Titanium(II) Porphyrin Complexes: Versatile One- and Two-Electron Reducing Agents. Reduction of Organic Chlorides, Epoxides, and Sulfoxides

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Treatment of the well-defined complexes (TTP)Ti(η^2-EtC≡CEt) or *trans*-(TTP)Ti(THF)$_2$ with vicinal dichloroalkanes or dichloroalkenes results in the production of alkenes or alkynes and 2 equiv of (TTP)TiCl. This net two-electron redox reaction arises from two formal one-electron reduction processes mediated by chlorine atom transfer. Oxygen atom transfer occurs when the Ti(II) porphyrins are treated with several different sulfoxides or epoxides, resulting in two-electron redox products, (TTP)Ti═O, the sulfide or alkene, and EtC≡CEt or THF. The electronic properties of the substituents on the sulfoxides or epoxides correlate with the yield and rate of the deoxygenation reactions.

Introduction

Numerous studies have demonstrated the versatility of metalloporphyrin complexes as reagents for a wide range of inner-sphere redox processes, including halogen and oxygen atom-transfer reactions.[2] We have been investigating the reactivity of Ti(II) porphyrin complexes since first reporting their synthesis and characterization in 1991.[3] Our findings indicate that Ti(II) tetratolylporphyrinato (TTP) complexes function as good oxygen, sulfur, or selenium atom acceptors in inner-sphere electron-transfer reactions.,[4,5] These atom-transfer reactions involving Ti(II) porphyrins were centered around reactions between two metal complexes—intermetal atom-transfer processes.

Low-valent titanium species have great utility in organic synthesis.[6] As part of our continuing program on early transition metal porphyrin chemistry, we recently examined the chlorine and oxygen atom-transfer reactions between some well-defined Ti(II) porphyrin complexes and nonmetal substrates such as organic halides, epoxides, and sulfoxides, in the hope that this effort would lead to useful methods for organic synthesis. In this report, we wish to present a detailed account of these reactions.

Experimental Section

General Considerations. Toluene, benzene-d_6, tetrahydrofuran, and hexanes for glovebox use were distilled from purple solutions of sodium benzophenone ketyl. Dry solvents were subsequently degassed on a vacuum line (10^{-5} Torr) with three successive freeze−pump−thaw cycles. Benzyl sulfoxide, 4-tolyl sulfoxide, 4-tolyl sulfone, and Ph$_3$CH were purchased from Aldrich and used without further purification. 1,2-Dichloroethane, *trans*-1,2-dichlorocyclohexane, *trans*-1,2-dichloroethylene, methyl sulfoxide, styrene oxide, and cyclohexene oxide were purchased from Aldrich and vacuum distilled for glovebox use. The Ti(II) tetratolylporphyrinato (TTP) complexes (TTP)Ti(η^2-EtC≡CEt) and *trans*-(TTP)Ti(THF)$_2$ were prepared as described elsewhere.[7]

All manipulations were performed either in a Vacuum Atmosphere glovebox equipped with a Model HE-553-2 Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV−visible data were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. ^{1}H NMR spectra were recorded on a Varian 300-MHz spectrometer, with Ph$_3$CH used as an internal standard for quantitative analyses. GC−MS analyses were performed on a Finnigan TSQ 700 mass spectrometer coupled to a Varian GC 3400 chromatograph using a 30-m DB5 column.

Reaction of (TTP)Ti(η^2-EtC≡CEt) with 1,2-Dichloroethane. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(η^2-EtC≡CEt) (1.9 mg, 2.38×10^{-3} mmol) and Ph$_3$CH (1.55 mg, 6.34×10^{-3} mmol) was added ca. 0.5 μL (6.34×10^{-3} mmol) of 1,2-dichloroethane. The tube was sealed under nitrogen. After standing at ambient temperature for 1 h, the sample was monitored by ^{1}H NMR and the spectrum showed no reaction. Subsequently, it was heated at 80 °C for 6 h and monitored by ^{1}H NMR again. The spectrum indicated the formation of (TTP)TiCl (2.1×10^{-3} mmol, 88%), free EtC≡CEt (2.1×10^{-3} mmol, 88%), and ethylene (3.5×10^{-4} mmol in solution), with no (TTP)Ti(η^2-EtC≡CEt) left. The product ethylene was further confirmed by its molecular peak ($m/e = 28$) by GC−MS obtained from a headspace sample. The Ti(III) complex, (TTP)TiCl, was also identified by UV−vis in toluene (428 nm, Soret; 552 nm).

