Group 4 metalloporphyrin diolato complexes and catalytic application of metalloporphyrins and related transition metal complexes

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LIST OF ABBREVIATIONS

Ar^{iPr}	2,6-diisopropylphenyl
av	average
^{t}Bu	tertiary butyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
EDA	ethyl diazoacetate
eq	equation
Et	ethyl
GC	gas chromatography
GC-MS	gas chromatography coupled to mass spectrometry
IR	infrared
Me	methyl
mg	milligram
MHz	megahertz
mL	milliliter
mmol	millimole
mol	mole
MS (CI)	mass spectrometry by chemical impact
MS (EI)	mass spectrometry by electron impact
nm	nanometer
NMR	nuclear magnetic resonance
OAc	Acetate anion, $CH_3C(O)O^-$
Ph	phenyl
Por	generic porphyrin dianion

ppm	parts per million
^{i}Pr	isopropyl
py	pyridine
THF	tetrahydrofuran
TMP	*meso*-tetramesitylporphyrinato dianion
TMS	trimethylsilyl
tmtaa	dibenzotetramethyltetraaza[14]annulene
tolyl	*p*-CH_3-C_6H_4
TPP	*meso*-tetraphenylporphyrinato dianion
TTP	*meso*-tetratolylporphyrinato dianion
UV-vis	ultraviolet-visible

ABSTRACT

Group 4 metalloporphyrin diolato complexes and catalytic application of metalloporphyrins and related transition metal complexes

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In this work, the first examples of group 4 metalloporphyrin 1,2-diolato complexes were synthesized through a number of strategies. In general, treatment of imido metalloporphyrin complexes, (TTP)M=NR, (M = Ti, Zr, Hf), with vicinal diols led to the formation of a series of diolato complexes. Alternatively, the chelating pinacolate complexes could be prepared by metathesis of (TTP)MCl_2 (M = Ti, Hf) with disodium pinacolate. These complexes were found to undergo C-C cleavage reactions to produce organic carbonyl compounds.

For titanium porphyrins, treatment of a titanium(II) alkyne adduct, (TTP)Ti(η^2-PhC≡CPh), with aromatic aldehydes or aryl ketones resulted in reductive coupling of the carbonyl groups to produce the corresponding diolato complexes. Aliphatic aldehydes or ketones were not reactive towards (TTP)Ti(η^2-PhC≡CPh). However, these carbonyl compounds could be incorporated into a diolato complex on reaction with a reactive precursor, (TTP)Ti[$O(Ph)_2C(Ph)_2O$] to provide unsymmetrical diolato complexes via cross

coupling reactions. In addition, an enediolato complex (TTP)Ti(OCPhCPhO) was obtained from the reaction of (TTP)Ti(η^2-PhC≡CPh) with benzoin.

Titanium porphyrin diolato complexes were found to be intermediates in the (TTP)Ti=O-catalyzed cleavage reactions of vicinal diols, in which atmospheric oxygen was the oxidant. Furthermore, (TTP)Ti=O was capable of catalyzing the oxidation of benzyl alcohol and α-hydroxy ketones to benzaldehyde and α-diketones, respectively. Other high valent metalloporphyrin complexes also can catalyze the oxidative diol cleavage and the benzyl alcohol oxidation reactions with dioxygen.

A comparison of Ti(IV) and Sn(IV) porphyrin chemistry was undertaken. While chelated diolato complexes were invariably obtained for titanium porphyrins on treatment with 1,2-diols, the reaction of vicinal diols with tin porphyrins gave a number of products, including mono-, bis-alkoxo, and chelating diolato complexes, depending on the identity of diols and the stoichiometry employed. It was also found that tin porphyrin complexes promoted the oxidative cleavage of vicinal diols and the oxidation of α-ketols to α-diketones with dioxygen.

In extending the chemistry of metalloporphyrins and analogous complexes, a series of chiral tetraaza macrocyclic ligands and metal complexes were designed and synthesized. Examination of iron(II) complexes showed that they were efficient catalysts for the cyclopropanation of styrene by diazo reagents. Good yields and high diastereoselectivity were obtained with modest enantioselectivity. A rationalization of the stereoselectivity was presented on the basis of structural factors in a carbene intermediate.

GENERAL INTRODUCTION

Dissertation organization

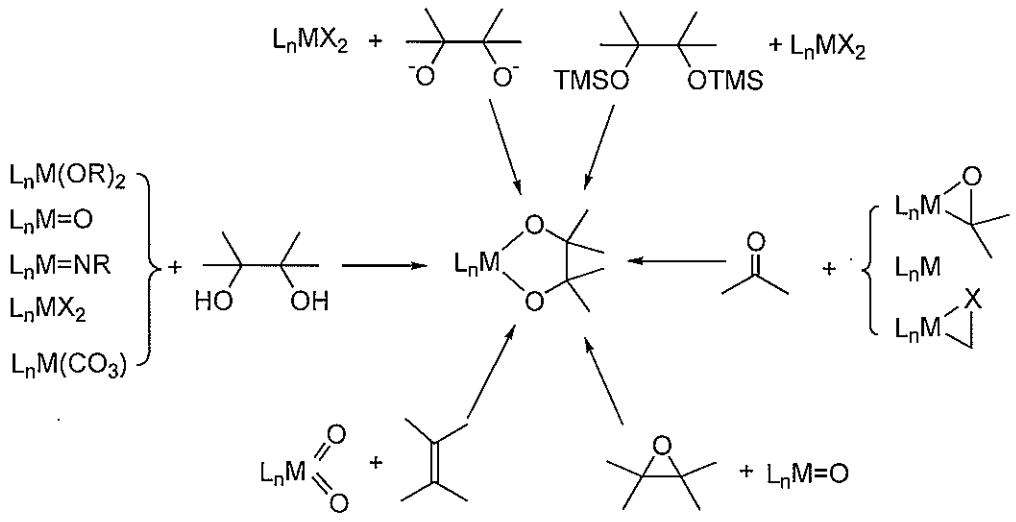
This dissertation starts with a general introduction consisting mainly of a literature review of transition metal diolato complexes. Chapters 1-7 are individual papers that have been published, submitted for publication, or are being prepared for submission. General conclusions follow the last chapter. Most of the work was performed by the author with two exceptions: Drs. Eric Rose and Bruno Andrioletti provided a chiral iron porphyrin used in Chapter 5, and Dr. Aziz Tekin carried out TLC separation in Chapter 7. The work was supported by a variety of funding agencies, including National Science Foundation, Petroleum Research Fund, and Research Corporation. Part of the work (Chapter 7) was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 2117 to this thesis.

Transition metal diolato complexes

Transition metal complexes containing alkoxide or aryloxide ligands have been well documented due to their structural diversity, reactivity, and relevance in biological and catalytic applications.[1] One of the subclasses, chelating bis(alkoxo) metal complexes, is relatively less studied, despite its versatile reactivity and involvement in several important organic transformations, such as the pinacol couping, the McMurry reaction, and dihydroxylation of olefins. Herein a mini review on metal diolato complexes is presented,

focusing on mononuclear transition metal complexes containing chelating 1,2-diolato ligands.

Synthesis. Chelating diolato complexes can be prepared via a number of synthetic strategies (scheme 1). Among these, alcohol exchange of diols with a bis alkoxo precursor, $L_nM(OR)_2$, was usually employed.[2] When $L_nM(OR)_2$ was not readily accessible, metal carbonate complexes, $L_nM(CO_3)$, if available, could serve as good starting materials, although the reactions were nearly thermoneutral.[3] Condensation of oxo metal complexes, $L_nM{=}O$, with diols also led to the formation of diolato complexes.[4] Alternatively, they could be obtained by treatment of dihalide complexes, L_nMX_2, with free diols in the presence of appropriate bases, or via a metathesis reaction with alkali metal salts of diols.[5] Rarely, bis-trimethylsilyl ethers of the diols were allowed to react with the trichloro titanium compound, $CpTiCl_3$, to afford the corresponding diolato complexes.[6]



Scheme 1: Synthesis of metal diolato complexes

The approaches mentioned above all start with a preformed diol skeleton. In a second strategy, diolato skeletons were generated by cycloaddition reactions. In one example, metal diolato complexes were prepared from epoxides and terminal oxo metal complexes.[7] In another case, the cycloaddition of olefins to the dioxo ligands of a metal complex provided the desired diolato products.[8]

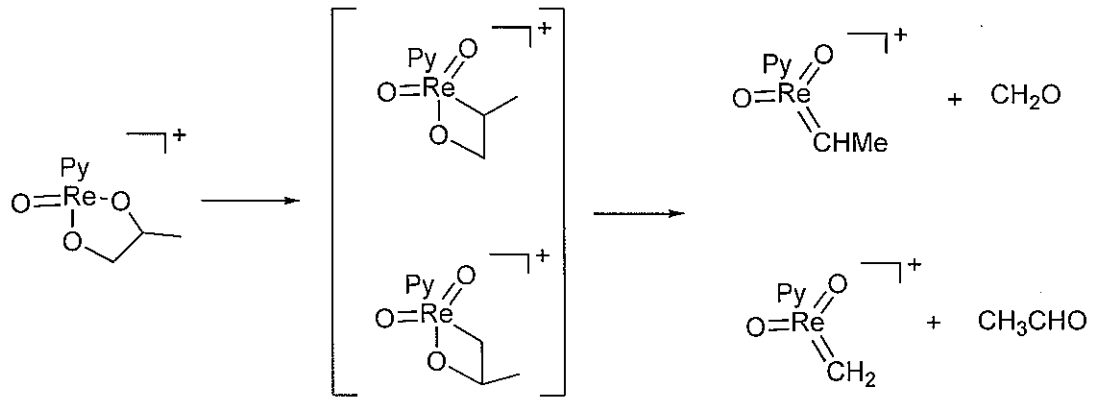
Another route involves formation of the diolato carbon skeleton during the reaction. For example, low valent early transition metals reductively couple organic carbonyl compounds to form diolato complexes. In a similar context, organic carbonyl compounds could be coupled upon reaction with η^2-imino, η^2-alkene or η^2-alkyne complexes.[9] Formal insertion of carbonyl compounds into η^2-carbonyl group 4 metal complexes, preformed or generated in situ from aminotroponiminate or tropocoronand macrocyclic ligands, also generated the corresponding diolato complexes.[10] This last route is very useful in obtaining unsymmetrical diolato complexes. In the latter cases, the starting metal complexes could be viewed as a low valent metal precursors, stabilized by η^2-ligands.

Reactivity. The M-O, O-C, and C-C bonds in the dioxametallacyclopentane ring of metal 1,2-diolato complexes comprise three different reactive sites. The chemoselecitivity of these sites depend on the nature of compounds involved and reaction conditions. Some of the potential reactions of diolato complexes are the reverse of reactions depicted in scheme 1.

Metal diolato complexes are generally susceptible to hydrolysis reactions, under neutral or acidic conditions, towards cleavage of M-O bonds and production of free diols. Diolato ligands can be displaced by more acidic diols or other chelates.[5b,c] This provides another approach to diolato complexes. M-O cleavage also occurred in reactions of group 9 transition metal pinacolato complexes Cp*M(pinacolate) (M = Co, Rh, Ir) with

heterocumulenes.[11] In such reactions, an initial insertion of heterocumulene into an M-O bond yielded a 7-membered metallacycle, followed by 1,2-elimination.

Metal diolato complexes also undergo cycloreversion reactions to extrude olefins by cleavage of two C-O bonds.[5a-b,8,12] Rhenium complexes were mostly studied in this context, partly due to their reverse relationship with OsO_4 mediated olefin dihydroxylations. A concerted [3+2] mechanism was initially proposed and was widely accepted. However, recent studies[13] of rhenium diolato complexes suggest a stepwise [2+2] mechanism, in which carbon migrates from oxygen to rhenium to form a metallaoxetane intermediate, followed by olefin extrusion. Very recently, rhenium carbene species, products uniquely derived from a metallaoxetane, were detected in an electrospray ionization tandem mass spectrometric study of a rhenium diolato cation, ReO(py)(1,2-propanediolato)$^+$.[14] This provides direct evidence that a metallaoxetane species is indeed involved (scheme 2). These controversies about the mechanism can be reconciled with the help of modern quantum chemical methods.[15] It seems that operating mechanisms may depend on the metals (Os, Re) and the supporting ligands. The concerted [3+2] mechanism is generally favored, with an asymmetric transition state in some systems.



Scheme 2. Rhenium carbene species from diolato through metallaoxetane

Under thermal or photochemical conditions, diolato complexes also undergo C-C cleavage reactions to release organic carbonyl compounds.[16] For example, pinacolato complexes Cp*M(pinacolato) (M = Co, Rh, Ir) undergo C-C cleavage reactions under photochemical conditions to produce acetone.[16a] This process was made catalytic in the presence of an oxidizing reagent. It was demonstrated that in calix[4]arene supported titanium diolato complexes, C-C bonds are significantly weakened so that a fast equilibrium exists between diolato complexes and η^2-ketone species.[17] Treatment of diolato complexes with terminal alkynes resulted in the formation of cross coupling products, 2-oxotitanacyclopent-4-ene complexes, together with the release of one equivalent of free carbonyl compounds.[17b] The η^2-ketone species could be trapped with diimine ligands such as 1,10-phenanthroline and 2,2-bipyridines to give isolable η^2-ketone complexes.[17c]

Lastly, it is conceivable that β-hydrogens, if present in diolato ligands, could undergo activation and afford dehydrogenated complexes, since alkoxo complexes are often unstable with respect to β-hydrogen elimination.[18] Oxidative dehydrogenation has been commonly observed in nitrogen-containing bidentate and macrocyclic ligands.[19] Furthermore, some mononuclear rhenium dithiolato complexes were shown to undergo a dehydrogenation reaction to form ethenedithiolate products, as well as olefin extrusion, under thermal or oxidative conditions.[20] However, a similar dehydrogenation reaction has not been reported in diolato complexes prior to this work.

Applications and implications. Metal diolato complexes can serve as precursors to a range of industrially important materials. For example, diolato ligands were incorporated into titanium alkoxo complexes to facilitate the growth of high quality TiO_2 thin film at

relatively low substrate temperatures in the metalorganic chemical vapor deposition (MOVCD) process.[21]

Due to the strong binding between early transition metals and oxygen, alkoxo and aryloxo ligands often behave as spectator ligands and allow for tuning of steric and electronic properties in metal complexes. One eminent example is that of chiral tartrate ester compounds functioning as chelating diolato ligands. These play a critical role in the Katsuki-Sharpless asymmetric epoxidation of allylic alcohols.[22] Also noteworthy are chiral binaphthol ligands used in many catalytic systems.

Diolato complexes function as active intermediates in many important organic transformations mediated by transition metals. Reductive coupling reactions of organic carbonyl compounds, producing olefins (the McMurry reaction) or 1,2-diols (pinacol coupling), are among the most useful C-C forming processes.[23] Metal diolato complexes have been implicated in these reactions, as they can be isolated in the reductive coupling reaction under some conditions.[23a,b] Only a few systems have been identified in which both the low valent metal complex and the diolato species are well characterized. With extensive efforts, the involvement of osmium diolato intermediates, generated via a cycloaddition reaction, has been firmly established in the osmium tetraoxide mediated dihydroxylation of olefins.[24] In the deoxygenation of epoxides and dedihydroxylation of vicinal diols catalyzed by transition metal complexes, diolato species also were demonstrated to be the key intermediates in the reaction pathway.[25] Such species are also involved in catalytic cycloaddition of epoxides with a number of substrates such as aldehydes, ketones, aromatic imines and diphenylketene.[7b]

Conversion of carbohydrates to useful industrial chemicals is very attractive as carbohydrates are among the most abundant and renewable biomass resources. Vicinal diol functionalities are ubiquitous in carbohydrates. Thus, transition metal diolato complexes offer a suitable model for understanding metal carbohydrate interactions and may facilitate the design of better transition metal catalysts.[3]

Metalloporphyrin complexes bearing the alkoxo and aryloxo ligands have been described.[26] However, chelating bis(alkoxo) metalloporphyrins are rarely reported, except in a few chelating 1,3-diolato metalloporphyrin complexes.[27] Their involvement in an iron porphyrin-catalyzed diol cleavage reaction has been suggested.[28] In this work, a series of group 4 metalloporphyrin diolato complexes were prepared through various synthetic approaches, and their reactivity and involvement in catalysis were investigated.

Porphyrin and related chiral tetraaza macrocyclic ligands

Porphyrins have been widely used as ligands in chemistry, due to a variety of reasons, including biological relevance, structural rigidity/stability, unique spectroscopic properties, etc. A great deal of metalloporphyrin chemistry deals with the catalytic oxidation of various organic substrates. For asymmetric catalysis, elaborate modification of the porphyrin ligands become necessary. Although a number of elegant porphyrins have been designed and prepared, it is generally difficult to systematically introduce chiral and/or bulky groups into porphyrins and the synthetic routes are often tedious with low yields.

Alternatively, more practical ligand systems are desirable. One approach utilized tetradentate salen ligands derived from chiral diamines. Such ligands can be easily prepared and readily modified. Moreover, they offer an environment where the chiral centers are in

close proximity to the active metal sites. In fact, chiral salen-based manganese epoxidation catalysts have been remarkable in achieving high enantioseletivities.[29,30] In a related approach, tetraaza macrocyclic ligands can be considered as close analogues to porphyrins, simply because of the macrocyclic nature of both systems. Various methodologies have been developed to construct this type of ligands. In our attempt of developing asymmetric cyclopropanation catalysts, we were able to introduce chiral centers into tetraaza macrocyclic ligands, by a template or non-template synthesis. These results, as well as catalytic studies, are the topics of chapter 5 and 6.

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CHARPTER 1. SYNTHESIS, CHARACTERICATION, AND REACTIVITY OF GROUP 4 METALLOPORPHYRIN DIOLATE COMPLEXES

A paper published in *Organometallics*[1]

Guodong Du and L. Keith Woo*

Abstract

A number of group 4 metalloporphyrin diolate complexes were synthesized via various approaches. For example, treatment of imido complex (TTP)Hf=NAr^{iPr} with diols resulted in formation of the corresponding diolato complexes (TTP)Hf[OCR$_1$R$_2$CR$_1$R$_2$O] (R$_1$ = R$_2$ = Me, **1**; R$_1$ = Me, R$_2$ = Ph, **2**; R$_1$ = R$_2$ = Ph, **3**). Treatment of (TTP)Ti=N^{i}Pr with diols generated (TTP)Ti[OCR$_1$R$_2$CR$_1$R$_2$O] (R$_1$ = R$_2$ = Me, **5**; R$_1$ = Me, R$_2$ = Ph, **6**; R$_1$ = H, R$_2$ = Ph, **7**; R$_1$ = H, R$_2$ = *p*-tolyl, **8**). Alternatively hafnium and titanium pinacolates **1** and **5** were prepared through metathetical reactions of (TTP)MCl$_2$ (M = Hf, Ti) with disodium pinacolate. The substitution chemistry of hafnium complexes correlated well with the basicity of the diolato ligands. Complexes **1-6** underwent oxidative cleavage reactions, producing carbonyl compounds and oxometalloporphyrin species. For less substituted diolates **7** and **8**, an array of products including the enediolate complexes

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(TTP)Ti[OC(Ar)C(Ar)O] (Ar = Ph, **9**; Ar = *p*-tolyl, **10**) was observed. The possible cleavage reaction pathways are discussed.

Introduction

Transition-metal complexes bearing alkoxo- or aryloxo-ligands have been widely investigated because of their structural diversity, reactivity and importance in biological and catalytic applications.[2] In early transition metal complexes, alkoxo- and aryloxo- ligands bind strongly with metals and often serve as spectator ligands, allowing for the adjustment of both steric and electronic properties.[3,4] Although chelating ligands containing phenolates are well known, especially in salen[5] chemistry, chelating bis(alkoxo) complexes are relatively less studied.[6]

A few group 4 metalloporphyrin complexes bearing alkoxide or aryloxide ligands have been reported. For example, (TTP)Ti$(OR)_2$ (R = Ph, Me, *t*-butyl),[7] (OEP)Zr$(OR)_2$ (R = *t*-butyl, $SiMe_3$)[8] were prepared by metathesis reactions of dichlorometalloporphyrins with appropriate alkali metal alkoxides and aryloxides. Treatment of imido- or hydrazidotitanium porphyrins with alcohols or phenols generated alkoxo- or aryloxo- complexes.[7,9] Metalloporphyrins bearing 1,3-dialkoxo chelating ligands, (TTP)Zr[OC(^{t}Bu)CHC(R)(Me)O] (R = *t*-butyl, *n*-hexyl)[10] and (OEP)M[OC(R)CHC(R)O] (M = Zr, Hf; R = Me, Ph)[11] were also reported.

We have expanded our work to group 4 metalloporphyrin diolato complexes. Herein, we describe the syntheses and characterization of a series of titanium, zirconium and hafnium η^2-diolates. The reactivity of these complexes will also be presented.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40-1 Dri-Train gas purifier. Toluene and hexane were dried and deoxygenated by passage through columns of activated alumina following the method of Grubbs.[12] Benzene-d_6 and THF were freshly distilled from purple solutions of sodium benzophenone and brought into the drybox without exposure to air. CH_2Cl_2 and CD_2Cl_2 were dried with P_2O_5, degassed with several freeze-pump-thaw cycles and brought into the drybox after being vacuum-transferred. The dichloro complexes, (TTP)MCl_2,[13] imido complexes, (TTP)M=NAr^{iPr} (M = Ti, Hf)[14] (where Ar^{iPr} = 2,6-diisopropylphenyl), (TTP)Ti=N^{i}Pr,[15] were obtained as described in previous studies. Disodium pinacolate was prepared by reaction of the free pinacol with NaH in toluene. Hydrobenzoin (1:1 *dl*:meso mixture), 1,2-di(*p*-tolyl)ethyleneglycol (1:1 *dl*:meso), and *dl*-2,3-diphenylbutane-2,3-diol were synthesized according to the literature procedures.[16]

^{1}H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts are referenced to proton solvent impurities (δ 7.15, C_6D_5H; 7.24, $CHCl_3$). UV-vis data were recorded on a HP8453 diode array spectrophotometer and reported as λ_{max} in nm (log ε). Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. GC-MS studies were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS).

Synthesis of (TTP)Hf[$OC(Me)_2C(Me)_2O$] (1). Method A. A solution of (TTP)Hf=NAr^{iPr} (142.9 mg, 0.140 mmol) and pinacol (17.6 mg, 0.149 mmol) in toluene (ca. 8 mL) was stirred for 12 h at room temperature and reduced to dryness in vacuo. The residue

was crystallized by layering a toluene solution (ca. 3 mL) with hexane (ca. 5 mL) and cooling the sample to –25 °C. The purple microcrystalline product was collected by filtration and dried under vacuum. Yield: 69.9 mg (52%). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.23 (s, 8H, β-H), 8.38 (d, 4H, *meso*-$C_6H_4CH_3$), 7.95 (d, 4H, *meso*-$C_6H_4CH_3$), 7.29 (dd, 8H, *meso*-$C_6H_4CH_3$), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -0.98 (s, 12H, $OCMe_2$). ^{13}C NMR (C_6D_6, 400 MHz): 150.2, 139.7, 137.3, 135.3, 133.9, 132.6, 124.7, 82.4, 25.1, 21.3. UV-vis (toluene): 323 (4.22), 421 (5.62), 548 (4.46). Anal. Calcd. for $C_{54}H_{48}N_4O_2Hf$: C, 67.32; H, 5.02; N, 5.81. Found: C, 66.93; H, 5.24; N, 5.57.

Method B. A slurry of (TTP)$HfCl_2$ (57.1 mg, 0.0622 mmol) and disodium pinacolate (45.0 mg, 0.278 mmol) in toluene (ca. 8 mL) was stirred for 16 h at room temperature. The resulting mixture was filtered through a pad (~1 cm) of Celite on a fritted funnel. The solvent was removed under vacuum to give the purple diolate **1**. Yield: 50 mg (83%). The ^{1}H NMR spectrum was identical to the above data.

Synthesis of (TTP)Hf[OC(Me)(Ph)C(Me)(Ph)O] (2). A solution of (TTP)Hf=NAr^{iPr} (59.0 mg, 0.0577 mmol) and *dl*-2,3-diphenylbutane-2,3-diol (16.7 mg, 0.0689 mmol) in toluene (ca. 6 mL) was stirred for 16 h at room temperature. Hexane (ca. 6 mL) was added and the resulting mixture was filtered through a pad (~1 cm) of activated neutral alumina. The solvent was removed under vacuum and the residue was triturated with hexane (ca. 4 mL). The purple-red diolate **2** was collected by filtration and dried under vacuum. Yield: 32 mg (51%). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.27 (q, 8H, β-H), 8.32 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, *meso*-$C_6H_4CH_3$), 8.03 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, *meso*-$C_6H_4CH_3$), 7.28 (t, 8H, *meso*-$C_6H_4CH_3$), 6.69 (m, 6H, *p*, *m*-C_6H_5), 5.79 (dd, 4H, *o*-C_6H_5), 2.41 (s, 12H, *meso*-$C_6H_4CH_3$), -1.36 (s, 6H, $OC(CH_3)(Ph)$). UV-vis (toluene): 421 (5.72), 551 (4.68).

Synthesis of (TTP)Hf[OC(Ph)$_2$C(Ph)$_2$O] (3). A solution of (TTP)Hf=NAr^{iPr} (45.1 mg, 0.0441 mmol) and benzopinacole (42.5 mg, 0.116 mmol) in toluene (ca. 5 mL) was stirred for 14 h at room temperature. Hexane (ca. 4 mL) was added and the resulting mixture was filtered through a pad (~1 cm) of activated neutral alumina. The solvent was removed under vacuum and the residue was triturated with hexane (ca. 3 mL). The purple-red diolate **3** was collected by filtration and dried under vacuum. Yield: 30 mg (57%). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.24 (s, 8H, β-H), 8.02 (m, 8H, *meso*-$C_6H_4CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 6.50 (t, 4H, $^3J_{H\text{-}H}$ = 7.6 Hz, *p*-C_6H_5), 6.39 (t, 8H, $^3J_{H\text{-}H}$ = 7.6 Hz, *m*-C_6H_5), 5.06 (d, 8H, $^3J_{H\text{-}H}$ = 7.6 Hz, *o*-C_6H_5), 2.42 (s, 12H, *meso*-$C_6H_4CH_3$). ^{13}C NMR (C_6D_6, 300 MHz): 150.2, 147.5, 139.5, 137.5, 135.6, 133.5, 133.0, 127.4, 125.8, 124.9, 124.4, 98.4, 21.3. UV-vis (toluene): 423 (4.97), 549 (3.80), 592 (2.78).

Synthesis of (TPP)Zr[OC(Me)$_2$C(Me)$_2$O] (4). A solution of (TPP)Zr=NAr^{iPr} (62.4 mg, 0.071 mmol) and pinacol (10.7 mg, 0.091 mmol) in toluene (ca. 6 mL) was stirred at room temperature. After 10 h, the solution was filtered over Celite and reduced to dryness in vacuo. The residue was triturated with hexane (ca. 3 mL), the mixture was filtered to afford the purple-red diolate **4** (27.5 mg, 47%). Analytically pure samples were obtained by layering a CH_2Cl_2 solution (ca. 2 mL) with hexane (ca. 4 mL), allowing the mixture to stand at –25 °C, filtering, and drying the solid in vacuo. ^{1}H NMR (C_6D_6, 300 MHz): δ 9.09 (s, 8H, β-H), 8.43 (d, 4H, *meso*-C_6H_5), 8.00 (d, 4H, *meso*-C_6H_5), 7.50 (dd, 8H, *meso*-C_6H_5), 7.44 (d, 4H, *meso*-C_6H_5), - 0.96 (s, 12H, OCMe_2). ^{13}C NMR (C_6D_6, 300 MHz): 149.9, 142.7, 135.4, 133.9, 132.5, 126.9, 124.6, 84.7, 24.7. UV-vis (toluene): 421 (5.71), 550 (4.45). MS: m/z 820 (818). Anal. Calcd. for $C_{50}H_{40}N_4O_2Zr$: C, 73.23; H, 4.92; N, 6.83. Found: C, 72.92; H, 5.12; N, 6.66.

Synthesis of (TTP)Ti[OC(Me)$_2$C(Me)$_2$O] (5). Method A. A solution of (TTP)Ti=N^{i}Pr (48.4 mg, 0.0625 mmol) and pinacol (21.1 mg, 0.178 mmol) in toluene (ca. 6 mL) was stirred for 12 h at room temperature and reduced to dryness in vacuo. The residue was recrystallized from a toluene solution (ca. 3 mL), layered with hexane (ca. 3 mL) and subsequently cooled to –25 °C. The purple solid **5** was collected by filtration. Yield: 13 mg (25%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.15 (s, 8H, β-H), 8.33 (br s, 4H, *meso*-$C_6H_4CH_3$), 8.05 (br s, 4H, *meso*-$C_6H_4CH_3$), 7.29 (br s, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -1.25 (s, 12H, OCMe_2). ^{13}C NMR (C_6D_6, 400 MHz): δ 150.1, 139.9, 137.2, 135.2, 134.2, 131.6, 124.1, 91.9, 23.5, 21.3. UV-vis (toluene): 428 (5.61), 532 (4.20), 552 (4.38).

Method B. A slurry of (TTP)TiCl$_2$ (35.5 mg, 0.0451 mmol) and disodium pinacolate (29.6 mg, 0.183 mmol) in toluene (ca. 6 mL) was stirred for 12 h at room temperature. The resulting mixture was filtered through a pad (~1 cm) of Celite. The solvent was removed under vacuum to afford the purple diolate **5**. Yield: 30 mg (80%). The ^{1}H NMR spectrum was identical to the above data. This sample was contaminated with 15% (TTP)TiO.

Synthesis of (TTP)Ti[OC(Me)(Ph)C(Me)(Ph)O] (6). A solution of (TTP)Ti=NAr^{iPr} (31.1 mg, 0.0402 mmol) and *dl*-2,3-diphenylbutane-2,3-diol (13.6 mg, 0.0561 mmol) in toluene (ca. 6 mL) was stirred for 12 h at room temperature. The reaction mixture was filtered through a pad (~1 cm) of activated neutral alumina. Removal of the solvent afforded the purple-red solid **6**. Yield: 26 mg (67%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-diolate: δ 9.19 (s, 8H, β-H), 8.27 (br s, 4H, *meso*-$C_6H_4CH_3$), 8.05 (br s, 4H, *meso*-$C_6H_4CH_3$), 7.27 (d, 8H, *meso*-$C_6H_4CH_3$), 6.68 (m, 6H, *p, m*-C_6H_5), 5.55 (d, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -1.57 (s, 6H, OC(Ph)CH_3). UV-vis (toluene): 553 (4.46), 426 (5.41), 413 (5.52).

Synthesis of (TTP)Ti[OCH(Ph)CH(Ph)O] (7). A solution of (TTP)Ti=N^{i}Pr (54 mg, 0.0698 mmol) and hydrobenzoin (20 mg, 0.0933 mmol, *dl*:meso = 1:1) in toluene (ca. 6 mL) was stirred for 12 h at room temperature, and then filtered through a pad (~1 cm) of activated neutral alumina. The solvent was removed *in vacuo* to afford a purple product. The ratio of *dl/meso* diolate was 2.4:1. Yield: 15 mg (23%). ^{1}H NMR (C_6D_6, 400 MHz): *dl*-diolate: δ 9.15 (q, 8H, J = 5.6 Hz, β-H), 8.14 (br s, 4H, *meso*-$C_6H_4CH_3$), 7.98 (br s, 4H, *meso*-$C_6H_4CH_3$), 7.26 (d, 8H, *meso*-$C_6H_4CH_3$), 6.61 (m, 6H, *p*, *m*-C_6H_5), 4.96 (d, 4H, $^{3}J_{H-H}$ = 6.6 Hz, *o*-C_6H_5), 2.90 (s, 2H), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$). *meso*-diolate: δ 9.19 (s, 8H, β-H), 6.32 (m, 6H, *p*, *m*-C_6H_5), 4.62 (d, 4H, $^{3}J_{H-H}$ = 7.5 Hz, *o*-C_6H_5), 3.20 (s, 2H), 2.37 (s, 12H, *meso*-$C_6H_4CH_3$). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis (toluene): 413 (5.36), 554 (4.31).

