smoothly and the remaining carbon atom positions were revealed using difference Fourier calculations. Further details concerning this method of structure determination will be published elsewhere.[9]

The two molecules in the asymmetric unit of **1** are shown in Figure 1 and both have some similar features to a molybdenum analog, (TTP)Mo(η^2-Ph-C≡C-Ph), characterized by Weiss.[10] The geometry about each Ti is square pyramidal with the four pyrrole nitrogens forming the basal plane and the alkyne triple bond at the apical site. The titanium atom is displaced from the mean


C13B
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C36
N6
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C42B
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C46A
C42
C37A
C39
C40
C41
C41A
C42A

24-atom porphyrin core towards the alkyne by 0.54 Å. The Ti_1-C_{27} and Ti_1-C_{28} distances are 2.016(5) and 2.015(5) Å and the C_{27}-C_{28} distance is 1.30(1) Å. In the second molecule, Ti_2-C_{61} and Ti_2-C_{62} distances are 2.007(7) and 2.028(7) Å and the C_{61}-C_{62} distance is 1.30(1) Å. Two structural aspects of **1** differ greatly from those of the Mo analog. In the Mo complex, the porphyrin ligand is saddle-shaped. The Ti complex **1** possesses a nearly-planar porphyrin core. The largest deviation from planarity is 0.064(6) Å at C_9. The planarity of the porphyrin core is very likely related to the formation of intermolecular π-π interactions[11] between pairs of porphyrins in the lattice as shown in Figure 2. The interplanar distance which separates the porphyrins in an associated pair is 3.36 Å. The other structural difference between these two alkyne complexes involves the orientation of the C≡C vector in the molecule. In the Mo case, this vector eclipses two *trans*- pyrrole nitrogens. However in the Ti complex, the C≡C vector bisects *cis*-pyrrole nitrogens. For example, the torsional angle between the C_{27}-C_{28} and N_1-N_3 vectors is 47.1°. This orientational difference presumably arises from steric factors. In both cases, the alkyne aligns in a manner which minimizes non-bonded interactions between the alkyne phenyl rings and the porphyrin substituents.

The bonding in the titanium complexes discussed here can be regarded as involving a four-electron donor alkyne ligand as was proposed for the Mo analog.[12] A comparison of (OEP)Ti(η^2-Ph-C≡C-Ph) with the structure $Cp_2Ti(CO)(\eta^2$-Ph-C≡C-Ph$)$[13] supports this classification. The 18-electron rule suggests that the acetylene ligand is formally a 2-electron donor in the cyclopendadienyl complex. The longer Ti-C_{alkyne} distances (2.107(7) and 2.330(7) Å) are in accord with this formalism. Althoughthe alkyne C-C distances are similar in the two structures (1.285(10) Å in $Cp_2Ti(\eta^2$-Ph-C≡C-Ph$)$CO), the C≡C stretching frequencies for the two complexes

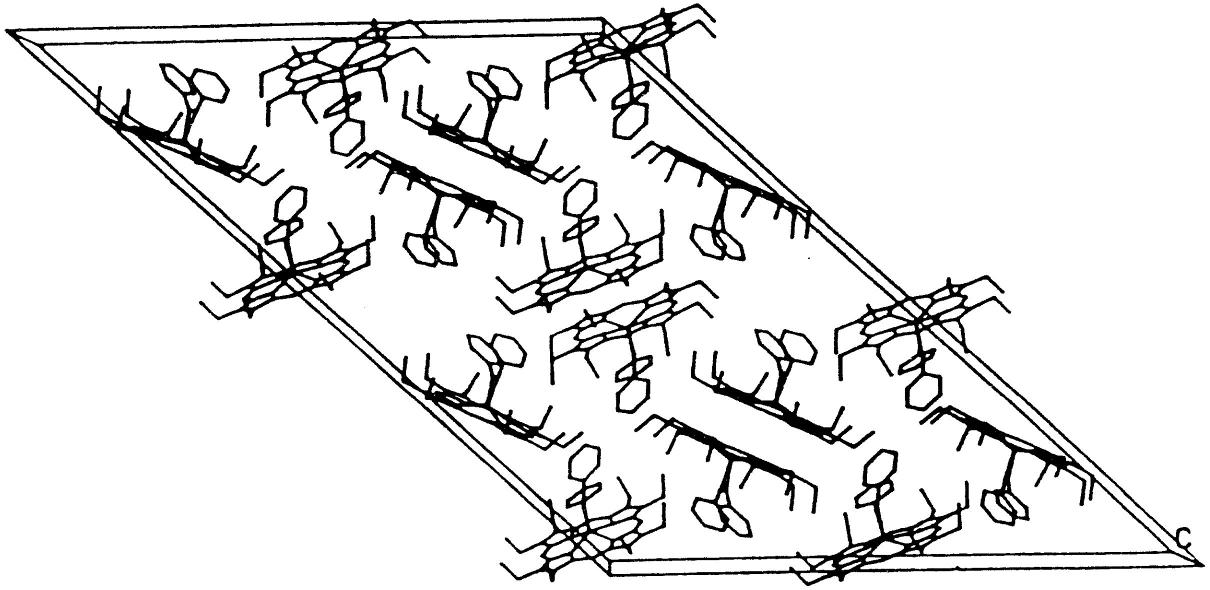

Figure 2. Crystal packing diagram for Ti(OEP)(η^2-Ph-C≡C-Ph).

are consistent with a 2-electron donor acetylene ($\upsilon_{C\equiv C}$ = 1780 cm^{-1}) in $Cp_2Ti(CO)(\eta^2$-Ph-C≡C-Ph) and a 4-electron donor acetylene ($\upsilon_{C\equiv C}$ = 1701 cm^{-1}) in (OEP)Ti(η^2-Ph-C≡C-Ph). Finally, the ^{13}C NMR spectrum for (OEP)Ti(η^2-Ph-C≡C-Ph) provides further support for this bonding interaction. The ^{13}C chemical shift for the C≡C carbons occurs at 219.4 ppm. Despite a significant upfield shift due to the porphyrin ring current,[14] this signal falls well within the region expected for a four-electron donor ligand.[15] In this regard, the alkyne complexes **1** and **2** represent the first metalloporphyrins thatcontain Ti(II). Reactivity studies of these novel complexes are also consistent with a Ti(II) formalism.[16]

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Supplementary Materials Available. Complete listings of data collection, atomic coordinates, thermal parameters, bond distances and angles, least-squares planes, and calculated and observed structure factors for **1** (85 pages). Ordering information is given on any masthead page.

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5. Abbreviations: OEP is the octaethylporphyrinato dianion and TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion.

6. Analytical Data. (TTP)Ti(PhC≡CPh): ^1H NMR (C_6D_6, 300 MHz); 9.06 (s, 8H, β-H), 7.97 (d, 7.52 Hz, 8H, $-C_6\underline{H}_4$-Me), 7.28 (m, 8H, $-C_6\underline{H}_4$-Me), 6.45 (m, 6H, *m*-, p-H), 4.65 (m, 4H, *o*-H), 2.40 (s, 12H, C_6H_4-$C\underline{H}_3$). UV-vis (toluene): 426 (Soret), 548, 582 nm. IR (mull): 1666 ($\upsilon_{C\equiv C}$). Anal. calcd. (found) for $C_{62}H_{46}N_4Ti$: C, 83.21 (82.55); H, 5.18 (5.23); N, 6.26 (6.04). (OEP)Ti(PhC≡CPh): ^1H NMR (C_6D_6, 300 MHz); 10.33 (s, 4H, *meso*-H), 6.29 (m, 6H, *m*-, p-H), 4.37 (m, 4H, *o*-H), 3.92 (q, 7.8 Hz, 16H, $C\underline{H}_2$-CH_3), 1.84 (t, 7.5 Hz, 24H, $CH_2C\underline{H}_3$). UV-vis (toluene): 408 (Soret), 532, 570 nm. IR (mull): 1701 ($\upsilon_{C\equiv C}$). Anal. calcd. (found) for $C_{50}H_{54}N_4Ti$: C, 79.14 (78.59); H, 7.17 (6.77); N, 7.38 (7.09).

7. Ti(OEP)(η^2-PhC≡CPh) crystallizes in the centrosymmetric space group C2/c with a = 49.369(7) Å, b = 13.734(9) Å, c = 36.042(5) Å, β = 136.622(7)°, V = 16784(9) $Å^3$, Z = 16, R = 0.061 and R_ω = 0.063. The calculated density ($C_{50}H_{54}N_4Ti$, M = 758.90) per unit cell is 1.201 g/cm^3. Data were collected at -40 °C on a Rigaku AFC6R diffractometer with Mo K_α radiation using an ω scan technique over the range $4.0 < 2\theta < 50.1°$. Unique reflections (6219) with $I > 3\sigma$ (I) were used after correction for absorption. All non-hydrogen atoms were refined anisotropically.

8. Patterson map calculations were carried out using: Powell, D. R., Jacobson, R. A., "FOUR: A Generated Crystallographic Fourier Program", U.S. DOE Report IS-4737, Iowa State University, Ames, IA, 1980; molecular mechanics calculations were performed using: PCMODEL, Serena Software, Box 3076, Bloomington, IN, 1989; least squares and difference Fourier calculations were carried out using: TEXSAN-TEXRAY Structure Solution Package, Molecular Structure Corporation, 1985; crystal structure diagrams were

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14. ^{13}C resonances for ligands held above a porphyrin are typically shifted 20 ppm upfield relative to the non-porphyrin analogs. See for example: (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

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PAPER 2: SYNTHESIS, CHARACTERIZATION, SUBSTITUTION, AND ATOM TRANSFER REACTIONS OF (η^2-ALKYNE)(TETRATOLYLPORPHYRINATO) TITANIUM(II). X-RAY STRUCTURE OF TRANS-BIS(4-PICOLINE)(TETRATOLYLPORPHYRINATO)TITANIUM(II).

Introduction

The great interest in titanium chemistry has been driven largely by the key role of titanium complexes in the Ziegler-Natta process.[1] Despite the importance of titanium, the chemistry of low-valent titanium is still lacking in scope. Nonetheless, efforts devoted towards developing this area are likely to reap significant rewards as exemplified by the ability of Ti(II) to activate small molecules such as CO,[2] CO_2,[3] N_2,[4] and H_2.[5] To date, only a few types of Ti(II) complexes have been developed. By far, the largest group is comprised of bis(cyclopentadienyl) complexes (Cp_2TiL_2).[6] The next largest class consists of bis-chelate complexes, $(\eta^2\text{-L}^\frown\text{L})_2TiX_2$, where the chelate ligand can be dimethylphosphinoethane,[7] dimethoxyethane, tetramethylethylenediamine,[8] or 2,2'-bipyridine[9] and X is halide, alkoxide, or alkyl. Less well-studied are the η^6-C_6H_6 complexes, $(\eta^6\text{-}C_6H_6)Ti(AlX_4)_2$ where X = halide,[10] and the η^8-cyclooctatetraene (COT^{-2}) complexes, $(\eta^8\text{-COT})Ti(\eta^4\text{-COT})$.[11] We have recently added a new category involving macrocycle ligands, porphyrinatotitanium(II) complexes.[12] Previously, Marchon, Guilard and coworkers implicated titanium(II) porphyrin species as transient intermediates in the photodecomposition of peroxotitanium(IV) porphyrin complexes.[13] 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[14] and +4[15] oxidation states. Furthermore, the chemistry of these complexes were primarily examined with regard to reactions with O_2 and oxygen or sulfur containing reagents. As part of our continuing studies on early transition metal porphyrin chemistry,[16] 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**).[13,17] Spectroscopic and structural data for these complexes are consistent with a formalism in which titanium is in the +2 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

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 vigorously 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_2O_5 and freshly distilled when needed. Alkynes (3-hexyne, 2-butyne, and 2-pentyne) were dried over Na prior to distillation. Phenylacetylene was dried over 4Å 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,18] Ti(TTP)(η^2-Ph-C≡C-Ph) 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 dry box (Vacuum Atmosphere) that contained less than 1 ppm of oxygen. The solvent used for electrochemistry was CH_2Cl_2 which was derived 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-Et-C≡C-Et), 1a. Et-C≡C-Et (0.100 mL, 0.924 mmole) was added to a solution of 126.4 mg (0.160 mmole) $TTPTiCl_2$ and 254 mg (6.69 mmole) $LiAlH_4$ in approximately 20 mL of toluene. After stirring the solution vigorously for 5 hrs, 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, 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_6D_6): 9.05 (s, 8H, β-H), 8.23 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.98 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.12 (q, 7.4 Hz, 4H, -CH_2CH_3), -0.87 (t, 7.5 Hz, 6H, -CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 225.9 (C≡C). UV-vis (toluene): 414 (Soret), 594 nm. Anal. Calcd. (found) for $C_{54}H_{46}N_4Ti$: C; 81.19 (80.41), H; 5.80 (5.58), N; 7.01 (7.00).