Reaction of (TTP)Ti(η^2-EtC≡CEt) with *trans*-1,2-Dichlorocyclohexane. This experiment was conducted in the same manner as above, using 1.1 mg (1.4×10^{-3} mmol) of (TTP)Ti(η^2-EtC≡CEt), 3.7 mg (1.5×10^{-2} mmol) of Ph$_3$CH, and 0.4 μL (3.0×10^{-3} mmol) of *trans*-1,2-dichlorocyclohexane. After being heated at 80 °C for 6 h, the sample was monitored by ^{1}H NMR, and the spectrum showed three products: cyclohexene (6.5×10^{-4} mmol, 93%), (TTP)TiCl (1.3×10^{-3} mmol, 93%), and free EtC≡CEt (1.3×10^{-3} mmol, 93%). The product

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(1) Camille and Henry Dreyfus Teacher−Scholar.

(2) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125 and references therein.

(3) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

(4) (a) Woo, L. K.; Hays, J. A. *Inorg. Chem.* ***1993***, *32*, 2228. (b) Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L.; Caron, C.; D'Souza F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.

(5) Hays, J. A.; Day, C. L.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1996**, *35*, 7601.

(6) (a) Lenoir, D. *Synthesis* **1989**, 883. (b) Dang, Y.; Geise, H. J. *J. Organomet. Chem.* **1991**, *405*, 1. (c) Pons, J. M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295. (d) Furstner, A.; Bogdanovic, B. *Angew. Chem.,Int. Ed. Engl.* **1996**, *35*, 2442.

(7) Wang, X.; Gray, S. D.; Chen, J.; Woo, L. K. *Inorg. Chem.*, in press.

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cyclohexene was further confirmed by its molecular peak (*m*/*e* = 80) using GC–MS.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with *trans*-1,2-Dichloroethylene. This experiment was conducted in the same manner as above, using 1.0 mg (1.2×10^{-3} mmol) of (TTP)Ti(η^2-EtC$\equiv$CEt), 2.5 mg (1.0×10^{-2} mmol) of Ph$_3$CH, and 0.3 μL (3.9×10^{-3} mmol) of *trans*-1,2-dichloroethylene. After being heated at 80 °C for 2 h, the sample was monitored by ^{1}H NMR and the spectrum showed three products: acetylene (2.2×10^{-4} mmol in solution), (TTP)TiCl (1.0×10^{-3} mmol, 83%), and free EtC$\equiv$CEt (1.1×10^{-3} mmol, 92%). The product acetylene was further confirmed by its molecular peak (*m*/*e* = 26) by GC–MS obtained from a headspace sample.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with 1,2-Dichloroethane. To an NMR tube containing a C$_6$D$_6$ suspension of *trans*-(TTP)Ti(THF)$_2$ (5.6 mg, 6.5×10^{-3} mmol) was added ca. 0.9 μL (1.1×10^{-2} mmol) of 1,2-dichloroethane. The tube was sealed under nitrogen. After being heated at 80 °C for 3 h, the sample was monitored by ^{1}H NMR and showed three products: ethylene, (TTP)TiCl, and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with *trans*-1,2-Dichlorocyclohexane. This experiment was conducted in the same manner as above, using 2.3 mg (2.7×10^{-3} mmol) of (TTP)Ti(THF)$_2$ and 0.5 μL (3.8×10^{-3} mmol) of *trans*-1,2-dichlorocyclohexane. After being heated at 80 °C for 2 h, the sample was monitored by ^{1}H NMR and the spectrum showed three products: cyclohexene, (TTP)TiCl, and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with *trans*-1,2-Dichloroethylene. This experiment was conducted in the same manner as above, using 2.8 mg (3.3×10^{-3} mmol) of (TTP)Ti(THF)$_2$ and 0.5 μL (6.5×10^{-3} mmol) of *trans*-1,2-dichloroethylene. After being heated at 80 °C for 2 h, the sample was monitored by ^{1}H NMR and the spectrum showed three products: HC$\equiv$CH, (TTP)TiCl and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with Styrene Oxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(η^2-EtC$\equiv$CEt) (1.0 mg, 1.25×10^{-3} mmol) and Ph$_3$CH (3.0 mg, 1.2×10^{-2} mmol) was added ca. 0.4 μL (3.5×10^{-3} mmol) of styrene oxide. The tube was sealed under nitrogen. After standing at ambient temperature for 30 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O (3.8×10^{-4} mmol), styrene (9.8×10^{-4} mmol), and free EtC$\equiv$CEt (1.2×10^{-3} mmol, 96%), with no (TTP)Ti(η^2-EtC$\equiv$CEt) left. In addition, a broad peak appeared at 2.5 ppm. As the reaction proceeded at ambient temperature, the quantities of styrene and (TTP)Ti=O kept growing to reach ca. 1.2×10^{-3} mmol (96%) after 9 h, whereas the peak at 2.5 ppm decreased to <5% intensity. The product styrene oxide was further confirmed by its molecular peak (*m*/*e* = 104) by GC–MS. Within experimental error, the reaction was quantitative.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with Cyclohexene Oxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(η^2-EtC$\equiv$CEt) (3.9 mg, 4.9×10^{-3} mmol) and Ph$_3$CH (2.6 mg, 1.1×10^{-2} mmol) was added ca. 1.5 μL (1.5×10^{-2} mmol) of cyclohexene oxide. The tube was sealed under nitrogen. After standing at ambient temperature for 1 h, the sample was monitored by ^{1}H NMR and the spectrum showed two products: cyclohexene (2.3×10^{-3} mmol, 47%) and free EtC$\equiv$CEt (4.9×10^{-3} mmol, 100%), with no (TTP)Ti(EtC$\equiv$CEt) left. In addition, a broad peak appeared at 2.5 ppm. No appreciable change in the ^{1}H NMR spectrum was observed as the sample stood at ambient temperature over a period of 7 h. Thus, it was heated at 80 °C and monitored by ^{1}H NMR every 24 h. The spectra showed the appearance of (TTP)Ti=O and that both it and cyclohexene were growing continuously over a period of 6 days to reach 3.0×10^{-3} (77%) and 2.9×10^{-3} mmol (60%), respectively. In the meantime, the peak at 2.5 ppm decreased by 88%. The product cyclohexene was further confirmed by its molecular peak (*m*/*e* = 82) by GC–MS.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with Styrene Oxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(THF)$_2$ (2.1 mg, 2.4×10^{-3} mmol) was added ca. 0.5 μL (4.4×10^{-3} mmol) of styrene oxide. The tube was sealed under nitrogen. After standing at ambient temperature for 20 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O, styrene, and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left. The ratio of (TTP)Ti=O to styrene was 1:1, as was expected.