Thermal decomposition of (TTP)Ti[OCH(Ph)CH(Ph)O] (7) under N_2. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti[OCH(Ph)CH(Ph)O] (7) (2.0 mg, 2.17 μmol), Ph_3CH (1.02 mg, 4.17 μmol, internal standard) and C_6D_6 (~0.5 mL) in a glovebox. Upon heating for 3 days at 80 °C, the diolate complex was consumed and an enediolate complex, (TTP)Ti[OC(Ph)C(Ph)O] (**9**) (13%), was observed as well as (TTP)TiO (73%). ^{1}H NMR of the enediolate (**9**): δ 9.04 (s, 8H, β-H), 8.18 (d, 4H, *meso*-$C_6H_4CH_3$), 7.92 (d, 4H, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, *meso*-$C_6H_4CH_3$), 6.61 (m, 6H), 5.71 (d, 4H), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$). Benzaldehyde (δ 9.61, -C*H*O, 12%), benzyl alcohol (δ 4.24, -CH_2OH, 12%), stilbene oxide (δ 3.84, PhC*H*, 24%) were also observed and confirmed by GC and GC-MS analysis.

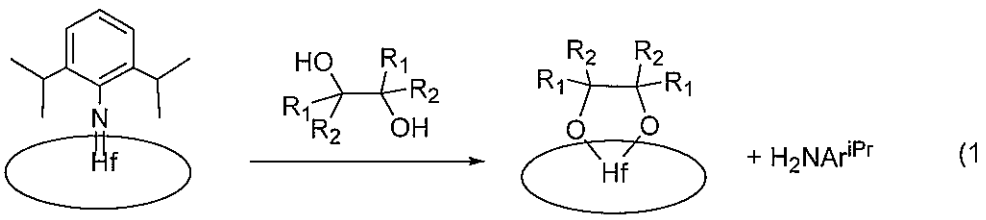
Thermal decomposition of (TTP)Ti[OCH(Ph)CH(Ph)O] (7) under air. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti[OCH(Ph)CH(Ph)O] (7) (1.0 mg, 1.07 μmol), Ph_3CH (1.2 mg, 4.91 μmol, internal standard) and C_6D_6 (~0.5 mL), flushed with air and sealed. Upon heating for 3 days at 80 °C, complex **7** was consumed. (TTP)Ti=O (85%) and (TTP)Ti(O_2) (14%) were identified by ^{1}H NMR as the titanium porphyrin species. Benzaldehyde (δ 9.61, -C*H*O, 75%), benzyl alcohol (δ 4.24, -CH_2OH, 4.6%), benzil (δ 7.90, *o*-C_6H_5, 20%) and H_2O (δ 0.40) were also observed and confirmed by GC and GC-MS analysis.

Synthesis of (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (8). A solution of (TTP)Ti=N^{i}Pr (63.6 mg, 0.0822 mmol) and 1,2-di(*p*-tolyl)ethyleneglycol (23.6 mg, 0.0975 mmol, *dl*:meso = 1:1) in toluene (ca. 6 mL) was stirred for 12 h at room temperature, and filtered through a pad (~1 cm) of activated neutral alumina. The solvent was removed in *vacuo* and the residue was recrystallized by layering a toluene solution (ca. 3 mL) with hexane (ca. 3 mL) and cooling the sample to -25 °C. The purple microcrystalline product was collected by filtration. The ratio of *dl*/*meso* diolate was 3.0:1. Yield: 25 mg (32%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-diolate: δ 9.17 (q, 8H, β-H), 8.15 (br s, 4H, *meso*- $C_6H_4CH_3$), 7.98 (br s, 4H, *meso*-$C_6H_4CH_3$), 7.26 (d, 8H, *meso*-$C_6H_4CH_3$), 6.41 (d, 4H, *m*-$C_6H_4CH_3$), 4.95 (d, 4H, *o*-$C_6H_4CH_3$), 2.91 (s, 2H), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), 1.84 (s, 6H, $C_6H_4CH_3$). *meso*-diolate: δ 9.21 (s, 8H, β-H), 6.17 (d, 4H, *m*-$C_6H_4CH_3$), 4.61 (d, 4H, *o*-$C_6H_4CH_3$), 3.22 (s, 2H), 2.37 (s, 12H, *meso*-$C_6H_4CH_3$), 1.61 (s, 6H, $C_6H_4CH_3$). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis (toluene): 414 (5.26), 425 (5.38), 553 (4.36).

Thermal decomposition of (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (8) under N_2. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (**8**) (2.0 mg, 2.17 μmol), Ph_3CH (1.02 mg, 4.17 μmol, as internal standard) and C_6D_6 (~0.5 mL) in a glovebox. Upon heating for 3 days at 80 °C, diolate complex was consumed and an enediolate complex, (TTP)Ti[OC(*p*-tolyl)C(*p*-tolyl)O] (**10**) (16%), was observed as well as (TTP)Ti=O (73%). ^{1}H NMR of the enediolate **10**: δ 9.07 (s, 8H, β-H), 6.48 (d, 4H), 5.71 (d, 4H), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), 1.78 (s, 6H, $C_6H_4CH_3$). Other peaks were obscured in aromatic region. Tolualdehyde (δ 9.68, -C*H*O, 20%), *p*-methylbenzyl alcohol (δ 4.31, -CH_2OH, 15%), 1,2-ditolylethylene epoxide (δ 3.91, tolyl-C*H*, 26%) were also observed and confirmed by GC and GC-MS analysis.

Results

Synthesis of diolates. In an effort to prepare group 4 metalloporphyrin diolates, the imido complexes were found to be suitable precursors. Treatment of (TTP)Hf=NAr^{iPr} with pinacol (eq. 1) cleanly afforded the corresponding diolate complex

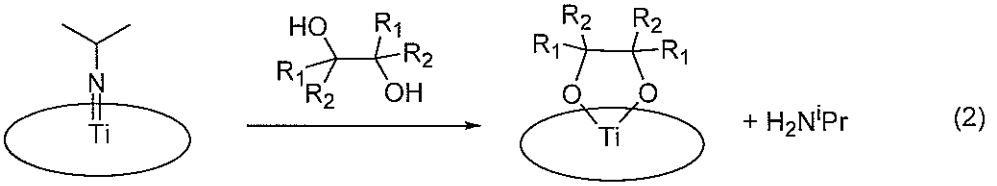


1: R_1=R_2=Me
2: R_1=Me, R_2=Ph
3: R_1=R_2=Ph

(TTP)Hf[$OC(Me)_2C(Me)_2O$] (**1**), as evidenced by ^{1}H NMR spectroscopy. This is in accord with the high oxophilicity of the group 4 transition metals. In a similar manner, (TTP)Hf[OC(Me)(Ph)C(Me)(Ph)O] (**2**) and (TTP)Hf[$OC(Ph)_2C(Ph)_2O$] (**3**) were prepared in

good yields. However, the reaction of (TTP)Hf=NAr^{iPr} with a less substituted diol, *meso*-hydrobenzoin, did not afford an isolable compound. A transient product was observed, accompanied by the disappearance of the starting imido complex and the appearance of free amine H_2NAr^{iPr}. The ^1H NMR spectrum of this product[17] was consistent with the expected (TTP)Hf[OCH(Ph)CH(Ph)O] and comparable with its titanium analogue. However, it decomposed upon recrystallization and prevented further characterization.

When (TTP)Ti=NAr^{iPr} was treated similarly with excess pinacol, only ~5% of (TTP)Ti=NAr^{iPr} was converted to the diolate (TTP)Ti[OC(Me)$_2$C(Me)$_2$O] (**5**). No diolate formation was observed when (TTP)Ti=NAr^{iPr} was treated with benzopinacole. In contrast, (TTP)Ti=N^{i}Pr, a sterically less congested imido complex, was a better starting material. Treatment of (TTP)Ti=N^{i}Pr with excess pinacol or 2,3-diphenylbutane-2,3-diol afforded the diolates **5** and (TTP)Ti[OC(Me)(Ph)C(Me)(Ph)O] (**6**) respectively, in good yields. Furthermore, this imido complex reacted with less substituted diols, such as hydrobenzoin or 1,2-di(*p*-tolyl)ethyleneglycol, resulting in the formation of the corresponding isolable diolates **7** and **8** (eq. 2). With the sterically more demanding benzopinacole, there was no observation of reaction.



(2)

5: R_1=R_2=Me
6: R_1=Me, R_2=Ph
7: R_1=H, R_2=Ph
8: R_1=H, R_2=p-tolyl

Alternatively, pinacolates could be prepared through salt elimination. Treatment of dichloro complexes, (TTP)MCl_2 (M = Ti, Hf), with disodium pinacolate in toluene afforded

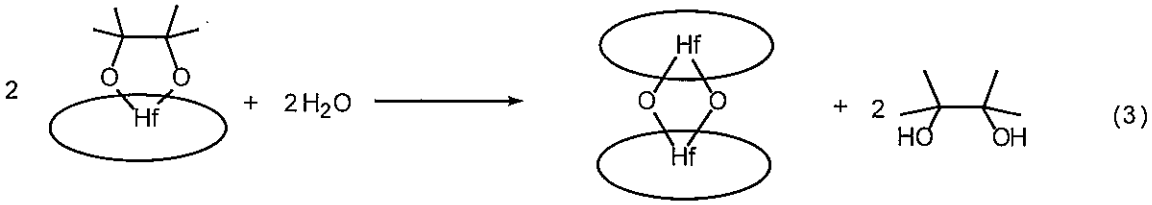
(TTP)M[OC(Me)$_2$C(Me)$_2$O)] (M = Ti (**5**); Hf (**1**)) in high yields. This direct approach for preparing diolato metalloporphyrin complexes failed with benzopinacole and only intractable products were obtained. In the presence of bases such as pyridine, no reaction was observed between (TTP)HfCl$_2$ and free diols.

It was reported that (TPP)Ti=O reacted with catechol (H$_2$cat) to afford the corresponding chelate complex (TTP)Ti(cat).[18] In a similar manner, (2,2'-biphenyldioxy)(tetra-*t*-butylphthalocyaninato)titanium(IV), (Pc)Ti(BP), was synthesized by the reaction of (Pc)Ti=O with 2,2'-biphenol.[19] Thus, the possibility of using (TTP)Ti=O as a starting material to prepare diolate complexes was explored and monitored by ^{1}H NMR spectroscopy. Treatment of (TTP)Ti=O with pinacol (~60 equiv) in CD_2Cl_2 produced only a trace of the diolate complex (TTP)Ti[OC(Me)$_2$C(Me)$_2$O] (**5**) at 22 °C. At elevated temperature (~120 °C), the diolate complex formed in 95% yield after 2 days. However, this reaction reversed upon cooling and ~45% of (TTP)Ti=O reappeared in 12 h. In the presence of molecular sieves (4 Å) in C_6D_6, diolate **5** was produced only in ~12% yield after days of heating. The major species, however, was the rearrangement product, pinacolone, which was confirmed by GC and ^{1}H NMR spectroscopy (δ = 1.71, 0.88 ppm). A small amount of acetone was also observed. Further study to address this reactivity is currently ongoing.

Characterization and properties of diolate complexes. The ^{1}H NMR spectra of these compounds are typical of metalloporphyrin complexes. The proton resonances associated with coordinated diolate ligands are shifted upfield relative to those of the free diols, due to the large porphyrin ring current effect. For example, the *o*-phenyl protons of (TTP)Hf[OC(Ph)$_2$C(Ph)$_2$O] (**3**) appear at 5.06 ppm, approximately 2.5 ppm upfield relative to those of the free diols. The resonances of *o*-tolyl protons of the TTP ligand generally

appear as two sets of signals. This is consistent with the enforced cis arrangement of the diolate ligands. Significant broadening was observed in the line widths of these signals in the titanium diolates. This may be due to the rotation of the *meso*-tolyl groups, facilitated by the deformation of the porphyrin ligand, which was noted previously in the literature.[20] Similar line broadening was also observed in the cis-ligated tin porphyrin complexes, $(TTP)Sn(Me)_2$[21] and $(TPP)Sn(Ph)_2$.[22]

Hafnium and zirconium diolato complexes **1-4** can be kept in the solid state at ambient temperature for weeks to months on exposure to air without decomposition. In solution, the pinacolate **1** reacted slowly with water, producing free pinacol and a diamagnetic product with a β-H resonance at 8.75 ppm. This was identified as a μ-oxo-dimeric species based on the similarity of its ^1H NMR spectrum with its zirconium analogue (eq. 3).[10,23] The zirconium diolate **4** undergoes a similar reaction with water. Diolate



(3)

complexes **2** and **3** are seemingly inert towards water, probably due to the stronger acidity and the greater bulkiness of these diol ligands. No hydrolysis was observed even after a prolonged period of exposure.

Titanium diolates are more labile compared to their hafnium and zirconium analogues. While they can be kept in the solid state, decomposition to release aldehydes or ketones at ambient temperature was observed in C_6D_6 solution over a period of days. Pinacolate complex $(TTP)Ti[OC(Me)_2C(Me)_2O]$ (**5**) readily reacts with water to yield

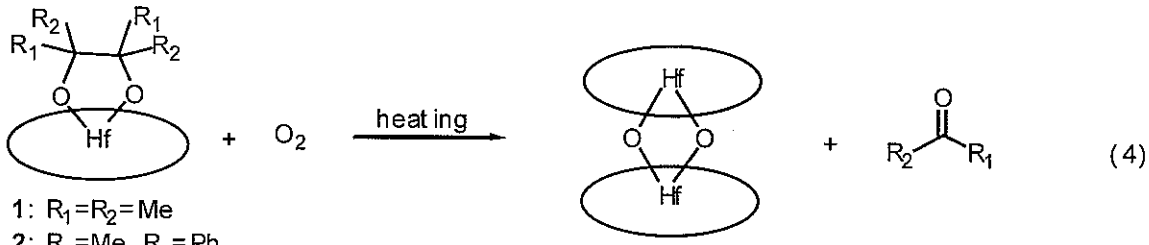
(TTP)Ti=O and free pinacol. The reactions of other titanium diolates with water are much slower.

Diolato displacement reactions. The hafnium and zirconium pinacolates undergo substitution reactions with other diols. For example, when hafnium pinacolate, (TTP)Hf[$OC(Me)_2C(Me)_2O$] (**1**), was treated with benzopinacole (3.0 equiv) in C_6D_6, (TTP)Hf[$OC(Ph)_2C(Ph)_2O$] (**3**) was produced quantitatively in hours. Similarly, treatment of **1** with 2,3-diphenylbutane-2,3-diol (4.7 equiv) generated (TTP)Hf[OC(Me)(Ph)C(Me)(Ph)O] (**2**) quantitatively in hours. However, pinacol (15 equiv) was not able to displace 2,3-diphenylbutane-2,3-diol from (TTP)Hf[OC(Me)(Ph)C(Me)(Ph)O] (**2**). It took 2 weeks for benzopinacole (~12 equiv) to displace 2,3-diphenylbutane-2,3-diol from **2**. No intermediate species were observed in the course of any of the substitution reactions. These reactions could also serve as an alternative route for preparing new diolate complexes.

The titanium pinacolate, (TTP)Ti[$OC(Me)_2C(Me)_2O$] (**5**), is less sensitive to displacement by other diols, presumably due to the smaller size of Ti(IV) compared with zirconium and hafnium. For example, (TTP)Ti[$OC(Me)_2C(Me)_2O$] (**5**) only partially reacted with excess hydrobenzoin (~5.0 equiv) reaching a steady state with an equilibrium constant of ~0.2. The reverse reaction from (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**) and pinacol (27 equiv) produced the pinacolate **5** smoothly in >95% conversion. With more bulky diols, no exchange reaction was observed.

Thermal reactivity. Although the hafnium and zirconium diolates were generally robust at ambient temperature, they underwent C–C bond cleavage reactions at elevated temperature. Heating an aerobic benzene-d_6 solution of (TTP)Hf[$OC(Ph)_2C(Ph)_2O$] (**3**) with a sand bath (~120 °C) in a sealed NMR tube resulted in the nearly quantitative formation of

benzophenone (92%, NMR yield) and three diamagnetic porphyrin species after 4 d. The major metal product (52% NMR yield) was a μ-oxo-dimer and the other two were not identifiable. Similarly, (TTP)Hf[OC(Me)(Ph)C(Me)(Ph)O] (**2**) and (TTP)Hf[$OC(Me)_2C(Me)_2O$] (**1**) thermalized to produce acetophenone and acetone, respectively (eq. 4). Under N_2, these reactions proceeded to a much lower extent, producing

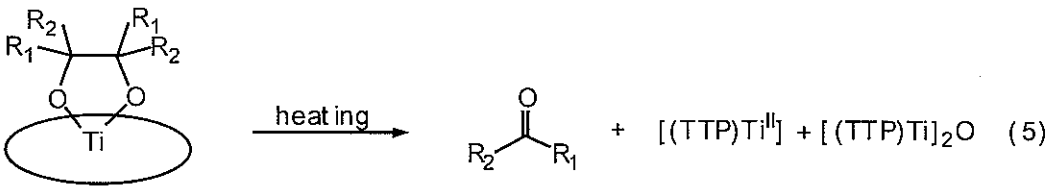


(4)

1: $R_1=R_2=Me$
2: $R_1=Me$, $R_2=Ph$
3: $R_1=R_2=Ph$

only small amounts of ketones and dimeric species, with starting diolates largely unchanged after extended heating in toluene-d_8 after 14 d. The presence of an oxygen acceptor, triphenylphosphine, did not change the course of the reaction.

The thermal treatment of the titanium analogues (TTP)Ti[$OC(Me)_2C(Me)_2O$] (**5**) and (TTP)Ti[OC(Me)(Ph)C(Me)(Ph)O] (**6**) under air in C_6D_6 resulted in the formation of (TTP)Ti=O and the corresponding ketones as observed for hafnium. Under N_2, the titanium pinacolate was converted initially to a paramagnetic species with δ 2.50 and 2.40-ppm resonances, accompanied by the production of acetone in 43-48% yield (eq. 5).[24] One



(5)

5: $R_1=R_2=Me$
6: $R_1=Me$, $R_2=Ph$

paramagnetic species could only be partially trapped by a large excess of pyridine to form a bis-pyridine adduct, (TTP)Ti(py)$_2$. The bis-pyridine complex has sharp ^{1}H NMR resonances and its spectrum matched that of a well-characterized sample.[25] The other unreactive species was probably a Ti(III) μ-oxo complex, [(TTP)Ti]$_2$O,[26] formed from traces of oxygen. After prolonged heating, the disappearance of both species was accompanied by the appearance of (TTP)Ti=O.

The thermal decomposition of a less substituted diolate complex, (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**), was more complicated. When a C_6D_6 solution of (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**) was heated under N_2 (~120 °C), an oxidative cleavage product, benzaldehyde (12%) was produced as before. Benzyl alcohol (12%) and stilbene oxide (24%) were also detected and confirmed by GC-MS and GC analysis. In addition to (TTP)Ti=O (72-75%), a new diamagnetic porphyrinato species formed in 13%-17% yield. This compound was confirmed to be an enediolate complex, (TTP)Ti[OC(Ph)C(Ph)O] (**9**), by an independent synthesis.[27] In the presence of excess free diol, (TTP)Ti=O was completely converted to the enediolate complex **9**. The thermolysis of (TTP)Ti[OCH(tolyl)CH(tolyl)O] (**8**) proceeded very similarly, producing (TTP)Ti=O (73-77%), enediolate **10** (13-16%), *p*-tolyl benzaldehyde (20%), *p*-methyl benzyl alcohol (15%), and 1,2-ditolylethylene epoxide (26%).

The thermal reaction of (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**) under air was somewhat different. After 3 days of heating (~120 °C) in C_6D_6 in an NMR tube, benzaldehyde was the major product (72-78%) and benzyl alcohol was present in small amounts (4-5%). No stilbene oxide was observed. Instead, a new organic species, benzil, was produced in ~20% yield. No enediolate complex was observed throughout the reaction. Instead two

diamagnetic titanium species, (TTP)Ti=O (85-90%) and (TTP)Ti(O_2) (11-14%), were observed.

Discussion

A variety of metalloporphyrin complexes, including alkoxo-, amido-, alkyl-, imido-complexes, have been prepared by the metathetical reaction of (por)MCl or (por)MCl_2 with various anion sources.[28] However, for group 4 metalloporphyrin diolate complexes only pinacolates were successfully prepared by this strategy. Intractable reaction products were obtained when the same approach was employed with hydrobenzoin or benzopinacole. It has been noted that alkoxide or amide salts can reduce metalloporphyrins.[7] Diols such as benzopinacole tend to decompose to free radicals under strongly basic conditions[29] and lead to intractable products in these reactions.

The approach delineated in eq. 1 and 2 is a more general route for preparing group 4 metalloporphyrin diolate complexes, since the imido complexes are readily accessible.[14,15] It makes use of the high oxophilicity of group 4 metals and the stronger acidity of alcohols over amines. Such reactivity was observed also in Ti, Zr, and Sn diamido- or imido-metalloporphyrin complexes.[7,9,21] The advantage of using (TTP)Ti=N^{i}Pr over (TTP)Ti=NAr^{iPr} as a starting material presumably derives from two aspects. The isopropylimido ligand is a stronger base than the aryl analog, NAr^{iPr} and drives the deprotonation of the diols. In addition, the ^{i}Pr group is less bulky than the Ar^{iPr} fragment, as indicated by the fact that 2,3-diphenylbutane-2,3-diol can displace N^{i}Pr from titanium, but does not replace NAr^{iPr}.

The diolate ligand substitution chemistry described for group 4 metalloporphyrin complexes reveals that the ligand affinity for hafnium porphyrin increases in the order of pinacol < 2,3-diphenylbutane-2,3-diol < benzopinacole. This trend correlates well with the increasing acidity of these diols. However, the steric factors of the metal and the diol appear to be important also. Due to the smaller size of titanium, pinacol provides enough steric hindrance that (TTP)Ti[$OC(Me)_2C(Me)_2O$] does not react with 2,3-diphenylbutane-2,3-diol.

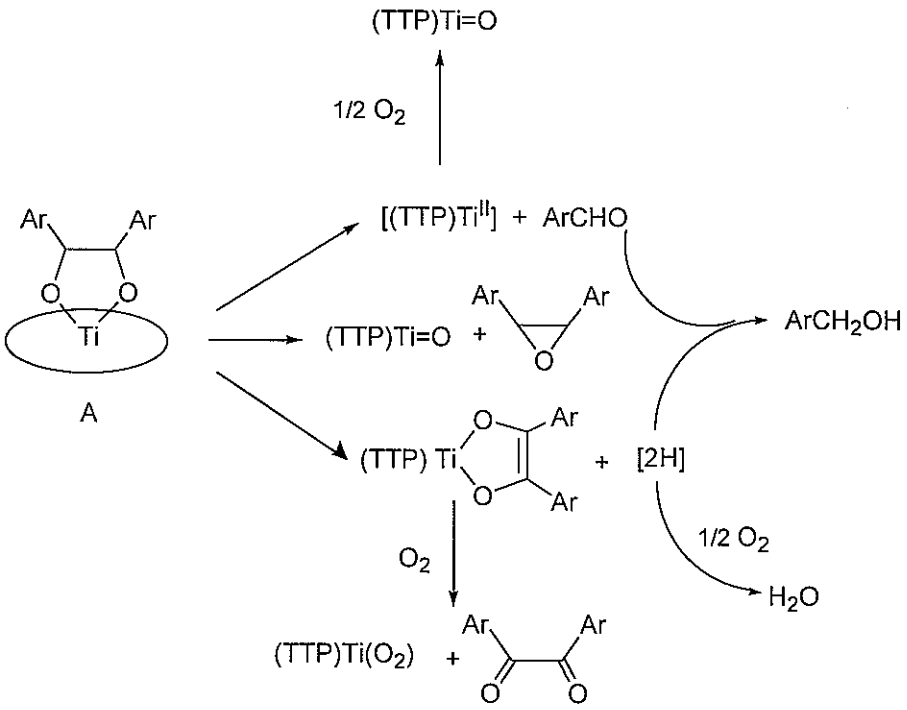
The reverse of the well-known reductive coupling of carbonyl compounds to form diolates, oxidative C–C cleavage, is rarely observed as a thermal process.[6a] Under thermal conditions, extrusion of alkenes from diolate complexes has been reported.[6d,30] Moreover, thermal treatment of alkali metal salts of secondary 1,2-diols results in cis/trans isomerization via a reversible elimination/addition of metal hydride and not through a retro-pinacol process.[31] However, photochemical conditions do promote oxidative C–C cleavage of diolates as shown for Pt(II)[32] and Rh(III)[6a] complexes. In addition, transition metal diolate complexes have been postulated as possible intermediates in catalytic diol C–C cleavage reactions.[33] The metalloporphyrin diolate complexes described here provide additional insight into thermal diolate cleavage reactions. Although reasonably robust at ambient temperature, they are found to undergo thermal cleavage reaction under oxidizing conditions. The corresponding carbonyl compounds are produced, accompanied by the formation of oxometalloporphyrins, (TTP)M=O, which further dimerize to μ-oxo species in the hafnium case. The use of (TTP)Ti=O as a diol cleavage catalyst has evolved from these studies and these results will be reported elsewhere.

Oxidative dehydrogenation is a well-known ligand degradation reaction, commonly observed in nitrogen-containing bidentate or macrocyclic ligands.[34] Enediolate complexes of

early transition metals are also common, mainly obtained by treatment of dialkyl precursors with CO[35] or by oxidation of low valent precursors with α-dicarbonyl compounds.[6c,36] However, the observation of dehydrogenation in diolate ligands to give enediolates is unprecedented to the best of our knowledge. Bergman[6a] *et al.* reported that group 9 diolate complexes, CpM(diolate) (M = Co, Rh, Ir), with primary or secondary diols underwent rapid decomposition, presumably via β-hydride elimination, but the decomposition products were not identified. The instability of (TTP)Hf[OCH(Ph)CH(Ph)O] complex is likely due to the decomposition via a similar hydrogen elimination process. Fortunately, the titanium analogue (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**) could be isolated and one of its thermolysis products was identified as the enediolate complex. A hydrogen elimination process must produce these products, although the reaction mechanism is unclear at this point.

Conclusion

In this study we have demonstrated that a variety of group 4 metalloporphyrin diolato complexes can be synthesized conveniently by the reaction of imido complexes with free diols. The reactivity of the hafnium chelate complexes toward diolato displacement is found to be primarily dominated by the acidity of the diolato ligands. In contrast, the reaction of the titanium analogs is dominated by steric factors. Oxidative cleavage of the diolato ligands was observed for these complexes. At least three reaction pathways are available for the thermolysis of the less substituted diolate complexes **7** and **8**. One is oxidative cleavage and the other is hydrogen elimination that leads to an enediolate complex. Benzaldehyde was reduced to benzyl alcohol synchronously (Scheme 1). A third pathway involving conversion of diolate to epoxide and (TTP)Ti=O is also possible. In the presence of dioxygen, this



Scheme 1

pathway becomes less favored. Benzil is likely produced via the enediolate complex, since the enediolate complex is found to release benzil and (TTP)Ti(O_2) upon exposure to air.[27] In air, the discrepancy between the amounts of benzyl alcohol (4-5%) and benzil (20%) suggests the existence of other pathways involved in the elimination of hydrogen. The formation of H_2O was also observed as a byproduct when O_2 is present.

Acknowledgments. We thank the Petroleum Research Fund, administered by American Chemical Society, for financial support.

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(5) Abbreviations: salen = dianion of a generic bis(salicylidene)diamine; TTP = dianion of *meso-tetra-p*-tolylporphyrin; TPP = dianion of *meso*-tetraphenylporphyrin; OEP = dianion of octaethylporphyrin.

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(17) ^{1}H NMR of (TTP)Hf[OCH(Ph)CH(Ph)O] (C_6D_6): δ 9.25 (s, 8H, β-H), 8.18 (d, 4H, *meso*-$C_6H_4CH_3$), 7.94 (d, 4H, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, *meso*-$C_6H_4CH_3$), 6.72 (m, 6H, *p*, *m*-C_6H_5), 5.37 (br s, 4H, *o*-C_6H_5), 3.14 (s, 2H), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$).

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CHAPTER 2. REDUCTIVE COUPLING REACTIONS OF CARBONYL COMPOUNDS WITH A LOW VALENT TITANIUM(II) PORPHYRIN COMPLEX

A paper to be submitted to *Organometallics*

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Abstract

The reactions of a low valent titanium(II) tetratolylporphyrin complex, (TTP)Ti(η^2-PhC≡CPh) (**1**), with various aromatic aldehydes or aryl ketones afforded the reductive coupling products, Ti(IV) diolato complexes (**2a-d**, **3a-d**). Treatment of **1** with two different carbonyl compounds selectively produced cross-coupled diolato complexes (**4a-d**). Interestingly, unreactive aliphatic aldehydes or ketones could be cross-coupled with aryl ketones. Reaction of **1** with benzil produced the enediolato complex (TTP)Ti[OC(Ph)C(Ph)O] (**5**). Putative η^2-carbonyl complexes were observed in the reactions of **1** with benzaldehyde and *p*-chlorobenzaldehyde, and their implication in reaction mechanisms is discussed.

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Introduction

Low valent titanium has a widespread use in metal-mediated organic synthesis.[1] As a result, titanium based pinacol coupling and McMurry reactions have been extensively investigated and elegantly employed in the syntheses of some complex natural products.[2] Recent studies focused on the stereo- and enantio- control of the pinacol coupling reactions under catalytic conditions. High diastereoselectivity has been achieved, however, the asymmetric version afforded only limited enantioselectivity.[3] Moreover, only a few systems have been reported in which both the low valent titanium complexes and the diolato species, putative intermediates in the C-C bond forming process, are well characterized.[4]

Titanium(II) porphyrin complexes were first synthesized and structurally characterized in 1991.[5] Subsequent investigations demonstrated that these complexes are potent reducing reagents and suitable acceptors for group or atom transfer reactions.[6] For example, (TTP)Ti(η^2-3-hexyne) was able to abstract chlorine, oxygen and sulfur from a variety of substrates including dichloroalkanes, epoxides, sulfoxides and triphenylphosphine sulfide.[6a,c] Reactions of (TTP)Ti(η^2-3-hexyne) with heterocumulenes generated group transfer products such as imido-complexes.[6b] Further studies showed that Ti(II) porphyrin complexes reacted with organic carbonyl compounds to form reductive coupling products. Herein we report a detailed account of this and related reactions. This study provides a new example of systems that support both Ti(II) species and ensuing Ti(IV) diolato complexes in well-defined forms.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40-1 Dri-Train gas purifier. Toluene and hexane were dried by passage through columns of activated alumina and a copper redox catalyst (Q-5) as described in the literature.[7] Benzene-d_6 and THF were freshly distilled from purple solutions of sodium benzophenone, degassed with several freeze-pump-thaw cycles and brought into the glovebox without exposure to air. CH_2Cl_2 was dried with P_2O_5, degassed with several freeze-pump-thaw cycles and brought into the glovebox after being vacuum-transferred into a glass vessel equipped with a high-vacuum teflon stopcock. Liquid aldehydes and ketones were degassed with several freeze-pump-thaw cycles before being brought into the glovebox and subsequently dried by passage though a pad of activated alumina. (TTP)Ti(η^2-PhC≡CPh) (**1**)[5] and (TTP)TiCl[8] were prepared according to literature procedures.