(TTP)Ti(η^2-Me-C≡C-Me), 1b. This compound was produced and isolated in the same manner as above using 162 mg (0.206 mmol) $(TTP)TiCl_2$, 358 mg (9.43 mmol) $LiAlH_4$., 0.100 mL (1.40 mmol) 2-butyne, and 15 mL of toluene. The isolated yield of purple crystals was 100 mg (65%). ^1H NMR (C_6D_6): 9.06 (s, 8H, β-H), 8.18 (d, 7.6 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.99 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.27 (m, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.54 (s, 6H, -CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 221.9 (C≡C). UV-vis (toluene): 414 (Soret), 554 nm.

(TTP)Ti(η^2-Me-C≡C-Et), 1c. This compound was produced and isolated in the same manner as above using 70 mg (0.089 mmol) (TTP)$TiCl_2$, 226 mg (6.1 mmol) $LiAlH_4$., 0.2 mL (2.1 mmol) 2-pentyne, and 10 mL of toluene. The isolated yield of purple crystals was 43 mg (62 %). ^1H NMR (C_6D_6): 9.06 (s, 8H, β-H), 8.21 (d, 7.2 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.98 (d, 7.2 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.26 (m, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.20 (q, 7.5 Hz, 2H -CH_2CH_3), -0.46 (s, 6H, -CH_3), -0.87 (t, 7.5 Hz, 3H, -CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 225.2 (C≡C-Et), 222.3 (Me-C≡C). UV-vis (toluene): 414 (Soret), 592 nm. Anal. Calcd. (found) for $C_{53}H_{44}N_4Ti$: C; 81.19 (81.00), H; 5.65 (5.66), N; 7.14 (7.47).

(TTP)Ti(*p*-CH_3-C_5H_4N)$_2$, 2a. Three mL of 4-picoline were added to 42.1 mg (0.0470 mmole) of (TTP)Ti(η^2-PhC≡CPh) (NB: other η^2-acetylene complexes can be used here also) in 15 mL 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, 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.* ^1H NMR (C_6D_6): 23.59 (br s, 4H, $NC_5H_4CH_3$), 13.45 (br s, 4H, $NC_5H_4CH_3$), 7.47 (s, 6H, $NC_5H_4CH_3$), 6.19 (d, 8H, *meso*-$C_6H_4CH_3$), 4.39 (d, 8H, *meso*-$C_6H_4CH_3$), 1.56 (s, 12H, *meso*-$C_6H_4CH_3$), -10.31 (br s, 8H, β-H). UV-vis (toluene): 426 (Soret), 552 nm. Anal. Calcd. (found) for $C_{60}H_{50}N_6Ti$: C, 79.81 (79.32); H, 5.58 (5.79).

(TTP)Ti(C_5H_5N)$_2$, 2b. Using the same reaction conditions and work-up as for the bis-picoline complex, (TTP)Ti(C_5H_5N)$_2$ was prepared from 75 mg (0.08 mmole)

(TTP)Ti(η^2-PhC≡CPh) and 1 mL of pyridine to yield 56 mg (76 %) of product. ^{1}H NMR (C_6D_6): 22.87 (br s, 4H, *o*-py), 13.78 (br s, 4H, *m*-py), 6.27 (d, 8H, 6.9 Hz, *meso*-$C_6H_4CH_3$), 4.31 (d, 8H, 7.2 Hz, *meso*-$C_6H_4CH_3$), 1.62 (s, 12H, *meso*-$C_6H_4CH_3$), -11.91 (br s, 8H, β-H). UV-vis (toluene): 412 (Soret), 556 nm.

(TTP)Ti(η^2-Ph-C≡C-H), 1e. Phenylacetylene (0.2 mL, 1.82 mmole) and 54 mg (0.070 mmole) (TTP)Ti(η^2-Me-C≡C-Me) were dissolved in 10 mL toluene and stirred for 4 h. After evaporating the solution to dryness under reduced pressure, the residues were redissolved in toluene and layered with hexane. The resulting purple crystals were filtered, washed with cold hexane, and dried in vacuo to yield 28 mg (49 %) of product. ^{1}H NMR (C_6D_6): 9.08 (s, 8H, β-H), 8.04 (d, 7.2 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.98 (d, 7.2 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.27 (m, 8H, *meso*-$C_6H_4CH_3$), 6.46 (m, 3H, *m*-, *p*-C_6H_5), 5.73 (s, 1H, ≡CH), 4.58 (m, 2H, *o*-C_6H_5), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$). ^{13}C{^{1}H} NMR (C_6D_6): 226.0 (Ph-*C*≡C-H), 211.3 (Ph-C≡*C*-H). UV-vis (toluene): 416 (Soret), 554 nm. Anal. Calcd. (found) for $C_{56}H_{42}N_4Ti$: C, 81.54 (81.30); H, 5.87 (5.34); N, 6.79 (6.15).

(TTP)Ti(η^2-H-C≡C-H), 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-Me-C≡C-Me) and evacuated to 10^{-5} Torr. After C_6D_6 (0.51 mL) was added by vacuum transfer, the tube was backfilled with acetylene, and flame sealed. ^{1}H NMR (C_6D_6): 9.09 (s, 8H, β-H), 8.12 (d, 7.8 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.97 (d, 7.4 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.21 (m, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), 5.81 (s, 2H, η^2-H-C≡C-H). ^{13}C NMR (C_6D_6): 216.0 (dd, $^1J_{CH}$ = 174.8 Hz, $^2J_{CH}$ = 1.96 Hz, C≡C).

(TTP)Ti=N-N=C(-$C_6H_4CH_3$)$_2$. A solution of (TTP)Ti(η^2-Ph-C≡C-Ph) (56.7 mg, 0.063 mmol) and di-*p*-tolyldiazomethane (16.9 mg, 0.076 mmol) in toluene (15 mL) were stirred under N_2 for 3 h. After removing the solvent under reduced pressure, the residues were redissolved in a minumum 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_6D_6): 9.11 (s, 8H, β-H), 8.16 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.95 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.34 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 7.28 (d, 7.5 Hz, 4H, *meso*-$C_6H_4CH_3$), 6.59 (d, 8.1 Hz, 2H, $N_2C(C_6H_4CH_3)_2$), 6.09 (m, 4H, $N_2C(C_6H_4CH_3)_2$), 5.01 (d, 8.1 Hz, 4H, $N_2C(C_6H_4CH_3)_2$), 2.43 (s, 12H, *meso*-$C_6H_4CH_3$), 2.24 (s, 3H, $N_2C(C_6H_4CH_3)_2$), 1.55 (s, 3H, $N_2C(C_6H_4CH_3)_2$). UV-vis (toluene) 426 (Soret), 550 nm. Anal. Calcd. (found) for $C_{63}H_{50}N_6Ti$: C; 80.58 (80.06), H; 5.37 (5.38), N; 8.95 (8.54).

Hydrolysis of (TTP)Ti=N-N=C(-$C_6H_4CH_3$)$_2$. An NMR tube containing a C_6D_6-solution of (TTP)Ti=N-N=C(-$C_6H_4CH_3$)$_2$ 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: 9.24 (s, 8H, β-H), 7.99 (d, 8H, *meso*-$C_6H_4CH_3$), 7.28 (d, 8H, *meso*-$C_6H_5CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 2.42 (s, 12H, *meso*-$C_6H_5CH_3$). Signals for H_2N-N=C($C_6H_4CH_3$)$_2$: 7.02 (m, H_2N-N=C($C_6H_4CH_3$)$_2$), 2.00 (s, 2H, H_2N-N=C($C_6H_4CH_3$)$_2$), 2.07 (s, 6H, H_2N-N=C($C_6H_4CH_3$)$_2$).

(TTP)Ti=S, 4. A solution of 56.0 mg (0.0621 mmole) (TTP)Ti(η^2-PhC≡CPh) and 20 mg (0.072 mmole) Ph_3P=S in 10 ml of toluene was heated to 50-60 °C for 11 hrs. The solution was then evaporated to dryness. The maroon solid was redissolved in a minimum of toluene, layered with hexane, and cooled to -20 °C overnight. The product (31 mg, 66%) was filtered, washed with hexane, and dried *in vacuo*, giving maroon crystals. ^{1}H NMR (C_6D_6): 9.2<x(s, 8H, β-H), 8.14 (d, 4H, -C_6H_4-Me), 7.95 (d, 4H, -C_6H_4-Me), 7.30 (m, -C_6H_4-Me), 2.41 (s, 12H, -CH_3). M.S. calcd. (found) for $C_{48}H_{36}$TiS: 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=Se using 56 mg (0.063 mmol) (TTP)Ti(η^2-Ph-C≡C-Ph), 22 mg (0.064 mmol) Ph_3P=Se, and 20 mL toluene. Dark purple crystals (36 mg, 73%) were isolated. ^{1}H NMR (C_6D_6): 9.30 (s, 8H, β-H), 8.18 (d, 4H, *meso*-$C_6H_4CH_3$), 7.95 (d, 4H, *meso*-$C_6H_5CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 2.42 (s, 12H, *meso*-$C_6H_5CH_3$). UV-vis (toluene): 432 (Soret), 554 nm. M.S. 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-Ph-C≡C-Ph) and 23.5 mg (0.092 mmol) 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, 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) S_8 were heated to 50 - 60 °C for 12 h. Work-up of the reaction mixture using the procedure described in method 1 produced 20.1 mg (95%) of purple crystals. ^{1}H NMR (C_6D_6): 9.11 (s, 8H, β-H), 8.12 (d, 8.1 Hz, 4H, -C_6H_4-Me), 7.92 (d, 6.9 Hz, 4H, -C_6H_4-Me), 7.26 (m, 8H, -C_6H_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-Me-C≡C-Me) and 39.6 mg (0.50 mmol) grey 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, 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) grey selenium were heated to 50 - 60 °C for 12 h. Work-up of the reaction mixture using the procedure described in method 1 produced 10.1 mg (79%) of purple crystals. ^{1}H NMR (C_6D_6): 9.08 (s, 8H, β-H), 8.15 (d, 7.2 Hz, 4H, -C_6H_4-Me), 7.89 (d, 6.6 Hz, 4H, -C_6H_4-Me), 7.26 (m, 8H, -C_6H_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 non-linear 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.[19] The positions of all non-hydrogen atoms were detemined 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 Corporation VaxStation 3100 using the SHELXTL PLUS version 4.0 programs.

Results

Synthesis of Ti(II) acetylene complexes. We have previously reported that porphyrinatotitanium(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 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

$$(TPP)TiCl_2 \ + \ R\text{-}C{\equiv}C\text{-}R' \ \xrightarrow{LiAlH_4} \ (TTP)Ti(\eta^2\text{-}R\text{-}C{\equiv}C\text{-}R') \qquad (1)$$

1a, R=R′=CH$_2$CH$_3$
b, R=R′=CH$_3$
c, R=CH$_3$, R′=CH$_2$CH$_3$
d, R=R′=C$_6$H$_5$

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 four-fold symmetry on the NMR time scale. Even in the most sterically congested case, (TTP)Ti(η^2-Ph-C≡C-Ph), 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_2H_4 or CO has not afforded Ti(II) complexes of ethylene or carbon monoxide.