Reaction of (TTP)Ti(THF)$_2$ with Cyclohexene Oxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(THF)$_2$ (1.9 mg, 2.2×10^{-3} mmol) and was added ca. 0.8 μL (7.9×10^{-3} mmol) of cyclohexene oxide. The tube was sealed under nitrogen. After standing at ambient temperature for 20 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O, cyclohexene, and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left. The ratio of (TTP)Ti=O to styrene was 1:1, as was expected.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with Methyl Sulfoxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of (TTP)Ti(η^2-EtC$\equiv$CEt) (2.4 mg, 3.0×10^{-3} mmol) and Ph$_3$CH (3.3 mg, 1.35×10^{-2} mmol) was added ca. 0.6 μL (8.5×10^{-3} mmol) of methyl sulfoxide. The tube was sealed under nitrogen. After standing at ambient temperature for 2 h, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O (4.7×10^{-4} mmol), methyl sulfide (1.7×10^{-3} mmol), and free EtC$\equiv$CEt (3.0×10^{-3} mmol), with no (TTP)Ti(EtC$\equiv$CEt) left. In addition, a broad peak appeared at 2.5 ppm. As the reaction proceeded at ambient temperature, the quantities of methyl sulfide and (TTP)Ti=O kept growing over a period of 49 h to reach ca. 1.9×10^{-3} mmol (79%), whereas the peak at 2.5 ppm decreased to <5%. The product methyl sulfide was further confirmed by its molecular peak (*m*/*e* = 62) by GC–MS.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with Benzyl Sulfoxide. The two reagents TTPTi(η^2-EtC$\equiv$CEt) (0.7 mg, 9.0×10^{-4} mmol) and benzyl sulfoxide (0.5 mg, 2.2×10^{-3} mmol) and the internal standard Ph$_3$CH (2.7 mg, 1.1×10^{-2}) were transferred into a 10-mL beaker. About 1 mL of C$_6$D$_6$ was added to the beaker. The mixture was agitated for 5 min and then transferred to a NMR tube and sealed under nitrogen. After standing at ambient temperature for 30 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O (8.3×10^{-5} mmol), benzyl sulfide (5.6×10^{-4} mmol), and free EtC$\equiv$CEt (9.0×10^{-4} mmol, 100%), with no (TTP)Ti(η^2-EtC$\equiv$CEt) left. In addition, a broad peak appeared at 2.5 ppm. As the reaction proceeded at ambient temperature, the quantities of benzyl sulfide and (TTP)Ti=O kept growing over a period of 57 h to reach ca. 9.0×10^{-4} mmol (100%), whereas the peak at 2.5 ppm disappeared. Within experimental error, the reaction was quantitative.