^{1}H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts are referenced to proton solvent impurities (δ 7.15, C_6D_5H). UV-vis data were recorded on a HP8453 diode array spectrophotometer and reported as λ_{max} in nm (log ε). Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. GC-MS studies were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS).

Preparation of (TTP)Ti[OCH(*p*-ClC$_6$H$_4$)CH(*p*-ClC$_6$H$_4$)O] (2a). To a toluene solution of *p*-chlorobenzaldehyde (30 mg, 0.21 mmol) was added a solution of (TTP)Ti(η^2-PhC≡CPh) (**1**) (91 mg, 0.10 mmol) in toluene (10 mL). The purple red solution was stirred

for ~40 min, filtered, and the solvent was removed in vacuo. The residue was taken up in toluene (2 mL), layered with hexane (6 mL), and placed in freezer at -25°C for ~18 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple material (TTP)Ti[OCH(*p*-ClC_6H_4)CH(*p*-ClC_6H_4)O] (**2a**), which contained both *dl* and *meso*-**2a** with a *dl*/*meso* ratio of 1.4 (63 mg, 63%). Samples for combustion analysis were obtained by layering a CH_2Cl_2 solution (2 mL) with hexane (4 mL), allowing the mixture to stand at –25°C, filtering and drying the solid in vacuo. ^{1}H NMR (C_6D_6, 400 MHz): *dl*-**2a**: δ 9.13 (q, 8H, β-H), 8.10 (br, 4H, *meso*-$C_6H_4CH_3$), 7.94 (br, 4H, *meso*-$C_6H_4CH_3$), 7.25 (t, 8H, *meso*-$C_6H_4CH_3$), 6.56 (d, 4H, *m*-C_6H_4Cl), 4.69 (d, 4H, *o*-C_6H_4Cl), 2.59 (s, 2H, OC*H*), 2.37 (s, 12H, *meso*-$C_6H_4CH_3$). *meso*-**2a**: δ 9.16 (s, 8H, β-H), 6.30 (d, 4H, *m*-C_6H_4Cl), 4.33 (d, 4H, *o*-C_6H_4Cl), 2.96 (s, 2H, OC*H*), 2.36 (s, 12H, *meso*-$C_6H_4CH_3$). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis (toluene): 553 (4.47), 427 (Soret, 5.48), 413 (sh, 4.18). Anal. Calcd for $C_{62}H_{46}N_4O_2TiCl_2 \cdot 0.5CH_2Cl_2$: C, 72.16; H, 4.55; N, 5.39. Found: C, 72.26; H, 5.02; N, 5.17.

Preparation of (TTP)Ti[OCH(Mes)CH(Mes)O] (2b). To a toluene solution of mesitylaldehyde (28 mg, 0.19 mmol) was added a solution of (TTP)Ti(η^2-PhC≡CPh) (**1**) (79 mg, 0.088 mmol) in toluene (10 mL). The purple red solution was stirred for ~40 min and filtered, then the solvent was removed in vacuo. The residue was taken up in toluene (4 mL), layered with hexane (4 mL), and placed in freezer at –25°C for ~21 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple material, which contained both *dl* and *meso* forms of **2b** with a *dl*/*meso* ratio of 2.2 (53 mg, 58%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-**2b**: δ 9.17 (q, 8H, β-H), 8.31 (br, 4H, *meso*-$C_6H_4CH_3$), 8.01 (br, 4H,

meso-$C_6H_4CH_3$), 7.25 (d, 8H, *meso*-$C_6H_4CH_3$), 6.05 (s, 2H, $C_6H_2(CH_3)_3$), 5.77 (s, 2H, $C_6H_2(CH_3)_3$), 3.59 (s, 2H, OC*H*Mes), 2.37 (s, 12H, *meso*-$C_6H_4CH_3$), 1.64(s, 12H, $C_6H_2(CH_3)_3$). *meso*-**2b**: δ 9.19 (s, 8H, β-H), 5.89 (4H, $C_6H_2(CH_3)_3$), 3.34 (s, 2H, OC*H*Mes), 2.36 (s, 12H, *meso*-$C_6H_4CH_3$). Other signals overlapped with the *dl* diolate. UV-vis (toluene): 591 (3.70), 552 (4.32), 426 (5.56).

Reaction of (TTP)Ti(η^2-PhC≡CPh) with *p*-$CH_3C_6H_4CHO$. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (3.2 mg, 3.6 μmol), *p*-$CH_3C_6H_4CHO$ (1.5 mg, 12 μmol), Ph_3CH (1.7 mg, 7.0 μmol, internal standard) and C_6D_6 (0.5 mL). Within 10 min, all of PhC≡CPh had been displaced and a diolato complex (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (**2c**) was produced in 87% yield with a *dl*/*meso* ratio of 1.8. The ^{1}H NMR and UV-vis spectra were identical to those for an authentic sample prepared by the reaction of (TTP)Ti=N^{i}Pr with 1,2-di(*p*-tolyl)ethan-1,2-diol.[9]

Preparation of (TTP)Ti[OC(Ph)(Me)C(Ph)(Me)O] (3a). To a hexane slurry of (TTP)Ti(η^2-PhC≡CPh) (**1**) (57 mg, 0.064 mmol) was added a solution of acetophenone (24 mg, 0.20 mmol) in hexane (10 mL). The dark red mixture was stirred for ~40 min. A purple product was collected by filtration and dried under vacuum, which contained both *dl* and *meso* forms of **3a** with a *dl*/*meso* ratio of 6.0 (35 mg, 58%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-**3a**: δ 9.19 (s, 8H, β-H), 8.27 (br, 4H, *meso*-$C_6H_4CH_3$), 8.05 (br, 4H, *meso*-$C_6H_4CH_3$), 7.27 (d, 8H, *meso*-$C_6H_4CH_3$), 6.68 (m, 6H, *p, m*-C_6H_5), 5.55 (d, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -1.57 (s, 6H, OC(Ph)CH_3). *meso*-**3a**: δ 6.35 (t, 2H, *p*-C_6H_5), 6.29 (t, 4H, *m*-C_6H_5), 4.48 (d, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -0.73 (s, 6H, OCPhCH_3). Other

signals overlapped with the *dl* diolate in the aromatic region. UV-vis(toluene): 553 (4.46), 426 (5.41), 413 (5.52). The *dl* form of this complex has been reported previously.[9]

Preparation of (TTP)Ti[OC(*p*-MeOPh)(Me)C(*p*-MeOPh)(Me)O] (3b). To a toluene solution of *p*-methoxyacetophenone (29 mg, 0.19 mmol) was added a solution of (TTP)Ti(η^2-PhC≡CPh) (**1**) (83 mg, 0.092 mmol) in toluene (10 mL). The purple red solution was stirred for ~40 min and filtered, then the solvent was removed in vacuo. The residue was taken up in toluene (2 mL), layered with hexane (6 mL), and placed in freezer at -25°C for ~20 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple material, which contained both *dl* and *meso* forms of **3b** with a *dl*/*meso* ratio of 5.5 (68 mg, 72%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-**3b**: δ 9.21 (s, 8H, β-H), 8.29 (br, 4H, *meso*-$C_6H_4CH_3$), 8.06 (br, 4H, *meso*-$C_6H_4CH_3$), 7.26 (br, 8H, *meso*-$C_6H_4CH_3$), 6.32 (d, 4H, *m*-$C_6H_4OCH_3$), 5.50 (d, 4H, *o*- $C_6H_4OCH_3$), 3.08 (s, 3H, $C_6H_4OCH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -1.53 (s, 6H, $OCCH_3$). *meso*-**3b**: δ 5.96 (d, 4H, *m*-$C_6H_4OCH_3$), 4.48 (d, 4H, *o*-$C_6H_4OCH_3$), 2.94 (s, 3H, $C_6H_4OCH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.72 (s, 6H, $OCCH_3$). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis(toluene): 553 (4.35), 427 (5.46).

Preparation of (TTP)Ti[OC(Ph)(Et)C(Ph)(Et)O] (3c). To a toluene solution of propiophenone (28 mg, 0.21 mmol) was added a solution of (TTP)Ti(η^2-PhC≡CPh) (**1**) (87 mg, 0.098 mmol) in toluene (10 mL). The purple red solution was stirred for ~40 min and filtered, then the solvent was removed under vacuum. The residue was taken up in toluene (3 mL), layered with hexane (5 mL), and placed in freezer at -25°C for ~22 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple material,

which consisted of both *dl* and *meso* forms of **3c** with a *dl/meso* ratio of 5.3 (66 mg, 69%). ^{1}H NMR (C_6D_6, 300 MHz): *dl*-**3c**: δ 9.19 (q, 8H, β-H), 8.47 (br, 4H, *meso*-$C_6H_4CH_3$), 7.98 (br, 4H, *meso*-$C_6H_4CH_3$), 7.29 (m, 8H, *meso*-$C_6H_4CH_3$), 6.99 (t, 2H, *m*-C_6H_5), 6.70 (t, 2H, *p*-C_6H_5), 6.52 (t, 2H, *m'*-C_6H_5), 5.75 (d, 2H, *o'*-C_6H_5), 5.31 (d, 2H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -0.48 (m, 2H, CH_2CH_3), -0.93 (t, 6H, CH_2CH_3), -2.27 (m, 2H, CH_2CH_3). *meso*-**3c**: δ 9.21 (s, 8H, β-H), 6.37 (t, 2H, *p*-C_6H_5), 6.31 (t, 4H, *m*-C_6H_5), 4.33 (d, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), 0.39 (m, 2H, CH_2CH_3), -0.56 (t, 6H, CH_2CH_3), -1.18 (m, 2H, CH_2CH_3). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis(toluene): 554 (4.14), 427 (5.28), 414 (5.22).

Reaction of (TTP)Ti(η^2-PhC≡CPh) with benzophenone. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (0.4 mg, 0.45 μmol), benzophenone (0.5 mg, 2.7 μmol), Ph_3CH (1.3 mg, 5.3 μmol, internal standard) and C_6D_6 (0.5 mL). Within 10 min, all of the PhC≡CPh had been displaced and benzopinacolate (TTP)Ti[$OC(Ph)_2C(Ph)_2O$] (**3d**) was produced in 84% yield. ^{1}H NMR (C_6D_6, 300 MHz): δ 9.16 (s, 8H, β-H), 8.04 (m, 4H, *meso*-$C_6H_4CH_3$), 7.70 (m, 4H, *meso*-$C_6H_4CH_3$, obscured by benzophenone), 7.25 (m, 8H, *meso*-$C_6H_4CH_3$), 6.52 (t, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *p*-C_{65}), 6.39 (t, 8H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-C_6H_5), 4.76 (d, 8H, $^3J_{H\text{-}H}$ = 7.5 Hz, *o*-C_6H_5), 2.41 (s, 12H, *meso*-$C_6H_4CH_3$). The amount of **3d** diminished rapidly in solution and only paramagnetic porphyrin species were observed after 3 h by ^{1}H NMR spectroscopy.

Preparation of (TTP)Ti[$OC(Ph)_2CH(Ph)O$] (4a). A round bottom flask was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (112 mg, 0.125 mmol) and benzophenone (95 mg, 0.52 mmol), and toluene (8 mL). After stirring for 1 min, a toluene solution (4 mL) of

benzaldehyde (47 mg, 0.44 mmol) was added and the mixture was stirred for an additional 2 min. Subsequently, the mixture was filtered through a pad of activated neutral alumina and the solvent was removed in vacuo. The residue was taken up in toluene (3 mL), layered with hexane (6 mL), and placed in freezer at -25°C for 12 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple product **4a** (73 mg, 58%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.10 (dd, 8H, β-H), 8.07 (br m, 4H, *meso*-$C_6H_4CH_3$), 7.96 (br m, 4H, *meso*-$C_6H_4CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 6.71 (t, 1H, *p*-C_6H_5), 6.64 (t, 2H, *m*-C_6H_5), 6.48 (t, 1H, *p*-C_6H_5), 6.34 (m, 5H, *m, p*-C_6H_5), 5.26 (d, 2H, *o*-C_6H_5), 5.17 (d, 2H, *o*-C_6H_5) 4.24 (d, 2H, *o*-C_6H_5), 3.91 (s, 1H, OC*H*), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$). ^{13}C NMR (C_6D_6, 400 MHz): δ 150.3 (α-pyrrole), 149.8 (α-pyrrole), 146.5, 144.5, 140.7, 139.7, 134.9 (*o*-tolyl), 133.5 (*o*-tolyl), 132.0 (β-pyrrole), 131.7 (β-pyrrole), 130.1, 127.8 (*m*-tolyl, obscured by solvent), 127.1, 126.8, 126.5, 126.2, 125.8, 125.6, 124.3, 100.3 (OCHPh), 100.0 ($OCPh_2$), 21.3 (*meso*-$C_6H_4CH_3$). UV-vis(toluene): 413 (5.29), 427 (5.21), 553 (4.22).

Preparation of (TTP)Ti[OC(Ph)$_2$C(Ph)(Me)O] (4b). A round bottom flask was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (62 mg, 0.070 mmol) and benzophenone (38 mg, 0.21 mmol) and toluene (8 mL). After stirring for 1 min, a toluene solution (3 mL) of acetophenone (59 mg, 0.49 mmol) was added and the mixture was stirred for an additional 5 min. Subsequently, the mixture was filtered through a pad of activated neutral alumina and the solvent was removed in vacuo. The residue was taken up in toluene (2 mL), layered with hexane (4 mL), and placed in freezer at -25°C for ~2 days. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple product **4b** (35 mg, 49%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.14 (s, 8H, β-H), 8.21 (br, 4H, *meso*-$C_6H_4CH_3$), 8.01 (br, 4H,

meso-$C_6H_4CH_3$), 7.27 (d, 8H, *meso*-$C_6H_4CH_3$), 6.72 (m, 3H, *m, p*-C_6H_5), 6.56 (m, 3H, *m, p*-C_6H_5), 6.45 (t, 1H, *p*-C_6H_5), 6.32 (t, 2H, *m*-C_6H_5), 5.80 (d, 2H, *o*-C_6H_5), 5.75 (d, 2H, *o*-C_6H_5), 4.76 (d, 2H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -1.51 (s, 3H, OCCH_3). UV-vis(toluene): 591 (3.81), 553 (4.29), 426 (5.52). Anal. Calcd for $C_{69}H_{54}N_4O_2Ti$: C, 81.32; H, 5.34; N, 5.50. Found: C, 80.90; H, 5.30; N, 5.20.

Preparation of (TTP)Ti[OC(Ph)$_2$C(Me)$_2$O] (4c). A round bottom flask was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (66 mg, 0.073 mmol) and benzophenone (42 mg, 0.23 mmol) and toluene (8 mL). After stirring for 1 min, a toluene solution (4 mL) of acetone (32 mg, 0.56 mmol) was added and the mixture was stirred for an additional 5 min. Subsequently, the mixture was filtered through a pad of activated neutral alumina and the solvent was removed in vacuo. The residue was taken up in toluene (0.5 mL), layered with hexane (5 mL), and placed in freezer at -25°C for ~2 days. Filtration, washing with hexane (1×2 mL) and drying under vacuum afforded a dard red product **4c** (26 mg, 37%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.13 (s, 8H, *β*-H), 8.12 (br, 4H, *meso*-$C_6H_4CH_3$), 7.98 (br, 4H, *meso*-$C_6H_4CH_3$), 7.29 (m, 8H, *meso*-$C_6H_4CH_3$), 6.69 (t, 2H, *p*-C_6H_5), 6.60 (t, 4H, *m*-C_6H_5), 5.18 (d, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -1.19 (s, 6H, C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 149.6 (*α*-pyrrole), 143.1, 139.3, 134.6 (*o*-tolyl), 133.4 (*o*-tolyl), 131.4 (*β*-pyrrole), 130.1, 128.3, 127.5 (*m*-tolyl), 126.1 (*o*-phenyl), 126.0 (*m*-phenyl), 125.0 (*p*-phenyl), 123.7, 100.9 (OCPh_2), 94.3 (OCMe_2), 26.0 (OCMe_2), 21.6 (*meso*-$C_6H_4CH_3$). UV-vis(toluene): 413 (5.33), 426 (5.41), 552 (4.22).

Cross coupling of actone with acetophenone. An NMR tube equipped with teflon stopcock was charged with (TTP)Ti(η^2-PhC≡CPh) (**1**) (1.4 mg, 1.6 μmol) and Ph_3CH (1.9

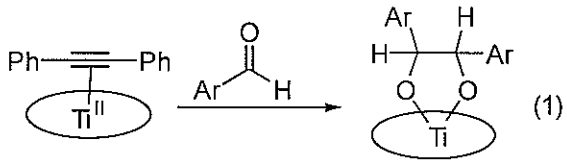
mg, 7.8 μmol, internal standard). A mixture of acetone (13.7 mg, 236 μmol) and acetophenone (1.4 mg, 12 μmol) in C_6D_6 was added. Within 20 min complex **1** was consumed and a new diolato complex (TTP)Ti[OC(Ph)(Me)C(Me)$_2$O] (**4d**) was produced in 85% yield. ^{1}H NMR data for **4d** (300 MHz, C_6D_6): δ 9.15 (s, 8H, *β*-H), 8.29 (br, 4H, *meso*-$C_6H_4CH_3$), 8.02 (br, 4H, *meso*-$C_6H_4CH_3$), 7.27 (d, 8H, *meso*-$C_6H_4CH_3$, obscured), 6.65 (m, 3H, *p,m*-C_6H_5), 5.48 (d, 2H, *o*-C_6H_5), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.67 (s, 3H), -1.26 (s, 3H), -2.03 (s, 3H). The homo coupling product of acetophenone, (TTP)Ti[OC(Ph)(Me)C(Ph)(Me)O] (**3a**), was also observed in ~5% yield.

Preparation of (TTP)Ti[OC(Ph)C(Ph)O] (5). To a stirred solution of benzil (27 mg, 0.13 mmol) in toluene (4 mL), was added a solution of (TTP)Ti(η^2-PhC≡CPh) (**1**) (110 mg, 0.122 mmol) in 10 mL of toluene. The purple red solution was stirred for 12 h, filtered, and the solvent was removed under vacuum. The residue was taken up in CH_2Cl_2 (3 mL), layered with hexane (6 mL), and placed in freezer at -25°C for 24 h. Filtration, washing with hexane (2×2 mL) and drying under vacuum afforded a red-purple material **5**. Yield: 76 mg (67%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.04 (s, 8H,), 8.19 (d, 4H, *meso*-$C_6H_4CH_3$), 7.91 (d, 4H, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, *meso*-$C_6H_4CH_3$), 6.62 (m, 6H, *m*- and *p*-C_6H_5), 5.71 (d, 4H, *o*-C_6H_5), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$). ^{13}C NMR: 150.6, 139.8, 137.2, 134.6 (*o*-$C_6H_4CH_3$), 134.5, 134.0 (*o*-$C_6H_4CH_3$), 132.7, 130.9 (*β*-pyrrole), 128.0 (*o*-C_6H_5), 127.7 (*m*-$C_6H_4CH_3$), 126.7 (*m*-C_6H_5), 125.3, 21.3 (*meso*-$C_6H_4CH_3$). UV-vis (toluene): 426 (5.43), 542 (4.34), 572 (3.75), 635 (3.29). Anal. Calcd for $C_{62}H_{46}N_4O_2Ti \cdot 0.2CH_2Cl_2$: C, 79.15; H, 4.95; N, 5.94. Found: C, 78.88; H, 5.06; N, 5.75.

Reaction of (TTP)TiCl with benzil. An NMR tube equipped with a teflon stopcock was charged with (TTP)TiCl (3.1 mg, 4.1 μmol), benzil (8.1 mg, 39 μmol), Ph_3CH (2.6 mg, 11 μmol) and C_6D_6. The reaction was monitored by NMR spectroscopy. After 2h, ^{1}H NMR analysis revealed the presence of (TTP)$TiCl_2$ and (TTP)Ti[OC(Ph)C(Ph)O] (**5**) in approximately a 1:1 ratio.

Results and Discussion

Reaction of (TTP)Ti(η^2-PhC≡CPh) with aldehydes. Aromatic aldehydes, ArCHO, (Ar = Ph, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, Mesityl), reacted cleanly and rapidly with (TTP)Ti(η^2-PhC≡CPh) (**1**) at ambient temperature to afford the reductive coupling products, (TTP)Ti[OCH(Ar)CH(Ar)O] (**2a-d**) (eq 1). The identity of these diolato complexes was



(1)

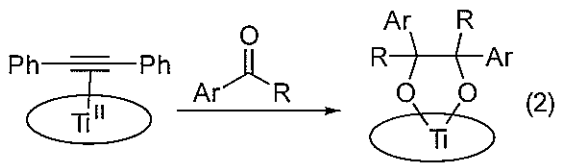
confirmed by an independent synthesis from free diols and an imido titaniumporphyrin complex.[9] The isolated yields were 50-75%, although the conversions of these reactions determined by ^{1}H NMR spectroscopy were generally greater than 85%. Both *dl* and *meso* diolato complexes were obtained, with *dl* isomers as the major products. The *dl*/*meso* ratio ranged over 1.4-2.9, but no evident trend could be derived that was consistent with electronic or steric properties of the aryl groups.

The ^{1}H NMR spectra of the diolato complexes **2a-d** displayed similar patterns. The *β*-pyrrole protons of the porphyrin with *dl*-diolate ligands generally appear as an AB quartet, due to the presence of the stereogenic center in the diolato ligand. In contrast, the *meso*

diolato complexes exhibit a singlet at a slightly lower field for the β-pyrrole protons. Owing to the large ring current effect of metalloporphyrins, the diolato protons resonate at higher fields relative to the free ligands. Note that the NMR signals of aryl groups in *dl* diolates are usually less shifted than those of *meso* diolates. For example, the *o*-C_6H_4Cl protons in *dl*-(TTP)Ti[OCH(*p*-ClC_6H_4)CH(*p*-ClC_6H_4)O] (**2a**) appear at 4.69 ppm, while their *meso* counterparts appear at 4.33 ppm. On the other hand, the protons on oxotitanacyclopentane ring are more upfield shifted in *dl* diolates, as demonstrated in the complex **2a** (2.59 ppm in *dl*-**2a** *vs* 2.96 ppm in *meso*-**2a**).

Aliphatic aldehydes are generally less active towards reductive coupling. Treatment of Ph_2CHCHO with (TTP)Ti(η^2-PhC≡CPh) (**1**) in C_6D_6 afforded a new product with a singlet at δ 9.15 (β-pyrrolic proton) and several upfield shifted signals, which were assignable to the coupling product. This diolato complex was labile and difficult to purify. Its facile decomposition may be due to a β-hydrogen elimination process.[10] Similar treatment of (TTP)Ti(η^2-PhC≡CPh) with propionaldehyde afforded no coupling product.

Reaction of (TTP)Ti(η^2-PhC≡CPh) with ketones. Aromatic ketones, ArCOR, (where Ar = Ph, R = Me, Et; Ar = *p*-CH_3O-C_6H_4, R = Me), reacted cleanly and rapidly with (TTP)Ti(η^2-PhC≡CPh) (**1**) in a toluene solution at ambient temperature to afford coupling products (TTP)Ti[OC(Ar)(R)C(Ar)(R)O] (**3a-c**) (eq 2). Both *dl* and *meso* diolato complexes



(2)

were obtained and isolated in overall yields of 55-75%. The *dl* diolates were in excess with a *dl*/*meso* ratio of 5-6. This higher stereoselectivity displayed by aromatic ketones is

presumably due to their lower activity and larger steric effect compared to aromatic aldehydes in these reactions.

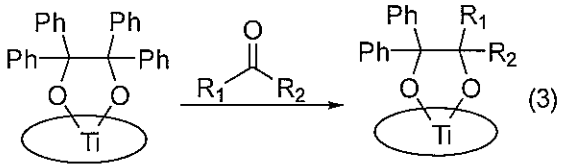
The ^{1}H NMR spectra of the diolato complexes **3a-c** have similar patterns as described above. An unusual phenomenon occurs for the diolate resonances in (TTP)Ti[OC(Et)(Ph)C(Et)(Ph)O] (**3c**). For *dl*-**3c**, the phenyl group of the diolato ligands displays five individual ^{1}H NMR signals, corresponding to the five positions on the phenyl ring. In contrast, only three signals were observed for the phenyl protons in the *meso*-**3c**. Apparently the rotation of phenyl ring in *dl* diolate is restricted on the NMR time scale, presumably due to the increased steric hindrance from the adjacent ethyl group. However, variable temperature NMR study of **3c** in $CDCl_3$ between –50-50 °C did not result in coalescence of the *dl* signals. In addition, the diastereotopic methylene protons in both *dl* and *meso*-**3c** display two well-separated 2H multiplets (–0.48 and –2.27 ppm for *dl*-**3c** and 0.39 and –1.18 ppm for *meso*-**3c**), indicating a large perturbation of the CH_2 unit by the porphyrin ring current.

Treatment of (TTP)Ti(η^2-PhC≡CPh) (**1**) with benzophenone in C_6D_6 afforded a new diamagnetic species in 85% yield, as determined by NMR spectroscopy. The presence of two broad 4H multiplets at 8.04 and 7.70 ppm for the *o*-protons of the *meso* tolyl groups indicated a cis coordination geometry.[11] The upfield signals at 4.76(d), 6.39(t) and 6.52(t) ppm were assignable to phenyl groups of a new ligand coordinated to Ti. The integration data suggested that 2 equiv of benzophenone were incorporated into a carbonyl coupling product, (TTP)Ti[OC(Ph)$_2$C(Ph)$_2$O] (**3d**). Similarly, reaction of (TTP)Ti(η^2-PhC≡CPh) with other diaryl ketones 4,4'-dimethylbenzophenone or 9-fluorenone also afforded the coupling products. However, these diolato products decomposed to a NMR inactive paramagnetic

species that precipitated out of the solution within hours, preventing further characterization. Upon exposure of the product mixtures to air, both oxo- and peroxo- species, (TTP)Ti=O and (TTP)Ti(O_2) were generated as detected by NMR spectroscopy. The lability of the tetra aryl substituted diolato complexes are attributed, in part, to the unfavorably crowded arrangement of four aryl groups. An alternative attempt to prepare **3d** from benzopinacole and an imidotitanium porphyrin, (TTP)Ti=N^{i}Pr, was not successful, while its hafnium analogue is readily accessible by this approach.[9] A sterically more congested aromatic ketone, 2,2,2-triphenyl acetophenone, also could not be reductively coupled with (TTP)Ti(η^2-PhC≡CPh).

Aliphatic ketones are often inert in the coupling reaction. Indeed the reactions of (TTP)Ti(η^2-PhC≡CPh) with acetone, 3-pentanone, and 2-octanone led to either no reaction or paramagnetic species without the formation of diolato complexes.

Cross coupling reaction of carbonyl compounds. Interestingly, the reactive complex (TTP)Ti[OC(Ph)$_2$C(Ph)$_2$O] (**3d**) is found to be a useful precursor for cross coupled diolato complexes. Addition of benzaldehyde or acetophenone to a toluene solution of preformed **3d** resulted in the formation of the cross-coupled diolato complexes, (TTP)Ti[OC(Ph)$_2$C(Ph)(R)O] (R = H, **4a**; Me, **4b**), in near quantitative yields (eq 3). Only traces of the homo-coupling product (**3a**) were observed. Furthermore, it is surprising to note

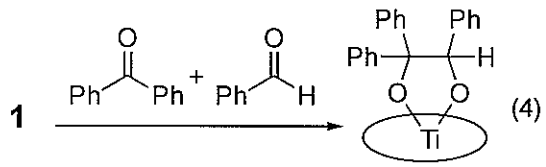


(3)

that treatment of **3d** with acetone, which itself is unreactive toward (TTP)Ti(η^2-PhC≡CPh) (**1**), produced a coupling product 1,1-dimethyl-2,2-diphenyl ethylenediolate,

(TTP)Ti[OC(Ph)$_2$C(Me)$_2$O] (**3c**). Similarly, reaction of **1** with propionaldehyde yielded the cross coupling product (TTP)Ti[OC(Ph)$_2$CH(Et)O].

It was also noted that the prior formation of (TTP)Ti[OC(Ph)$_2$C(Ph)$_2$O] (**3d**) was not necessary, as two carbonyl compounds could be added at the same time and the cross coupled diolates were still the major products. Thus, treatment of (TTP)Ti(η^2-PhC≡CPh) (7.8 μmol) with a mixture of benzophenone (10 μmol) and benzaldehyde (15 μmol) afforded (TTP)Ti[OC(Ph)$_2$CH(Ph)O] (**4a**) in 95% yield (eq 4). Addition of a solution of benzophenone (122 μmol) and acetone (121 μmol) to a solution of (TTP)Ti(η^2-PhC≡CPh) (1.9 μmol) resulted in the formation of diolate (TTP)Ti[OC(Ph)$_2$C(Me)$_2$O] (**4c**) in 61% yield (eq 5). Furthermore, carbonyl compounds other than benzophenone could be used as coupling partner to activate acetone in these coupling reactions. For example, treatment of (TTP)Ti(η^2-PhC≡CPh) with a mixture of acetophenone and acetone generated the cross



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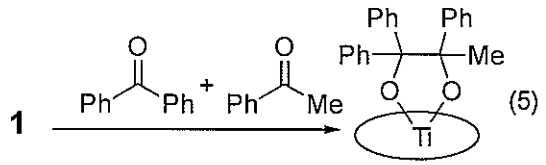

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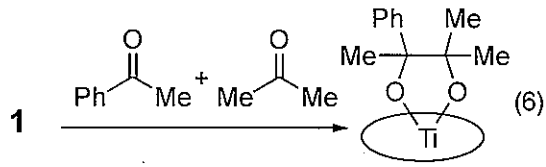


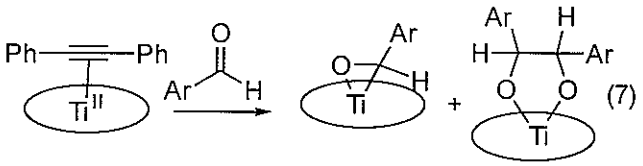
(6)

coupling product (TTP)Ti[OC(Ph)(Me)C(Me)$_2$O] in 85% yield, as determined by NMR spectroscopy (eq 6). However, a complex mixture was observed when (TTP)Ti(η^2-

PhC≡CPh) was treated with a mixture of equal molar amounts of acetophenone and benzaldehyde,.

In light of acetone being coupled as described previously, attempts were made to couple (TTP)Ti[$OC(Ph)_2C(Ph)_2O$] with a variety of other substrates, such as methyl benzoate, ^{i}PrNCO, PhCH=NPh, or CS_2, but no further reactions were observed.