Substitution reactions of (TTP)Ti(η^2-R-C≡C-R). 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

$$\text{(TTP)Ti}(\eta^2\text{-R-C}\equiv\text{C-R}) \; + \; 2\text{L} \rightarrow \text{(TTP)TiL}_2 + \text{R-C}\equiv\text{C-R} \qquad (2)$$

2a, L=4-CH_3-C_5H_4N
2b, L=C_5H_5N

titanium complex. These displacement reactions occurs readily at ambient temperature in less than 1 h. The new substitution products are paramagnetic in solution as indicated by the broad range of proton resonances (~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_6D_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** and **2b**, 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. one equivalent 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 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≡C-CH_3) as a starting material. 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-H-C≡C-H) 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

$$\text{(TTP)Ti}(\eta^2\text{-CH}_3\text{-C}\equiv\text{C-CH}_3) + \text{Ph-C}\equiv\text{C-Ph} \rightarrow \text{(TTP)Ti}(\eta^2\text{-Ph-C}\equiv\text{C-Ph}) + \text{CH}_3\text{-C}\equiv\text{C-CH}_3 \qquad (3)$$

$$\text{(TTP)Ti}(\eta^2\text{-CH}_3\text{-C}\equiv\text{C-CH}_3) + \text{Ph-C}\equiv\text{C-H} \rightarrow \underset{\textbf{1e}}{\text{(TTP)Ti}(\eta^2\text{-Ph-C}\equiv\text{C-H})} + \text{CH}_3\text{-C}\equiv\text{C-CH}_3 \qquad (4)$$

$$\text{(TTP)Ti}(\eta^2\text{-CH}_3\text{-C}\equiv\text{C-CH}_3) + \text{H-C}\equiv\text{C-H} \rightarrow \underset{\textbf{1f}}{\text{(TTP)Ti}(\eta^2\text{-H-C}\equiv\text{C-H})} + \text{CH}_3\text{-C}\equiv\text{C-CH}_3 \qquad (5)$$

taken. The ^{13}C NMR spectrum of this complex exhibits a single acetylenic carbon resonance at 216 ppm (dd, $^{1}J_{CH}$ = 174.8 Hz, $^{2}J_{CH}$ = 2.0 Hz). The one-bond C-H coupling constant is low in this complex compared to other π-acetylene complexes for which $^{1}J_{CH}$ = 190 - 230 Hz.[20] However, it is higher than for typical uncoordinated sp^2-hybridized carbons ($^{1}J_{CH}$ = 143 - 160 Hz).[21]

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 Fig. 1. Crystallographic data for the structure determination, tables for fraction coordinates of non-hydrogen atoms, and tables of bond distances and angles are listed in Tables I-IV of Appendix A. Table II of Appendix A lists thermal parameters of the non-hydrogen atoms. 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 range from 57-86°. 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 their planes make an angle of 43° with the Ti-N_1 bond, as illustrated in Fig. 2. A few other bis-pyridine metalloporphyrin complexes have been structurally characterized by single-crystal X-ray diffraction.[22] The complexes Cr(TPP)(py)$_2$,[23], Mo(TTP)(py)$_2$,[24] Fe(TPP)(py)$_2$,[25] and Ru(OEP)(py)$_2$,[26] all show structural features which are similar to Ti(TTP)(pic)$_2$.

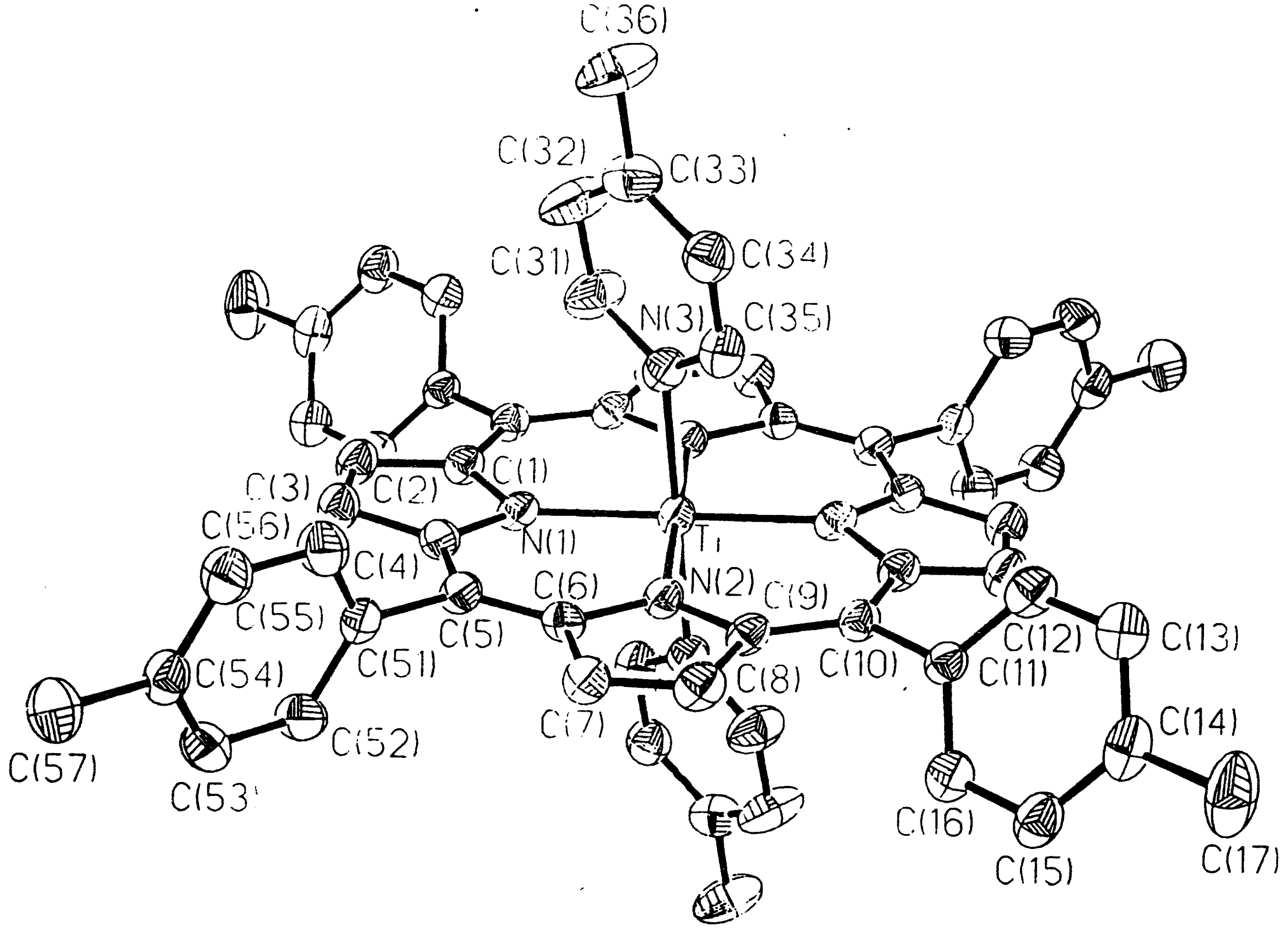


Figure 1. Molecular structure and atom labelling scheme for $(TTP)Ti(NC_5H_4\text{-}p\text{-}CH_3)_2$

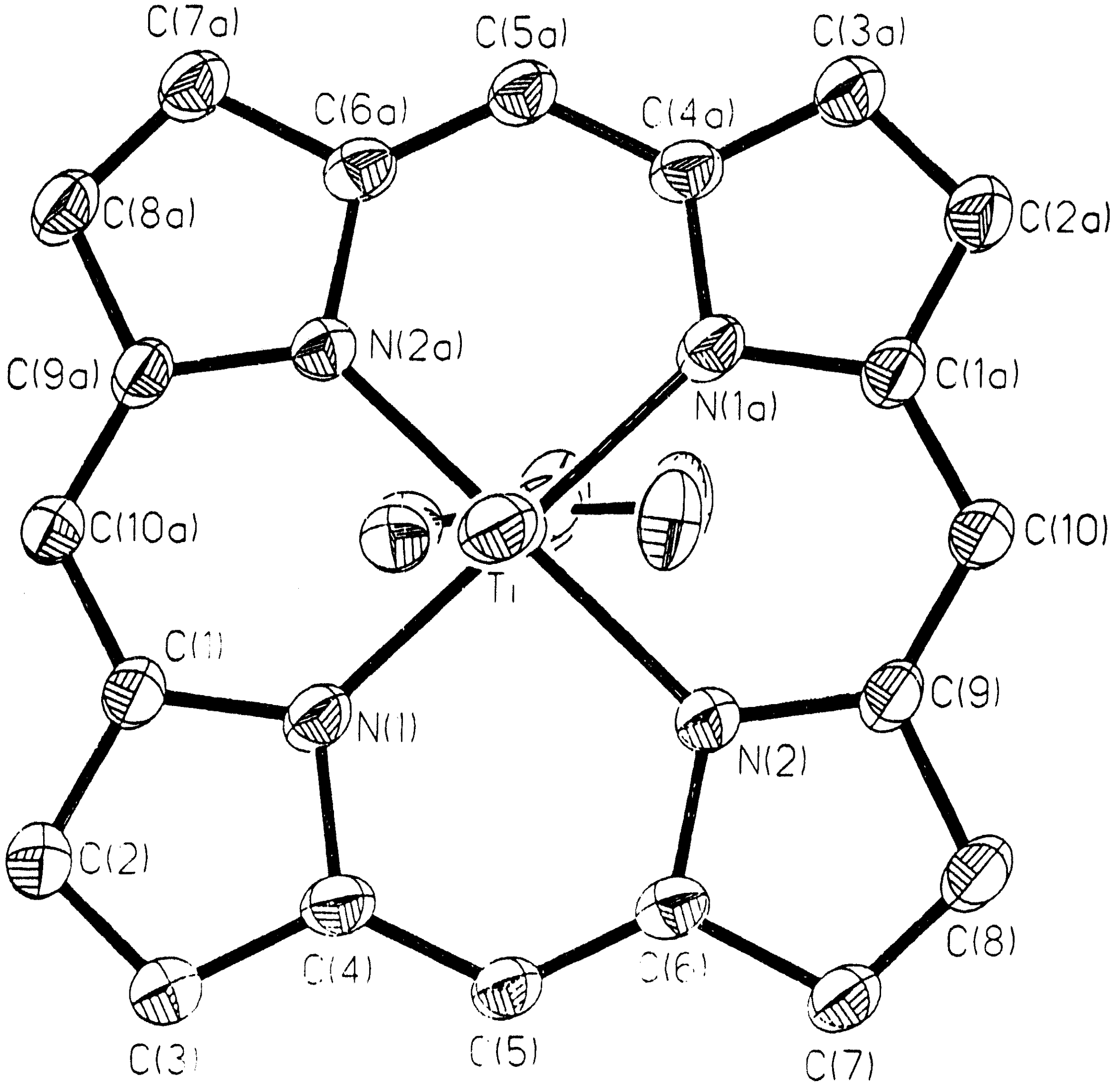
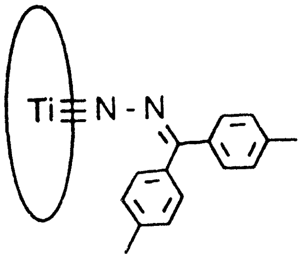


Figure 2.Axial view of (TTP)Ti(NC$_5$H$_4$-*p*-CH$_3$)$_2$ showing relationship of the picoline ring to the porphyrin plane

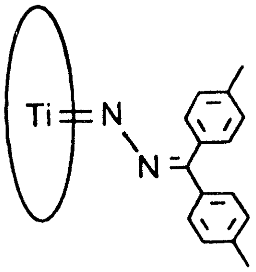
Magnetic properties of (TTP)Ti(pic)$_2$. Solid state SQUID magnetic susceptibility measurements on (TPP)Ti(pic)$_2$ from 6 to 300 K confirm the paramagnetism of the *bis*-picoline complex. The magnetic moment of the complex is 1.2 BM at 300 K and decreases to 0.58 BM at 50 K. This is significantly lower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

Reaction of (TTP)Ti(η^2-Ph-C≡C-Ph) with a diazo compound. Treatment of **1d** with di(*p*-tolyl)diazomethane did not yield a carbene complex, but instead produced a hydrazido (or a "metalloazine") titanium(IV) complex, **3**, as shown in eq. 6. 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. These data are consistent with either a linear (A) or bent (B) hydrazido ligand.

$$(\mathrm{TTP})\mathrm{Ti}(\eta^2\text{-Ph-C}\equiv\text{C-Ph}) + N_2C(C_6H_4\text{-}CH_3)_2 \rightarrow \underset{\mathbf{3}}{(\mathrm{TTP})\mathrm{Ti{=}N{-}N{=}C}(C_6H_4\text{-}CH_3)_2} + \text{Ph-C}\equiv\text{C-Ph} \qquad (6)$$



A



B

Hydrolysis of the hydrazido complex, **3**, produces (TTP)Ti=O and the hydrazone, $H_2N\text{-}N{=}C(C_6H_4\text{-}CH_3)_2$, as observed by ^{1}H NMR. This confirms the composition of complex **3**.