Reaction of (TTP)Ti(η^2-EtC$\equiv$CEt) with 4-Tolyl Sulfoxide. This experiment was conducted in the same manner as above, using 0.9 mg (1.1×10^{-3} mmol) of (TTP)Ti(η^2-EtC$\equiv$CEt), 2.2 mg (9.0×10^{-3} mmol) of Ph$_3$CH, and 0.5 mg (2.1×10^{-3} mmol) of 4-tolyl sulfoxide. After standing at ambient temperature for 25 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O (3.1×10^{-4} mmol), 4-tolyl sulfide (7.9×10^{-4} mmol), and free EtC$\equiv$CEt (1.1×10^{-3} mmol), with no (TTP)Ti(EtC$\equiv$CEt) left. In addition, a broad peak appeared at 2.5 ppm. As the reaction proceeded at ambient temperature, the quantities of 4-tolyl sulfide and (TTP)Ti=O kept growing over a period of 22 h to reach 1.1×10^{-3} mmol (100%), whereas the peak at 2.5 ppm disappeared. The product 4-tolyl sulfide was further confirmed by its molecular peak (*m*/*e* = 214) by GC–MS. Within experimental error, the reaction was quantitative.

Reaction of *trans*-(TTP)Ti(THF)$_2$ with Methyl Sulfoxide. To an NMR tube containing a C$_6$D$_6$ solution (0.65 mL) of *trans*-(TTP)Ti(THF)$_2$ (1.1 mg, 1.2×10^{-3} mmol) and was added ca. 0.4 μL (5.6×10^{-3} mmol) of methyl sulfoxide. The tube was sealed under nitrogen. After standing at ambient temperature for 20 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O, methyl sulfide, and free THF, with no *trans*-(TTP)Ti(THF)$_2$ left. In addition, a broad peak appeared at 2.5 ppm. As the reaction proceeded to 36 h, this broad peak disappeared. The final ratio of (TTP)Ti=O to methyl sulfide was 10:8. The slightly lower than expected observed amount of methyl sulfide is presumably due to its volatility.

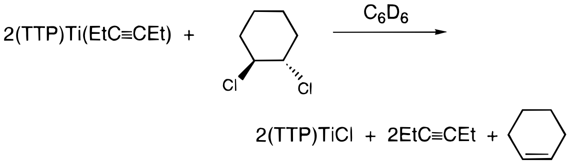
Reaction of *trans*-(TTP)Ti(THF)$_2$ with Benzyl Sulfoxide. The two reagents, *trans*-(TTP)Ti(THF)$_2$ (2.0 mg, 2.3×10^{-3} mmol) and benzyl sulfoxide (1.0 mg, 4.3×10^{-3} mmol), were transferred into a 10-mL beaker. About 1 mL of C_6D_6 was added to the beaker. The mixture was agitated for 5 min, and then transferred to an NMR tube and sealed under nitrogen. After standing at ambient temperature for 20 min, the sample was monitored by ^{1}H NMR and the spectrum showed three products: (TTP)Ti=O, benzyl sulfide, and free EtC≡CEt, with no *trans*-(TTP)Ti(THF)$_2$ left. The final ratio of (TTP)Ti=O to benzyl sulfide was 1:1 as expected.

Results

Reactions of Ti(II) Porphyrins with Vicinal Dichloroalkanes and Dichloroalkenes. In the process of characterizing (TTP)Ti(η^2-EtC≡CEt) and *trans*-(TTP)Ti(THF)$_2$, we noticed that these Ti(II) porphyrins react with chlorinated NMR solvents such as $CDCl_3$ and CD_2Cl_2, yielding the known Ti(III) complex (TTP)TiCl. To unravel the reactivity of Ti(II) porphyrins with organic halides, the diamagnetic (TTP)Ti(η^2-EtC≡CEt) and a few vicinal dichloroalkanes and dichloroalkenes were selected as reactants, and exploratory reactions were conducted in C_6D_6 using Ph_3CH as internal reference to quantify product formation.