Observation of η^2-carbonyl complexes. Upon treatment of *p*-chlorobenzaldehyde with excess (TTP)Ti(η^2-PhC≡CPh) in C_6D_6, a new diamagnetic species was observed, as a minor product, along with the coupling diolato product (eq 7). This species showed two



Ar = Ph, p-Cl-C_6H_4

highly upfield shifted 2H doublets at 6.26 and 3.69 ppm, a 1H singlet at –1.0 ppm as well as an 8H *β*-pyrrole singlet at 9.02 ppm. A similar species was observed in the reaction of benzaldehyde with (TTP)Ti(η^2-PhC≡CPh) in hexane, featuring two upfield phenyl signals at 6.34 and 3.97 ppm and a one-proton singlet at –0.82 ppm. A close proximity of the axial ligand to the porphyrin ring was indicated by the relative magnitude of the upfield shifts. These species are assigned as η^2-carbonyl complexes (eq 7). Zirconium and hafnium η^2-carbonyl complexes have been prepared by treatment of dialkyl[12] or alkyl hydride[13] complexes with CO. Titanium η^2-carbonyl complexes were proposed as reactive intermediates that couple with carbonyl compounds, although they could not be isolated.[14] Regarding the extremely large upfield shift of aldehydic hydrogens (from 9.68 to –1.0 ppm in (TTP)Ti(η^2-$OCHC_6H_4Cl$)), it has been reported that η^2-carbonyl complexes possess a

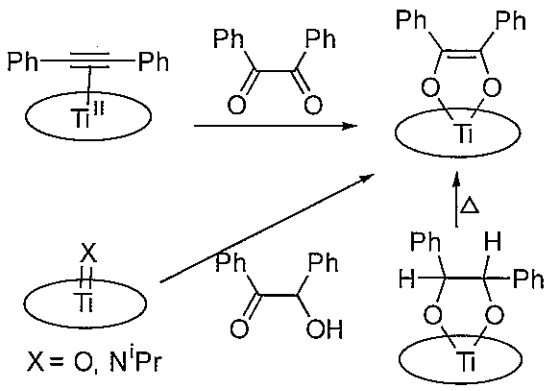
metalloxocyclopropyl-like ring due to the back donation of electrons from the metal dπ orbital to C=O π* orbital.[15] Consequently, the ^{1}H NMR signal of aldehydic hydrogen in $Cp_2Mo(\eta^2$-PhCHO), e. g., appears at 4.51 ppm in CD_2Cl_2.[15a] On the other hand, the upfield shift of 5-6 ppm magnitude for α-hydrogen signals of the axial ligands in metalloporphyrin complexes is not uncommon, due to the large ring current effect. However these species (TTP)Ti(η^2-OCHAr) were labile and it was not possible to purify them.

Mechanistic aspects of coupling reactions. Two pathways are generally invoked in the reductive coupling of carbonyl compounds. While the dimerization of ketyl radicals is often assumed to be responsible for the formation of metallapinacolate intermediates,[16] some researchers prefer an alternative pathway involving a carbonyl insertion into the M-C bond of a η^2-carbonyl intermediate.[17] The latter process is supported by DFT calculations.[18]

It seems reasonable to assume that different reaction pathways exist in these coupling reactions, depending on the metal system utilized and reaction conditions employed. In the present study, the observation of η^2-carbonyl species suggested that a carbonyl insertion pathway might be operative. The rapid formation of cross coupling products from diolato complexes and carbonyl compounds indicates that an equilibrium exists between (TTP)Ti[$OC(Ph)_2C(Ph)_2O$] and an η^2-carbonyl complex (TTP)Ti(η^2-$OCPh_2$). The reversibility between a pinacolate and an η^2-carbonyl compound has been demonstrated in other titanium-based systems recently.[19] Furthermore, the enhanced reactivity of preformed (TTP)Ti[$OC(Ph)_2C(Ph)_2O$] toward acetone also agrees with such a scheme involving reversible cleavage of a C-C bond and a carbonyl insertion pathway, since aryl ketones are better π-acid ligands to form η^2-carbonyl complexes. Such a pathway is also consistent with

our investigation of (TTP)Ti=O catalyzed diol cleavage reaction, where a radical pathway appears to be less likely.[20]

Reaction of (TTP)Ti(η^2-PhC≡CPh) with diketone. The reaction of (TTP)Ti(η^2-PhC≡CPh) (**1**) with a vicinal diketone, benzil, in toluene yielded a new complex with a 6H multiplet at 6.62 ppm and a 4H double of doublet at 5.71 ppm, as well as an 8H β-pyrrolic singlet at 9.04 ppm. This new compound was identified as an enediolato complex, (TTP)Ti[OC(Ph)C(Ph)O] (**5**). Treatment of (TTP)Ti=N^{i}Pr or (TTP)TiO with benzoin yielded the same product. This species was also observed in the thermal decomposition reaction of the diolato complex (TTP)Ti[OCH(Ph)CH(Ph)O] (scheme 1).[9] A tantalum



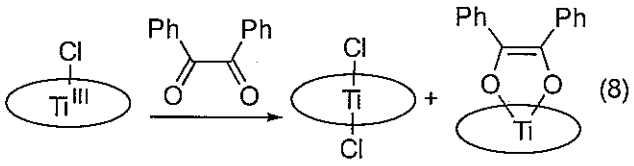
Scheme 1

porphyrin enediolato complex was also detected upon treatment of dialkyl metalloporphyrin complex [(OEP)TaMe$_2$]BPh$_4$ with CO.[21] Upon exposure to air, (TTP)Ti[OC(Ph)C(Ph)O] (**5**) decomposed slowly to produce benzil and a diamagnetic species with a singlet at 9.14 ppm, consistent with the formulation of the peroxo titaniumporphyrin, (TTP)Ti(O$_2$). The peroxo complex further decayed to (TTP)Ti=O in air.

Reactivity of diolato complexes. As reported earlier,[9] the titanium porphyrin diolato complexes are fairly robust in air as solids. For example, (TTP)Ti[OCH(*p*-ClC_6H_4)CH(*p*-ClC_6H_4)O] can be stored in air for months without significant decomposition. In solution, however, release of free aldehydes or ketones was noticeable within 1 day at ambient temperature. The *meso* diolates are found to be more labile than the *dl* isomer in all cases.

Upon heating under N_2, diolato complexes **3a-c** decomposed to free ketones and paramagnetic porphyrin species with broad NMR signals at 2.40 ppm and/or 2.50 ppm. Trapping with a large excess of pyridine partially generated a well-defined bispyridine adduct, (TTP)Ti$(py)_2$,[6c] while trapping with benzaldehyde gave no coupling product. It is noteworthy that during the thermal decomposition of (TTP)Ti[OC(Ph)(Me)C(Ph)(Me)O] (**3a**), an olefin, Ph(Me)C=C(Me)Ph was also detected by GC-MS (m/z=208), although the yield was low (<10%). This is reminiscent of McMurry reactions, which afford olefins at elevated temperature or diols at lower temperature.[22] In comparison, the thermal decomposition of (TTP)Ti[OCH(Ph)CH(Ph)O] (**2d**) under N_2 afforded a complex mixture of products, including (TTP)TiO, enediolate (TTP)Ti[OC(Ph)C(Ph)O] (**5**), benzaldehyde and benzyl alcohol, as well as stilbene oxide.[9]

Reactivity of (TTP)TiCl. Ti(III) complexes have been shown to be efficient reducing reagents and capable of mediating pinacolic coupling reactions.[23] $CpTiCl_2$ reacts with R_2CO to form dimeric coupling complexes.[24] We also found that (TTP)TiCl reacts with azide to afford imido Ti(IV) porphyrin complexes.[25] To extend the scope of chemistry described in previous sections, the investigation of (TTP)TiCl with carbonyl compounds was conducted. Treatment of (TTP)TiCl with excess benzil in C_6D_6 produced equal amounts of (TTP)$TiCl_2$ and the enediolate (TTP)Ti[OCPhCPhO] within 2 h (eq 8). However, no



(8)

coupling reaction was observed when (TTP)TiCl was treated with benzaldehyde or *p*-tolualdehyde in C_6D_6. Interestingly, transformation of (TTP)TiCl to (TTP)Ti=O and $(TTP)TiCl_2$ in approximately 2:1 ratio was observed by ^1H NMR spectroscopy. The oxygen source was probably from adventitious traces of dioxygen in the glovebox. Similar reactivity was observed for (TPP)TiF.[26] The reaction of (TTP)TiCl with a diol, 1,2-di(*p*-tolyl)-ethan-1,2-diol, was also investigated. The formation of a diolato complex, (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (**2a**) was observed in up to 50% yield, but no Ti(II) species, $(TTP)Ti(py)_2$, could be trapped even in neat pyridine solvent.

Conclusion

In this study we have described the reductive coupling reactions of carbonyl compounds with a low valent titanium(II) porphyrin complex, (TTP)Ti(η^2-PhC≡CPh). A series of titanium (IV) diolato complexes were obtained. Notably cross-coupled diolato complexes could be produced, even when one of the coupling partners itself was not reactive toward (TTP)Ti(η^2-PhC≡CPh). With the observation of η^2-carbonyl species, a carbonyl insertion process was suggested for the coupling reactions. A radical pathway seems unlikely based on previous studies with a radical clock.

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CHAPTER 3. ALCOHOL OXIDATION WITH DIOXYGEN MEDIATED BY OXOTITANIUM PORPHYRIN AND RELATED TRANSITION METAL COMPLEXES

A paper to be submitted to *Organometallics*

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Abstract

Oxotitanium porphyrin (TTP)Ti=O and related transition metal complexes were shown to catalyzed the oxidation of various alcohols using atmospheric oxygen as the oxidant. Vicinal diols were cleaved to carbonyl compounds in the presence of catalytic amounts of (TTP)Ti=O, (TTP)V=O or (Saldach)V=O. α-Hydroxy ketones were oxidized to α-diketones with (TTP)Ti=O. Benzyl alcohol was oxidized to benzaldehyde in modest to high yields by a number of high valent transition metal complexes. Reaction pathways for the transformations mediated by (TTP)Ti=O are discussed. Formation of diolato and enediolato complexes is believed to be the key step in the diol cleavage and α-hydroxy ketone oxidation, respectively.

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Introduction

The involvement of oxometalloporphyrins as active intermediates has long been recognized in the catalytic cycle of many heme metalloenzymes, particularly the cytochrome P450 family.[1] Extensive research devoted to this area has confirmed the presence of such species in the oxidation reactions by using synthetic metalloporphyrin model systems.[2] Iron and manganese porphyrins received much attention due to their remarkable activity and versatility in oxidation reactions.[2,3] On the other hand, early transition metal porphyrins such as oxotitanium or oxovanadium porphyrins are often regarded as inert due to the strength of their metal-oxygen multiple bonds.[4]

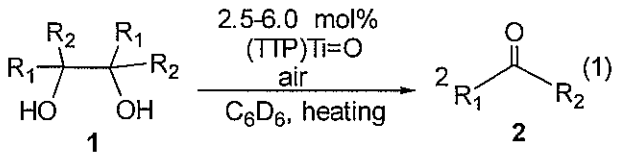
In the course of our study of group 4 metalloporphyrin diolato complexes, it was found that (TTP)Ti=O[5] reacts with free diols to yield diolato complexes.[6] It was also noted that these diolato complexes undergo oxidative cleavage reactions at elevated temperature to release carbonyl compounds. A catalytic cycle converting vicinal diols into ketones and/or aldehydes was designed. It was further extended to other types of substrates, including α-hydroxy ketones and simple alcohols. Here we report our study on these and related systems.

Results and Discussion

(TTP)Ti=O mediated vicinal diol oxidation. Oxidation of diols is an important organic transformation, partially due to its connection with the enzyme hemoprotein ligninase.[7] The usual oxidation products of vicinal diols are aldehydes/ketones,[8] carboxylic acids,[9] or a pair of compounds consisting of a carbonyl compound and an alcohol,[10] resulting from the oxidative cleavage of C-C bonds. Oxidation of vicinal diols to α-hydroxy ketones or α-diketones without C-C scission is also possible.[11] Selective oxidation has been achieved

by employing different oxidants and/or catalytic systems. While a number of stoichiometric processes exist for these transformations, metal-based catalytic systems are more favorable due to increasing environmental consciousness. Particularly, those systems using dioxygen as the oxidant are very attractive from both economic and ecological standpoints.[12]

Prompted by our previous study of group 4 metalloporphyrin diolato complexes,[6] we examined the utility of (TTP)Ti=O as a catalyst for the oxidative cleavage of vicinal diols. Indeed, (TTP)Ti=O was found to catalyze the diol cleavage under aerobic conditions (eq. 1).[13] Heating a C_6D_6 solution of 2,3-diphenylbutane-2,3-diol and 4.6 mol% (TTP)Ti=O in the presence of air in a sealed NMR tube resulted in the conversion of the diol to



1 **2**

	R_1	R_2
a	Ph	Ph
b	Me	Ph
c	Me	Me
d	H	Ph
e	H	*p*-tolyl

acetophenone in nearly quantitative yield (98%), Table 1. A diolato complex, (TTP)Ti[OC(Ph)(Me)C(Ph)(Me)O],[6] was observed during the reaction by ^{1}H NMR spectroscopy. Likewise, benzopinacole was converted into benzophenone in high yield, but the reaction reached completion faster than that of 2,3-diphenylbutane-2,3-diol. While a peroxo species (TTP)Ti(O_2) was the only intermediate observed in this transformation, both (TTP)Ti=O and (TTP)Ti(O_2) were present after all of the diol was consumed. The formation of water was also observed in these two reactions.

When *meso*-hydrobenzoin, a less substituted diol, was subjected to the same catalytic conditions, only a 37% yield of benzaldehyde was obtained after the complete consumption

Table 1: (TTP)Ti=O-mediated vicinal diol cleavages

Run	Substrate	Time h	Conv%	Yield %	t.o.n	Other products[d]
1	**1a**	10	68	67	36	
		31	100	98	53	H_2O(16%)
2	**1b**	17	24	20	8.5	H_2O
		48	98	98	37	
3[b]	**1b**	20	39	20	13	Pyridine
		43	100	67	44	
4	**1c**	165	6.3	3.6	11	
5	**1d**	71	47	15	11	Alc 3.5, bzl 15
		135	83	22	17	Alc 7.4, bzl 22
		210	98	37	27	Alc 9.0, bzl 29
6[c]	**1e**	22	58	9.8	9.2	Alc, benzil
		82	76	20	19	Alc(1.2), bzl(6.8)
		168	96	23	22	Alc(1.5), bzl(6.5)

(a) t.o.n= mole of cleavage product/mole of (TTP)Ti=O; (b) this reaction was run under N_2 in the presence of excess PyNO (8 equiv). (c) in the presence of 2 equiv CH_3COOH. (d) alc: benzyl alcohol; bzl: benzil.

of the starting diol. Other products, benzyl alcohol and benzil were detected in significant amounts, 9% and 29%, respectively. This is consistent with diolato complexes serving as intermediates in these catalytic reactions. In an independent experiment, thermolysis of the

diolato complex (TTP)Ti[OCH(Ph)CH(Ph)O] was found to afford benzaldehyde, as well as benzil and benzyl alcohol.[6]

Unactivated diols were also examined as substrates. Under similar conditions, pinacol was cleaved in a much longer time span to give acetone. It took 265 h to achieve 20 turnovers. Diolato complex (TTP)Ti[$OC(Me)_2C(Me)_2O$] was observed during the reaction by ^{1}H NMR spectroscopy. However, when cyclic diols such as *trans*-1,2-cyclohexanediol or *trans*-1,2-cycloheptanediol were used, no formation of the corresponding diolates was detected and no cleavage products were observed even after 7 days of heating, although other uncharacterized species were present.

Attempts were made to improve the yield, reaction rate and selectivity. Pinacol and hydrobenzoin were chosen as substrates for optimization of the catalytic reaction conditions. A variety of acids and bases were tested in this context (Table 2). For the oxidative cleavage of *meso*-hydrobenzoin, addition of benzoic acid (BA), *m*-chlorobenzoic acid (mCBA), acetic acid or pyridine showed moderate acceleration effects, although the reaction was still quite sluggish. The reaction was cleaner, producing less benzyl alcohol (2.0-4.6%) and benzil (9-13%). When a stronger acid, *p*-toluenesulfonic acid (TsOH) was used, the conversion of diol was complete within 31 h and less benzyl alcohol and benzil were produced (run 4, Table 2). However, the yield of benzaldehyde was still low (~38%) and a number of unidentified signals appeared in the ^{1}H NMR spectrum. For the cleavage of pinacol, addition of benzoic acid or triethyl amine showed no effect. In the presence of TsOH, however, pinacolone was obtained as the major product (>80%).

Reaction mechanism. Based on the results described above, a probable reaction pathway for the (TTP)Ti=O-catalyzed diol cleavage is shown in Scheme 1. (TTP)Ti=O first

reacts with diols to form diolato complexes, as we have demonstrated previously, although the reaction is not thermodynamically favored.[6] The diolato complexes then undergo

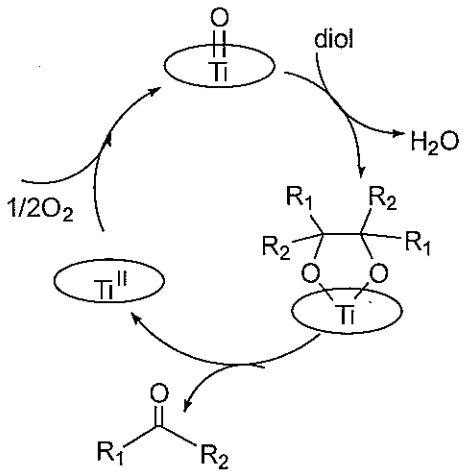
Table 2: (TTP)Ti=O mediated pinacol and *meso*-hydrobenzoin oxidation

Run	Substrate	Additive[a]	Time h	Conv %	Yield %	t.o.n	Other products[b] Alc, benzil	
1	**1d**	-	135	83	22	17	7.4	22
			210	98	37	27	9.0	29
2	**1d**	BA(1.3)	27	59	35	23	1.7	8.0
			75	86	53	36	2.2	9.0
			217	100	58	38	2.2	9.9
3	**1d**	mCBA(0.96)	72	79	37	26	3.3	8.8
			164	85	44	31	3.8	11
4	**1d**	TsOH(0.11)	31	99	38	23	2.8	7.8
5	**1d**	Pyridine (8)	17	49	32	26	1.3	7.3
			82	89	38	30	4.6	13
			166	97	37	30	4.7	16
6	**1c**	BA(0.16)	105	4.9	2.7	7.0		
			165	8.0	4.1	11		
7	**1c**	TsOH(0.79)	7	100	-		Pinacolone (>80%)	

(a) additive used with mol equivalent in parentheses: BA, benzoic acid; mCBA, *m*-chlorobenzoic acid; TsOH, *p*-toluenesulfonic acid. (b) alc: benzyl alcohol; bzl: benzil.

oxidative cleavage to release carbonyl compounds and a transient Ti^{II} species. This species is subsequently oxidized back to (TTP)Ti=O or to (TTP)Ti(O_2) by molecular oxygen in the

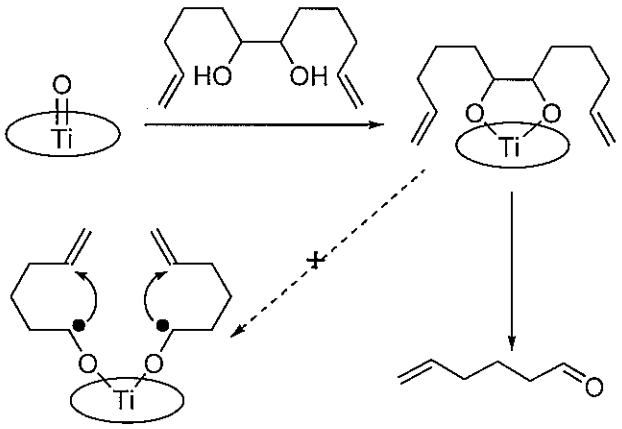
air. Both (TTP)Ti=O and (TTP)Ti(O_2) species appear to be active for this catalytic transformation. For activated and sterically hindered diols such as benzopinacole, the cleavage of the corresponding diolates is facile and no diolato complexes are observed in the reaction, although we have independently demonstrated the existence of such diolato complexes.[14] For other diols including hydrobenzoin, the cleavage is slow and diolato complexes were observed. Since (TTP)Ti=O was usually observed despite its catalytic amount during the reaction, the diolato complex formation was likely also a slow step. Acids and bases accelerated these reactions, probably by facilitating the formation of diolato complexes.



Scheme 1

In an effort to intercept possible radical intermediates arising from the C-C homolysis of diolato ligands, a diol with terminal C=C double bonds, 1,11-dodecadiene-6,7-diol,[15] was prepared and subject to the catalytic conditions described above. The formation of a diolato complex was evident. However, cyclized products were not detected and only the aldehyde, 5-hexen-1-al was observed in low yield. This suggests that the cleavage step in the above

catalytic cycle is mainly through a concerted two-electron process, rather than a radical mechanism (Scheme 2).



Scheme 2

A few metalloporphyrin complexes have been investigated as catalysts in diol cleavage reactions.[16] A chelating dialkoxo complex was considered as a reactive intermediate but deemed less probable compared to the noncyclic monodiol complex. However, The formation of diolato complexes seems to be the key step in the (TTP)Ti=O-catalyzed reaction. The corresponding diolato complexes were observed in all cases expect for benzopinacole, due to rapid cleavage of the benzopinacolate species. Diols such as *trans*-1,2-cyclohexanediol and *trans*-1,2-cycloheptanediol do not react with (TTP)Ti=O and no cleavage products were observed.

Other oxidizing reagents that are capable of converting (TTP)Ti(II) to (TTP)Ti=O can be substituted for dioxygen. Indeed, in the presence of excess pyridine N-oxide under N_2, 2,3-diphenylbutane-2,3-diol was smoothly converted to acetophenone by catalytic amounts

of (TTP)Ti=O (run 3, Table 1). As expected, no (TTP)Ti(O_2) was observed and pyridine was present after the reaction.

Stereoselectivity. The oxidation of a mixture of *dl*- and *meso*-1,2-di(*p*-tolyl) ethyleneglycol was monitored by ^{1}H NMR spectroscopy in the presence of (TTP)Ti=O. Although the *dl*-diolato complex may be preferably formed from diol and (TTP)Ti=O, as observed by NMR spectroscopy (initial *dl*/*meso* ratio ~10:1), the *meso*-diolate is more labile towards cleavage, as noted in other titanium porphyrins diolato complexes.[14] The overall effect is no significant differentiation between *meso*- and *dl*-diols. This stereochemical outcome is similar to that obtained in (TPP)FeCl-catalyzed diol cleavages.[16a] The disadvantage of the (TPP)FeCl systems is that a stoichiometric co-reductant is necessary.

Vanadyl complex-mediated diol cleavage. Based on the proposed mechanism, other oxometalloporphyrins should also catalyze the diol cleavage reaction, provided that the low-valent metal intermediate species can be readily oxidized by molecular oxygen. In this context we extended this catalytic process to other transition metals and other supporting ligands. Two vanadyl complexes, (TTP)V=O and (Saldach)V=O,[5] were examined in oxidative diol cleavage reactions. The reactions were carried out in sealed NMR tubes, using C_6D_6 as a solvent. The results are summarized in Table 3. For benzopinacole, both complexes worked well, affording 100% conversion of diol and 84-89% yield of benzophenone in comparable times (runs 1 and 5). However, other products, including tetraphenylethylene, tetraphenylethane and diphenylmethane, were detected by NMR and/or GC-MS. In comparison, the (TTP)Ti=O-catalyzed benzopinacole cleavage under air produced benzophenone in 99% yield without any detectable side products.

For the cleavage of *meso*-hydrobenzoin, the (TTP)V=O-catalyzed reaction afforded a benzaldehyde yield of 22% (turnover number = 12) after 50 h of heating (run 2). No benzyl

Table 3: Vanadium complexes mediated diol cleavage

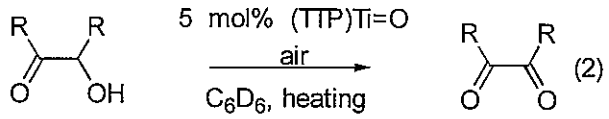
run	substrate	catalyst	time (h)	conv (%)	yield (%)	t.o.n[a]	note[b]
1	**1a**	(TTP)V=O	15	86	84	21	
			34	100	89	22	
2	**1b**	(TTP)V=O	17	17	17	6.3	
			62	100	97	36	
2	**1d**	(TTP)V=O	50	64	22	12	30
			108	65	28	15	32
3[c]	**1d**	(TTP)V=O	18	64	26	13	31
			89	69	32	16	30
			185	78	35	17	25
4	**1c**	(TTP)V=O	19	9.0	8.9	4.0	
			84	13	12	5.1	
			191	25	21	9.6	
5	**1a**	(saldach)V=O	36	100	84	14	
6	**1d**	(saldach)V=O	38	64	48	21	28
			92	82	63	28	22

(a) t.o.n= mole of aldehyde or ketone/mole of catalyst. (b) yield of isomerization to *dl*-hydrobenzoin. (c) with 2 equiv (relative to diol) acetic acid.

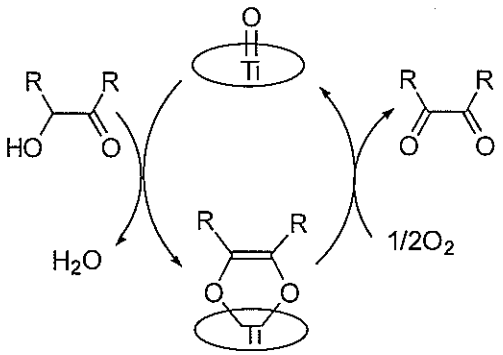
alcohol or benzil were observed, while 31% of *meso*-hydrobenzoin isomerized to the *dl*-form, as observed by ^{1}H NMR spectroscopy (δ: *meso*-diol 4.61; *dl*-diol 4.46 ppm). *Meso-dl* isomerization of vicinal diols has been observed under thermal conditions or in the presence of transition metal complexes.[17] Longer reaction times gave no improvement for the yield of aldedhyde or for the conversion of diol. For the same transformation, (Saldach)V=O performed better, giving higher conversion, higher yield of benzaldehyde (63%) and less isomerization to *dl*-hydrobenzoin (22%) after 92 h (run 6). It was observed that the color of (Saldach)V=O changed from grey-green to brown during the reaction. Both reactions slowed down with time, which suggests a deactivation of the catalysts. In comparison, the (TTP)Ti=O-catalyzed *meso*-hydrobenzoin reaction produced significant amounts of benzil and benzyl alcohol as side products, while little or no isomerization was observed.

When acetic acid was added to the (TTP)V=O-catalyzed hydrobenzoin cleavage, the conversion of diol and formation of benzaldehyde was slightly accelerated (runs 2 & 3, Table 3). When TsOH was used, the major product was the rearrangement product, Ph_2CHCHO, as well as a small amount of benzil. For the cleavage of pinacol to actone, both (TTP)V=O and (Saldach)V=O were poor catalysts, and the addition of benzoic acid did not seem to accelerate this transformation.

Catalytic oxidation of α-hydroxy ketones to α-diketones by (TTP)Ti=O. Oxidation of α-hydroxy ketones often affords α-diketones, which are useful synthetic intermediates.[18] Many methods have been developed for this transformation, though few of them utilize dioxygen as the oxidant.[19] Thus α-hydroxy ketones were found to be effectively oxidized to α-diketones using atmospheric oxygen (eq. 2) by catalytic amounts of (TTP)Ti=O.[13]



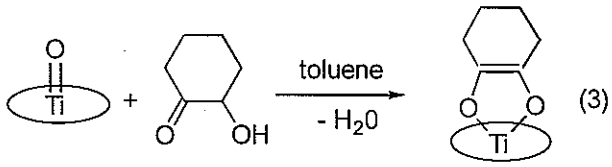
Heating an aerobic C_6D_6 solution of benzoin in the presence of 5 mol% (TTP)Ti=O in an NMR tube resulted in the smooth conversion of benzoin to benzil. Total consumption of benzoin occurred within 20 h and benzil was obtained in 92% yield, as well as a small amount of benzaldehye (2.7%). Presumably the reaction proceeds through an enediolato intermediate (TTP)Ti[OC(Ph)C(Ph)O],[6] that is formed via the reaction between (TTP)Ti=O and benzoin (Scheme 3). This species further reacts with dioxygen in air to provide benzil and (TTP)Ti=O and/or (TTP)Ti(O_2), as we have shown previously.[14] Indeed, ^{1}H NMR monitoring of the reaction showed the presence of (TTP)Ti[OC(Ph)C(Ph)O] throughout the reaction. The release of benzil from the enediolato complex appears to be the rate-limiting step.



Scheme 3

Cyclic α-hydroxy ketones can be converted to α-diketones as well. When 2-hydroxy-cyclohexnone (adipoin) was subjected to catalytic conditions similar to those for the oxidation of benzoin, 1,2-cyclohexanedione was obtained in 87% yield after 41 h of heating.

No cleavage product was observed for this case. Again, an enediolato intermediate (TTP)Ti(OC_6H_8O) was observed throughout the reaction. Moreover, this enediolato species can be isolated from the reaction between (TTP)Ti=O and excess adipoin under N_2 (eq. 3).



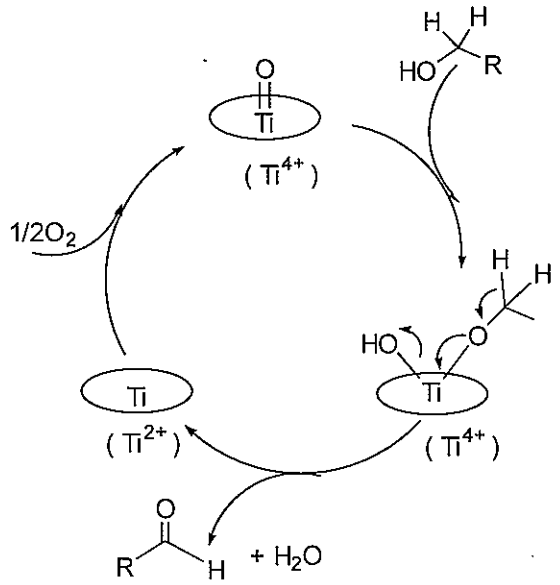
(3)

Oxidation of benzyl alcohol with (TTP)Ti=O. (Por)Ti=O has been used catalytically with alkyl hydrogen peroxide for the epoxidation of alkenes.[20] Since (TTP)Ti=O is capable of mediating the oxidation of vicinal diols and α-hydroxy ketones, we were interested in the oxidation of simple alcohols with molecular oxygen.

Initially the oxidation reaction was carried out under the conditions described above, using benzyl alcohol as the substrate. However, only trace amounts of benzaldehyde were observed at best. Thus, a variety of solvents were examined in the benzyl alcohol oxidation reactions. No aldehyde was observed when reactions were performed in THF or $CHCl_3$, while in xylene or pyridine the oxidation of benzyl alcohol afforded benzaldehyde in low yields (10~20%) after days of refluxing. The optimal oxidation with (TTP)Ti=O performed in refluxing chlorobenzene was sluggish, taking 4-5 days to achieve >90% conversion of benzyl alcohol and a modest yield (~48%) of benzaldehyde. Longer reaction times further diminished the yield of aldehyde. The formation of over-oxidized product, benzoic acid, was confirmed by GC-MS analysis (m/z 122).

Mechanistic consideration of oxidation of simple alcohols. It is quite clear that the oxidations of vicinal diols and α-ketols mediated by (TTP)Ti=O make use of the chelating ability of these substrates to form the diolato or enediolato intermediates. Without a chelate

effect, the oxidation of simple alcohols must proceed by a different pathway. Alkoxo complexes have been invoked as intermediates in transition metal-catalyzed alcohol oxidations.[21,22] It has been proposed also that a cis (TPP)Ti(OH)(OOR) species, which was not detected or isolated, was responsible for the epoxidation of alkenes.[20] An analogous alkoxo intermediate may be involved in the oxidation of benzyl alcohol, as shown in Scheme 4.



Scheme 4

More supporting evidence was obtained in the oxidation reaction of benzhydrol in C_6D_6 monitored via ^1H NMR spectroscopy. The oxidation to benzophenone occurred very slowly. However some upfield-shifted signals were observed in the early stages of reaction and eventually disappeared. The integration and multiplicity of signals at 6.40 (t, 1H), 6.21 (t, 2H), 4.07 (d, 2H) ppm were consistent with a phenyl group that was strongly perturbed by

the porphyrin ring current effect, presumably from an intermediate (TTP)Ti(OH)($OCHPh_2$) species.