$$(\mathrm{TTP})\mathrm{Ti{=}N{-}N{=}C}(C_6H_4\text{-}CH_3)_2 + H_2O \rightarrow (\mathrm{TTP})\mathrm{Ti{=}O} + H_2N\text{-}N{=}C(C_6H_4\text{-}CH_3)_2 \qquad (7)$$

The formation of hydrazones from the hydrolysis of hydrazido complexes has been previously reported.[27]

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-Ph-C≡C-Ph) is heated in toluene at 50 - 60 °C with triphenylphosphine sulfide, Ph_3P=S, or triphenylphosphine selenide, Ph_3P=Se, formation of the corresponding titanium(IV) complexes (TTP)Ti=S, **4**, and (TTP)Ti=Se, **5**, occurs. The resulting by-products are free diphenylacetylene

$$\text{(TTP)Ti}(\eta^2\text{-Ph-C}\equiv\text{C-Ph}) + \text{X=PPh}_3 \rightarrow \underset{\textbf{4}, X = S \;\; \textbf{5}, X = Se}{\text{(TTP)Ti=X}} + \text{Ph-C}\equiv\text{C-Ph} + \text{PPh}_3 \qquad (8)$$

and triphenylphosphine. However, when the acetylene complex, **1d**, is treated with elemental sulfur, the per-sulfido complex, **6**, is produced. A similar product, **7**, can be prepared with

$$\text{(TTP)Ti}(\eta^2\text{-Me-C}\equiv\text{C-Me}) + \tfrac{1}{4}\,\text{S}_8 \rightarrow \underset{\textbf{6}}{\text{(TTP)Ti(S}_2)} + \text{Me-C}\equiv\text{C-Me} \qquad (9)$$

$$\text{(TTP)Ti}(\eta^2\text{-Me-C}\equiv\text{C-Me}) + \text{Se} \rightarrow \underset{\textbf{7}}{\text{(TTP)Ti(Se}_2)} + \text{Me-C}\equiv\text{C-Me} \qquad (10)$$

elemental selenium. The same η^2-X_2 complexes can be prepared by treating the terminal (TTP)Ti=X complex with elemental chalcogenides (eq. 11-12).

$$\text{(TTP)Ti=S} + \tfrac{1}{8}\,\text{S}_8 \rightarrow \text{(TTP)Ti}(\eta^2\text{-S}_2) \qquad (11)$$

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

Electrochemistry of (TTP)Ti=S and (TTP)Ti=Se in CH_2Cl_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 non-aqueous 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_2Cl_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 macrocyles.[29]

Figure 3 shows cyclic voltammograms of (TTP)Ti=S and (TTP)Ti=Se in CH_2Cl_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_2Cl_2 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

Table V. Half-wave and Peak Potentials (V vs. SCE) for the Reduction and Oxidation of Titanium(IV) Porphyrins in CH_2Cl_2, 0.1 M TBAP

	Oxidation		Reduction		
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
(TPP)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.

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_2Cl_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 to 0.80 V/s and the peak potential shifts positively with increase in the scan rate. The irreversible nature of the first of 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 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.[28] Finally, it can be noted that the peak potential for the first irreversible oxidation of (TTP)Ti=S (0.97 V) and (TPP)Ti(S_2) (0.98 V) are similar to each other and this contrasts with data for (TTP)Ti=Se and (TPP)Ti(Se_2), 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.

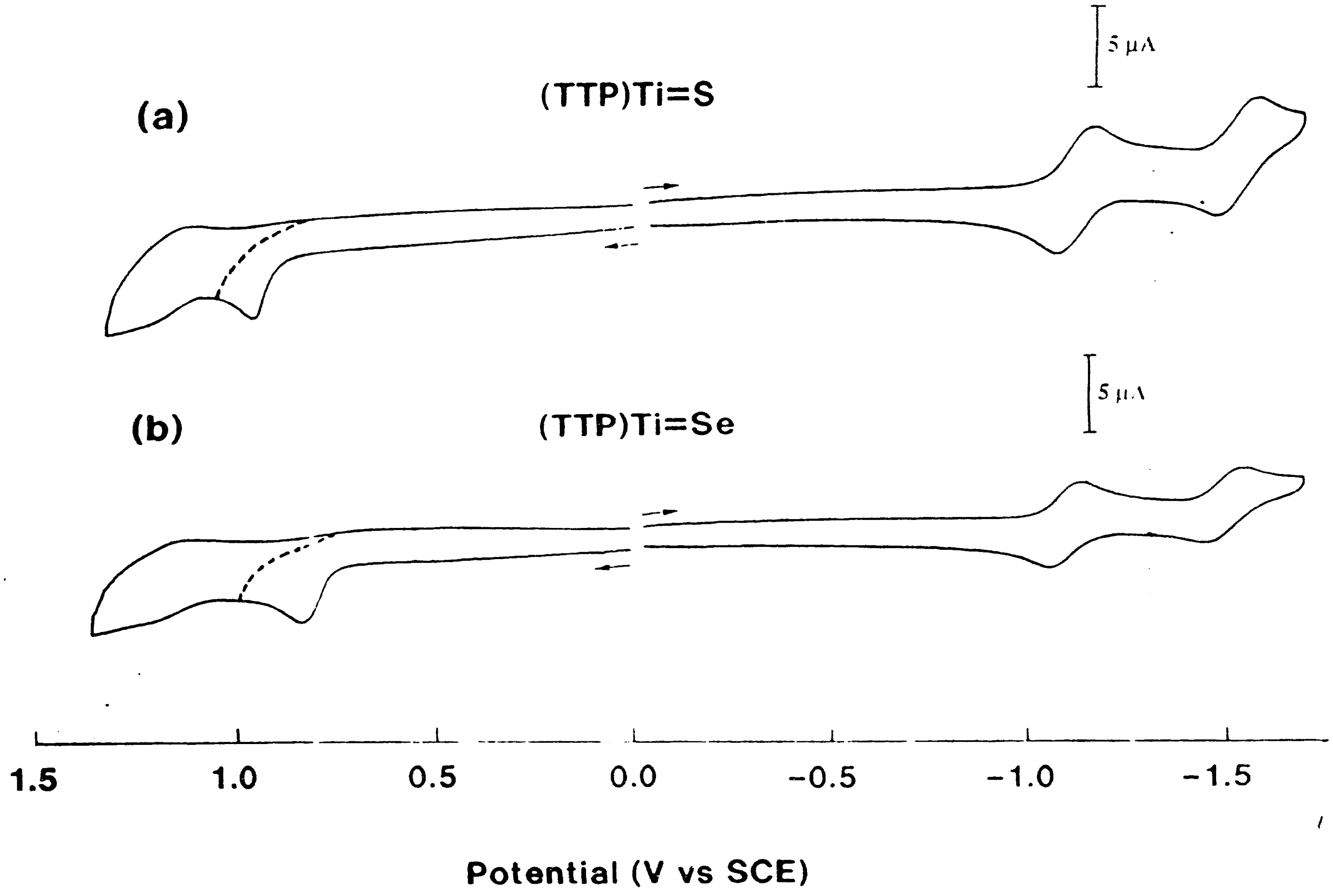


Figure 3.Cyclic voltammograms of (a) (TTP)Ti=S and (b) (TTP)Ti=Se in CH_2Cl_2, 0.1 M TBAP (scan rate 0.1 V/s)

Discussion

The acetylene and *bis*-ligand complexes of the titanium porphyrins presented here can be viewed as containing titanium in the formal +2 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.[21] 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 appear to be important in stabilizing the titanium(II) complexes. Thus, the analogous CO or ethylene complexes cannot be prepared by either reducing (TTP)TiCl$_2$ in the presence of these ligands or by displacement of acetylene from (TTP)Ti(η^2-Ph-C≡C-Ph). 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 one equivalent of 4-picoline is added to (TTP)Ti(η^2-Ph-C≡C-Ph). 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(η^2-Ph-C≡C-Ph) occurs. However, the reverse reactions do not occur. For example, addition of 2-butyne to (TTP)Ti(η^2-Ph-C≡C-Ph) 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. However, when (TTP)Ti(η^2-Ph-C≡C-Ph) is treated with di(*p*-tolyl)diazomethane, loss of N_2 and formation of a carbene complex is not observed. Instead, a reaction to produce a hydrazido complex, (TTP)Ti=N-N=C(C_6H_5-CH_3)$_2$, results. Apparently, the reactivity of the titanium complexes discussed here is driven by their strong reducing potential. This behavior is also consistant with the Ti(II) formalism proposed here.

Furthermore, (TTP)Ti(η^2-Ph-C≡C-Ph) 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-Ph-C≡C-Ph) and produces the corresponding Ti(IV) selenide. These chalcogenide complexes are the first terminal sulfide and selenide complexes of titanium porphyrins. When elemental forms of sulfur or 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.[29] The titanium η^2-S_2 and η^2-Se_2 complexes have been prepared previously by Guilard *et al.* by reaction of (TTP)Ti-F or (TTP)TiF$_2$ with Cp_2TiS_5 or Cp_2TiSe_5.[16p] Eq. 11-12 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 consistant 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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17. Abbreviations: TTP is *meso*-tetra-*p*-tolylporphyrinato and OEP is octaethylporphyrinato.

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APPENDIX A.

Table I. Structure Determination Summary for (TTP)Ti(4-picoline)$_2$

Empirical Formula	$C_{66}H_{56}N_6Ti$
Color; Habit	Brown; Prism
Crystal Size (mm)	0.40 x 0.10 x 0.10
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	
a (Å)	9.764(2)
b (Å)	10.899(2)
c (Å)	13.530(2)
α (°)	92.18(2)
β (°)	98.10(2)
γ (°)	114.14(2)
Volume (Å^3)	1293.6(4)
Z	1
Formula Weight	981.1
Density (calc.)	1.259 mg/m^3
Absorption Coefficient	1.771 mm^{-1}
F(000)	516
Diffractometer Used	Siemens P4/RA
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	213
Monochromator	Highly oriented graphite crystal

2θ Range	5.0 to 115.0 °
Scan Type	2θ-θ
Reflections Collected	4759
Independent Reflections	3490 (R_{int} = 5.46%)
Observed Reflections	2736 ($F > 4.0\sigma(F)$)
Hydrogen Atoms	Riding model, fixed isotropic
Number of Parameters Refined	332
Final R Indices (obs. data)	R = 5.17 %, R_w = 5.42 %
Goodness-of-Fit	2.64
Data-to-Parameter Ratio	8.2:1
Largest Difference Peak	0.27 $e\text{Å}^{-3}$
Largest Difference Hole	-0.38 $e\text{Å}^{-3}$

Table II. Atomic coordinates (x10^{-4}) and equivalent isotropic displacement coefficients (Å^2 x 10^3)

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

* Equivalent isotropic U defined as one third of the trace of the orthogonalized 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 (°)