When (TTP)Ti(η^2-EtC≡CEt) was treated with 1,2-dichloroethane in slight excess (ca. 2.7-fold), no appreciable reaction was detected by ^{1}H NMR at ambient temperature up to 1 h. At 80 °C for 6 h, the reaction was complete as monitored by ^{1}H NMR. The spectrum clearly indicated the formation of ethylene ($\delta = 5.25$ ppm in C_6D_6), (TTP)TiCl,[8] and free EtC≡CEt (eq 1). Moreover, the identities of (TTP)TiCl and ethylene were further confirmed by UV−vis and GC−MS analyses, respectively. When treated with (TTP)Ti(η^2-EtC≡CEt) at 80 °C, *trans*-1,2-dichlorocyclohexane afforded analogous products: cyclohexene, (TTP)TiCl, and free EtC≡CEt (eq 2). This newly discovered reactivity was also extended to 1,2-*trans*-dichloroethylene, a vicinal dichloroalkene, whose reaction with (TTP)Ti(η^2-EtC≡CEt) at 80 °C gave acetylene, (TTP)TiCl, and free EtC≡CEt (eq 3). The NMR yields of the aforementioned reactions were determined by comparing the product integrals with that of the internal reference. Yields were relatively high, ranging from 88% to 94%.

$$2(TTP)Ti(EtC{\equiv}CEt) + ClCH_2CH_2Cl \xrightarrow{C_6D_6} 2(TTP)TiCl + 2EtC{\equiv}CEt + H_2C{=}CH_2 \qquad (1)$$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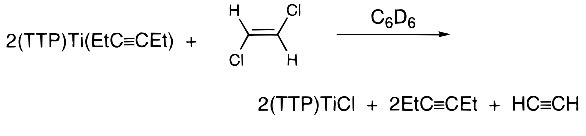
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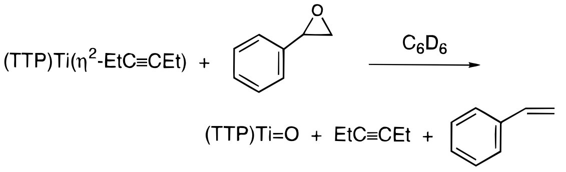
Another well-defined Ti(II) porphyrin complex, *trans*-(TTP)Ti(THF)$_2$, demonstrated analogous reactivity with organic vicinal dichlorides.

Reactions of Ti(II) Porphyrins with Epoxides and Sulfoxides. When (TTP)Ti(η^2-EtC≡CEt) was treated with styrene oxide in C_6D_6 solution at ambient temperature, facile reactions were recorded by ^{1}H NMR after 20 min. The release of free EtC≡CEt was quantitative, some (TTP)Ti=O[9] and styrene were produced, and a new species with a broad ^{1}H NMR peak at 2.5 ppm was observed. Quantitative yields for styrene and (TTP)Ti=O were achieved after 9 h, while the signal for the intermediate species disappeared. Similarly, the reaction of (TTP)Ti(η^2-EtC≡CEt) with cyclohexene oxide at ambient temperature quantitatively released free EtC≡CEt, produced cyclohexene in 47% yield, and gave a new species indicated by a 2.5 ppm peak in the ^{1}H NMR spectrum. However, no (TTP)Ti=O was afforded until the reaction was heated to 80 °C. At this elevated temperature, both (TTP)Ti=O and cyclohexene slowly grew in quantity over the course of 6 days to reach a maximum yield of 60%, while the ^{1}H NMR peak at 2.5 ppm associated with the intermediate species decreased by 88%. These oxygen-transfer reactions are illustrated in eqs 4 and 5.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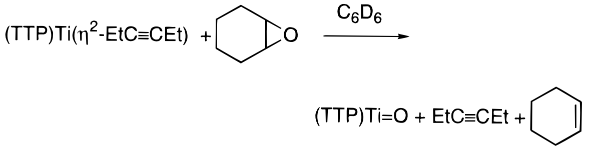
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Treatment of (TTP)Ti(η^2-EtC≡CEt) with methyl, benzyl, and 4-tolyl sulfoxides at ambient temperature also resulted in oxygen-transfer reactions, affording (TTP)Ti=O and the corresponding sulfides (eqs 6−8). The reaction with methyl sulfoxide afforded dimethyl sulfide in a yield of 64% over a period of 49 h, and those with benzyl and 4-tolyl sulfoxides were quantitative and complete after 57 and 22 h, respectively. Furthermore, an intermediate with an ^{1}H NMR signal at 2.5 ppm was observed during the course of all three reactions.