Oxidation of alcohols with various transition metal complexes. A number of high valent transition metal complexes were also examined in the oxidations of benzyl alcohol. Selected results are summarized in Table 4. Oxovanadium complexes were first tested in refluxing chlorobenzene. (TTP)V=O afforded a 67% yield of benzaldehyde in 6 days and (Saldach)V=O afforded a 71% yield of benzaldehyde with a slightly faster rate (in 4 days). The yield of benzaldehyde diminished at longer reaction time. Under similar conditions, the more active (TTP)Cr=O was found to afford 56% yield of benzaldehyde in 47 h with 97% conversion. (TTP)Cr=O was shown to effect the conversion of benzyl alcohol to benzaldehyde with iodosobenzene.[23]

Nitridometalloporphyrin complexes, (TTP)Cr≡N and (TTP)Mn≡N, with metals in the formal +5 oxidation state, are remarkably inert. Nevertheless, their capacity for alcohol oxidation was also examined. In refluxing chlorobenzene, (TTP)Mn≡N afforded a 99% yield of benzaldehyde in 22 h. When (TTP)Cr≡N was used, an 86% benzaldehyde was produced with 100% conversion within 45 h. The active catalysts may not be the nitrido species, however. An induction period was observed for (TTP)Cr≡N and only 23% benzaldehyde was obtained in the first 19 h of reaction. The color of the reaction mixture changed from deep red to dark green in the second day of the reaction. On the other hand, when a lower oxidation state species of Mn, (TTP)Mn(III)Cl, was used, only 9.8% yield of benzaldehyde was obtained after 67 h of refluxing. Thus, a high-valent form of the complex appears to be necessary as the precatalyst.

Table 4: Benzyl alcohol oxidation mediated by various metal complexes[a]

run	catalyst	time (h)	Conv (%)	Yield (%)	t.o.n[b]
1	(TTP)Ti=O	46	37	31	7.2
		70	68	44	10
2	(TTP)V=O	69	39	24	12
		94	60	39	20
		142	90	67	35
3	(saldach)V=O	49	36	34	6.9
		71	75	66	14
		96	100	71	15
		127	100	39	
4	(TTP)Cr=O	21	34	31	13
		47	97	56	23
5	(TTP)Cr≡N	19	19	23	6.2
		45	100	86	23
6	(TTP)Mn≡N	25	100	99	20
7	(TTP)MnCl	67	15	9.8	2.0

(a) see Experiment section for reaction conditions.
(b) t.o.n= mole of benzaldehyde/mole of catalyst.

Summary

In summary, we have demonstrated that (TTP)Ti=O and related transition metal complexes are able to mediate the oxidation of various alcohols under aerobic conditions. Oxidations of vicinal diols, α-hydroxy ketones and benzyl alcohol could be achieved with

near quantitative yields obtained in several cases. In addition, these studies lend some new insight into the nature of intermediates involved in metalloporphyrin-catalyzed oxidations.

Experimental Section

^{1}H NMR experiments were performed on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts were referenced to residual solvent peaks (δ 7.15, C_6D_5H). GC-MS studies were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS). GC analyses were performed on a HP 5890 gas chromatograph equipped with a flame ionization detector and a DB-5 capillary column (30 m × 0.32 mm i.d.).

Metal complexes used in this study, (TTP)Ti=O,[24] (TTP)V=O,[25] (saldach)V=O,[26] (TTP)Cr=O,[23] (TTP)Cr≡N,[27] (TTP)Mn≡N,[28] were prepared according to literature procedures. Diols, 1,11-dodecadiene-6,7-diol,[15] 1,2-di(*p*-tolyl) ethyleneglycol and *dl*-2,3-diphenylbutane-2,3-diol,[29] were synthesized via reported methods. Other chemicals were obtained from commercial sources and used as received.

Oxidation of diols mediated by transition metal complexes. In a typical experiment, diol (35 μmol), oxometal complex (2.5-6.0 mol%), Ph_3CH (2.5 mg, 10 μmol, internal standard) and C_6D_6 (~0.6 mL) were placed in an NMR tube equipped with a teflon stopcock. The tube was sealed and heated in a sand bath (~120 °C). The reaction was monitored via ^{1}H NMR spectroscopy. The tube was flushed with air after each NMR spectrum was taken.

Oxidation of 1,11-dodecadiene-6,7-diol mediated by (TTP)Ti=O. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti=O (1.1 mg, 1.5 μmol), 1,11-

dodecadiene-6,7-diol (5.3 mg, 27 μmol), Ph_3CH (2.1 mg, 8.6 μmol) and ~0.5 mL of C_6D_6. The tube was capped after exposure with air. Heating in a sand bath (~120 °C) for 48 h resulted in the consumption of (TTP)Ti=O and the formation of a diolato species. ^1H NMR (C_6D_6, 400 MHz): δ 9.15 (q, 8H, *β*-H), 8.39 (br, 4H, *meso*-$C_6H_4CH_3$), 7.90 (br, 4H, *meso*-$C_6H_4CH_3$), 7.34 (br, 4H, *meso*-$C_6H_4CH_3$), 7.28 (br, 4H, *meso*-$C_6H_4CH_3$), 5.41 (m, 2H), 4.83 (m, 2H), 4.72 (m, 2H), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), -0.15 (m, 2H), -0.26 (m, 2H), -0.87 (m, 2H), -1.54 (m, 2H). Other signals around 1.2 and 1.6 ppm, as determined by the ^1H-^1H COSY spectroscopy, were buried under other peaks. Further heating generated a small triplet (J = 1.6 Hz) at 9.24 ppm, which was assigned to the aldehydic proton of 5-hexen-1-al. The NMR spectrum taken in $CDCl_3$ showed a 9.77 ppm triplet (J = 1.6 Hz), which agreed with reported data.[30]

Benzoin oxidation mediated by (TTP)Ti=O. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti=O (1.5 mg, 2.0 μmol), benzoin (8.8 mg, 39 μmol), Ph_3CH (2.1 mg, 8.6 μmol) and ~0.5 mL of C_6D_6. The tube was sealed after introducing air. Heating in a sand bath (~120 °C) for 20 h resulted in the consumption of benzoin and the production of benzil (92% yield) and a small amount of benzaldehyde (2.7% yield), as determined by ^1H NMR. An enediolato intermediate, (TTP)Ti[OC(Ph)C(Ph)O],[6] was observed during the reaction.

Preparation of an enediolato complex (TTP)Ti($OC_6H_{10}O$). Under N_2, a round bottom flask was charged with (TTP)Ti=O (24.8 mg, 0.0338 mmol), adipoin (8.5 mg, 0.0745 mmol), and toluene (5 mL). The stirred mixture was heated gently (~80 °C) for 48 h, at which time ^1H NMR spectroscopy revealed only ~20% (TTP)Ti=O was converted to a new species. After addition of more adipion (12.4 mg), the mixture was again heated at ~90 °C

for 52 h and reduced to dryness in vacuo. The residue was taken in CH_2Cl_2 (1 mL), layered with hexane (2 mL), placed in freezer (~-25°C) for days. Filtration afforded an enediolate complex (TTP)Ti($OC_6H_{10}O$). Yield: 12 mg (42%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.13 (s, 8H, *β*-H), 8.22 (br, 4H, *meso*-$C_6H_4CH_3$), 7.95 (br, 4H, *meso*-$C_6H_4CH_3$), 7.28 (m, 8H, *meso*-$C_6H_4CH_3$), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), 0.30 (br, 4H, C_6H_8) -0.40 (br, 4H, C_6H_8). UV-vis (toluene): 426 (Soret), 543, 629 nm.

Adipoin oxidation mediated by (TTP)Ti=O. An NMR tube equipped with a teflon stopcock was charged with (TTP)Ti=O (1.4 mg, 1.9 μmol), adipoin (3.6 mg, 32 μmol), Ph_3CH (3.5 mg, 14 μmol) and ~0.5 mL of C_6D_6 under N_2. (TTP)Ti=O was consumed after heating in a sand bath (~120 °C) for 24 h and the resultant porphyrin species was identified to be the enediolato complex (TTP)Ti($OC_6H_{10}O$). The NMR tube was then open to air and recapped. Heating in a sand bath (~120 °C) for another 41 h resulted in the consumption of adipoin and the production of 1,2-cyclohexanedione (87% yield) in its enol form, as determined by ^{1}H NMR spectroscopy. ^{1}H NMR data for 1,2-cyclohexanedione (C_6D_6, 400 MHz): δ 6.17 (br, 1H, O*H*), 5.73 (t, 1H, vinyl-*H*), 1.95 (t, 2H, $COCH_2$), 1.60 (appr q, 2H, $COCH_2CH_2CH_2$), 1.22 (quintet, 2H, $COCH_2CH_2$).[31] EI-MS: *m/z* 112 (M^+, base peak), 97, 83, 70, 55.

Oxidation of benzyl alcohol mediated by transition metal complexes. In a typical experiment, benzyl alcohol (0.25 mmol), metal complex (2.5-6.0 mol%), *n*-dodecane (15 mg, internal standard) and PhCl (~6 mL) were placed in a round bottom flask. The mixture was heated to reflux and the reaction was monitored via GC analysis.

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(5) Abbreviations: TTP = dianion of *meso-tetra-p*-tolylporphyrin; TPP = dianion of *meso*-tetraphenylporphyrin; Saldach = dianion of trans-1,2-bis(salicylidene) cyclohexane-diamine.

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(13) Control experiments were carried out by heating a C_6D_6 solution of 2,3-diphenylbutane-2,3-diol, *meso*-hydrobenzoin or benzoin in the presence or absence of air without (TTP)Ti=O. No oxidation was observed after extended heating (up to 2 weeks).

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CHAPTER 4. REACTION OF TIN PORPHYRINS WITH VICINAL DIOLS

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Abstract

Reactions of tin porphyrins with vicinal diols were investigated. Treatment of $(TTP)Sn(C{\equiv}CPh)_2$ or $(TTP)Sn(NHtolyl)_2$ with pinacol and 2,3-diphenyl-butane-2,3-diol afforded diolato complexes $(TTP)Sn[OC(Me)_2C(Me)_2O]$ (**1**) and (TTP)Sn[OC(Ph)(Me)C(Ph)(Me)O] (**2**), respectively. Both complexes underwent C-C cleavage reactions to give $(TTP)Sn^{II}$ and ketones. Reaction of $(TTP)Sn(C{\equiv}CPh)_2$ with 1 equivalent of *o*-catechol generated $(TTP)Sn(C{\equiv}CPh)(OC_6H_4OH)$ (**3**), which subsequently transformed into $(TTP)Sn(OC_6H_4O)$ (**4**). With excess catechol, disubstituted $(TTP)Sn(OC_6H_4OH)_2$ (**5**) was obtained. (TTP)Sn(C≡CPh)(OCHRCHROH) (R = H, **6**; R = Ph, **8**) and $(TTP)Sn(OCHRCHROH)_2$ (R = H, **7**; R = Ph, **9**) were obtained analogously by treatment of $(TTP)Sn(C{\equiv}CPh)_2$ with appropriate diols. In the presence of dioxygen, tin porphyrin complexes were found to promote the oxidative cleavage of vicinal diols and the

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oxidation of α-ketols to α-diketones. Possible reaction mechanisms involving diolato or enediolato intermediates are discussed. The molecular structure of (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**) was determined by X-ray crystallography.

Introduction

The structural and physical similarities between the highest oxidation state chemistry of the early transition metals (Group n) and their corresponding main group elements (Group n+10) was originally observed during Mendeleev's time. This analogy still retains utility. Thus, vanadyl (V=O) complexes, which have shown promise as insulin mimics, are proposed to function as P=O analogues.[1] Considerable analogies are also observed between the chemistry of organoscandium and organoaluminum complexes.[2]

We have been interested in the chemistry of group 4 metalloporphyrins[3] as well as tin (group 14) porphyrins.[4] Although some chemical similarities exist, significant differences are often observed. For example, treatment of (TTP)$SnCl_2$ with lithium phenylacetylide generated a σ-bonded bisalkynyl complex, trans-(TTP)Sn(C≡CPh)$_2$.[5] Quite surprisingly, the same reaction with (TTP)$TiCl_2$ resulted in oxidative coupling of the acetylides and formation of a Ti(II) alkyne adduct, (TTP)Ti(1,2-η^2-PhC≡CC≡CPh).[6]

In continuing our investigation of group 4 metalloporphyin diolato complexes,[7] efforts were extended to reactions of tin porphyrins with various diols. While chelated diolato complexes are invariably obtained for titanium porphyrins, tin porphyrin-diol complexes show more structural diversity with *trans* bisalkoxo substituted species being regularly obtained. Both titanium and tin complexes are able to promote the oxidative cleavage of diols with molecular dioxygen.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40-1 Dri-Train gas purifier, unless noted otherwise. Toluene and hexane were dried by passage through columns of activated alumina and supported copper redox catalyst (Q-5) as described in the literature.[8] Benzene-d_6 and THF were freshly distilled from purple solutions of sodium benzophenone, degassed with several freeze-pump-thaw cycles and brought into the drybox without exposure to air. CH_2Cl_2 was dried with P_2O_5, degassed with several freeze-pump-thaw cycles and brought into the drybox after trap-to-trap vacuum distillation. (TTP)$SnCl_2$,[9] (TTP)Sn(C≡CPh)$_2$,[5] (TTP)Sn(OH)$_2$,[10] (TTP)Sn[4d] were prepared according to literature procedures. A *d,l* mixture of 2,3-diphenylbutane-2,3-diol was obtained using a previously reported procedure.[11]

^{1}H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts are referenced to proton solvent impurities (C_6D_5H, δ 7.15; $CHCl_3$, δ 7.24). UV-vis data were recorded on a HP8453 diode array spectrophotometer and reported as λ_{max} in nm (log ε). Fourier Transform Infrared spectra were recorded on a FT-DL spectrometer. Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services.

Synthesis of (TTP)Sn(NHtolyl)$_2$. To a stirred solution of (TTP)$SnCl_2$ (183 mg, 0.213 mmol) in 16 mL of toluene at –25 °C was added LiNHtolyl (85 mg, 0.75 mmol). The solution was warmed to ambient temperature and stirred for 18 h. After filtering the mixture through a coarse frit, the filtrate was dried in vacuo, triturated with hexane, and filtered. Removal of solvent from the filtrate under reduced pressure afforded a dark green product.

Yield: 101 mg, 47%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.97 (s, 8H, β-H), 8.03 (d, 8H, J = 7.8 Hz, *meso*-$C_6H_4CH_3$), 7.58 (d, 8H, J = 7.8 Hz, *meso*-$C_6H_4CH_3$), 5.40 (d, 4H, J = 7.8 Hz, *m*-$NHC_6H_4CH_3$) 2.72 (s, 12H, *meso*-$C_6H_4CH_3$), 1.81 (d, 4H, J = 7.8 Hz, *o*-$NHC_6H_4CH_3$), 1.69 (s, 6H, $NHC_6H_4CH_3$), -5.08 (s, 2H, $NHC_6H_4CH_3$). The ^{1}H NMR spectrum (C_6D_6) of (TTP)Sn(NHtolyl)$_2$ prepared by an amine exchange reaction,[5] has been reported.

Synthesis of (TTP)Sn[OC(Me)$_2$C(Me)$_2$O] (1). To a solution of (TTP)Sn(NHtolyl)$_2$ (32 mg, 0.032 mmol) in toluene (3 mL) was added a solution of pinacol (8 mg, 0.06 mmol) in toluene (3 mL). The mixture was stirred at ambient temperature for 1.5 h as the color changed from green to dark red. After the removal of solvent under reduced pressure, the residue was taken up in toluene (1 mL), layered with hexane (3 mL) and placed in freezer at –25 °C for 6 d. The resulting dark red product was collected by filtration. Yield: 15 mg (53%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.19 (s, 8H, β-H), 8.31 (br, 4H, *meso*-$C_6H_4CH_3$), 7.97 (br, 4H, *meso*-$C_6H_4CH_3$), 7.29 (m, 8H, *meso*-$C_6H_4CH_3$), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), -1.07 (s, 12H, $OCMe_2$). UV-vis (toluene): 406 (4.73), 429 (5.44), 488 (3.86), 565 (3.96), 603 (3.68). MS (EI): *m/z* 904 (M^+), 787 ((TTP)Sn^+). Anal. Found: C, 72.32; H, 5.90; N, 5.85. Calcd for $C_{54}H_{48}N_4O_2Sn$: C, 71.77; H, 5.35; N, 6.20.

Synthesis of (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (2). To a solution of (TTP)Sn(NHtolyl)$_2$ (32 mg, 0.032 mmol) in CH_2Cl_2 (5 mL) was added a solution of 2,3-diphenylbutane-2,3-diol (16 mg, 0.066 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at ambient temperature for 40 min during which the color changed from green to dark red. After the solvent was removed under reduced pressure, the residue was taken up in toluene and filtered. The filtrate was dried under vacuum, redissolved in CH_2Cl_2 (1 mL), layered with hexane (3 mL) and placed in freezer at –25 °C for 3d. Filtration provided the desired

product (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O]. Yield: 16 mg (48%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.24 (s, 8H, *β*-H), 8.25 (br, 4H, *meso*-$C_6H_4CH_3$), 8.05 (br, 4H, *meso*- $C_6H_4CH_3$), 7.26 (d, 8H, J = 7.6 Hz, *meso*- $C_6H_4CH_3$), 6.68 (m, 6H, *p,m*-C_6H_5), 5.88 (m, 4H, *o*-C_6H_5), 2.40 (s, 12H, *meso*-$C_6H_4CH_3$), -1.69 (s, 6H, $OCCH_3$). UV-vis (toluene): 410 (sh), 430 (Soret), 490, 564, 604 nm. The presence of (TTP)Sn (~8%) was observed by its ^{1}H NMR *β*-H signal at 9.19 ppm.

Synthesis of (TTP)Sn(C≡CPh)(OC$_6$H$_4$OH) (3). A solution of (TTP)Sn(C≡CPh)$_2$ (31 mg, 0.031 mmol) and catechol (3.5 mg, 0.032 mmol) in toluene (ca. 8 mL) was stirred for 24 h at ambient temperature and reduced to dryness in vacuo. The residue was taken up in toluene (1 mL), layered with hexane (3 mL) and placed in freezer at –25°C for 23 h. The purple microcrystalline product **3** was collected by filtration and dried under vacuum. This compound could be stored with air over weeks. Yields: 24 mg (77%). ^{1}H NMR (C_6D_6, 400 MHz): δ 9.18 (s, 8H, *β*-H), 8.02 (m, 8H, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, J = 8.4 Hz, *meso*-$C_6H_4CH_3$), 6.13 (t, 1H, J = 7.6 Hz, *p*-C_6H_5), 5.97 (t, 2H, J = 7.6 Hz, *m*-C_6H_5), 5.78 (t, 1H, J = 7.2 Hz, OC_6H_4OH), 5.71 (d, 1H, J = 6.0 Hz, OC_6H_4OH), 5.44 (m, 3H, *o*-C_6H_5 and OC_6H_4OH), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), 1.67 (d, 1H, J = 7.2 Hz, OC_6H_4OH), 0.57 (s, 1H, OC_6H_4OH). IR (KBr): 3440 (OH), 2129 (C≡C) cm^{-1}. UV-vis (toluene): 412 (sh, 4.71), 433 (5.67), 531 (3.68), 571 (4.25), 613 (4.25). MS (EI): *m/z* 897 (M^+-C≡CPh), 787 ((TTP)Sn^+). The molecular structure of this complex was solved by X-ray crystallography (vide infra).

Generation of (TTP)Sn(OC$_6$H$_4$O) (4) from 3. An NMR tube equipped with a teflon stopcock was charged with (TTP)Sn(C≡CPh)(OC$_6$H$_4$OH) (**3**) (1.4 mg, 1.4 μmol) and C_6D_6. After 12 d of heating in a sand bath (~120 °C), (TTP)Sn(C≡CPh)(OC$_6$H$_4$OH) (**3**) was

consumed and a new species (TTP)Sn(OC_6H_4O) (**4**) was observed by ^{1}H NMR spectroscopy. This species could be stored in air over months without noticeable change. ^{1}H NMR data for **4**: δ 9.15 (s, 8H, *β*-H), 8.02 (m, 4H, *meso*-$C_6H_4CH_3$), 7.87 (m, 4H, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, J = 8.4 Hz, *meso*-$C_6H_4CH_3$), 5.65 (m, 2H, OC_6H_4O), 5.38 (m, 2H, OC_6H_4O), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$). UV-vis (CH_2Cl_2): 427 (Soret), 561, 602 nm. Free PhC≡CH (1 equiv) was also observed.

Synthesis of (TTP)Sn(*o*-$OC_6H_4OH)_2$ (5). A solution of (TTP)Sn(NHtolyl)$_2$ (22 mg, 0.022 mmol) and catechol (7.6 mg, 0.069 mmol) in toluene (ca. 6 mL) was stirred for 6 h at ambient temperature. The mixture was filtered and the filtrate reduced to 3 mL in vacuo. Then it was layered with hexane (2 mL) and placed in freezer at –25°C for 14 h. The brown-red product was collected by filtration and dried under vacuum. Yields: 18 mg (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.14 (s, 8H, *β*-H), 8.07 (d, 8H, J = 8.0 Hz, *meso*-$C_6H_4CH_3$), 7.59 (d, 8H, J = 7.6 Hz, *meso*-$C_6H_4CH_3$), 5.63 (td, 2H, OC_6H_4OH), 5.31 (dd, 2H, OC_6H_4OH), 5.16 (td, 2H, OC_6H_4OH), 2.72 (s, 12H, *meso*-$C_6H_4CH_3$), 1.37 (dd, 2H, OC_6H_4OH), 0.01 (s, 2H, OC_6H_4OH). IR (KBr): 3455 (OH). UV-vis (toluene): 426 (5.26), 523 (3.52), 563 (3.95), 603 (3.79).

Synthesis of (TTP)Sn(C≡CPh)(OCH_2CH_2OH) (6). A mixture of (TTP)Sn(C≡CPh)$_2$ (37 mg, 0.037 mmol) and ethylene glycol (25 mg, 0.40 mmol) in toluene (ca. 8 mL) was stirred at ambient temperature for 14 h and reduced to dryness in vacuo. The residue was taken up in THF (1 mL), layered with hexane (3 mL) and placed in freezer at –25°C for 8 h. The purple product was collected in two crops by filtration and dried under vacuum. Yield: 27 mg (75%). Samples for combustion analysis were obtained by layering a CH_2Cl_2 (1 mL)

solution with hexane (2 mL), allowing the mixture to stand at –25 °C, filtering and drying the solid in vacuo. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.18 (s, 8H, *β*-H), 8.03 (m, 8H, *meso*-$C_6H_4CH_3$), 7.24 (d, 8H, *meso*-$C_6H_4CH_3$), 6.14 (t, 1H, *p*-C_6H_5), 5.99 (t, 2H, *m*-C_6H_5), 5.41 (d, 2H, *o*-C_6H_5), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), 0.61 (m, 2H, OCH_2CH_2OH), -1.65 (m, 1H, OCH_2CH_2OH), -1.95 (m, 2H, OCH_2CH_2OH). IR (KBr): 3432 (OH), 2123 (C≡C). UV-vis (toluene): 414 (4.59), 434 (5.56), 532 (3.47), 572 (4.08), 613 (4.12). MS (EI): *m/z* 888 (M^+-OCH_2CH_2OH), 787 ((TTP)Sn^+). Anal. Found: C, 70.87; H, 5.53; N, 5.37. Calcd. for $C_{58}H_{46}N_4O_2Sn\cdot CH_2Cl_2$: C, 70.92; H, 4.84; N, 5.61.

Synthesis of (TTP)Sn(OCH_2CH_2OH)$_2$ (7). A mixture of (TTP)Sn(C≡CPh)$_2$ (28 mg, 0.028 mmol) and ethylene glycol (110 mg, 1.77 mmol) in toluene (ca. 6 mL) was heated at ~80 °C for 18 h. The resulting mixture was filtered and reduced to dryness in vacuo. The residue was triturated with hexane (2 mL), then filtered. The solid was dried under vacuum. Yield: 10 mg (40%). Samples for combustion analysis were obtained by layering a CH_2Cl_2 (1 mL) solution with hexane (2 mL), allowing the mixture to stand at –25 °C, filtering and drying the solid in vacuo. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.16 (s, 8H, *β*-H), 8.03 (d, 8H, J = 8.0 Hz, *meso*-$C_6H_4CH_3$), 7.25 (d, 8H, J = 8.0 Hz, *meso*-$C_6H_4CH_3$), 2.38 (s, 12H, *meso*-$C_6H_4CH_3$), 0.61 (m, 4H, OCH_2CH_2OH), -1.54 (m, 2H, OCH_2CH_2OH), -1.95 (m, 4H, OCH_2CH_2OH). UV-vis (toluene): 409 (4.69), 429 (5.65), 523 (3.67), 563 (4.25), 603 (4.18), 624 (3.88). Anal. Found: C, 67.21; H, 5.62; N, 5.78. Calcd. for $C_{52}H_{46}N_4O_4Sn\cdot 0.25CH_2Cl_2$: C, 67.42; H, 5.03; N, 6.02.

Reaction of (TTP)Sn(C≡CPh)$_2$ with *meso*-hydrobenzoin. An NMR tube equipped with a teflon stopcock was charged with (TTP)Sn(C≡CPh)$_2$ (0.8 mg, 0.8 μmol), *meso*-

hydrobenzoin (0.7 mg, 3.3 μmol), Ph_3CH (1.2 mg, 4.9 μmol) and ~0.5 mL of C_6D_6. After 6 h at ambient temperature, ^1H NMR spectroscopy revealed the formation of a major product, (TTP)Sn(C≡CPh)[OCH(Ph)CH(Ph)OH] (**8**). ^1H NMR (C_6D_6, 400 MHz): 9.15 (s, 8H, *β*-H), 8.06 (t, 8H, J = 9.2 Hz, *meso*-$C_6H_4CH_3$), 7.27 (t, 8H, J = 9.2 Hz, *meso*-$C_6H_4CH_3$), 6.46 (t, 1H, J = 7.6 Hz, *p*-C_6H_5), 6.42 (t, 1H, J = 7.2 Hz, *p*-C_6H_5), 6.33 (t, 2H, J = 7.6 Hz, *m*-C_6H_5), 6.12 (m, 3H, *m*-C_6H_5 and *p*-CCC_6H_5), 5.97 (t, 2H, J = 8.0 Hz, *m*-CCC_6H_5), 5.42 (d, 2H, J = 8.0 Hz, *o*-CCC_6H_5), 4.97 (d, 2H, J = 7.6 Hz, *o*-C_6H_5), 3.69 (d, 2H, J = 7.2 Hz, *o*-C_6H_5), 2.39 (s, 12H, *meso*-$C_6H_4CH_3$), 1.60 (m, C*H*PhOH), -1.11 (d, 1H, J = 6.8 Hz, CHPhO*H*), -1.88 (d, 1H, J = 3.2 Hz, OC*H*Ph). UV-vis (toluene): 412 (sh), 435 (Soret), 531, 571, 612 nm. Heating over a sand bath (~120 °C) for 3 h resulted in the production of (TTP)Sn[OCH(Ph)CH(Ph)OH]$_2$ (**9**) as the major product. ^1H NMR (C_6D_6, 400 MHz): 9.09 (s, 8H, *β*-H), 8.09 (d, 8H, J = 8.0 Hz, *meso*-$C_6H_4CH_3$), 7.30 (d, 8H, J = 7.6 Hz, *meso*-$C_6H_4CH_3$), 6.45 (m, 8H, *m,p*-C6H5), 6.17 (t, 4H, J = 7.2 Hz, *m*-C_6H_5), 5.22 (d, 4H, J = 7.6 Hz, *o*-C_6H_5), 3.95 (d, 4H, J = 7.2 Hz, *o*-C_6H_5), 2.42 (s, 12H, *meso*-$C_6H_4CH_3$), 1.64 (m, 2H, C*H*PhOH), -0.73 (d, 2H, CHPhO*H*), -1.62 (d, 2H, OC*H*Ph). UV-vis (toluene): 409 (sh), 430 (Soret), 562, 602, 626 nm. Further heating decomposed the bisalkoxo complex **9**, with (TTP)Sn observed as one of the products.

Diol oxidation mediated by tin porphyrin complexes. In a typical experiment, diol (35 μmol), tin(IV) porphyrin (4-6 mol%), Ph_3CH (2.5 mg, 10 μmol, internal standard) and C_6D_6 (~0.5 mL) were placed in a NMR tube equipped with a teflon stopcock. The tube was sealed and heated in a sand bath (~120 °C). The reaction was monitored via ^1H NMR spectroscopy. The yields of products were determined based on appropriate NMR signal integration relative to the internal standard.

Reaction of (TTP)Sn with ethylene glycol. An NMR tube equipped with a teflon stopcock was charged with (TTP)Sn (0.9 mg, 1.1 μmol), ethylene glycol (3.2 mg, 52 μmol), Ph_3CH (1.7 mg, 7.0 μmol) and ~0.6 mL of C_6D_6. Heating the mixture in a sand bath (~120 °C) over 30 h resulted in no change in the ^1H NMR signals for the porphyrin. The NMR tube was then flushed with air and capped. Another 3 h of heating resulted in the color of the solution changing from dark green to purple-red. The ^1H NMR spectrum revealed the total consumption of (TTP)Sn and the quantitative generation of (TTP)Sn(OCH_2CH_2OH)$_2$ (**7**).

Benzoin oxidation mediated by (TTP)Sn(C≡CPh)$_2$. An NMR tube equipped with a teflon stopcock was charged with (TTP)Sn(C≡CPh)$_2$ (1.2 mg, 1.2 μmol), benzoin (5.0 mg, 22 μmol), Ph_3CH (2.4 mg, 9.8 μmol) and ~0.5 mL of C_6D_6. The tube was sealed after exposure to air. Heating the tube in a sand bath (~120 °C) for 22 h resulted in the consumption of benzoin and the production of benzil (87 % yield) and a small amount of benzaldehyde (8.7% yield), as determined by ^1H NMR spectroscopy.

Adipoin oxidation mediated by (TTP)Sn(C≡CPh)$_2$. An NMR tube equipped with a teflon stopcock was charged with (TTP)Sn(C≡CPh)$_2$ (1.8 mg, 1.8 μmol), adipoin (4.0 mg, 35 μmol), Ph_3CH (2.4 mg, 9.8 μmol) and ~0.5 mL of C_6D_6. The tube was sealed after exposure to air. Heating the tube in a sand bath (~120 °C) for 35 h resulted in 69% conversion of adipoin and the production of 1,2-cyclohexanedione (31% yield) in its enol form, as determined by ^1H NMR spectroscopy. ^1H NMR of 1,2-cyclohexanedione in its enol form (C_6D_6, 400 MHz): δ 6.17 (s, 1H, O*H*), 5.73 (t, 1H, J = 4.6 Hz, vinyl-*H*), 1.95 (t, 2H, COCH_2), 1.60 (q, 2H, CHCH_2), 1.22 (quintet, 2H, $COCH_2CH_2$). ^1H NMR in CDCl3 (400 MHz): δ

6.13 (t, 1H, J = 4.6 Hz, vinyl-*H*), 5.95 (s, 1H, O*H*), 2.52 (t, 2H, COCH_2), 2.38 (q, 2H, CHCH_2), 1.99 (quintet, 2H, $COCH_2CH_2$).[12] EI-MS: *m/z* 112 (M^+, base peak), 97, 83, 70, 55.

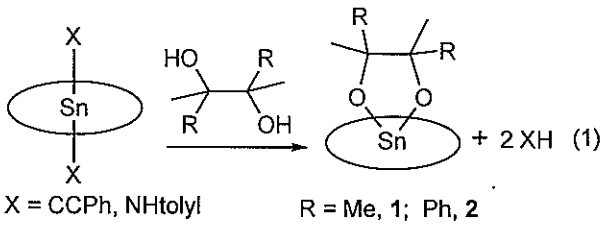
X-ray Crystallography. A dark purple crystal with approximate dimensions 0.3 x 0.3 x 0.3 mm^3 was mounted on a glass fiber. The crystal evaluation and data collections at 173 K were performed on a BRUKER SMART 1000 CCD-based diffractometer with Mo K_α radiation (0.71073 Å), using the full-sphere routine. The datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiply equivalent measurements[13] using DADABS software.[14] Details of the X-ray structure determination are summarized in Table 1 (see Appendix).