N(1)-Ti-N(2)	91.4(1)	N(1)-C(4)-C(3)	109.5(3)	C(11)-C(10)-C(1A)	116.6(4)
N(1)-Ti-N(3)	87.4(1)	N(1)-C(4)-C(5)	124.6(4)	C(10)-C(11)-C(12)	120.2(3)
N(2)-Ti-N(3)	87.4(1)	C(3)-C(4)-C(5)	125.9(4)	C(10)-C(11)-C(16)	122.0(4)
N(1)-Ti-N(1A)	180.0(1)	C(4)-C(5)-C(51)	116.6(4)	C(12)-C(11)-C(16)	117.8(4)
N(2)-Ti-N(1A)	88.6(1)	C(4)-C(5)-C(6)	127.1(4)	C(11)-C(12)-C(13)	121.5(3)
N(3)-Ti-N(1A)	92.6(1)	C(51)-C(5)-C(6)	116.2(3)	C(12)-C(13)-C(14)	120.2(4)
N(1)-Ti-N(2A)	88.6(1)	C(5)-C(51)-C(52)	121.9(3)	C(13)-C(14)-C(15)	118.4(4)
N(2)-Ti-N(2A)	180.0(1)	C(5)-C(51)-C(56)	120.0(4)	C(13)-C(14)-C(17)	119.3(4)
N(3)-Ti-N(2A)	92.6(1)	C(52)-C(51)-C(56)	118.1(4)	C(15)-C(14)-C(17)	122.4(4)
N(1A)-Ti-N(2A)	91.4(1)	C(51)-C(52)-C(53)	120.8(3)	C(14)-C(15)-C(16)	121.3(4)
N(1)-Ti-N(3A)	92.6(1)	C(52)-C(53)-C(54)	121.3(4)	C(11)-C(16)-C(15)	120.8(4)
N(2)-Ti-N(3A)	92.6(1)	C(53)-C(54)-C(55)	118.0(4)	Ti-N(3)-C(31)	121.8(3)
N(3)-Ti-N(3A)	180.0(1)	C(53)-C(54)-C(57)	121.1(4)	Ti-N(3)-C(35)	121.8(3)
N(1A)-Ti-N(3A)	87.4(1)	C(55)-C(54)-C(57)	120.9(3)	C(31)-N(3)-C(35)	116.1(3)
N(2A)-Ti-N(3A)	87.4(1)	C(54)-C(55)-C(56)	120.8(3)	N(3)-C(31)-C(32)	123.3(4)
Ti-N(1)-C(1)	127.8(2)	C(51)-C(56)-C(55)	121.0(4)	C(31)-C(32)-C(33)	120.3(5)
Ti-N(1)-C(4)	125.3(2)	N(2)-C(6)-C(5)	125.7(3)	C(32)-C(33)-C(34)	116.7(4)
C(1)-N(1)-C(4)	105.9(3)	N(2)-C(6)-C(7)	108.4(4)	C(32)-C(33)-C(36)	121.7(4)
Ti-N(2)-C(6)	125.0(3)	C(5)-C(6)-C(7)	125.8(4)	C(34)-C(33)-C(36)	121.5(4)
Ti-N(2)-C(9)	128.1(3)	C(6)-C(7)-C(8)	108.5(3)	C(33)-C(34)-C(35)	120.5(4)
C(6)-N(2)-C(9)	106.6(3)	C(7)-C(8)-C(9)	107.8(3)	N(3)-C(35)-C(34)	123.1(4)
N(1)-C(1)-C(2)	109.2(3)	N(2)-C(9)-C(8)	108.6(4)	C(41)-C(40)-C(42A)	119.9(6)
N(1)-C(1)-C(10A)	125.4(4)	N(2)-C(9)-C(10)	125.3(3)	C(40)-C(41)-C(42)	120.2(6)
C(2)-C(1)-C(10A)	125.3(4)	C(8)-C(9)-C(10)	126.0(4)	C(41)-C(42)-C(40A)	119.9(8)
C(1)-C(2)-C(3)	108.2(4)	C(9)-C(10)-C(11)	118.8(3)		
C(2)-C(3)-C(4)	107.2(4)	C(9)-C(10)-C(1A)	124.6(4)		

PAPER 3: OXYGEN ATOM TRANSFER REACTIONS OF TITANIUM PORPHYRINS

INTRODUCTION

Although atom transfer reactions are very common and have been known for over forty years, an understanding of oxygen atom transfer processes that occur between two metal complexes is still emerging.[1] A large portion of the documented oxygen atom transfer reactions occur between a metal oxo donor and non-metal oxo acceptor, such as phosphines and alkenes. Examples of intermetal oxygen-transfer reactions are less common. In most cases, reaction of a metal oxo donor with metal acceptor results in the formation of a μ-oxo species, eq. 1. Holm has termed this type of reaction as incomplete atom transfer.[2] In contrast, complete atom transfer specifies the case when the oxo ligand is totally cleaved from the donor complex, (eq. 2). This case has been documented in molybdenum,[2] tungsten,[2,3] and vanadium[4] complexes, and implicated in the ruthenium oxo porphyrin-catalyzed aerobic epoxidation of alkenes.[5]

$$L_nM{=}O \;+\; L_nM' \rightarrow L_nM{-}O{-}M'L_n \qquad 1$$

$$L_nM{=}O \;+\; M'L_n \rightarrow L_nM \;+\; O{=}ML_n \qquad 2$$

The fundamental factors which dictate the occurrence of complete versus incomplete oxygen atom transfer are not well understood. However, it is clear that steric factors can promote complete oxygen atom transfer by destabilizing the μ-oxo species.[6] Incomplete oxygen atom transfer typically involves a net one electron change. However, complete oxygen atom transfer can mediate both one- or two-electron redox processes. Thus an understanding of the factors that influence the electron stoichiometry involved in an oxygen atom transfer is also not well developed. Our approach towards studying these important issues has focussed on systems which approach the self-exchange category ($\Delta G^{\ddagger} = 0$). This allows an assessment of the relative stability of the μ-oxo species relative to those of the oxo donor and acceptor complexes without complications arising from a thermodynamic driving force. The energetics of this bridged M-O-M unit clearly dictates the type of reaction (complete versus incomplete oxygen atom transfer) and determines the rate of atom transfer.

We have found that electronic factors are extremely important in intermetal atom transfer reactions of metalloporphyrins. In the work presented here, we describe a more detailed account of oxygen atom transfer reaction between titanium porphyrin complexes.

EXPERIMENTAL

General. All manipulations were carried out under an atmosphere of nitrogen using either a Vacuum Atmosphere glove-box equipped with a Model MO40H Dri-Train gas purifier or on a high vacuum line using standard Schlenk techniques. All solvents were rigorously dried and degassed prior to use. Benzene-d_6, toluene, tetrahydrofuran, hexane were vacuum distilled from solutions of sodium benzophenone. Methanol was distilled from sodium under nitrogen over to 4 Å molecular sieves and then vacuum distilled a second time prior to use. CH_2Cl_2, $CDCl_3$ and CD_2Cl_2 were stored over either P_2O_5 or CaH_2 and vacuum distilled prior to use. Triphenylmethane was sublimed under reduced pressure at 100 °C prior to use. Sodium pivulate was obtained from Aldrich Chemical Company and recrystallized from methanol/CH_2Cl_2. (TTP)Ti=O,[7] (OEP)Ti=O,[7], (TTP)TiCl,[8] (OEP)TiCl[8] were prepared using literature procedures. (OEP)Ti($O_2CC(CH_3)_3$ was prepared using a modification of a previously developed procedure.[9] All reagents used for kinetic and equilibrium studies were twice recrystallized prior to use. Concentrations of stock solutions were checked before use either by UV-vis or ^1H NMR spectroscopies. ^1H NMR spectra were recorded on either a Nicolet 300-MHz or a Varian VXR 300-MHz Fourier transform spectrometer. UV-vis were recorded on a HP8452A diode array spectrophotometer. IR spectra were recorded on a either a IBM IR98 or a Digilab Fourier transform spectrometer. Elemental analyses were obtained from Desert Analytics, Tuscon AZ.

Equilibrium Measurements. Samples for equilibrium determinations for the titanium oxo-chloride exchange and the oxo-dichloride system were prepared by adding specific volumes of known concentrations of an oxo complex, the opposing chloride or dichloride complex, and an internal standard, triphenylmethane, into a 5-mm. NMR tube attached to a ground glass joint. The solvent was evaporated off under low vacuum in the glovebox. The NMR solvent, either d_8-toluene (oxo-chloride exchange) or $CDCl_3$ (oxo-dichloride) were pipeted in and a high vacuum line adaptor attached. The tube was then placed on a high vacuum line, the tube frozen with liquid nitrogen and, without evacuating, the NMR tube was flamed sealed. For the oxo-chloride system, the equilibrium constant was determined by integrating the meso-proton signal of the (OEP)Ti=O and the β-pyrrole signal of the (TTP)Ti=O. These signals were compared to the methine proton of the triphenylmethane to verify that mass balance was maintained and to determine concentrations. The tubes were monitored in a temperature controlled NMR probe until no further change in the spectrum was observed. For the oxo-dichloride system, all species were diagmagnetic, so meso-protons and β-pyrrole protons were integrated with respect to the triphenylmethane to assure that mass balance was maintained.

Kinetic measurements. Rate data for the (POR)Ti=O/(POR)Ti-X (X = chloride, pivalate anion) systems were obtained on a UV-visible spectrometer equipped with a thermally regulated cell holder. Solutions of the oxo and the appropriate titanium(III) complexes were loaded into a 1-cm. quartz cuvette under nitrogen atmosphere and capped with a septum. The cuvette was placed in the cell holder, and the run was monitored at 572 nm. Molar absorptivities of the porphyrin complexes are given in Table I. A final spectrum from 500 to 700 nm. was taken to verify that decomposition of the chloride complex did not occur. Kinetic runs were also done in the presence of excess chloride in the form of bis(triphenylphosphoranylidene)ammonium chloride. Typical initial concentrations ranged 7.37×10^{-6} to 4.1×10^{-5} M. Rate constants were obtained

Table I. Molar absorptivities for metalloporphyrins in toluene at 572 nm

compd.	molar absorptivity x 10^{-4} ($M^{-1}s^{-1}$)	compd.	molar absorptivity x 10^{-4} ($M^{-1}s^{-1}$)
(TTP)Ti=O	0.313	(OEP)Ti=O	3.02
(TTP)Ti-Cl	0.900	(OEP)Ti-Cl	1.06

using an integrated rate law for second order equilibrium reactions derived by King.[10]

Rate data for the (POR)Ti=O/(POR)TiCl$_2$ systems were obtained on either a UV-vis spectrophotometer with a thermally regulated cell holder (for runs at 20, 30, and 50 °C) or on a thermally regulated Varian VXR 300 MHz NMR spectrometer. For runs on the UV-vis spectrophotometer, CHCl$_3$ solutions of the oxo and the appropriate dichloride are loaded into a 1-cm. quartz cuvette fitted with a stopcock. The cuvette is placed in the cell holder, allowed time to equilibrate to the proper temperature, and the run monitored at 550 nm. Molar absorptivities of the porphyrin complexes in CHCl$_3$ are given in Table II. A final spectrum from 500 to 700 nm. was obtained to verify that the dichloride complexes had not decomposed. Typical concentrations of oxo and dichloride complexes are approximately 4.5 x10^{-5} M. For kinetic runs at 0 °C, solutions of the oxo complex, the appropriate dichloride complex, and a

Table II. Molar absorptivities for metallaporphyrins in CHCl$_3$ at 550 nm

compd.	molar absorptivity x 10^{-4} ($M^{-1}s^{-1}$)	compd.	molar absorptivity x 10^{-4} ($M^{-1}s^{-1}$)
(TTP)Ti=O	2.41	(OEP)Ti=O	0.484
(TTP)TiCl$_2$	1.33	(OEP)TiCl$_2$	0.479

internal standard, triphenylmethane, are transfered into a 5-mm. NMR tube fitted with a ground glass joint. The solvents are evaporated off under reduced pressure and a high vacuum line adapter is attached. Deuterated solvent is vacuum transferred into the tube on a high vacuum line, the tube is backfilled with N_2 to approximately 550 mmHg, and the NMR tube was flame sealed. The tube is kept in liquid N_2 prior to insertion into the instrument, then it is thawed sightly and placed into the magnet and allowed to equilibrate to the proper temperature. Runs are monitored with either the meso-protons of the OEP complexes or the β-pyrrole protons of the TPP complexes and intergrated with rspect to the methine proton of the internal standard. Comparison of these signals is used to verify that mass balance was maintained during the run. In both cases, rate constants were obtained using an intergrated rate law for second order equilibrium reactions derived by King.[10]

RESULTS

Reduction of Oxotitanium(IV) Porphyrin with Titanium(III) Porphyrin. Treatment of (TTP)Ti=O with (OEP)Ti-Cl in d_8-toluene results in spectral changes which are consistent with the transfer of a terminally bound oxygen ligand between two metal complexes shown in eq 3. The

$$(TTP)Ti{=}O \;+\; (OEP)Ti{-}Cl \;\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\; (TTP)Ti{-}Cl \;+\; (OEP)Ti{=}O \qquad 3$$

^1H NMR spectrum of the resulting mixture contains a new resonance at 10.54 indicating the formation of (OEP)Ti=O. The resonance at 9.24 ppm. does not completely disappear indicating that eq. 3 is an equilibrium process. Since the titanium(III) complexes are d^1 and paramagnetic, the signals for these species are broadened and thus difficult to observe. The reversibility of eq 3 can be confirmed by the complementary experiment in which (OEP)Ti=O is treated with (TTP)Ti-Cl. This generates a final spectrum with peak positions identical to that observed for the forward process.

Equilibrium constants for eq. 3 are conveniently established by ^1H NMR by monitoring the β-pyrrole of the (TTP)Ti=O (9.24 ppm.), the meso-proton signal of (OEP)Ti=O (10.54 ppm.), and the methine proton of the internal standard, triphenylmethane (5.34 ppm). Flamed-sealed NMR tubes containing (TTP)Ti=O, (OEP)Ti-Cl, and triphenylmethane in d_8-toluene were prepared. During the course of the experiment, mass balance was maintained in terms of total oxo complex concentration. The equilibrium constants for eq 3 were determined over a 40-deg. range and are listed in Table III. The thermodynamic parameters, $\Delta H^{\circ} = 2.0 \pm 0.3$ kcal/mol and $\Delta S^{\circ} = 7.6 \pm 0.1$ cal(mol·K)$^{-1}$, were determined from this temperature dependence.