The Ti(II) porphyrin complex *trans*-(TTP)Ti(THF)$_2$ also undergoes oxygen atom-transfer reactions with epoxides or sulfoxides, affording (TTP)Ti=O, THF, alkenes, or sulfides. These reactions are qualitatively faster than those involving (TTP)Ti(η^2-EtC≡CEt). In general, an intermediate with an ^{1}H NMR signal at 2.5 ppm was also observed with reactions involving *trans*-(TTP)Ti(THF)$_2$.

Discussion

Dechlorination of *vic*-Dichlorides through Ti(II) Porphyrins. Dechlorination of *vic*-dichlorides to alkenes can be useful in organic synthesis. Although a variety

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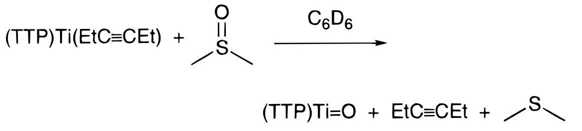
[8] Berrreau, L. M.; Hays, J. A.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105.

[9] Fournari, C.; Guilard, R.; Fontesse, M.; Latour, J.-M.; Marchon, J.-C. *J. Organomet. Chem.* **1976**, *110*, 205.



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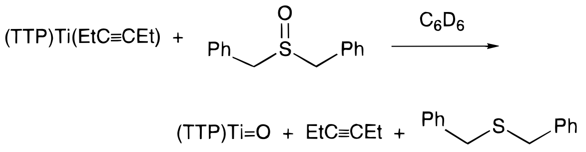

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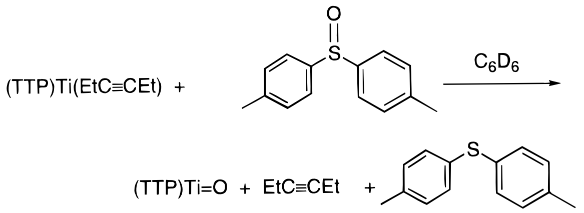

(8)

of methods have been developed to afford such transformations,[10] examples involving the use of well-defined transition metal complexes are rare. For instance, a system comprising $TiCl_3$- or $TiCl_4/LiAlH_4$ in tetrahydrofuran was utilized to convert *trans*-1,2-dichlorocyclohexane to cyclohexene in 72% yield, but the identity of the active Ti reagent was unclear.[11] Chromium(II) reagents are capable of reducing 1,2-dihalides to olefins, but 1,2-dichlorides are reportedly inert or very slow toward this process.[12] In addition, Zn reagents will also dechlorinate 1,2-dihalides, albeit in modest yields.[13]

When treated with *vic*-dichloroalkanes in homogeneous solution at elevated temperature (80 °C), the well-defined Ti(II) porphyrin complexes such as (TTP)Ti(η^2-EtC≡CEt) generated alkenes and (TTP)TiCl in good yield. These are chlorine-transfer reactions in which every product can be conclusively identified. It is interesting to note that these reactions are single-electron oxidations rather than two-electron oxidations that would give six-coordinate Ti(IV) porphyrin alkyl chlorides. Two-electron processes are characteristic of the oxidation chemistry of some cyclopentadinenyl-based Ti(II) complexes,[14] as manifested by the reaction of $Cp_2Ti(PMe_3)_2$ with MeI, which yields $Cp_2Ti(Me)(I)$.,[15,16] However, six-coordinate Ti(IV) porphyrin complexes (ionic radius 0.605 Å) have trans geometries except in cases with bidentate ligands.[17] The rigid macrocyclic porphyrin ligand may prevent Ti(II) porphyrins from undergoing a *cis*-constrained oxidative addition reaction to give six-coordinate Ti(IV) complexes.

Scheme 1

(i) homolytic β-cleavage

$$\bullet CH_2CH_2Cl \longrightarrow H_2C{=}CH_2 + \bullet Cl$$

(ii) reduction by (TTP)Ti(η^2-EtC≡CEt)

$$(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) + \bullet CH_2CH_2Cl \xrightarrow{-EtC\equiv CEt} (TTP)TiCl + H_2C{=}CH_2$$

The initial step in the reactions of *vic*-dichloroalkanes with (TTP)Ti(η^2-EtC≡CEt) appears to be the reduction of the dichlorides, as represented by eq 9. This step is

$$(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) + ClCH_2CH_2Cl \xrightarrow{-EtC\equiv CEt} (TTP)TiCl + \bullet CH_2CH_2Cl \qquad (9)$$

presumably inner- sphere in nature. Two possibilities can explain the fate of the radical $^\bullet CH_2CH_2Cl$. They are illustrated in Scheme 1.