The systematic absences in the diffraction data were consistent for the monoclinic space group $P2_{1/c}$. The position of Sn atom was found by the Patterson method. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps and their positions were refined in a full-matrix anisotropic approximation. All hydrogen atoms were placed at calculated positions and refined using a riding model.

Results

Synthesis of tin porphyrin diolato complexes. It has been shown that tin porphyrins have high affinity for oxygen donor ligands.[15] This is reflected in the reactions of MeOH with (TTP)Sn(C≡CPh)$_2$ that sequentially afforded (TTP)Sn(C≡CPh)(OMe) and then (TTP)Sn(OMe)$_2$.[5] Replacement of MeOH with vicinal diols was expected to generate chelated diolato complexes, analogous to titanium porphyrin chemistry.[7] Surprisingly, the

reactions of vicinal diols with tin porphyrins are somewhat diol-dependent. Thus, treatment of (TTP)Sn(C≡CPh)$_2$ with *dl*-2,3-diphenylbutane-2,3-diol led to the formation of the diolato complex (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) in ~50% yield. The bis substituted complex, (TTP)Sn[OC(Ph)(Me)C(Ph)(Me)OH]$_2$ was observed in only ~40% yield even when a large excess of diol was used in the reaction. With the more labile bisamido tin porphyrin complex, (TTP)Sn(NHtolyl)$_2$, clean formation of (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) was observed, but it required more than 1 equiv of diol to complete this conversion. The same was true with pinacol (eq. 1). The reaction

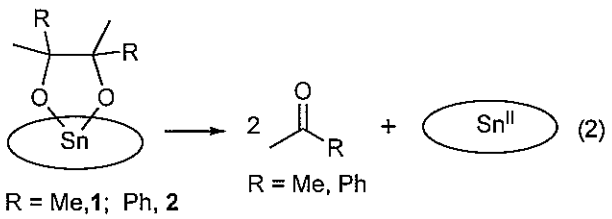


of pinacol with (TTP)Sn(NHtolyl)$_2$ yielded the diolato complex (TTP)Sn[OC(Me)$_2$C(Me)$_2$O] (**1**) in good yield. In the reaction of (TTP)Sn(C≡CPh)$_2$ with excess pinacol (~10 equiv), complex **1** was afforded as a major product, as well as mono- and bis-substituted complexes, (TTP)Sn(C≡CPh)[OC(Me)$_2$C(Me)$_2$OH] (**1a**) and (TTP)Sn[OC(Me)$_2$C(Me)$_2$OH]$_2$ (**1b**), as monitored by ^{1}H NMR spectroscopy. However, attempts to isolate either **1a** or **1b** under a variety of conditions proved unsuccessful. Treatment of benzopinacole with (TTP)Sn(C≡CPh)$_2$ at ambient temperature in C_6D_6 resulted in the consumption of diol and the generation of benzophenone, but no diolato species was observed during the reaction. Treatment of the disodium salt of pinacol with (TTP)SnCl$_2$ or (TTP)Sn(OTf)$_2$ resulted in the

formation of a complex mixture in which diolato complex **1** was a minor component. Other products could not be identified.

The tin porphyrin diolato complexes (TTP)Sn[OC(Me)$_2$C(Me)$_2$O] (**1**) and (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) share similar ^{1}H NMR characteristics. The presence of two broad resonances for the *o*-protons of the *meso* tolyl groups on the porphyrin ring is consistent with the enforced *cis* geometry of the chelating diolato ligands. The upfield shifted signals of the diolato ligands, due to the large porphyrin current effect, are also comparable to their titanium analogues.[7]

(TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) decomposed partially (~40%) to (TTP)Sn^{II} and 2 equiv acetophenone at ambient temperature over 14 h. Appreciable decomposition was noticed even in the solid state. Isolation of analytically pure **2** was thus precluded. On heating in C_6D_6, the decomposition of **2** was much faster, as indicated by the rapid color change from a deep red of **2** to the green color of (TTP)Sn^{II} over 30 min (eq. 2). The decomposition of (TTP)Sn[OC(Me)$_2$C(Me)$_2$O] (**1**) proceeded

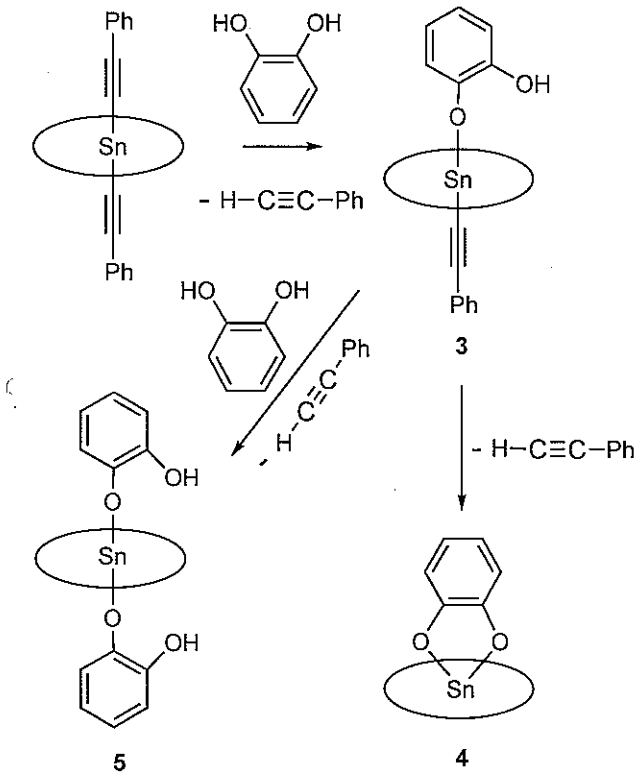


similarly, yielding (TTP)Sn^{II} and 2 equiv of acetone, although the process was much slower. Upon exposure with air, diolato complex **1** reacted with moisture to release free pinacol. The porphyrin product was identified as (TTP)Sn(OH)$_2$ by its ^{1}H NMR spectrum, although the signal for the OH group was not observed.

Reaction of tin porphyrins with *o*-catechol. (TTP)Sn(C≡CPh)$_2$ and (TTP)Sn(NHtolyl)$_2$ react readily with excess *o*-catechol, resulting in the formation of a bis catecholato complex, (TTP)Sn(OC$_6$H$_4$OH)$_2$ (**5**), with two pendant -OH groups. This complex is sparingly soluble in non-polar solvents such as C$_6$D$_6$, but readily soluble in polar CDCl$_3$. The axial catecholato ligands adopt a trans geometry, as indicated by the appearance of the *o*-protons of the *meso*-tolyl groups as an 8H doublet in its ^{1}H NMR spectrum. This is in contrast to the reaction of *o*-phenylenediamine with (TTP)Sn(NHPh)$_2$, where a chelating diamido complex, (TTP)Sn(*o*-C$_6$H$_4$(NH)$_2$) formed readily.[5] The *trans* substituted complex with pendant amines was not observed.

The reaction of (TTP)Sn(C≡CPh)$_2$ with *o*-catechol proceeded presumably in a stepwise manner. Indeed, treatment of (TTP)Sn(C≡CPh)$_2$ with 1 equivalent of catechol afforded an unsymmetrically substituted complex (TTP)Sn(C≡CPh)(OC$_6$H$_4$OH) (**3**). In the ^{1}H NMR spectrum of **3**, the *o*-protons of the *meso*-tolyl groups appear as a multiplet and not as a doublet observed for symmetrical *trans* metalloporphyrin complexes. The IR spectrum for **3** showed the presence of both C≡C (2129 cm^{-1}) and OH (3440 cm^{-1}) functional groups, thus verifying its formulation. On heating in C$_6$D$_6$ (~120 °C), this complex slowly transformed to a new species, as monitored by ^{1}H NMR spectroscopy. The β-H signal for (TTP)Sn(C≡CPh)(OC$_6$H$_4$OH) (**3**) at 9.18 ppm diminished while a new signal at 9.15 ppm increased over a period of 12 days. This new species was assigned as the chelated diolato complex, (TTP)Sn(OC$_6$H$_4$O) (**4**) (Scheme 1). The presence of two broad 4H multiplets for the *o*-protons of the *meso*-tolyl groups was similar to that observed for the Ti(TTP) analogue and other diolato complexes[7,16] and indicated an enforced *cis*-ligation by the chelating

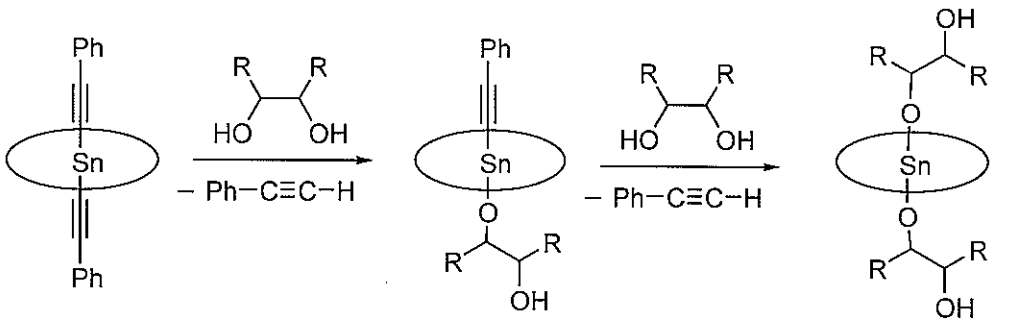
catecholato ligand. IR spectroscopy revealed the loss of the C≡C and OH functional groups. Unlike (TTP)Sn[OC(Me)$_2$C(Me)$_2$O] (**1**) and (TTP)Sn[OC(Ph)(Me)C(Ph)(Me)O] (**2**), this species was very inert to heating at 120 °C. Alternative routes to **4** were attempted. Reaction of (TTP)$SnCl_2$ with the dilithium salt of catechol did not afford the expected diolato complex. Treatment of (TTP)Sn(NHtolyl)$_2$ with 1 equiv of catechol in toluene resulted in no reaction; while with more than 2 equiv of catechol, the disubstituted product (TTP)Sn(OC_6H_4OH)$_2$ (**5**) was obtained.



Scheme 1

Reaction of (TTP)Sn(C≡CPh)$_2$ with other diols. As observed in the reaction of catechol, (TTP)Sn(C≡CPh)$_2$ generally reacts with other diols in a stepwise manner. In the

first step, the substitution of one acetylide ligand by an alkoxide generated the unsymmetrically substituted tin porphyrin complexes. A number of such complexes, (TTP)Sn(C≡CPh)(OCHRCHROH) (R = H, **6**; R = Ph, **8**), can be observed in NMR tube reactions and/or isolated (Scheme 2). This step is facile and is usually complete within hours. The second substitution, however, is more difficult, and often requires a longer reaction time and/or heating. Nevertheless, bis alkoxo complexes (TTP)Sn(OCHRCHROH)$_2$ (R = H, **7**; R = Ph, **9**) can be obtained cleanly.



R = H, **6**; Ph, **8**

R = H, **7**; Ph, **9**

Scheme 2

The ^{1}H NMR spectra of (TTP)Sn(C≡CPh)(OCH$_2$CH$_2$OH) (**6**) and (TTP)Sn(C≡CPh)[OCH(Ph)CH(Ph)OH] (**8**) are typical for unsymmetrically substituted *trans* metalloporphyrins. The *o*-protons of the tolyl groups resonate as multiplets, due to the loss of mirror symmetry along the porphyrin plane. With symmetric disubstitution, the mirror symmetry is regained and these signals appear as regular 8H doublets in bis alkoxo complexes **7** and **9**. Compared to monoalkoxo complexes **6** and **8**, the ^{1}H NMR signal of alkoxo ligands in complexes **7** and **9** are shifted downfield. In addition, it is observed that in (TTP)Sn(C≡CPh)(OCH$_2$CH$_2$OH) (**6**), the alkoxo ligand is more labile than -C≡CPh toward

water, as $HOCH_2CH_2OH$ was detected within days upon exposure with air, while the acetylide ligand remained bound.

When pure (TTP)Sn(C≡CPh)(OCH_2CH_2OH) (**6**) was heated in C_6D_6 in a sealed NMR tube, the generation of a diolato complex was observed, as indicated by the appearance of two broad signals at aromatic region around 8 ppm. However, this reaction was not clean and (TTP)Sn (β-H: 9.19 ppm) was observed as well as other unidentifiable species.

Structure of (TTP)Sn(C≡CPh)(OC_6H_4OH) (3). The molecular structure of (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**) is one of the few examples of tin porphyrins with a Sn-C bond (Figure 1) structurally characterized by X-ray diffraction. Selected bond lengths and bond angles are listed in Table 2. The central Sn atom possesses a pseudooctahedral coordination geometry with phenylacetylide and catecholato at mutually trans positions. The porphyrin ring adopts a planar conformation. The RMS deviation for the N4 plane is 0.015 and the Sn atom is displaced 0.116(4) Å towards the acetylide group. The Sn-C bond distance is 2.139(12) Å and is noticeably shorter than the Sn-C distances observed in other tin porphyrin complexes (2.167(2) Å in (TTP)Sn($C\equiv CPh)_2$,[5] 2.212(4) and 2.196(4) Å in *trans*-(TPP)$SnPh_2(CH_2Cl_2)$, 2.210(7) and 2.193(7) Å in *cis*-(TBPP)$SnPh_2$[16]) while still in the normal range observed for Sn-C single bonds. The Sn-O bond distance (2.083(7) Å) is in good accord with data for six-coordinate tin complexes.[17] The acetylenic bond distance of 1.194(15) Å is in the range of C≡C triple bonds and is consistent with the IR signal observed at 2129 cm^{-1}.

The most notable feature in the structure of (TTP)Sn(C≡CPh)(OC_6H_4OH) is large voids of 218.4 $Å^3$ found in the lattice that could capture organic solvents with up to 9 non-

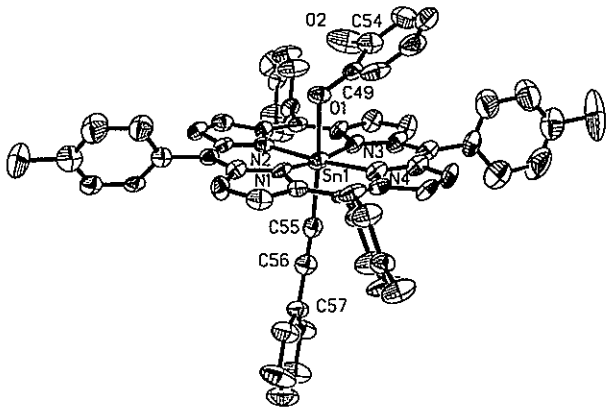


Figure 1: ORTEP representation of the structure of (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**).

Table 2. Selected bond lengths [Å] and bond angles [°] for complex **3**.

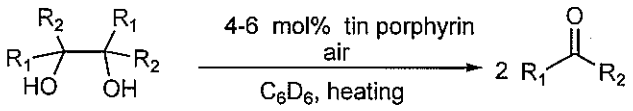
Sn(1)-N(1)	2.090(9)	Sn(1)-N(2)	2.100(8)
Sn(1)-N(3)	2.101(9)	Sn(1)-N(4)	2.102(9)
Sn(1)-O(1)	2.083(7)	Sn(1)-C(55)	2.139(12)
C(55)-C(56)	1.194(15)	C(56)-C(57)	1.434(16)
O(1)-C(49)	1.311(12)	O(2)-C(54)	1.381(15)
O(1)-Sn(1)-N(1)	86.7(3)	C(55)-Sn(1)-N(1)	89.8(4)
O(1)-Sn(1)-N(2)	83.6(3)	C(55)-Sn(1)-N(2)	93.1(3)
O(1)-Sn(1)-N(3)	86.1(3)	C(55)-Sn(1)-N(3)	97.4(4)
O(1)-Sn(1)-N(4)	90.9(3)	C(55)-Sn(1)-N(4)	92.4(4)
N(1)-Sn(1)-N(3)	172.8(3)	N(2)-Sn(1)-N(4)	174.5(3)
O(1)-Sn(1)-C(55)	175.2(4)	C(49)-O(1)-Sn(1)	127.3(6)
C(56)-C(55)-Sn(1)	168.5(10)	C(55)-C(56)-C(57)	177.1(12)

hydrogen atoms. However, the SQUEEZE routine from PLATON package[18] found only three "unaccounted" electrons per cell. The negative and positive residuals are almost equal (1.348 and -1.359 e. $Å^{-3}$), therefore the existence of diffuse solvent in this structure is very unlikely. Such sieves-like lattices were obtained in other tin porphyrin complexes,[19] holding promise for new types of porous materials.[20]

Oxidation of vicinal diols and α-ketols mediated by tin porphyrins. We have shown that (TTP)Ti=O is able to catalyze the oxidative cleavage of vicinal diols to carbonyl compounds and the oxidation of α-ketols to α-diketones, probably via the formation of titanium porphyrin diolato or enediolato intermediates.[21] Similar reactivity is observed in tin porphyrin chemistry, i.e. the formation of diolato complexes from tin porphyrin precursors and the decomposition of diolato complexes to $(TTP)Sn^{II}$ and carbonyl compounds. This prompted us to investigate oxidative transformations mediated by tin porphyrin complexes. Selected results are summarized in Table 3. Heating (~120 °C) an aerobic C_6D_6 solution of 2,3-diphenylbutane-2,3-diol and 5.7 mol% $(TTP)Sn(C{\equiv}CPh)_2$ in a sealed NMR tube resulted in the conversion of diol to acetophenone in modest yield (55%, entry 1). Benzopinacole was converted into benzophenone in high yield (97%, entry 2) within 15 h. With unactivated diols, this cleavage reaction proceeded very slowly. For example, pinacol was cleaved to acetone under similar conditions with a turnover number of 2.3 after 8 days of heating (entry 3). Diolato complexes $(TTP)Sn[OC(Me)_2C(Me)_2O]$ (**1**) and (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) were observed in these reactions, respectively, by ^1H NMR spectroscopy. When the less substituted hydrobenzoin was subjected to the same reaction conditions, up to 10% yield of benzaldehyde was obtained. Benzyl alcohol (~0.8%) and benzil (~16%) were also detected (entry 4). With *trans*-1,2-cyclohexanediol, only a

trans-bisalkoxo complex (TTP)Sn($OC_6H_{10}OH)_2$ was observed without the formation of oxidation products.

Table 3: Vicinal diol cleavage mediated by tin porphyrins[a]



entry	R_1	R_2	catalyst	Time h	Conv %	Yield %
1	Ph	Me	(TTP)Sn($CCPh)_2$	44	46	42
				85	60	55
2	Ph	Ph	(TTP)Sn($CCPh)_2$	15	100	97
3	Me	Me	(TTP)Sn($CCPh)_2$	190	28	16
4	Ph	H	(TTP)Sn($CCPh)_2$	36	50	4.3
				188	52	8.8[b]
5	tolyl	H	(TTP)Sn($CCPh)_2$	42	90	11[c]
6	Ph	Me	$(TTP)Sn^{II}$	38	32	28
				83	51	46
7	Ph	Me	(TTP)Sn($OH)_2$	41	36	35
				83	60	53
8	Ph	Ph	(TTP)Sn($OH)_2$	18	100	86
9	Ph	Ph	(TTP)$SnCl_2$	96	83	71

Note: (a) for reaction conditions, see experimental section for details. (b) Other products were also observed: benzyl alcohol (0.5-0.8%), benzil (9.4-17%). (c) Other products were also observed: *p*-methyl benzyl alcohol (5.4%), dimethyl benzil (29%).

A number of other tin porphyrin complexes were found to mediate the oxidative cleavage of vicinal diols as well. In the presence of catalytic amounts of (TTP)Sn or

(TTP)Sn(OH)$_2$, 2,3-diphenylbutane-2,3-diol was oxidized to acetophenone in similar yields (entries 6 and 7). With (TTP)SnCl$_2$, which possesses robust Sn-Cl bonds, the cleavage of benzopinacole to benzophenone was observed, although substantially slow (entry 9).

Given the ability of (TTP)Ti=O to catalyze the oxidation of α-ketol to α-diketones, we further examined the utility of tin porphyrin complexes in this transformation. Heating an aerobic C_6D_6 solution of benzoin in the presence of 5.5 mol% (TTP)Sn(C≡CPh)$_2$ in an NMR tube resulted in the smooth conversion of benzoin to benzil. After total consumption of benzoin within 22 h, benzil was obtained in 87% NMR yield, as well as a small amount of benzaldehye (8.7%). Similarly, 2-hydroxy cyclohexanone (adipoin) was oxidized to cyclohexan-1,2-dione under identical conditions with 70% conversion, although the yield of cyclohexan-1,2-dione was low (31% after 35 h), as determined by ^{1}H NMR spectroscopy.

Discussion

Reaction of tin porphyrins with diols. The structure and coordination geometry of metal diolato complexes have been shown to be influenced greatly by the type of diolato moiety.[22] While chelated diolato complexes were invariably obtained for Ti porphyrins,[7] the outcome of reactions between (TTP)Sn(C≡CPh)$_2$ or (TTP)Sn(NHtolyl)$_2$ and vicinal diols was dependent on the diols employed. Highly substituted vicinal diols tended to yield diolato chelate complexes, while less substituted diols preferred to form mono- and bisalkoxo complexes. With pinacol and 2,3-diphenyl-butane-2,3-diol, the diolato chelate complexes **1** and **2** were readily obtained. In contrast, attempts to prepare chelated diolato complexes from ethylene glycol and hydrobenzoin in a similar manner proved to be elusive. Only mono- and/or bisalkoxo complexes were observed. Higher temperature and longer reaction

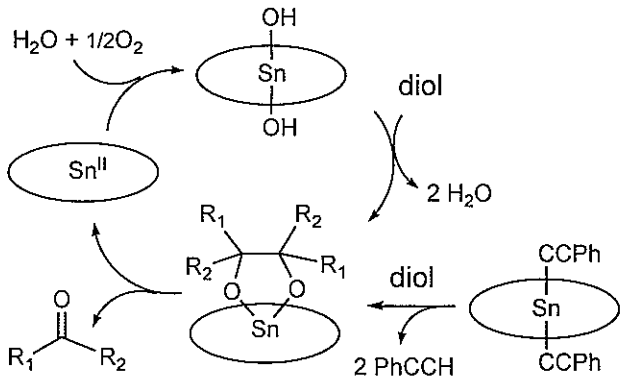
times appeared to favor the production of diolato complex **1** in the pinacol reaction. However, under these conditions the decomposition of **1** to (TTP)Sn become significant and clean formation of **1** was not achieved. In the presence of methanol, reaction of $(TTP)Sn(C{\equiv}CPh)_2$ with pinacol or *meso*-hydrobenzoin did not give a clean formation of diolato complexes, thus a weak protic acid catalyzed diolate formation is not likely.

On the other hand, it is possible to produce the diolato complex $(TTP)Sn(OC_6H_4O)$ (**4**) by heating a C_6D_6 solution of $(TTP)Sn(C{\equiv}CPh)(OC_6H_4OH)$ (**3**) over a long period of time (12 d). This is in part, due to the thermal stability of the resulting diolato complex and in part, due to the inability of the pendant OH groups to form dimers or oligomers with other tin porphyrin species. In contrast, heating a $(TTP)Sn(C{\equiv}CPh)(OCH_2CH_2OH)$ (**6**) solution did generate the diolato complex as a minor product, while accompanied by the decomposition to (TTP)Sn (β-H: 9.19 ppm) and other uncharacterizable products.

The nature of the starting tin porphyrin complexes was also important in the reaction outcome. In the reactions of $(TTP)Sn(C{\equiv}CPh)_2$ with pinacol and 2,3-diphenyl-butane-2,3-diol, the formation of mono- and bisalkoxo complexes were often observed. With a more labile diamido complex, $(TTP)Sn(NHtolyl)_2$, the diolato complexes $(TTP)Sn[OC(Me)_2C(Me)_2O]$ (**1**) and (TTP)Sn[OC(Ph)(Me)C(Ph)(Me)O] (**2**) could be obtained in good yields with trace or no formation of mono- or bisalkoxo species. However, the requirement of excess diol was somewhat unexpected. Presumably the formation of the diolato complexes proceeds through an alkoxo-alkynyl- substituted intermediate, as demonstrated by the generation of $(TTP)Sn(OC_6H_4O)$ (**4**) from $(TTP)Sn(C{\equiv}CPh)(OC_6H_4OH)$ (**3**). The ease of dissociation of the amido group, relative to that of the C≡CPh group, greatly

facilitates the formation of diolato complexes from the intermediates mentioned above. Surprisingly, the reaction of a labile tin porphyrin, $(TTP)Sn(OTf)_2$, with disodium pinacolate did not produce the desired diolato complex cleanly.

Mechanistic aspects of tin porphyrin mediated diol cleavage and ketol oxidation. Based on previous studies with (TTP)Ti=O-mediated oxidations,[21] a probable catalytic cycle for the tin porphyrin-mediated diol cleavage is shown in Scheme 3. Sn(IV) complexes, such as $(TTP)Sn(C{\equiv}CPh)_2$, react with diols to form diolato intermediates, which in turn undergo oxidative cleavage to release carbonyl compounds and $(TTP)Sn^{II}$. This latter step was observed independently in the decomposition of the diolato complexes under N_2. The Sn^{II} species is subsequently oxidized to $(TTP)Sn(OH)_2$ by molecular oxygen in moist air, which is known to be a very facile process.[23] This was further supported by the reaction of 2,3-



Scheme 3

diphenylbutan-2,3-diol in the presence of $(TTP)Sn^{II}$. Under N_2, no acetophenone production was observed, while under air, the formation of the diolato complex **2** was observed and acetophenone was produced in a rate similar to that of the $(TTP)Sn(C{\equiv}CPh)_2$-mediated reaction. Although $(TTP)Sn(OH)_2$ is quite inert, it has been known to react with an array of

phenols and carboxylic acids under mild conditions.[10,24] We have shown here that (TTP)Sn reacted readily with ethylene glycol to afford (TTP)Sn($OCH_2CH_2OH)_2$ (**7**) upon exposure to air. Thus the formation of diolato complexes from (TTP)Sn$(OH)_2$ and diols completes the catalytic cycle. We also found that (TTP)Sn$(OH)_2$ was able to cleave diols oxidatively, under catalytic conditions (Table 3, entries 7 and 8).

To probe the reaction pathway of tin porphyrin-mediated α-ketol oxidation, the reaction of benzoin with (TTP)Sn$(C{\equiv}CPh)_2$ under N_2 was monitored by ^{1}H NMR spectroscopy. The reaction proceeded stepwise, first yielding monosubstituted (TTP)Sn(C≡CPh)[OCH(Ph)COPh], then disubstituted (TTP)Sn$[OCH(Ph)COPh]_2$. (TTP)Sn and benzil were produced very slowly after prolonged heating. However, unlike the oxotitanium porphyrin-mediated reaction, where an enediolato species (TTP)Ti[OC(Ph)=C(Ph)O] was readily observed,[21] the formation of the tin porphyrin enediolato species was not directly detected by ^{1}H NMR spectroscopy. The generation of such tin (IV) species has been elusive, although tin(II) enediolato species are known.[25] We have also shown that titanium(II) porphyrins react with benzil to afford the enediolato complex (TTP)Ti[OC(Ph)=C(Ph)O], while the analogous product with (TTP)Sn(II) is not observed. Nonetheless, by analogy with the (TTP)Ti=O-mediated reaction, we believe a similar mechanism involving an enediolato intermediate is operative in the tin porphyrin-mediated α-ketol oxidation. The presence of coordinating groups (carbonyl CO or OH) vicinal to the alcohol group seems to be crucial for these reactions. Simple alcohols such as benzhydrol and *p*-methyl benzyl alcohol can not be oxidized under the same conditions.

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Supporting Information Available: Tables giving crystallographic data for **3** including atomic coordinates, bond lengths and angels, and anisotropic displacement parameters. This information is available free of charge via the internet at http://pubs.acs.org.

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APPENDIX

Table I. Crystal data and structure refinement for (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**).

Empirical formula	C62 H46 N4 O2 Sn	
Formula weight	997.72	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.594(3) Å	α = 90°
	b = 32.673(9) Å	β = 98.477(5)°
	c = 15.814(4) Å	γ = 90°
Volume	5414(2) $Å^3$	
Z	4	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.517 mm^{-1}	
F(000)	2048	
Crystal size	0.32 x 0.29 x 0.21 mm^3	
Theta range for data collection	1.80 to 21.98°	
Index ranges	-11<=h<=11, -34<=k<=34, -16<=l<=16	
Reflections collected	34104	
Independent reflections	6589 [R(int) = 0.1129]	
Completeness to theta = 21.98°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.81	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6589 / 0 / 622	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0864, wR2 = 0.2083	
R indices (all data)	R1 = 0.1255, wR2 = 0.2308	
Largest diff. peak and hole	1.348 and -1.359 $eÅ^{-3}$	

$R1 = \Sigma \, | \, |F_O| - |F_c| \, | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table II. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Sn(1)	5763(1)	8575(1)	5947(1)	35(1)
C(1)	3606(9)	8858(3)	4550(6)	30(2)
C(2)	3205(11)	8819(3)	3662(8)	45(3)
C(3)	4154(10)	8631(3)	3297(7)	40(3)
C(4)	5170(9)	8563(3)	3971(6)	32(2)
C(5)	6322(10)	8352(3)	3894(7)	33(3)
C(6)	6527(10)	8236(3)	3018(7)	35(3)
C(7)	6672(13)	8538(4)	2418(8)	61(4)
C(8)	6864(16)	8431(4)	1600(9)	78(5)
C(9)	6885(12)	8023(4)	1349(9)	54(3)
C(10)	7022(16)	7910(5)	439(9)	79(5)
C(11)	6787(10)	7736(4)	1951(8)	44(3)
C(12)	6618(9)	7838(3)	2759(7)	35(3)
C(13)	7273(9)	8235(3)	4566(7)	32(3)
C(14)	8471(10)	8044(3)	4482(8)	39(3)
C(15)	9118(10)	7994(3)	5270(7)	41(3)
C(16)	8366(10)	8158(3)	5878(7)	35(3)
C(17)	8708(10)	8175(3)	6750(7)	36(3)
C(18)	10024(10)	8019(3)	7116(7)	40(3)
C(19)	11024(11)	8282(4)	7285(9)	65(4)
C(20)	12211(12)	8144(4)	7614(9)	66(4)
C(21)	12438(10)	7744(4)	7798(8)	50(3)
C(22)	13758(11)	7603(5)	8215(10)	80(5)
C(23)	11458(12)	7482(4)	7643(10)	69(4)
C(24)	10236(11)	7616(4)	7294(9)	58(4)
C(25)	8021(10)	8341(3)	7359(7)	34(3)
C(26)	8435(11)	8388(3)	8256(7)	45(3)
C(27)	7525(11)	8597(4)	8594(7)	48(3)
C(28)	6514(10)	8683(3)	7913(8)	45(3)

Table II. (continued)

C(29)	5413(11)	8915(3)	7995(7)	44(3)
C(30)	5341(12)	9083(4)	8856(7)	46(3)
C(31)	5976(17)	9431(5)	9098(10)	80(5)
C(32)	6032(19)	9580(5)	9926(10)	90(5)
C(33)	5459(18)	9401(5)	10512(10)	75(5)
C(34)	5530(20)	9551(6)	11424(10)	143(10)
C(35)	4763(18)	9067(7)	10266(10)	100(6)
C(36)	4689(15)	8898(5)	9429(10)	81(5)
C(37)	4431(10)	9014(3)	7318(7)	39(3)
C(38)	3307(11)	9247(3)	7407(8)	43(3)
C(39)	2607(10)	9263(3)	6630(7)	41(3)
C(40)	3275(9)	9056(3)	6032(7)	33(3)
C(41)	2908(9)	9024(3)	5159(7)	32(3)
C(42)	1585(9)	9185(3)	4821(7)	32(2)
C(43)	1400(10)	9537(3)	4362(7)	42(3)
C(44)	148(10)	9681(4)	4100(8)	48(3)
C(45)	-893(10)	9463(3)	4258(7)	40(3)
C(46)	-2243(10)	9609(4)	3963(9)	56(4)
C(47)	-688(11)	9114(4)	4722(10)	65(4)
C(48)	543(11)	8976(4)	5007(9)	61(4)
C(49)	6777(10)	9448(3)	6255(7)	36(3)
C(50)	5790(12)	9732(4)	6148(9)	58(4)
C(51)	5813(15)	10083(4)	6633(11)	71(4)
C(52)	6840(18)	10144(5)	7257(11)	75(5)
C(53)	7848(16)	9882(4)	7389(9)	67(4)
C(54)	7801(12)	9544(4)	6898(8)	51(3)
C(55)	4704(11)	8019(3)	5961(7)	38(3)
C(56)	4003(11)	7732(4)	5835(7)	42(3)
C(57)	3114(10)	7401(3)	5659(8)	41(3)
C(58)	3273(12)	7050(4)	6097(9)	66(4)
C(59)	2395(16)	6727(4)	5935(11)	86(5)
C(60)	1342(14)	6775(5)	5302(12)	87(5)

Table II. (continued)

C(61)	1192(14)	7140(5)	4842(11)	85(5)
C(62)	2087(12)	7446(4)	5018(9)	60(4)
N(1)	4821(7)	8700(2)	4718(5)	31(2)
N(2)	7247(8)	8292(2)	5419(5)	32(2)
N(3)	6834(8)	8519(3)	7170(6)	35(2)
N(4)	4379(8)	8911(3)	6478(6)	37(2)
O(1)	6815(6)	9105(2)	5828(5)	41(2)
O(2)	8817(9)	9275(3)	6963(7)	95(4)

Table III. Bond lengths [Å] and angles [°] for (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**).