Table III. Equilibrium constants for eq. 3 in d_8-toluene

temperature (°C)	K_{eq}	temperature (°C)	K_{eq}
0	1.3 ± 0.3	20	1.7 ± 0.4
10	1.4 ± 0.4	30	1.4 ± 0.3

The forward rates of eq 3 in toluene were determined spectrophotometrically by following the absorbance changes at 572 nm. and listed in Table IV. All of the compounds involved, (TTP)Ti=O, (TTP)Ti-Cl, (OEPTi=O, and (OEP)Ti-Cl, obey Beer's law over the concentration range used in these experiments. This indicates self-association does not complicate the mechanistic analysis. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions shown in eq 4. Plots of $\ln[\Delta/(\alpha + \Delta(1-1/K))]$ vs. time are linear

Table IV. Forward rate constants for eq 3 in toluene

Temperature (°C)	k_f (x10^{-2} M^{-1}s^{-1})
40	8.1 ± 1.1
30	4.6 ± 0.2
20	2.4 ± 0.2
10	1.4 ± 0.3
0	0.56 ± 0.09

$$\ln\left[\frac{\Delta}{\alpha + \Delta(1 + 1/K)}\right] = -\alpha k_1 t + \mathit{constant} \qquad 4$$

for at least 3 half lives. An absorbance versus time curve of a typical kinetic run and a log plot of the data are located in Figures 1 and 2 respectively.

Effect of Coordinating Ligand. (POR)Ti-X (X is an anionic ligand) are known to coordinate neutral donor ligands on the back side of the metal,[11,12] so forward rates of eq. 3 in THF were examined. In all runs the data were found to follow second-order reversible rate law for more than 3 half-lives. Rates for eq. 3 were found to exhibit a dependence on solvent used ($k_{THF} = 60\ M^{-1}s^{-1}$ and $k_{toluene} = 240\ M^{-1}s^{-1}$)

Effect of Axial Ligand. Axial ligand effects were studied in these systems by changing the monoanionic ligand of the starting titanium(III) porphyrin complexes as shown in eq 5. A

$$(TTP)Ti{=}O + (OEP)Ti{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (TTP)Ti{-}X + (OEP)Ti{=}O \qquad 5$$

comparison of two different axial ligands, pivalate and chloride, was made at 20 °C in THF. Kinetic runs for the pivulate system were found to follow an integrated rate law for second-order reversible reactions. Rates for eq 5 were found to have little dependence on the nature of the axial ligand (at 20 °C: $k_{piv} = 100 \pm 10\ M^{-1}s^{-1}$ and $k_{chloride} = 70 \pm 10\ M^{-1}s^{-1}$).

Effect of Added Axial Ligand. The rate of oxygen atom transfer was studied as a function of added chloride ion. Bis(triphenylphosphoranylidene)ammonium chloride, (PPN)Cl,

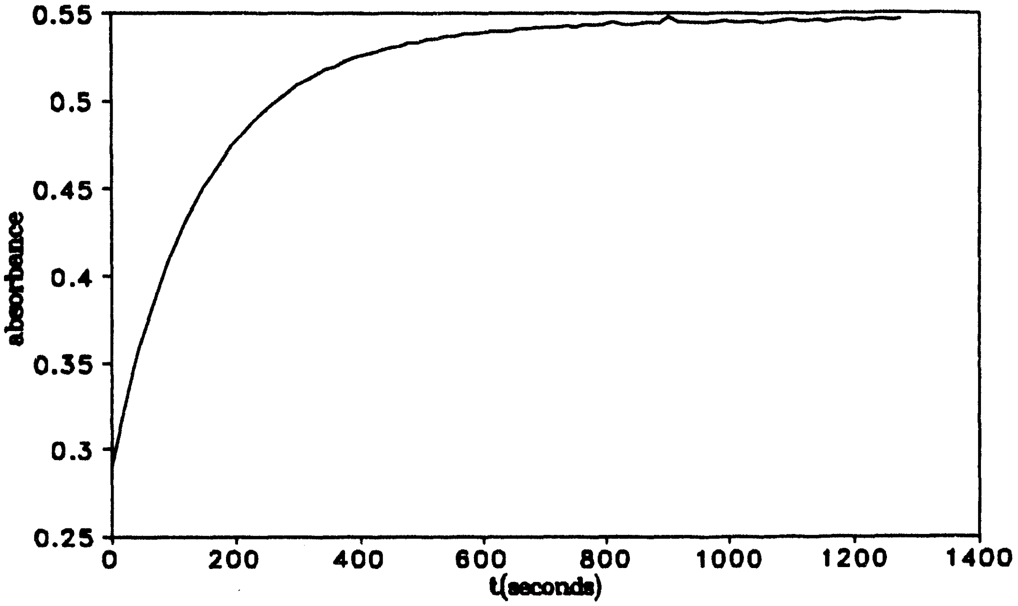


Figure 1. Representative absorption vs. time plot for equation 3. [(TTP)Ti=O] = 1.95 x 10^{-5}, [(OEP)TiCl] = 1.94 x 10^{-5}, in toluene at 20 °C

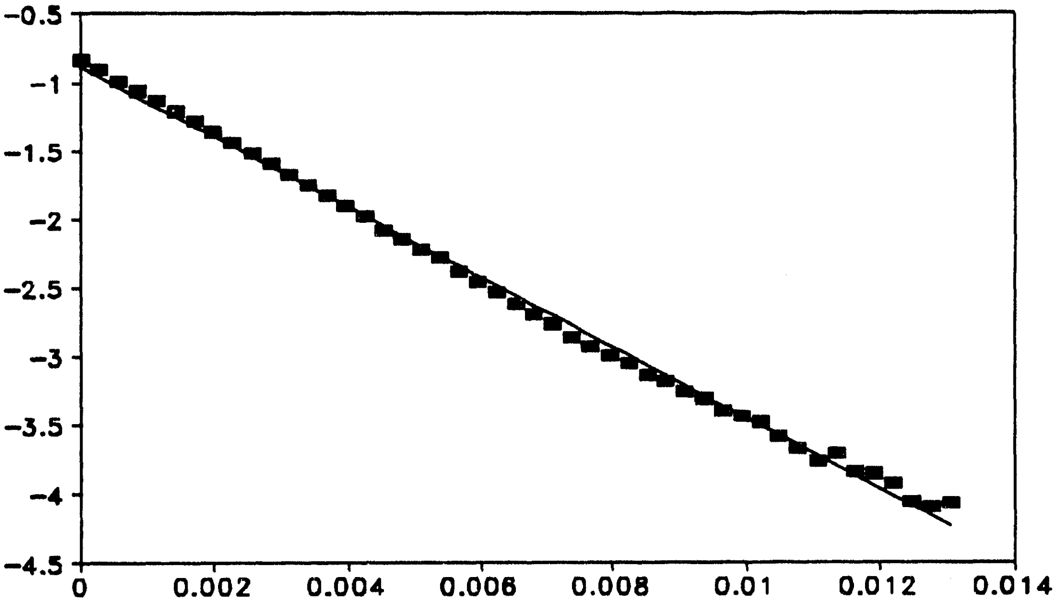


Figure 2. Plot of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs. αt for figure 1, $k_f = 256 \pm 2\ M^{-1}s^{-1}$

was used as the source of chloride. Due to the low solubility of the chloride source in toluene, kinetic runs were performed in CH_2Cl_2 solutions. The dissociation constant for (PPN)Cl at 20 °C in CH_2Cl_2 is 5.10×10^{-4}.[13]

The rate data for all runs in CH_2Cl_2 were found to follow a second-order reversible rate law at 20 °C. In the absence of any added chloride, the rate constant for the eq 3 in CH_2Cl_2 at 20 °C is $4.6 \pm 0.4 \times 10^2$ $M^{-1}s^{-1}$. Using a 10 fold excess of Cl^- with respect to (OEP)TiCl, decreases the rate constant to $3.6 \pm 0.3 \times 10^{-2}$ $M^{-1}s^{-1}$. Using a 500 fold excess, the rate constant was reduced to $2.7 \pm 0.3 \times 10^{-2}$ $M^{-1}s^{-1}$. Additionally, these experiments allow a comparison of the rate of atom transfer in two different solvents. Rates were found to increase upon changing the solvent from toluene to CH_2Cl_2 at 20 °C. For CH_2Cl_2, the rate constant was found to be 460 $M^{-1}s^{-1}$ and for toluene, 240 $M^{-1}s^{-1}$. A similar solvent effect was observed for the system where chromium was used instead of titanium.[14]

Oxygen Atom Transfer between (TTP)TiCl$_2$ and (OEP)Ti=O. Treatment of (TTP)$TiCl_2$ with (OEP)Ti=O in $CDCl_3$ results in spectral changes consistent with the transfer of a terminally bound oxo ligand between two metal centers (eq 6). All species are diamagnetic

$$(TTP)TiCl_2 \;+\; (OEP)Ti{=}O \;\rightleftharpoons\; (TTP)Ti{=}O \;+\; (OEP)TiCl_2 \qquad 6$$

making it easy to verify that transfer has occurred. The ^1H NMR spectrum of the resulting mixture contains two new signals at 10.48 and 9.12 ppm. indicating the formation of (OEP)$TiCl_2$ and (TTP)Ti=O, respectively. The signals for (TTP)Ti=O (8.99 ppm.) and (OEP)Ti=O (10.54 ppm) do not entirely disappear indicating that eq 6 is an equilibrium process. The equililbrium (eq 6) can be verified by the reverse process in which (TTP)Ti=O is treated with (OEP)$TiCl_2$.

This generates a final spectrum identical to that observed for the forward process.

Equilibrium constants for eq 6 are once again conveniently established by ^1H by monitoring all meso-proton and β-pyrrole signals, since all species are diamagnetic. Flamed-sealed NMR tubes were prepared containing $(TTP)TiCl_2$ and (OEP)Ti=O plus an internal standard, triphenylmethane in $CDCl_3$. Initial concentrations for the porphyrin complexes range from 0.5 mM to 2.0 mM. During the course of the experiment mass balance was maintained in terms of total oxo complex concentration. The equilibrium constants to eq 6 were determined over a 50-deg range and are listed in Table IV. The thermodynamic parameters, ΔH° = -3.7 ± 0.8 kcal/mol and $\Delta S^\circ = -5.1 \pm 0.7$ cal(mol·K)$^{-1}$, were determined from this temperature dependence.

Table IV. Equilibrium constants for eq. 6 in $CDCl_3$

Temperature (°C)	K_{eq}	Temperature (°C)	K_{eq}
0	71 ± 11	30	31 ± 8
20	47 ± 13	50	26 ± 10

The forward rates of eq. 6 in $CHCl_3$ were examined both by spectrophotmetric methods , monitoring the absorbance changes at 550 nm, and by ^1H NMR, observing the spectral changes of the meso- and β-pyrrole protons as shown in Table V. For the UV-vis runs, all

Table V. Forward rate constants for eq 6 in $CHCl_3$

temperture (°C)	k_f ($M^{-1}s^{-1}$)	temperture (°C)	k_f ($M^{-1}s^{-1}$)
50	58 ± 7	20	5 ± 1
30	7 ± 2	0	0.18 ± 0.08

compounds listed in Table II obey Beer's law over the concentration range of the experiments. This indicates self-association does not complicate the mechanistic analysis. In all kinetic runs, the data are found to obey an integrated rate law for reversible second-order reactions as shown in eq. 4. Plots of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs. time are linear for at least 3 half lives. Plots of a typical kinetic and worked up data are located in Figure 3 and 4.