Of the two options, pathway ii is more likely because it is thermodynamically favored with formation of a strong Ti−Cl bond. Moreover, there is a precedent in which a similar pathway was demonstrated for the reaction between $ClCH_2CH_2Cl$ and a Ni(I) complex that yielded ethylene and a Ni(II) species.[18] For the reaction of (TTP)Ti(η^2-EtC≡CEt) with *trans*-1,2-dichloroethylene that produces (TTP)TiCl and acetylene, we propose a mechanism analogous to that for 1,2-dichloroethane.

This mechanism appears to be in contrast to the E2 pathway (halonium ion abstraction) proposed by Savéant, Schäfer, and co-workers for the electrochemical reduction of vicinal dibromides mediated by iron and cobalt porphyrin complexes.[19] However, in Savéant's system, electrochemically generated $Fe(I)^-$ and $Co(I)^-$ complexes serve as two-electron reductants that form inert Fe(III) and Co(III) halide complexes on halonium ion transfer. While a two-electron process with our Ti(II) complex is possible (*vida infra*), this would produce a diamagnetic Ti(IV) product that we do not observe.

Deoxygenation of Epoxides and Sulfoxides through Ti(II) Porphyrins. Both deoxygenation of epoxide to alkene[20] and sulfoxide to sulfide[21] are useful organic transformations. For the deoxygenating reagents derived from low-valent transition metal compounds, the exact nature of the active reductant is poorly understood and the reaction is usually conducted under heterogeneous conditions, giving intractable metal oxo species. Recently, Chan and co-workers reported the deoxygen-

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[10] Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers Inc.: New York, 1989; p 133.

[11] Olah, G. A.; Prakash, G. K. S. *Synthesis* **1976**, 607.

[12] Kray, W. C., Jr.; Castro, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4603.

[13] (a) Butenandt, A.; Schmidt-Thomé, J. *Ber. Otsch. Ges.* **1936**, *69*, 882. (b) Bohlmann, F.; Kieslich, K. *Chem. Ber.* **1954**, *87*, 1363. (c) McCutcheon, J. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 526. (d) Smith, C. W.; Norton, D. G. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 348. (e) Allred, E. L.; Beck, B. R.; Voorhees, K. J. *J. Org. Chem.* **1974**, *39*, 1426.

[14] Cloke, F. G. N. Titanium Complexes in Oxidation States +2 and +3”; In *Comprehensive Organometallic Chemistry II*; Lappert, M. F., Ed.; Elsevier Science Inc.: New York, 1995; Vol. 4, p 221.

[15] Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewald, U. *J. Organomet. Chem.* **1987**, *320*, 37.

[16] Treatment of (TTP)Ti(EtC≡CEt) with MeI in C_6D_6 at 80 °C resulted in what appears to be two paramagnetic species with broad ^1H NMR peaks at 2.36 and 2.48 ppm, respectively. No Ti(IV) compounds were observed. In comparison with the ^1H NMR spectrum of (TTP)TiCl, we tentatively assign these two products as Ti(III) compounds (TTP)TiI and (TTP)TiMe. Further studies of this reaction will be undertaken.

[17] Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137.

[18] Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 4231.

[19] (a) Lexa, D.; Savéant, J.-M.; Schäfer, H. J.; Su, K.-B.; Vering, B.; Wang, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 6162. (b) Lexa, D.; Savéant, J.-M.; Su, K.-B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464.

[20] Murai, S.; Murai, T.; Kato, S. Reduction of Epoxides. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Inc.; New York, 1991; Vol. 8, p 871.

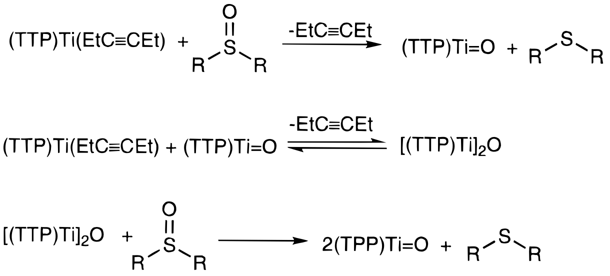
[21] (a) Madesclaire, M. *Tetrahedron* **1988**, *44*, 6537. (b) Kukushkin, V. Y. *Russ. Chem. Rev.* **1990**, *59*, 844.

ation of sulfoxides by the well-defined $Cp_2Ti(CO)_2$ to give sulfides. However, the titanium oxo products were uncharacterized, with partial loss of Cp.[22] Other examples of oxygen atom abstraction from sulfoxides are reported in a review by Kukushkin.[23] Bergman has shown that photolysis of $Cp_2TaCH_3(\eta^2\text{-}CH_2{=}CH_2)$ generates a transient species that behaves as Cp_2TaCH_3 and that efficiently abstracts heteroatoms from epoxides, thiiranes, and aziridines.[24] In this system, the metal product is $Cp_2Ta({=}X)(CH_3)$, where X = O, S, NR. Mayer has also shown that Mo(II) and W(II) complexes are also capable of abstracting oxygen or sulfur from epoxides and thiiranes.[25] To our knowledge, no reactions of epoxides with well-defined Ti(II) complexes have been described in the literature.