Sn(1)-O(1)	2.083(7)	C(28)-N(3)	1.378(14)
Sn(1)-N(1)	2.090(9)	C(28)-C(29)	1.413(15)
Sn(1)-N(2)	2.100(8)	C(29)-C(37)	1.416(15)
Sn(1)-N(3)	2.101(9)	C(29)-C(30)	1.480(16)
Sn(1)-N(4)	2.102(9)	C(30)-C(31)	1.346(19)
Sn(1)-C(55)	2.139(12)	C(30)-C(36)	1.360(18)
C(1)-N(1)	1.376(12)	C(31)-C(32)	1.39(2)
C(1)-C(41)	1.406(14)	C(32)-C(33)	1.32(2)
C(1)-C(2)	1.412(15)	C(33)-C(35)	1.34(2)
C(2)-C(3)	1.376(15)	C(33)-C(34)	1.51(2)
C(3)-C(4)	1.417(15)	C(35)-C(36)	1.43(2)
C(4)-N(1)	1.365(13)	C(37)-N(4)	1.363(13)
C(4)-C(5)	1.422(14)	C(37)-C(38)	1.438(15)
C(5)-C(13)	1.406(15)	C(38)-C(39)	1.339(15)
C(5)-C(6)	1.483(14)	C(39)-C(40)	1.431(15)
C(6)-C(12)	1.371(14)	C(40)-N(4)	1.360(13)
C(6)-C(7)	1.393(15)	C(40)-C(41)	1.383(14)
C(7)-C(8)	1.384(18)	C(41)-C(42)	1.519(14)
C(8)-C(9)	1.392(18)	C(42)-C(43)	1.358(14)
C(9)-C(11)	1.352(16)	C(42)-C(48)	1.368(15)
C(9)-C(10)	1.514(18)	C(43)-C(44)	1.410(15)
C(11)-C(12)	1.359(15)	C(44)-C(45)	1.367(15)
C(13)-N(2)	1.366(13)	C(45)-C(47)	1.355(16)
C(13)-C(14)	1.438(14)	C(45)-C(46)	1.514(15)
C(14)-C(15)	1.341(15)	C(47)-C(48)	1.390(16)
C(15)-C(16)	1.438(15)	C(49)-O(1)	1.311(12)
C(16)-N(2)	1.367(13)	C(49)-C(50)	1.389(16)
C(16)-C(17)	1.375(14)	C(49)-C(54)	1.408(16)
C(17)-C(25)	1.400(14)	C(50)-C(51)	1.379(18)
C(17)-C(18)	1.517(15)	C(51)-C(52)	1.37(2)
C(18)-C(24)	1.359(15)	C(52)-C(53)	1.36(2)
C(18)-C(19)	1.360(16)	C(53)-C(54)	1.346(17)

Table III. (continued)

C(19)-C(20)	1.364(17)	C(54)-O(2)	1.381(15)
C(20)-C(21)	1.352(17)	C(55)-C(56)	1.194(15)
C(21)-C(23)	1.341(18)	C(56)-C(57)	1.434(16)
C(21)-C(22)	1.527(16)	C(57)-C(58)	1.338(17)
C(23)-C(24)	1.401(17)	C(57)-C(62)	1.381(16)
C(25)-N(3)	1.378(13)	C(58)-C(59)	1.404(18)
C(25)-C(26)	1.430(15)	C(59)-C(60)	1.39(2)
C(26)-C(27)	1.354(15)	C(60)-C(61)	1.39(2)
C(27)-C(28)	1.430(16)	C(61)-C(62)	1.377(18)
O(1)-Sn(1)-N(1)	86.7(3)	C(28)-C(29)-C(30)	116.1(10)
O(1)-Sn(1)-N(2)	83.6(3)	C(37)-C(29)-C(30)	118.6(10)
N(1)-Sn(1)-N(2)	90.0(3)	C(31)-C(30)-C(36)	117.9(13)
O(1)-Sn(1)-N(3)	86.1(3)	C(31)-C(30)-C(29)	118.9(11)
N(1)-Sn(1)-N(3)	172.8(3)	C(36)-C(30)-C(29)	123.1(13)
N(2)-Sn(1)-N(3)	89.6(3)	C(30)-C(31)-C(32)	120.9(14)
O(1)-Sn(1)-N(4)	90.9(3)	C(33)-C(32)-C(31)	123.2(17)
N(1)-Sn(1)-N(4)	90.2(3)	C(32)-C(33)-C(35)	116.6(16)
N(2)-Sn(1)-N(4)	174.5(3)	C(32)-C(33)-C(34)	124.4(19)
N(3)-Sn(1)-N(4)	89.5(3)	C(35)-C(33)-C(34)	119.1(17)
O(1)-Sn(1)-C(55)	175.2(4)	C(33)-C(35)-C(36)	122.5(15)
N(1)-Sn(1)-C(55)	89.8(4)	C(30)-C(36)-C(35)	118.7(16)
N(2)-Sn(1)-C(55)	93.1(3)	N(4)-C(37)-C(29)	126.9(10)
N(3)-Sn(1)-C(55)	97.4(4)	N(4)-C(37)-C(38)	108.1(9)
N(4)-Sn(1)-C(55)	92.4(4)	C(29)-C(37)-C(38)	124.9(11)
N(1)-C(1)-C(41)	125.8(9)	C(39)-C(38)-C(37)	106.6(10)
N(1)-C(1)-C(2)	107.1(9)	C(38)-C(39)-C(40)	109.1(10)
C(41)-C(1)-C(2)	127.1(10)	N(4)-C(40)-C(41)	125.8(10)
C(3)-C(2)-C(1)	109.0(10)	N(4)-C(40)-C(39)	107.1(9)
C(2)-C(3)-C(4)	106.0(10)	C(41)-C(40)-C(39)	127.1(10)
N(1)-C(4)-C(3)	109.1(9)	C(40)-C(41)-C(1)	127.9(9)
N(1)-C(4)-C(5)	125.3(9)	C(40)-C(41)-C(42)	115.7(9)

Table III. (continued)

C(3)-C(4)-C(5)	125.4(10)	C(1)-C(41)-C(42)	116.4(9)
C(13)-C(5)-C(4)	126.6(10)	C(43)-C(42)-C(48)	118.7(10)
C(13)-C(5)-C(6)	116.7(9)	C(43)-C(42)-C(41)	122.3(9)
C(4)-C(5)-C(6)	116.7(9)	C(48)-C(42)-C(41)	119.0(9)
C(12)-C(6)-C(7)	116.7(11)	C(42)-C(43)-C(44)	119.6(10)
C(12)-C(6)-C(5)	123.2(10)	C(45)-C(44)-C(43)	121.5(11)
C(7)-C(6)-C(5)	120.1(10)	C(47)-C(45)-C(44)	117.8(10)
C(8)-C(7)-C(6)	120.3(12)	C(47)-C(45)-C(46)	120.1(10)
C(7)-C(8)-C(9)	121.2(13)	C(44)-C(45)-C(46)	122.1(10)
C(11)-C(9)-C(8)	117.3(12)	C(45)-C(47)-C(48)	121.2(11)
C(11)-C(9)-C(10)	121.9(12)	C(42)-C(48)-C(47)	121.0(11)
C(8)-C(9)-C(10)	120.8(12)	O(1)-C(49)-C(50)	125.9(11)
C(9)-C(11)-C(12)	121.8(11)	O(1)-C(49)-C(54)	118.9(10)
C(11)-C(12)-C(6)	122.6(11)	C(50)-C(49)-C(54)	115.2(11)
N(2)-C(13)-C(5)	126.4(9)	C(51)-C(50)-C(49)	122.5(13)
N(2)-C(13)-C(14)	107.3(9)	C(52)-C(51)-C(50)	117.9(14)
C(5)-C(13)-C(14)	126.3(10)	C(53)-C(52)-C(51)	122.8(14)
C(15)-C(14)-C(13)	107.7(10)	C(54)-C(53)-C(52)	117.7(14)
C(14)-C(15)-C(16)	108.6(10)	C(53)-C(54)-O(2)	121.1(13)
N(2)-C(16)-C(17)	126.8(10)	C(53)-C(54)-C(49)	123.9(12)
N(2)-C(16)-C(15)	106.7(9)	O(2)-C(54)-C(49)	114.9(11)
C(17)-C(16)-C(15)	126.5(10)	C(56)-C(55)-Sn(1)	168.5(10)
C(16)-C(17)-C(25)	128.2(10)	C(55)-C(56)-C(57)	177.1(12)
C(16)-C(17)-C(18)	117.4(9)	C(58)-C(57)-C(62)	119.7(11)
C(25)-C(17)-C(18)	114.2(10)	C(58)-C(57)-C(56)	121.2(11)
C(24)-C(18)-C(19)	118.2(11)	C(62)-C(57)-C(56)	119.2(11)
C(24)-C(18)-C(17)	121.3(10)	C(57)-C(58)-C(59)	121.3(13)
C(19)-C(18)-C(17)	120.5(10)	C(60)-C(59)-C(58)	119.1(15)
C(18)-C(19)-C(20)	120.9(12)	C(61)-C(60)-C(59)	119.2(14)
C(21)-C(20)-C(19)	121.8(12)	C(62)-C(61)-C(60)	119.6(14)
C(23)-C(21)-C(20)	118.0(11)	C(61)-C(62)-C(57)	121.1(13)
C(23)-C(21)-C(22)	121.4(13)	C(4)-N(1)-C(1)	108.8(8)

Table III. (continued)

C(20)-C(21)-C(22)	120.5(13)	C(4)-N(1)-Sn(1)	126.0(6)
C(21)-C(23)-C(24)	121.2(12)	C(1)-N(1)-Sn(1)	123.9(7)
C(18)-C(24)-C(23)	119.9(12)	C(13)-N(2)-C(16)	109.7(8)
N(3)-C(25)-C(17)	124.4(10)	C(13)-N(2)-Sn(1)	125.3(6)
N(3)-C(25)-C(26)	107.8(9)	C(16)-N(2)-Sn(1)	124.9(7)
C(17)-C(25)-C(26)	127.5(10)	C(28)-N(3)-C(25)	108.1(9)
C(27)-C(26)-C(25)	108.3(10)	C(28)-N(3)-Sn(1)	125.8(7)
C(26)-C(27)-C(28)	107.4(10)	C(25)-N(3)-Sn(1)	126.0(7)
N(3)-C(28)-C(29)	126.6(11)	C(40)-N(4)-C(37)	109.1(9)
N(3)-C(28)-C(27)	108.4(9)	C(40)-N(4)-Sn(1)	125.0(7)
C(29)-C(28)-C(27)	124.9(11)	C(37)-N(4)-Sn(1)	125.9(7)
C(28)-C(29)-C(37)	125.2(11)	C(49)-O(1)-Sn(1)	127.3(6)

Table IV. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (TTP)Sn(C≡CPh)(OC_6H_4OH) (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	19(1)	38(1)	50(1)	4(1)	5(1)	3(1)
C(1)	26(6)	29(6)	32(6)	5(5)	0(5)	-4(5)
C(2)	35(7)	38(7)	60(9)	5(6)	-1(6)	1(6)
C(3)	36(7)	45(7)	41(7)	-8(5)	7(6)	11(6)
C(4)	30(6)	30(6)	37(6)	9(5)	6(5)	4(5)
C(5)	31(6)	24(6)	45(7)	0(5)	11(5)	-1(5)
C(6)	27(6)	34(6)	43(7)	1(5)	4(5)	8(5)
C(7)	85(10)	42(7)	61(9)	10(7)	28(8)	4(7)
C(8)	117(14)	60(10)	62(10)	21(8)	28(9)	2(9)
C(9)	45(8)	49(8)	68(9)	3(7)	7(7)	15(6)
C(10)	104(13)	82(11)	60(10)	5(8)	39(9)	23(9)
C(11)	26(6)	43(7)	64(9)	-7(7)	13(6)	2(5)
C(12)	13(5)	41(7)	50(8)	-1(6)	5(5)	-3(5)
C(13)	23(6)	31(6)	44(7)	4(5)	12(5)	-3(5)
C(14)	18(6)	50(7)	51(8)	2(6)	11(6)	2(5)
C(15)	27(6)	37(7)	58(8)	2(6)	5(6)	0(5)
C(16)	28(6)	38(6)	38(7)	0(5)	5(5)	3(5)
C(17)	30(6)	28(6)	49(8)	4(5)	10(6)	-3(5)
C(18)	25(6)	48(7)	47(7)	1(6)	9(5)	6(6)
C(19)	26(7)	59(9)	102(11)	29(8)	-12(7)	-4(6)
C(20)	28(8)	65(10)	103(12)	20(8)	2(7)	-8(7)
C(21)	19(7)	80(10)	52(8)	6(7)	8(6)	19(7)
C(22)	21(7)	115(13)	100(12)	20(10)	-1(7)	22(8)
C(23)	32(8)	56(8)	118(13)	8(8)	1(8)	21(7)
C(24)	30(7)	43(8)	98(11)	0(7)	-2(7)	9(6)
C(25)	27(6)	39(6)	39(7)	12(5)	13(5)	8(5)
C(26)	36(7)	55(7)	42(8)	10(6)	2(6)	11(6)

Table IV. (continued)

C(27)	39(7)	68(8)	35(7)	9(6)	5(6)	21(7)
C(28)	26(7)	52(8)	60(8)	10(6)	14(6)	11(6)
C(29)	37(7)	47(7)	51(8)	16(6)	14(6)	5(6)
C(30)	48(8)	62(9)	31(7)	15(6)	13(6)	19(7)
C(31)	125(15)	58(10)	65(11)	5(8)	38(10)	2(10)
C(32)	142(17)	65(10)	65(11)	-2(9)	26(11)	3(10)
C(33)	103(13)	72(11)	55(10)	16(9)	22(10)	26(10)
C(34)	240(30)	139(17)	55(11)	-4(11)	42(14)	99(18)
C(35)	105(15)	152(18)	53(11)	12(11)	42(10)	-10(13)
C(36)	79(11)	94(12)	73(11)	12(9)	21(9)	1(9)
C(37)	31(6)	46(7)	41(8)	17(6)	7(5)	6(5)
C(38)	42(7)	45(7)	47(8)	8(6)	27(6)	18(6)
C(39)	25(6)	55(7)	46(8)	10(6)	16(6)	2(5)
C(40)	20(6)	39(6)	38(7)	10(5)	1(5)	-4(5)
C(41)	13(5)	29(6)	53(8)	10(5)	5(5)	-2(4)
C(42)	21(6)	30(6)	45(7)	0(5)	6(5)	0(5)
C(43)	19(6)	45(7)	62(8)	15(6)	9(6)	-5(5)
C(44)	23(7)	51(7)	68(9)	14(6)	1(6)	6(6)
C(45)	28(7)	35(6)	56(8)	-1(6)	3(6)	1(5)
C(46)	14(6)	71(9)	82(10)	19(7)	1(6)	6(6)
C(47)	24(7)	53(8)	120(12)	28(8)	14(7)	-3(6)
C(48)	32(7)	49(8)	98(11)	27(7)	1(7)	4(6)
C(49)	35(7)	31(6)	44(7)	8(5)	13(6)	-1(5)
C(50)	32(7)	46(8)	98(11)	17(7)	18(7)	-5(6)
C(51)	49(9)	50(9)	125(14)	-8(9)	49(10)	-3(7)
C(52)	92(13)	61(10)	87(12)	-5(9)	57(11)	-16(10)
C(53)	86(12)	57(9)	57(9)	0(7)	2(8)	-24(9)
C(54)	40(8)	46(8)	64(9)	7(7)	2(7)	0(6)
C(55)	32(7)	42(7)	40(7)	1(5)	6(5)	6(6)
C(56)	29(7)	40(7)	54(8)	0(6)	2(6)	6(6)
C(57)	29(7)	33(7)	60(8)	-6(6)	7(6)	-3(5)
C(58)	43(8)	56(9)	93(11)	-5(8)	-10(7)	-7(7)

Table IV. (continued)

C(59)	76(12)	57(10)	121(14)	-2(9)	-5(11)	-22(9)
C(60)	44(9)	81(12)	135(15)	-27(11)	9(10)	-22(8)
C(61)	57(10)	72(11)	114(14)	-15(10)	-31(9)	-15(8)
C(62)	49(8)	51(8)	77(10)	-9(7)	-2(7)	-6(7)
N(1)	18(5)	30(5)	47(6)	5(4)	14(4)	-1(4)
N(2)	21(5)	31(5)	43(6)	2(4)	1(4)	-2(4)
N(3)	20(5)	40(5)	45(6)	7(4)	10(4)	6(4)
N(4)	29(5)	42(5)	40(6)	10(4)	8(4)	2(4)
O(1)	23(4)	35(4)	64(5)	-2(4)	6(4)	-1(3)
O(2)	64(7)	69(7)	133(9)	24(6)	-45(6)	-11(6)

CHAPTER 5: ASYMMETRIC CYCLOPROPANATION OF STYRENE CATALYZED BY CHIRAL MACROCYCLIC IRON(II) COMPLEXES

A paper published in *Organometallics*[1]

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Abstract

Three chiral tetraaza macrocyclic ligands (**4a-c**) were synthesized by the cyclization reaction of diamines with dithioaldehydes. The iron(II) complexes of ligands **4a** and **4c**, as well as two chiral iron(II) porphyrin complexes, $Fe^{II}(D_4\text{-TpAP})$ and $Fe(\alpha_2\beta_2\text{-BNP})$, are efficient catalysts for the cyclopropanation of styrene with diazoacetate reagents. The cyclopropyl esters were produced with high diastereoselectivities and good yields. However, the enantioselectivities were modest to poor. The rationalization of the stereoselectivity in these cyclopropanation reactions is presented. The results of a single-crystal X-ray analysis of the ligand **4a** are also reported.

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Introduction

Transition metal-catalyzed cyclopropanation has been an area of intensive study over the past several decades.[2] Since the first report[3] of chiral induction in cyclopropanation, a number of excellent catalyst systems have been developed that achieve highly selective asymmetric results.[4] In this context, chiral ruthenium porphyrin catalysts have received much attention recently.[5] However, despite the presence of a wide variety of chiral iron porphyrins and their remarkable efficiency and selectivity in catalytic epoxidation of olefins,[6] few of these have been tested as cyclopropanation catalysts. In fact, chiral iron porphyrins were not used in cyclopropanation until 1999.[7]

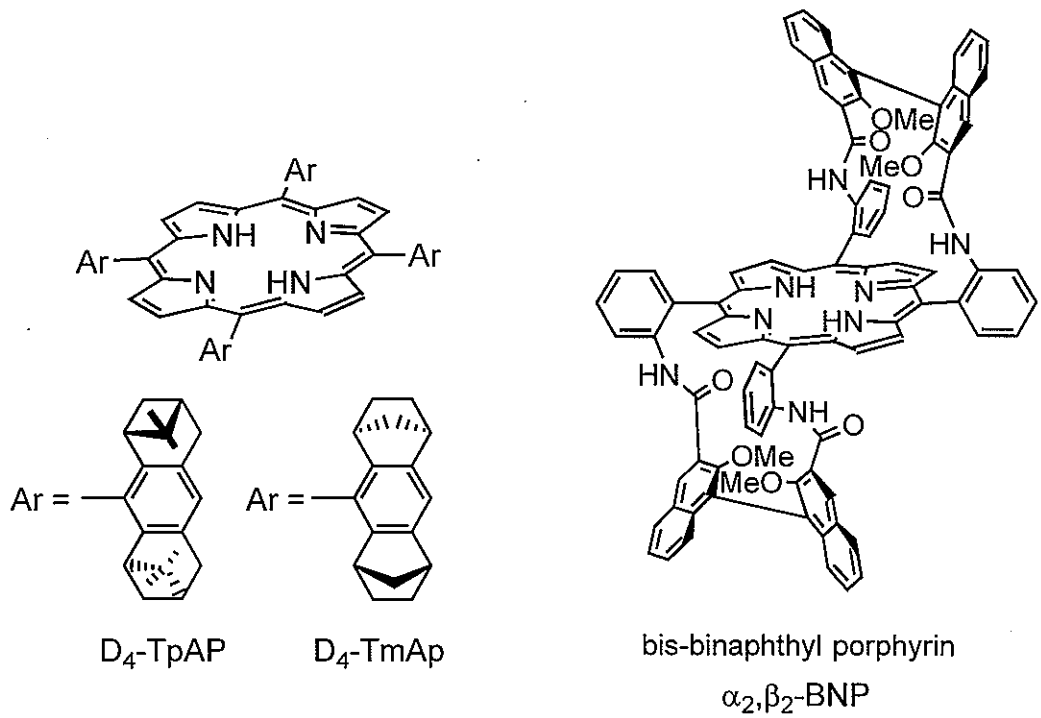
Due to the structural resemblance to porphyrins, the related tetraaza macrocyclic ligands seemed to be a logical extension to metalloporphyrin chemistry. We have examined the application of an iron complex of tetramethyldibenzotetraaza[14]annulene (tmtaa) in catalytic non-chiral cyclopropanation reactions.[8] These ligands provide the possibility of introducing auxiliary stereogenic centers in close proximity to the active metal sites, making them promising candidates in asymmetric catalysis studies.

In this paper, we report the non-template synthesis of a number of chiral macrocyclic ligands, and the application of their iron(II) complexes in asymmetric cyclopropanation catalysis. In addition, we report the catalytic results of two chiral iron porphyrin complexes (Chart 1).

Experimental Section

General Procedures. All manipulations involving air or moisture sensitive iron(II) complexes were performed under a nitrogen atmosphere using a Vacuum Atmospheres

glovebox equipped with a Model MO40-1 Dri-Train gas purifier. Solvents used in the catalytic reactions were dried and degassed. The starting materials, 4-phenyl-1,2-dithiolium iodide (**2a**), 4-(*p*-nitrophenyl)-1,2-dithiolium iodide (**2b**) were prepared according to literature methods.[9] The chiral diamine, (*R,R*)-(-)-1,2-diaminocyclohexane (dach), was resolved from a commercial mixture by a published procedure.[10] A reported method was used to synthesize (*1R,3R,4S*)-(-)-menthyl diazoacetate.[11] Fe(D_4-TpAP) was prepared by reaction of the free base porphyrin[12] and anhydrous iron(II) bromide in the presence of 2,6-lutidine according to the procedure of Collman.[13] Fe($\alpha_2\beta_2$-BNP) was prepared by reduction of Fe($\alpha_2\beta_2$-BNP)Cl[14] with Zn/Hg amalgam in THF or toluene.[15] The reactivity pattern and UV-vis spectral properties were similar with those of Fe(TTP). All other reagents were used as purchased.



D_4-TpAP D_4-TmAp bis-binaphthyl porphyrin α_2,β_2-BNP

Chart 1. Structures of chiral porphyrins used in this study.

^{1}H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts were referenced to residual solvent peaks (δ 7.24, $CHCl_3$; 7.15, C_6D_5H). UV-vis data were recorded on a HP8452A diode array spectrophotometer and reported as λ_{max} in nm (log ε). Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. Optical rotation data were measured on a JASCO DIP-370 digital polarimeter at 589 nm. GC-MS studies were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS). GC analyses were performed on a HP 5890 gas chromatograph equipped with a flame ionization detector and a DB-5 capillary column (30 m × 0.32 mm i.d.). Chiral capillary GC analyses were performed on a HP 5890 gas chromatograph equipped with a flame ionization detector and a CP-Chirasil-Dex CB capillary column (25 m × 0.25 mm i.d.).

Preparation of dithioaldehyde 3a. In a typical preparation, 4-phenyl-1,2-dithiolium iodide, **2a** (8.24 g, 26.9 mmol) was suspended in dry benzene (200 mL) and (*R,R*)-dach (3.18 g, 27.8 mmol) in benzene (50 mL) was added slowly. After stirring for 1 h, the yellow precipitate was removed by filtration and the filtrate taken to dryness under reduced pressure to afford **3a**, which was used for the next step without further purification. Yield: 5.04 g (92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 14.30 (s, 2H, N*H*), 10.15 (d, $^3J_{H\text{-}H}$ = 3 Hz, 2H, C*H*(=S)), 7.47 (dd, $^3J_{H\text{-}H}$ = 12.9 Hz, 3Hz, 2H, C=C*H*NH), 7.09-7.29 (m, 10H, aromatic), 3.21 (m, 2H, C*H*N), 2.31 (m, 2H, C_6H_{10}), 1.91 (m, 2H, C_6H_{10}), 1.63 (m, 2H, C_6H_{10}), 1.48 (m, 2H, C_6H_{10}).

Preparation of dithioaldehyde 3b. In a typical preparation, 4-(*p*-nitrophenyl)-1,2-dithiolium iodide, **2b** (350 mg, 0.997 mmol) was suspended in dry benzene (10 mL) and (*R,R*)-dach (113 mg, 0.990 mmol) in benzene (6 mL) was added slowly. After stirring for 1 h, the yellow precipitate was removed by filtration and the filtrate taken to dryness under reduced pressure to afford **3b**, which was used for the next step without further purification. Yield: 198 mg (80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 14.32 (s, 2H, N*H*), 10.30 (d, $^{3}J_{H\text{-}H}$ = 3 Hz; 2H, C*H*(=S)), 3.29 (m, 2H, C*H*N), 2.34 (m, 2H, C_6H_{10}), 1.98 (m, 2H, C_6H_{10}), 1.4-1.7 (m, 4H, C_6H_{10}). Imine and aromatic peaks between 7.2-8.2 ppm were obscured by impurities.

Synthesis of H_2[HPhH(dach)$_2$] (4a). To a hot solution of **3a** (2.52 g, 6.20 mmol) in benzene (250 mL) was added (*R,R*)-dach (1.29 g, 11.30 mmol) in benzene (70 mL) through a pressure-equalizing dropping funnel over 3 hours. The mixture was kept briskly boiling for 12 hours and reduced to dryness *in vacuo*. Addition of methanol induced the separation of a yellow solid. Further purification was achieved by layering a filtered chloroform solution of **4a** and precipitating with methanol (1:2 v/v). Filtering the solid and drying in air produced light yellow crystals. Yield: 0.772 g (28%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.62 (s, 2H, N*H*), 7.71 (s, 4H, C=C*H*N), 7.26 (m, 4H, *m*-C_6H_5), 7.20 (m, 4H, *o*-C_6H_5), 7.09 (m, 2H, *p*-C_6H_5), 3.19 (m, 4H, C*H*N), 2.18 (m, 4H, C_6H_{10}), 1.89 (m, 4H, C_6H_{10}), 1.47 (m, 4H, C_6H_{10}), 1.39 (m, 4H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 150.7(C=CHN), 141.9, 128.5, 125.3, 124.2, 105.8, 64.6 (*C*HN on C_6H_{10}), 29.5, 24.9. IR (KBr): 3500, 2930, 2851, 1635, 1578, 1290, 1265 cm^{-1}. UV-vis ($CHCl_3$): 296 nm (4.82), 331 (4.72), 420 (3.46). MS (EI): 452

(M^+). $[\alpha]_D^{26\,°C} = -739.5$ ($c = 0.0064$, $CHCl_3$). Anal. Calcd. for $C_{30}H_{36}N_4 \cdot 0.5H_2O$: C, 78.05; H, 8.08; N, 12.14. Found: C, 78.10; H, 7.79; N, 11.95.

Alternatively, **4a** could be prepared from dithioaldehyde **3c** and excess (*R,R*)-dach by an amine exchange reaction. To a hot solution of **3c** (70.0 mg, 0.191 mmol) in benzene (20 mL) was added (*R,R*)-dach (72.6 mg, 0.636 mmol) in benzene (5 mL) through a pressure-equalizing dropping funnel over 3 hours. The mixture was kept briskly boiling for 12 hours and reduced to dryness *in vacuo*. The workup procedure as described above yielded light yellow crystals. Yield: 24 mg (28%). The ^{1}H NMR spectrum was identical to the above data.

Synthesis of H_2[H(*p*-NO_2-Ph)H(dach)$_2$] (4b). To a hot solution of **3b** (669 mg, 1.35 mmol) in benzene (120 mL) was added (*R,R*)-dach (293 mg, 2.57 mmol) in benzene (20 mL) through a pressure-equalizing dropping funnel over 3 hours. The mixture was kept briskly boiling for 12 hours and reduced to dryness *in vacuo*. The workup procedure as described for **4a** was used to afford a red-orange product. Yield: 341 mg (47%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 12.25 (s, 2H, N*H*), 8.10 (d, $^3J_{H\text{-}H}$ =9 Hz, 4H, $C_6H_4NO_2$), 7.90 (s, 4H, C=C*H*N), 7.27 (d, $^3J_{H\text{-}H}$ =9 Hz, 4H, $C_6H_4NO_2$), 3.26 (m, 4H, C*H*N), 2.27 (m, 4H, C_6H_{10}), 1.98 (m, 4H, C_6H_{10}), 1.45 (m, 8H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): 151.3 (C=*C*HN), 148.9, 124.6, 123.5, 103.7, 64.5 (*C*HN on C_6H_{10}), 29.5, 24.8. IR (KBr): 3500, 2930, 2857, 1635, 1578, 1334, 1284, 1280, 1110 cm^{-1}. UV-vis (THF): 437 (4.43). MS (EI): 542 (M^+). MS (CI/NH_3): 543 ($M+H^+$), 560 ($M+NH_4^+$). $[\alpha]_D^{26\,°C} = -466.0$ ($c = 0.0013$, $CHCl_3$).