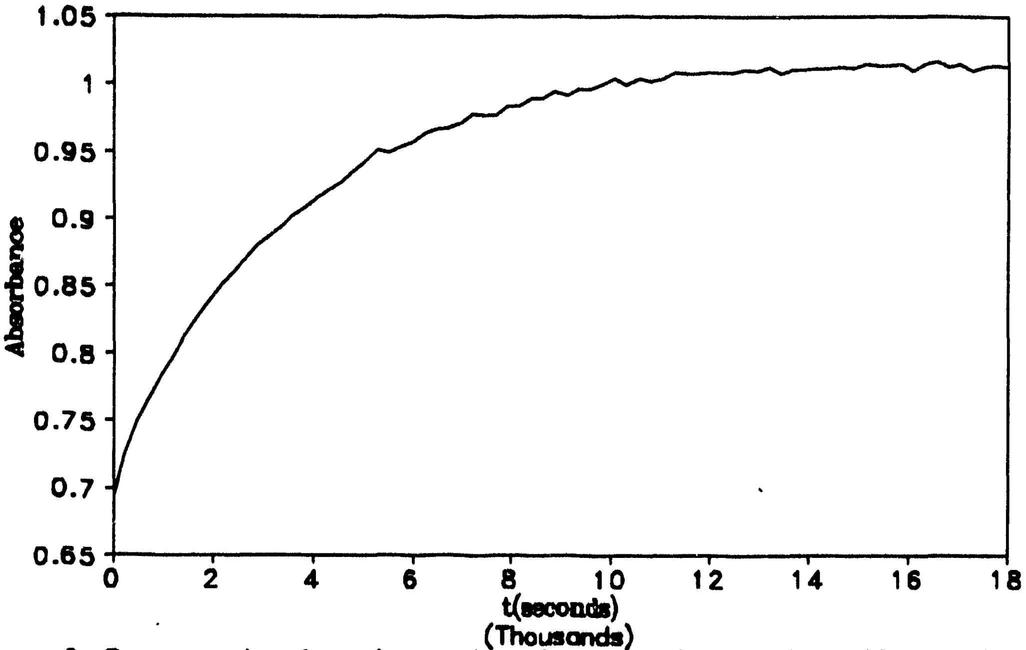


Figure 3. Representative absorption vs. time plot of equation 6. [(TTP)TiCl$_2$] = 4.44 x 10^{-5} M, [(OEP)Ti=O] = 4.41 x 10^{-5} M, in CHCl$_3$ at 20 °C

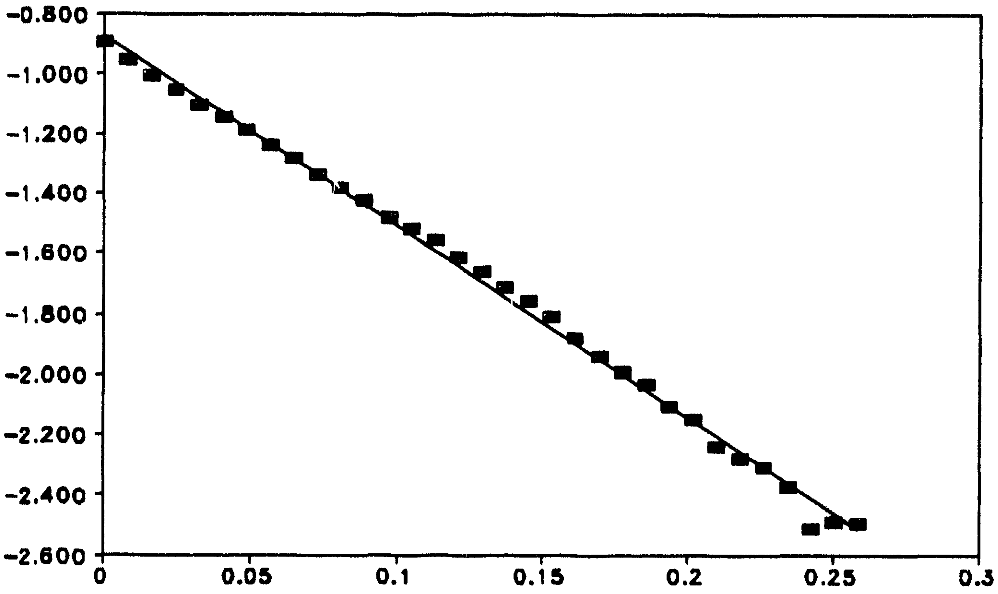
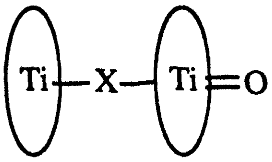


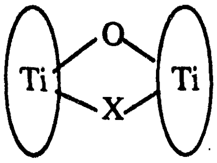
Figure 4. Plot of ln[Δ/(α + Δ(1 - 1/K))] vs. αt for figure 3, k_f = 6.34 ± 0.06 M^{-1}s^{-1}

DISCUSSION

We have found that complete oxygen atom transfer resulting in either one- or zero-electron transfer between two metalloporphyrins can be achieved. It is possible to observe this process by using different porphyrin ligands as UV-vis and ^1H NMR spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction, eliminating complications due to ligand loss. Furthermore, stereochemical rearrangements found in other systems that undergo complete atom transfer are not possible here.[3,15] Rate constants for eq. 3 have been measured in the forward direction over a 40-deg. temperature span. These rate constants range between 60 and 810 $M^{-1}s^{-1}$ The temperature dependence of the forward rate yields activation parameters of $\Delta H^‡$ = 10.8 ± 0.4 kcal/mol and $\Delta S^‡ = -10.7 \pm 0.3$ cal(mol·K)$^{-1}$. Rate constants for eq. 6 have been measured in the forward direction over a 50-deg. temperature range. These rate constants range between 0.18 and 58 $M^{-1}s^{-1}$. The temperature dependence of the forward rate constants yield activation parameters of $\Delta H^‡ = 11 \pm 1$ kcal/mol and $\Delta S^‡ = 11 \pm 3$ cal(mol·K)$^{-1}$. Although eq. 3 proceeds, in all probability, by an inner sphere process, mechanistic aspects of this reaction are complicated by the bridging abilities of both the chloride and oxo ligands. In order to address this issue, we have compared the reduction of (TTP)Ti=O with that of both (OEP)Ti-Cl and (OEP)Ti-$O_2CC(CH_3)_3$. The rate constants for these two reaction are similar, regardless of whether chloride ($k_{Cl} = 60$ $M^{-1}s^{-1}$) or pivalate ($k_{piv} = 100$ $M^{-1}s^{-1}$) is the axial ligand on titanium(III). Because pivalate is a much bulkier ligand, this rate comparison serves to rule out a binuclear intermediate in which the monanionic ligand is involved in bridging the two metals. Thus the μchloro-bridged adduct, A, and the doubly bridged species, B, must not be important intermediates



A



B

along the reaction pathway.

It is likely that the redox reaction between (TTP)Ti=O and (OEP)Ti-Cl involves a μ-oxo intermediate. Formation of this intermediate can occur either by an S_N1 type mechanism (scheme I) or by a S_N2 type mechanism (scheme II). These two processes can normally be distinguished

Scheme I

$$^{*}\text{Ti-Cl} \rightarrow {}^{*}\text{Ti(III)}^{+} + \text{Cl}^{-}$$

$$^{*}\text{Ti(III)}^{+} + \text{Ti=O} \rightarrow {}^{*}\text{Ti=O} + \text{Ti(III)}^{+}$$

$$\text{Ti(III)}^{+} + \text{Cl}^{-} \rightarrow \text{Ti-Cl}$$

Scheme II

$$^{*}\text{Ti-Cl} + \text{Ti=O} \rightarrow [{}^{*}\text{Ti-O-Ti}]^{+} + \text{Cl}^{-}$$

$$\text{Cl}^{-} + [{}^{*}\text{Ti-O-Ti}]^{+} \rightarrow {}^{*}\text{Ti=O} + \text{Ti-Cl}$$

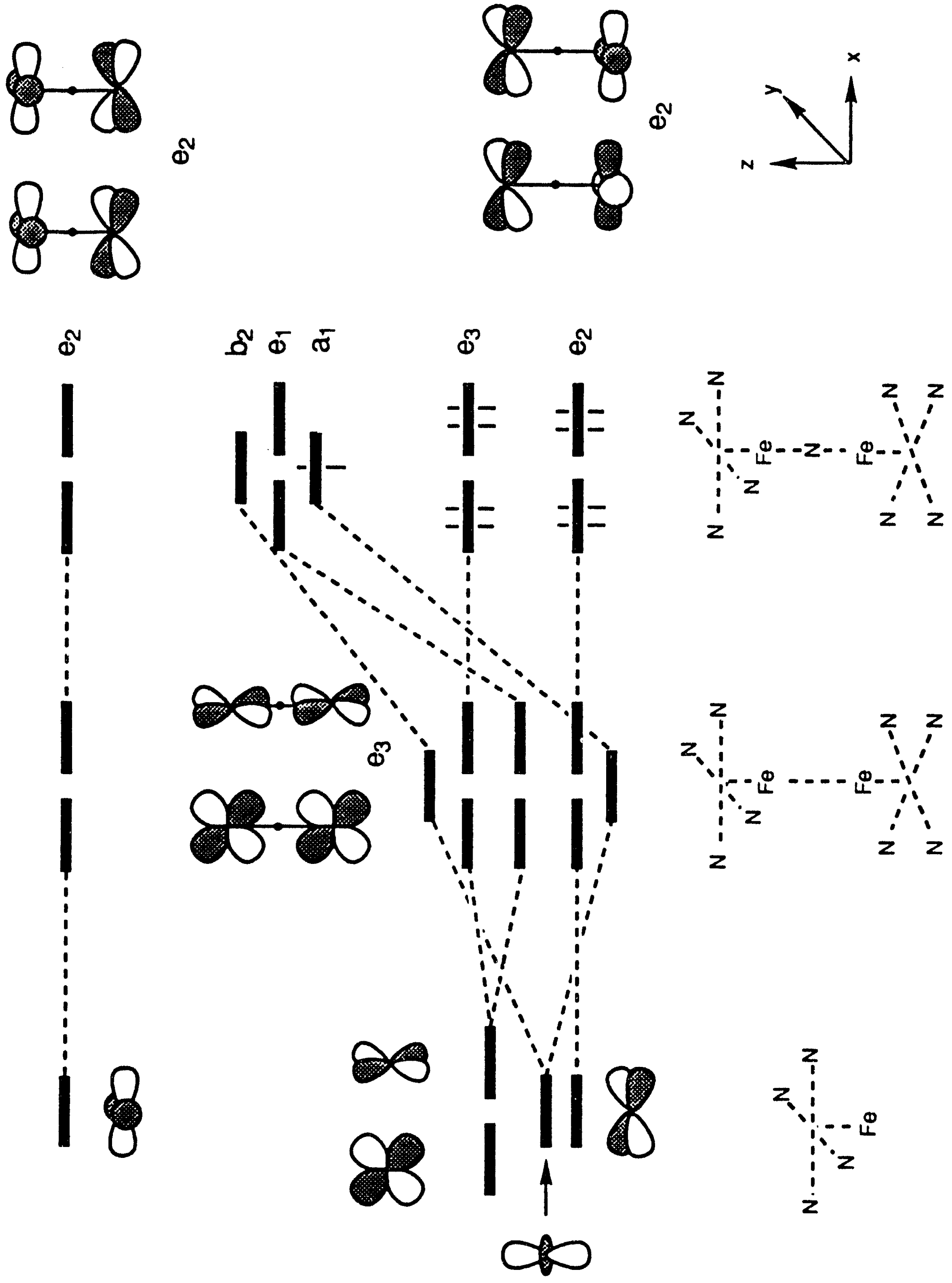
*Ti = (OEP)Ti and Ti = (TTP)Ti

by their chloride ion dependence. Unfortunately, this system is complicated by the fact that titanium(III) porphyrin complexes can coordinate a second anionic ligand trans to the first axial ligand (eq ?). Consequently, a pre-equilibrium between the five-coordinate titanium(III)

$$(TPP)Ti\text{-}F \;+\; Et_4NF \;\rightarrow\; Et_4N^+[(TPP)TiF_2]^- \qquad 7$$

porphyrin starting material and a six-coordinate titainum(III) adduct complicates any mechanistic analysis when excess chloride is present. It is then found that both the S_N1 and S_N2 mechanisms become inversely dependent upon chloride concentration. Additional studies are under way to attempt to elucidate the mechanism further.