Because of the extreme oxophilicity of the Ti(II) center, upon exposure to oxygen, $TTPTi^{(II)}$-based complexes rapidly convert to the fully characterized (TTP)Ti=O. Thus, these Ti(II) porphyrins may serve as efficient deoxygenating agents. The reaction of $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ with styrene oxide was quantitative after 9 h at ambient temperature, yielding styrene and (TTP)Ti=O. In contrast, the reaction between $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ and cyclohexene oxide required higher temperature and was incomplete even after 6 days. We attribute the significant differences in reaction rates and yields to the electronic effect induced by the α-carbon substituents of the epoxide substrate. With an electron-withdrawing phenyl group,[26] styrene oxide is more susceptible to reduction than is cyclohexene oxide, in which the α-carbon substituents are methylenes. This observation, based on electronic effects, was corroborated by the reactions of $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ with various sulfoxides ($R_2S{=}O$), where R = Me, benzyl, and 4-totyl, which generate the corresponding sulfides and (TTP)Ti=O. As the electronic withdrawing effect of R increases in the order of Me, benzyl, and 4-tolyl, the deoxygenation reaction of $R_2S{=}O$ with $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ becomes faster and gives higher yields.

In all reactions of $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ with the epoxides or sulfoxides, consumption of $(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt)$ was fast and complete in less than 1 h, accompanied by formation of (TTP)Ti=O, the alkene or sulfide, and a paramagnetic intermediate. This intermediate shows the same resonance in the ^1H NMR spectra (δ = 2.5 ppm) in all reactions. Hence, it is unlikely that this intermediate is an adduct of the $(TTP)Ti^{(II)}$ fragment with various epoxides or sulfoxides. In addition, after initial formation of this intermediate, its slow decay correlated with the growth of (TTP)Ti=O and additional alkene or sulfide. On the basis of these experimental observations, we suggest that this intermediate is the known Ti(III) μ-oxo complex $[(TTP)Ti]_2O$. This complex has been synthesized independently from a reaction between (TTP)Ti=O and $(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh)$.[5] Moreover, we propose a mechanism for these oxygen-transfer reactions, as represented by Scheme 2. The first two steps are facile, but the third step involves oxidizing a Ti(III) complex and is slow. The reactivity of $[(TTP)Ti]_2O$ with oxygen atom donors is currently under investigation.

Scheme 2



Attempts to reduce sulfones to sulfoxides by Ti(II) porphyrins at ambient or elevated temperature were unsuccessful, resulting in either no reaction or decomposition of the Ti(II) starting materials.

Concluding Remarks

A series of new reactions of Ti(II) porphyrin complexes has been demonstrated. Of particular interest is the observation that when treated with organic electrophiles, $(TTP)Ti^{(II)}$-based complexes may undergo both one- and two-electron processes depending on the substrate. Ti(II) reductions with vicinal dichloroalkanes or dichloroalkenes are tandem single-electron oxidation processes mediated by chlorine atom transfer, affording (TTP)TiCl and alkenes or alkynes. We believe that this novel reactivity for Ti(II) complexes is enforced by the porphyrin ligand geometry. In addition, reactions of $(TTP)Ti^{(II)}$ complexes with epoxides or sulfoxides are two-electron processes mediated by oxygen atom transfer. These deoxygenation reactions lead to (TTP)Ti=O and alkenes or sulfides. The electronic effects of the substituents account for the difference in the yield and rate of these reactions. The extent of these reactions is consistent with the nature of both the reactants and products. The scope and mechanistic details of these reactions are being studied further.

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[22] Chen, T. L.; Shaver, A.; Chan, T. H. *J. Organomet. Chem.* **1989**, *367*, C5.

[23] Kukushkin, V. Y. *Coord. Chem. Rev.* **1995**, *139*, 375.

[24] (a) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7953. (b) Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 133.

[25] Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402.

[26] March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons, Inc.: New York, 1992; p 15.