The reduction products of oxotitanium porphyrins are strongly dependent on the nature of the reducing agent. This has already been established for oxochromium complexes. When chromium(II) porphyrin is the reducing agent, the reaction halts at the μ-oxo dimer (eq.).[16] However, when a chromium (III) porphyrin is used as the reductant, the result is reverisble oxygen atom transfer. In the case of oxotitanium porphyrins, we observe similar results. An examination of the electronic structure of μ-oxometalloporphyrin dimers provides a possible rationale for this contrasting behavior. The d-orbital energy level for $[Fe(TTP)]_2O$ shown in Figure 5 was derived by Tatsumi and Hoffmann[17] using extended Hückel calculations on $[(NH_2^-)_4Fe\text{-}OFe(NH_2^-)_4]^{-4}$ as a computational model. To a first approximation, this energy level diagram should apply to the $[(POR)M\text{-}O\text{-}M(POR)]^{0,+}$ (M = Cr, Ti) system. In the chromium case, when chromium(II) is the reductant, the neutral (POR)Cr-O-Cr(POR) dimer has six d-electrons. This leads to a $(e_2)^4(e_3)^2$ ground state which is electronically stable with respect to complete oxygen atom transfer. However, when chromium(III) is the reductant, the cationic d^5 μ-oxo species must have either a low-spin $(e_2)^4(e_3)^1$ or high-spin $(e_2)^2(e_3)^2(e_1)^1$ ground state. Either state


e$_2$
b$_2$
e$_1$
a$_1$
e$_3$
e$_2$
e$_2$
e$_3$
e$_2$
z
y
x
N
Fe
N
Fe

is electronically degenerate and Jahn-Teller destabillized, leading to cleavage of the μ-oxo species. In similar manner, we can describe the titanium system. If titanium(II) is used as the reductant, the neutral μ-oxo species has a $(e_2)^2$ ground state which is electronically stable as with the chromium case. If titanium(III) is used as the reductant, the cationic d^1 μ-oxo intermediate has a $(e_2)^1$ ground state and is electronically degenerate, leading to cleavage of the μ-oxo intermediate.

CONCLUDING REMARKS

A number of results have evolved from this study. Of particular interest is the observation that complete inter-metal oxygen atom transfer is possible and facile for titanium porphyrins. Oxygen atom transfer in titanium porphyrin complexes can mediate both a one- and zero-electron process. The reversible processes reported here are the first such examples involving titanium porphyrins. Although mechanistic studies are incomplete, it is clear that the oxo ligand is the preferred bridging species despite the presence of other good bridging ligands (e.g chlorides and carboxylates). Finally, a simplified molecular orbital analysis suggests that the complete oxo transfer between (POR)Ti=O and (POR)TiCl is promoted by electronic factors.

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PAPER 4: INTERMETAL OXYGEN, SULFUR, AND SELENIUM ATOM TRANSFER REACTIONS INVOLVING TITANIUM PORPHYRIN COMPLEXES.

INTRODUCTION

Metalloporphyrin complexes are extremely versatile reagents for a wide variety of inner sphere redox processes involving intermetal halogen-,[1] oxygen-,[2] and nitrogen-atom transfers.[3,4] Of particular interest is the fact that the number of redox equivalents exchanged during an atom transfer process can be varied by changing the nature of the reducing agent.[3,5] In addition, inner sphere redox reactions can involve what Holm has termed complete vs. incomplete atom transfer.[6] We have utilized metalloporphyrin complexes to address fundamental issues which dictate the redox changes and the course of the reaction. For the (POR)Cr=O/(POR)Cr^{II} and (POR)Cr=O/[(POR)$Cr^{III}]^+$ redox couples,[7] we recently suggested that electronic factors dictate the nature of the reaction.[2b] When Cr(II) is the reductant, incomplete oxygen atom transfer occurs to yield a μ-oxo Cr(III) dimer.[8] However, when Cr(III) is the reductant, reversible oxygen atom transfer occurs between the two chromium porphyrin complexes. Correspondingly, Ti(III) porphyrins also undergo reversible oxygen atom transfer with oxotitanium(IV) porphyrins.[2a] From these observations and earlier work, metalloporphyrin chemistry is clearly relevant to the fundamental issue of dioxygen activation by metal ions. For example, the reaction of ferrous porphyrins with O_2 produces a μ-oxo complex, (PHx)Fe-O-Fe(POR).[9] This reaction is thought to proceed through a μ-peroxo species, (POR)Fe-O-O-Fe(POR) which homolytically cleaves to form a ferryl intermediate (Fe=O).[10] In addition, treatment of chromous porphyrin with oxygen yields (POR)Cr=O or (POR)Cr-O-Cr(POR) under conditions of excess or limiting O_2, respectively.[8b] However, the reaction of the titanium porphyrin complex, (POR)Ti-Cl, with oxygen affords an η^2-O_2 product, (POR)Ti(η^2-O_2).[11]

These examples indicate that the role of transition metals in the activation of oxygen is complicated by the many different reaction pathways that are possible. As a continuation of our atom transfer chemistry and our interest in oxygen activation, we have examined the intermetal oxygen atom transfer capabilities of titanium peroxo complexes and the related sulfur and selenium analogs with (TTP)Ti(η^2-R-C≡C-R).[12]

RESULTS AND DISCUSSION

When (OEP)Ti(O_2)[13] (7.78 mM) is treated with (TTP)Ti(η^2-Ph-C≡C-Ph) (4.53 mM) in C_6D_6 under anaerobic conditions, diagnostic changes in the ^{1}H NMR spectrum of the reaction sample are observed. For example, the meso-proton resonance (10.44 ppm) for the peroxo complex diminishes, the β-pyrrolic proton signal (9.06 ppm) for the acetylene complex completely disappears, and signals for free diphenyl acetylene appear. A new meso-proton signal (10.54 ppm) and a new β-pyrrolic proton resonance (9.24 ppm) emerge which signify the formation of the terminal oxo complexes, (OEP)Ti=O and (TTP)Ti=O,[14] respectively (eq 1).

$$\text{(TTP)Ti(PhC}{\equiv}\text{CPh)} + \text{(OEP)Ti}(\eta^2\text{-}O_2) \rightarrow \text{(TTP)Ti=O} + \text{(OEP)Ti=O} + \text{PhC}{\equiv}\text{CPh} \tag{1}$$

The timescale for the reaction to reach completion at ambient temperatures is on the order of minutes. Integration of the NMR signals indicate that the products form quantitatively in a 1:1 ratio and that mass balance is maintained. Thus, formation of the oxo complexes cannot be due to a reaction with adventitious dioxygen or water. Equation 1 is analogous to the product forming step in a mechanism proposed by Marchon and Guilard to explain the formation of (TPP)Ti=O from the photolysis of (TPP)Ti(O_2) as shown in eq 2-3.[15] The postulated

$$2\ (TmTP)Ti(\eta^2\text{-}O_2) \xrightarrow{h\nu} [\ (TmTP)Ti(II)\ ] + O_2 \tag{2}$$

$$(TmTP)Ti(\eta^2\text{-}O_2) + [(TmTP)Ti(II)] \rightarrow 2\ (TmTP)Ti{=}O \tag{3}$$

(TTP)Ti(II) intermediate was not detected, but implicated by ^{18}O labelling studies. Eq 1 formally involves a two-electron reduction and O-O bond cleaveage of bound O_2^{2-} to 2 O^{2-} by titanium(II) mediated by oxygen atom transfer. It is clear that this type of reaction must be given serious consideration in processes which involve metal ion activation of dioxygen.

In a similar manner, the persulfido and perselenido complexes, (OEP)Ti(S_2)[16] and (OEP)Ti(Se_2)[16] undergo related atom transfer processes (eq 4-5). In these examples, an η^2-3-

$$\text{(TTP)Ti(PhC}\equiv\text{CPh) + (OEP)Ti(}\eta^2\text{-S}_2\text{)} \rightarrow \text{(TTP)Ti=S + (OEP)Ti=S + PhC}\equiv\text{CPh} \qquad 4$$

$$\text{(TTP)Ti(PhC}\equiv\text{CPh) + (OEP)Ti(}\eta^2\text{-Se}_2\text{)} \rightarrow \text{(TTP)Ti=Se + (OEP)Ti=Se + PhC}\equiv\text{CPh} \qquad 5$$

hexyne complex[17] was used as the reductant. ^{1}H NMR spectroscopy was a convenient method for monitoring these reactions also. For example, in eq 5 new signals which are diagnostic for (TTP)Ti=Se[17] (9.30 ppm, β-pyrrolic H) and (OEP)Ti=Se[17] (10.64 ppm, meso-H) are observed with an integrated intensity ratio of 1:1. Eq 4 and 5 represent rare examples of intermetal sulfur or selenium atom transfer reactions. Other known intermetal sulfur or selenium transfer reactions involve the use of Cp_2TiS_5 and Cp_2TiSe_5 as transfer reagents. In general these typically deliver S_2 or Se_2 fragments as shown in reactions 6-8.[18,16] The exception is shown in reaction 9 in which a single selenium atom has been transferred from Cp_2TiSe_5 to a vanadium(II) complex.[19]

$$[Ir(dppe)_2]Cl \; + \; Cp_2TiS_5 \; \rightarrow \; [Ir(dppe)_2S_2]Cl \qquad 6$$

$$[Ir(dppe)_2]Cl \; + \; Cp_2TiSe_5 \; \rightarrow \; [Ir(dppe)_2Se_2]Cl \qquad 7$$

$$(TTP)TiF \ + \ Cp_2TiS_5 \ \rightarrow (TTP)Ti(S_2) \qquad 8$$

$$(OEP)V(THF)_2 \ + \ Cp_2TiSe_5 \ \rightarrow (OEP)V{=}Se \qquad 9$$

Activation of molecular oxygen is a multi-step process involving the transfer of several electrons and cleavage of the O-O bond. No single metal species is capable of accomplishing these tasks by itself. Due to the intricacies involved, detailed mechanisms for the activation of oxygen by transition metal complexes are generally not known. Furthermore, elaborate schemes are often needed to account for the observed behavior. For example, in the outer sphere reduction of (TPP)Ti(η^2-O_2), a series of one-electron steps have been proposed to explain the observed cyclic voltammetry results.[20] The first reduction involves the porphyrin ligand, forming an anion radical complex, Ti^{IV}(η^2-O_2)($TPP^{\bullet -}$). Presumably, protonation of the η^2-O_2 ligand weakens the Ti-peroxo bonding and allows internal electron transfer to occur, leading to (TPP)Ti^{III}(OOH). Subsequent addition of an electron to the hydroperoxo complex is relatively easier than the first reduction of the initial η^2-O_2 complex. The overall reaction involves an ECEC mechanism in the two-electron reduction of the peroxo ligand. In reaction 1, it is likely that Ti(II) complex can serve as the Lewis acid which activates the peroxo ligand of (OEP)Ti(η^2-O_2) towards reduction. Furthermore, the ability of Ti(II) to supply both electrons in the reduction step is also crucial. Thus, reactions such as that represented in eq 1 are essential in understanding fundamental steps involved in the activation of O_2.

Frequently, coordinated superoxide or peroxide intermediates are implicated in the reduction of dioxygen. The lifetimes of these intermediates can depend dramatically on the metal and ancillary ligands. Porphyrins have an especially strong stabilizing effect on such intermediates.[21] In the work discussed here, the utility of porphyrin ligands in atom transfer chemistry is clearly apparent from an inorganic functional group aspect. The porphyrin is an innocent ligand in these examples. It essentially serves as a spectator group and allows only reaction at the axial ligand to take place. In this manner, it should be possible to examine in detail, one step in the reduction of O_2 to O^{2-}. Few systems are known in which such a study can be undertaken. Moreover, reactions 1, 4 and 5 should enable a systematic comparison of the relative intrinsic tendencies for intermetal oxygen, sulfur, or selenium atom transfer to occur in an isoelectronic and isostructural series of complexes without complications arising from unwanted side reactions or structrual reorganization. To date, the only other intra-group comparison of atom transfer capability has been done on the halogens. Further aspects of these novel intermetal group 16 atom processes are under study.

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General Summary

A number of new results have evolved from this study. First, we have shown that it is possible to synthesize η^2-alkyne titanium(II) porphyrin complexes. These complexes undergo a variety of reactions. The bound alkyne can be displaced by neutral donor ligands such as 4-picoline. The titanium(II) metal center is found to be a good reductant as exemplified by the reductions of a diazomethane and phosphine chalcogenides. Secondly, complete inter-metal oxygen atom transfer is possible and facile for titanium porphyrins. The reversible processes reported here are the first such examples involving titanium porphyrins. Both one- and zero-electrons can be transferred in this process. Finally, titanium(II) complexes have been found to be an excellent reductant of axial ligands on other metal centers specifically (TTP)Ti(E_2), where E = O, S, Se.

Further work needs to be done in several areas. Mechanistic studies of the oxo/chloro and oxo/dichloride systems need to be continued to elucidate the mechanism. Also kinetic studies of the perchalcogenide reduction with Ti(II) need to be carried out.

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