Synthesis of H_2[HPhH(dpen)$_2$] (4c). An amine exchange reaction was used to prepare **4c** from dithioaldehyde **3c** and (*R,R*)-1,2-diphenylethylenediamine. To a hot solution

of **3c** (174 mg, 0.474 mmol) in benzene (50 mL) was added (*R,R*)-1,2-diphenylethylenediamine (203 mg, 0.956 mmol) in benzene (25 mL) through a pressure-equalizing dropping funnel over 3 hours. The mixture was kept briskly boiling for 12 hours and reduced to dryness *in vacuo*. The workup procedure as described for **4a** was used to produce light yellow crystals. Yield: 76 mg (25%). ^{1}H NMR($CDCl_3$, 400 MHz): δ 12.42 (s, 2H, N*H*), 7.51 (d, $^{3}J_{H\text{-}H}$ =7.6 Hz, 8H, *o*-C_6H_5 on ethylene bridge), 7.44 (d, $^{3}J_{H\text{-}H}$ =6.4 Hz, 4H), 7.38 (t, $^{3}J_{H\text{-}H}$ =7.6 Hz, 8H, *m*-C_6H_5 on ethylene bridge), 7.29 (t, $^{3}J_{H\text{-}H}$ =7.6 Hz, 4H, *p*-C_6H_5 on ethylene bridge), 7.09 (t, $^{3}J_{H\text{-}H}$ =7.6 Hz, 4H, *m*-C_6H_5), 6.95 (m, 6H, *o,p*-C_6H_5), 4.80 (s, 4H, NC*H*). ^{13}C NMR ($CDCl_3$, 300 MHz): 155.5, 144.0, 140.8, 128.7, 128.5, 127.5, 127.3, 125.1, 124.4, 73.3 (N*C*H). UV-vis (THF): 302 (3.92), 339 (3.94). MS (EI): 648 (M^+). MS(CI/NH_3): 649 ($M+H^+$). $[\alpha]_D^{26\,°C} = -28.9$ (c = 0.0020, $CHCl_3$).

Preparation of lithium salt Li_2[HPhH(dach)$_2$]. A solution of **4a** (133 mg, 0.294 mmol) and $LiN(TMS)_2$ (644 mg, 3.85 mmol) in dry THF (20 mL) was allowed to stir at ambient temperature under an inert atmosphere for 12 hours and then reduced to dryness under vacuum. The residue was taken up with THF (4 mL) and layered with hexane (12 mL). After cooling overnight at –25°C, an orange product was filtered, washed with hexane and dried *in vacuo*. Yield: 102 mg (74%). ^{1}H NMR (C_6D_6, 300 MHz): δ 8.40 (s, 4H, C=C*H*N), 7.56 (d, $^{3}J_{H\text{-}H}$ =7.8 Hz, 4H, *o*-C_6H_5), 7.37 (t, $^{3}J_{H\text{-}H}$ =7.8 Hz, 4H, *m*-C_6H_5), 7.07 (t, $^{3}J_{H\text{-}H}$ =7.8 Hz, 2H, *p*-C_6H_5), 3.05 (m, 4H, C*H*N), 2.29 (m, 4H), 1.83 (m, 4H), 1.30 (m, 8H). Variable amounts of THF were included in crystals as observed by ^{1}H NMR.

Iron(II) complexes: Compound Fe[HPhH(dach)$_2$] (**4a**-Fe) was prepared by reaction of the lithiated ligand and anhydrous $FeBr_2$ in THF and purified by column chromatography

on alumina eluted with THF-toluene(1:10) as a purple solid. Due to the high sensitivity to air, no satisfactory analytical data could be obtained. However, a broad peak around 21 ppm was observed in ^{1}H NMR, and the mass analysis showed the molecular ion at m/z 504. The complexes were used in catalytic reactions immediately. Complexes **4b**-Fe and **4c**-Fe were prepared similarly.

Catalytic cyclopropanation reactions by iron porphyrin complexes. In a typical experiment, styrene (2 mmol), iron porphyrin (0.1-0.4 mol% relative to diazoacetates) and *n*-dodecane (30 μL, internal standard) were placed into a round bottom flask and dissolved in 3 mL of solvent. A solution of ethyl diazoacetate (0.2 mmol) in 10 mL of solvent was added dropwise through a pressure-equalizing dropping funnel over 30 min - 6 h. After the addition was finished, an aliquot of the reaction mixture was taken and analyzed by GC.

Catalytic cyclopropanation reactions by Fe(II) complexes of 4a, 4b, and 4c. In a typical experiment, styrene (2 mmol), iron complex (1-2 mol% relative to diazoacetates), and *n*-dodecane (30 μL, internal standard) were placed into a round bottom flask and dissolved in 3 mL of solvent. A solution of ethyl diazoacetate (0.2 mmol) in 10 mL of solvent was added dropwise through a pressure-equalizing dropping funnel over 30 min - 6 h. After the addition was finished, an aliquot of the reaction mixture was taken and analyzed by GC.

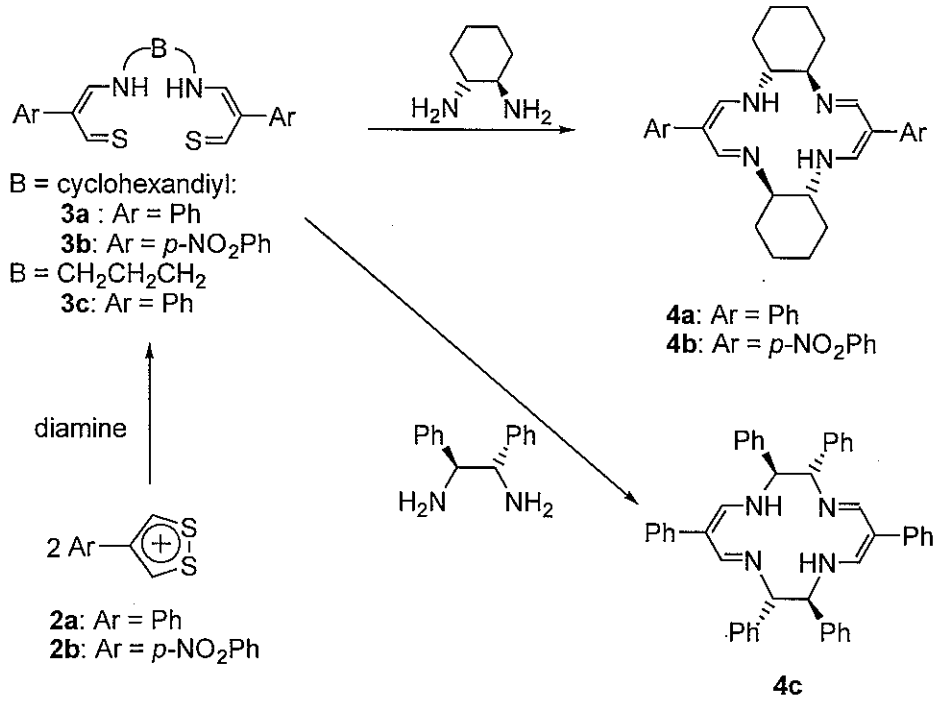
Structural determination of 4a. A yellow prismatic crystal with approximate dimensions 0.5 x 0.5 x 0.2 mm^3 was mounted on a glass fiber. Data collections at 173 K were performed on a BRUKER SMART 1000 CCD-based diffractometer with graphite monochromated MoK_α radiation (0.71073 Å), using the full-sphere $\omega/2\theta$ scan routine. The datasets were corrected for Lorentz and polarization effects. The absorption correction was

based on fitting a function to the empirical transmission surface as sampled by multiply equivalent measurements.[16]

The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2/m$. The *E*-statistics suggested strongly the non-centrosymmetric space group $P2_1$. This yielded chemically reasonable and computationally stable results of refinement. The structure has a pseudo inversion center. However, all attempts to convert the unit cell to higher symmetry failed. The positions of all non-hydrogen atoms were found by direct methods and refined in a full-matrix anisotropic approximation. All hydrogen atoms except those bonded to N atoms were placed at calculated positions and refined using a riding model. The hydrogen atoms bonded to N atoms were found from a Fourier map and were treated with a riding model using fixed temperature factors and an occupancy of 0.5.

Results

Synthesis of the chiral ligands. New chiral tetraaza macrocycles were synthesized by a modification of a literature procedure that was used for non-chiral N_4-ligands.[17] The iodide salt of 4-phenyl-1,2-dithiolium was treated with (*R,R*)-dach to afford the open chain dithioaldehyde **3a**, which was further cyclized by excess diamine under high dilution conditions to afford H_2[HPhH(dach)$_2$] (**4a**) as light yellow crystals in 17-32% yield (Scheme 1). No attempt was made to optimize the yield. Analogously, macrocycle **4b** was prepared as a brick-red powder, starting from 4-(*p*-nitrophenyl)-1,2-dithiolium iodide. In an alternative route, **4a** could be prepared from the open chain dithioaldehyde **3c** and excess (*R,R*)-dach by amine exchange to afford similar yields. Ligand **4c** was obtained in this way from **3c** and (*R,R*)-diphenylethylenediamine.



Scheme 1. Synthesis of Chiral Macrocyclic Ligands

The structure of macrocyclic ligand **4a** was further determined by a diffraction analysis (Figure 1). X-ray crystallographic data for **4a** are compiled in Table 1 and significant bond lengths and bond angles are collected in Table 2. The N-C distances within the 1,3-propanediiminato linkages are virtually identical, ranging over 1.298-1.310 Å. The C-C distances within the 1,3-propanediiminato linkages averaged between 1.460-1.471 Å. This is somewhat different from those found for a closely related tetraaza macrocyclic free ligand, H_2tmtaa, where the corresponding N-C distances are slightly longer and the C-C distances are slightly shorter.[18] Due to the steric interaction of the methyl groups and the benzenoid rings, H_2tmaa adopts a non-planar saddle shape with two N-H atoms directed out of the N_4-plane. The free ligand **4a** however has a planar geometry with in-plane N-H bonds.

Table 1. Crystal data and structure refinement for ligand **4a**.

Empirical formula	$C_{30}H_{36}N_4$
Formula weight	452.63
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
a	6.2799(5) Å
b	11.1105(9) Å
c	17.5679(14) Å
α	90°
β	96.6780(10)°
γ	90°
Volume	1217.45(17) $Å^3$
Z	2
Density (calculated)	1.235 Mg/m^3
Data / restraints / parameters	5566 / 1 / 323
Goodness-of-fit on F^2	0.848
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0437, wR2 = 0.0826
R indices (all data)	R1 = 0.0759, wR2 = 0.0902
Absolute structure parameter	0(2)
Largest diff. peak and hole	0.165 and -0.200 $e.Å^{-3}$

Table 2. Selected bond lengths [Å] and bond angles [°] for **4a**.

C(1)-N(1)	1.460(2)	N(1)-C(1)-C(2)	114.46(16)
C(1)-C(2)	1.520(3)	N(1)-C(1)-C(6)	108.27(14)
C(1)-C(6)	1.534(2)	C(2)-C(1)-C(6)	110.32(15)
C(2)-C(3)	1.528(2)	C(1)-C(2)-C(3)	111.51(16)
C(3)-C(4)	1.522(2)	C(4)-C(3)-C(2)	110.57(16)
C(4)-C(5)	1.521(3)		
C(5)-C(6)	1.528(2)		
C(6)-N(2)	1.463(2)		
C(7)-N(2)	1.306(2)		
C(7)-C(8)	1.414(3)		
C(8)-C(15)	1.399(2)		
C(15)-N(3)	1.306(2)		

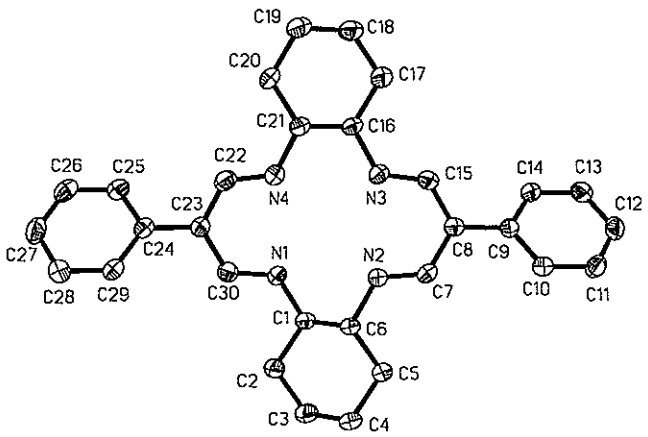
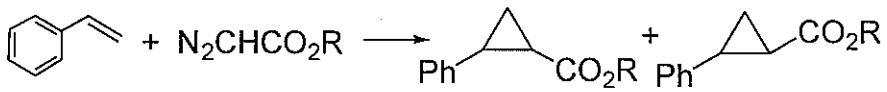


Figure 1. Thermal ellipsoid representation of the molecular structure of ligand **4a**.

Asymmetric cyclopropanation catalyzed by $Fe^{II}(D_4$-TpAP). Iron(II) porphyrins are effective catalysts in the cyclopropanation of olefins with ethyl diazoacetate (EDA).[19] With suitable chiral auxiliaries incorporated into the periphery of iron porphyrin complexes, asymmetric cyclopropanation was anticipated. Two chiral iron(II) porphyrins (Chart 1) were examined as catalysts in the cyclopropanation of styrene and the results are summarized in Table 3. Fe(D_4-TpAP) was found to be an efficient cyclopropanation catalyst for styrene and alkyl diazoacetate. Slow addition of a toluene solution of EDA to a toluene solution containing styrene and Fe(D_4-TpAP) afforded cyclopropyl esters in excellent yield, 99% based on EDA, with a trans/cis ratio of 21. No EDA coupling products, fumarate or maleate, were detected. However, the asymmetric induction was poor to modest at 45% ee for the trans isomer and 21% ee for the cis isomer. This result is inferior to an analogous chiral ruthenium porphyrin catalyst, Ru(D_4-TmAP) (Chart 1). As observed in other iron porphyrin catalyzed cyclopropanation reactions, the trans/cis ratio displayed a modest solvent dependence. When THF was used as the solvent, the trans/cis ratio increased to 44. This is among the highest trans selectivity obtained to date for these reagents. In CH_3CN, the ratio dropped to 12.

The effect of diazo reagents on the stereo- and enantioselectivity was examined by applying two bulkier diazo reagents, *t*-butyl and (-)-menthyl diazoacetates as the carbene sources in catalytic cyclopropanation reactions. The cyclopropanation yields were good to excellent, 99% and 78%, respectively. However, the stereochemical outcome was not as good as hoped. Both stereo- and enantioselectivity decreased. For example, a trans/cis ratio of 7.5 and 20% ee for the trans isomer were obtained with *t*-butyl diazoacetate.

Table 3. Asymmetric cyclopropanation of styrene with chiral iron(II) porphyrin complexes.[a]



R	ligand	yield%	t/c	%ee[b] trans	%ee[b] cis	solv
Et	D_4-TpAP	99	21	45(S,S)[c]	21(1R,2S)	PhMe
t-Bu	D_4-TpAP	99	7.5	20	30	PhMe
Menthyl	D_4-TpAP	78	10	27	78	PhMe
Et	$\alpha_2\beta_2$-BNP	94.8	5.8	27(R,R)	25(1R,2S)	PhMe
t-Bu	$\alpha_2\beta_2$-BNP	85.6	3.2	24	74	PhMe
Menthyl	$\alpha_2\beta_2$-BNP	64.3	3.3	55	40	PhMe

(a) See Experimental Section for reaction conditions. (b) de for menthyl ester. (c) Absolute configurations were assigned according to references 22c and 25.

Asymmetric cyclopropanation catalyzed by $Fe^{II}(\alpha_2\beta_2$-BNP). $Fe^{III}(\alpha_2\beta_2$-BNP)Cl was shown to be an efficient catalyst for asymmetric epoxidation of terminal olefins, with up to 90% ee achieved for some simple olefins. However, when $Fe^{II}(\alpha_2\beta_2$-BNP) was employed as a catalyst in the cyclopropanation reaction of styrene, poor results were obtained. The trans/cis ratio of 3-6 was generally observed. Performing the reaction in donor solvents such as THF did not improve the selectivity significantly. The enantioselectivity was also inferior. Only 27% and 25% ee were observed for trans and cis cyclopropane isomers from the EDA reaction, respectively. The chiral induction for the trans isomer was opposite to that obtained in the Fe(D_4-TpAP) catalyzed reaction, while the same chiral preference for the cis isomer

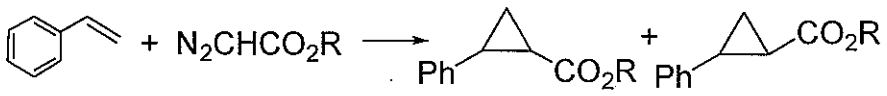
was observed for both catalysts. Again, no significant improvement resulted when diazo reagents bearing bulky ester groups were used as carbene sources.

Asymmetric cyclopropanation catalyzed by Fe(II)[HPhH(dach)$_2$] and Fe(II)[H(*p*-NO$_2$-Ph)H(dach)$_2$]. Enantiomerically pure trans-1,2-diaminocyclohexane derivatives have found great utility as chiral auxiliaries or ligands in asymmetric catalysis.[20] We thus synthesized a tetraaza macrocyclic ligand, **4a**, incorporating two (*R,R*)-dach bridges. The iron(II) complex of this ligand was investigated in catalytic cyclopropanation of styrene. The results are contained in Table 4. A total yield of 87% was obtained with a trans/cis ratio of 7.4 when EDA was used. However, the enantioselective outcome was only modest, 42% ee for both cis and trans products. Changing the ester substituents from ethyl to *t*-butyl resulted in a significant drop of both productivity (15%) and diastereoselectivity (trans/cis 4.5) of cyclopropanation products, while (-)-menthyl diazoacetate resulted in higher yield (95%) and higher selectivity (trans/cis 13.3).

Furthermore, Fe-**4a** was also found active in catalyzing cyclopropanation of styrene with aryl diazomethane. When mesityl diazomethane was used as the carbene source a 90% yield of cyclopropanation was obtained with a trans/cis ratio of 2.3. However, only trivial enantioselectivity was observed.

For metalloporphyrin catalysts, attachment of electron withdrawing groups at *meso*- or β- pyrrole positions generally increases the reactivity of catalysts.[21] Thus **4b**, an analogue of **4a** bearing two *para* nitro groups, was examined as a ligand in the cyclopropanation reaction of styrene and EDA. Similar asymmetric induction was achieved. However, the chemical yield and diastereoselectivities were low, only a 16% yield of cyclopropane was obtained with a trans/cis ratio of 3.1.

Table 4. Asymmetric cyclopropanation of styrene by iron(II) chiral macrocyclic complexes with **4a**, **4b** and **4c**[a].



R	ligand	yield %	t/c	% ee[b] trans	% ee[b] cis	solv
Et	**4a**	87	7.4	42(R,R)[c]	42(1S,2R)[c]	PhMe
t-Bu	**4a**	15	4.5	19	32	PhMe
Menthyl	**4a**	95	13.3	79	n.d.[d]	PhMe
Et	**4b**	16	3.1	38	48	PhMe
Et	**4c**	54	9.1	~0	~0	PhMe
t-Bu	**4c**	46	10.1	~0	~0	PhMe
Menthyl	**4c**	71	14.9	55	45	PhMe

(a) See Experimental Section for reaction conditions. (b) de for menthyl ester. (c) Absolute configurations were assigned according to references 22c and 25. (d) Not determined.

Asymmetric cyclopropanation catalyzed by Fe(II)[HPhH(dpen)$_2$]. In an attempt at tuning the steric properties of the N_4-macrocyclic ligands, (*R,R*)-diphenylethylenediamine bridges were introduced into the macrocyclic ligand, in place of (*R,R*)-dach. The corresponding iron complexes gave reasonable chemical yields and good trans selectivity of cyclopropyl esters by treatment of styrene with ethyl, *t*-butyl, or (-)-menthyl diazoacetates in the presence of the catalyst, but failed to produce any notable enantio- differentiation in the

former two diazoacetates. With (-)-menthyl diazoacetate, 55% de and 45% de were observed for the trans and cis isomers, respectively.

Discussion

Effect of diazo reagent and ligand on cyclopropanation. As with other iron porphyrins, $Fe^{II}(D_4\text{-TpAP})$ and $Fe^{II}(\alpha_2\beta_2\text{-BNP})$ both were efficient catalysts for the catalytic cyclopropanation of styrene with diazoacetates. $Fe^{II}(D_4\text{-TpAP})$ usually gave higher cyclopropanation yields and better diastereoselective control than $Fe^{II}(\alpha_2\beta_2\text{-BNP})$ did. When compared with the reaction of styrene and ethyl diazoacetate catalyzed by $Ru(D_4\text{-TmAP})$, a similar catalyst with less bulky *meso*-substituents, $Fe^{II}(D_4\text{-TpAP})$ gave comparable stereoselective control and the same sense of chiral induction for both trans and cis cyclopropyl esters. The difference was that $Ru(D_4\text{-TmAP})$ induced high enantiomeric excesses for the trans product (81-91% ee) and very low enantiomeric excesses for the cis product (2-9% ee).[5a] $Fe(D_4\text{-TpAP})$ gave modest enantiomeric excesses for both diastereomers. It appears that the increase of steric bulk at the porphyrin periphery is not very beneficial for cyclopropanation of styrene in terms of enantioselectivity, although a higher trans/cis ratio was achieved.

In cyclopropanation reactions, bulkier diazo reagents are commonly used to improve the enantio- and stereoselectivity.[22] In the catalytic systems investigated here, however, increasing the steric bulk from ethyl to menthyl diazoacetates, did not result in better trans/cis ratios or enantiomeric excesses. This is suggestive of a subtle interaction between the ligands and the diazo reagents.

Explanation of the enantioselectivity in iron macrocycle-catalyzed cyclopropanation. The active intermediate in the iron porphyrin-catalyzed reactions is likely to be an iron carbene species formed by reaction of the iron porphyrin with diazo reagents. We have spectroscopically observed the formation of iron carbene complexes, (TTP)Fe=CHR (R=mesityl or trimethylsilyl).[8] An iron carbene complex supported by a non-porphyrin macrocyclic ligand, (tmtaa)Fe=CPh_2,[23] was isolated and characterized by X-ray crystallography. In this complex, the carbene plane defined by $C(C_{ipso})_2$ is nearly parallel to a pair of trans Fe-N bonds. In contrast, the carbene plane usually bisects the adjacent M-N bonds in metalloporphyrin carbene complexes.[5a, 24]

The enantioselectivity occurring in these cyclopropanation reactions can be correlated to the orientation of the carbene ligand and the approach of the incoming olefin. In cyclopropanation by group 8 metalloporphyrin carbene complexes, the approach of the olefin with its C=C axis parallel to the M=C bond is strongly preferred.[8] The likely orientation of the carbene intermediate in the Fe[HPhH$(dach)_2$] reaction is shown in Figure 2, with the carbene plane parallel to either pair of trans Fe-N bonds. Minimizing steric interactions between the ester group and the axial proton of the chiral cyclohexyl ring should favor the orientation in Fig 2A. Approach of styrene along path "a" minimizes the steric interference of the axial proton of the cyclohexyl bridge with the olefin phenyl group. This produces the favored trans product with an (*R,R*)-configuration. The major cis enantiomer results from approach along path "b". This is also in agreement with the observed data.

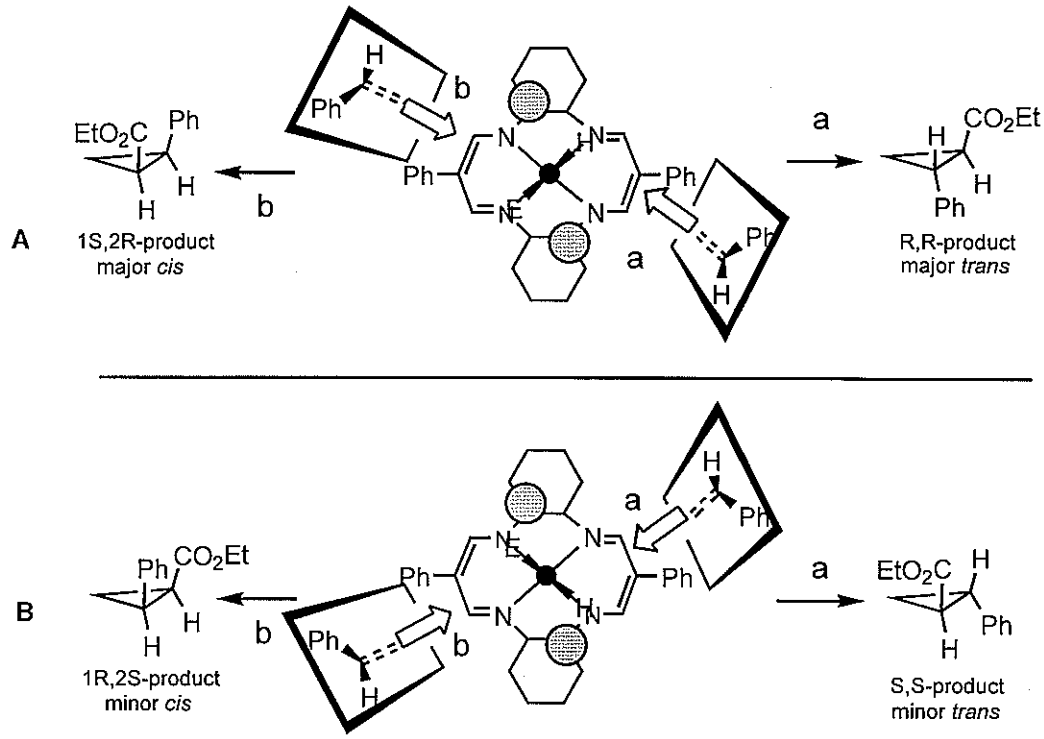


Figure 2. Illustration of enantiocontrol in **4a** catalyzed cyclopropanation viewed from above the carbene complex. The carbene ligand (E = carboethoxy) is oriented out of the plane of the page and the styrene double bond is perpendicular to the page.

The Fe(D_4-TpAP) catalyzed cyclopropanation gave the same sense of chiral induction as did the analogous Ru(D_4-TmAP) complex, indicting a similar preferred orientation in both catalytic reactions. The favored carbene orientation is shown in Figure 3A. Approach of styrene from the left side in Fig 3A results in a large steric interaction of the phenyl group with the isopropylidene fragment of the *meso*-substituent. Thus, styrene prefers to approach from right side of carbene plane. This leads to the major trans enantiomer with an (*S,S*)-configuration. Likewise, using the steric model proposed for $Fe^{III}(\alpha_2\beta_2$-BNP)Cl in the epoxidation of olefins,[14] the stereochemical outcome of the $Fe^{II}(\alpha_2\beta_2$-BNP)-catalyzed

cyclopropanation can be reasonably predicted. Figure 3B shows the carbene orientation with the minimum steric interaction between the carbene ester group and the binaphthyl bridge. This leads to the major trans enantiomer having an (*R,R*)-configuration. The trans/cis ratio of cyclopropyl esters produced in these reactions are merely 3-6 to 1, lower than the selectivity induced by simple porphyrins such as H_2TTP ligand.

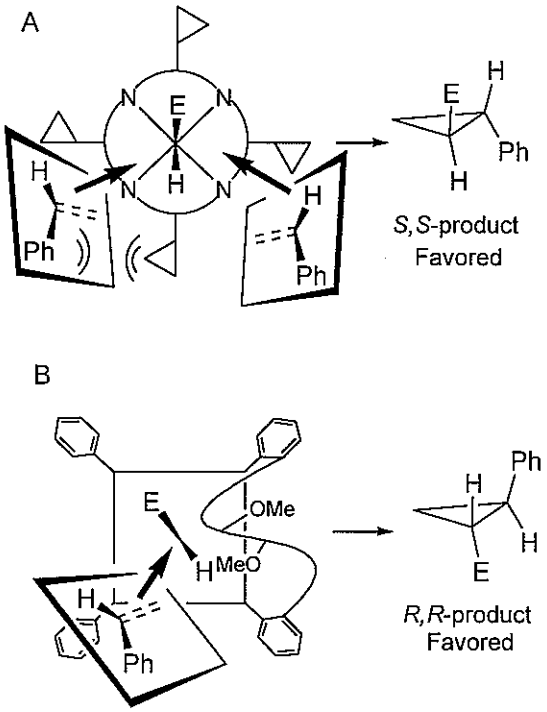


Figure 3. Chiral induction of iron porphyrin complexes. The carbene ligand is oriented out of the plane of the page with the styrene double bond perpendicular to the page. See text for discussion.

It should be noted that the orientation of the ester substituents in the carbene intermediate alone does not determine the overall stereochemical outcome of the cyclopropanation reactions.[25] Nevertheless, this simplified analysis provides useful information about the reaction mechanism and for the future design of new ligands.

Conclusion

We have shown that a number of chiral iron(II) complexes, with macrocyclic ligands, serve as effective catalysts for the cyclopropanation of styrene by diazoacetates. On the basis of previous structural data on the orientation of carbene ligand in macrocyclic iron complexes and the approach of the incoming styrene, the stereochemical outcome can be reasonably understood. However, the chiral induction of these catalysts is modest, at best. Further rational modification of ligands is needed to achieve higher enantioselectivity.

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Supporting Information Available: Tables giving crystallographic data for **4a** including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This information is available free of charge via the internet at http://pubs.acs.org.

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APPENDIX

Table I. Crystal data and structure refinement for $H_2[H(Ph)H(dach)_2]$ (**4a**).

Empirical formula	C30 H36 N4	
Formula weight	452.63	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.2799(5) Å	α = 90°
	b = 11.1105(9) Å	β = 96.6780(10)°
	c = 17.5679(14) Å	γ = 90°
Volume	1217.45(17) $Å^3$	
Z	2	
Density (calculated)	1.235 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	488	
Crystal size	0.5 x 0.2 x 0.2 mm^3	
Theta range for data collection	1.17 to 28.30°	
Index ranges	-8<=h<=8, -14<=k<=14, -23<=l<=22	
Reflections collected	13514	
Independent reflections	5566 [R(int) = 0.0313]	
Completeness to theta = 28.30°	95.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1 and 0.81	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5566 / 1 / 323	
Goodness-of-fit on F^2	0.848	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0826	
R indices (all data)	R1 = 0.0759, wR2 = 0.0902	
Absolute structure parameter	0(2)	
Largest diff. peak and hole	0.165 and -0.200 $eÅ^{-3}$	

Table II. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for H_2[H(Ph)H(dach)$_2$] (**4a**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	7806(3)	-1372(2)	8178(1)	29(1)
C(2)	8114(3)	-2729(2)	8175(1)	34(1)
C(3)	6986(3)	-3338(2)	8797(1)	39(1)
C(4)	4610(3)	-3025(2)	8703(1)	37(1)
C(5)	4299(3)	-1668(2)	8722(1)	32(1)
C(6)	5410(3)	-1060(2)	8094(1)	27(1)
C(7)	3863(3)	863(2)	8424(1)	30(1)
C(8)	3637(3)	2129(2)	8396(1)	29(1)
C(9)	2142(3)	2719(2)	8868(1)	27(1)
C(10)	217(3)	2169(2)	9011(1)	32(1)
C(11)	-1194(3)	2733(2)	9440(1)	37(1)
C(12)	-757(3)	3867(2)	9734(1)	39(1)
C(13)	1133(3)	4431(2)	9608(1)	40(1)
C(14)	2566(3)	3854(2)	9189(1)	34(1)
C(15)	4868(3)	2829(2)	7950(1)	32(1)
C(16)	7781(3)	3178(2)	7164(1)	33(1)
C(17)	6960(3)	4410(2)	6921(1)	44(1)
C(18)	8687(4)	5136(2)	6581(1)	45(1)
C(19)	9423(4)	4477(2)	5907(1)	46(1)
C(20)	10228(3)	3228(2)	6134(1)	44(1)
C(21)	8534(3)	2495(2)	6491(1)	33(1)
C(22)	10590(3)	653(2)	6418(1)	33(1)
C(23)	11116(3)	-560(2)	6594(1)	29(1)
C(24)	12681(3)	-1181(2)	6166(1)	29(1)
C(25)	14515(3)	-604(2)	5975(1)	33(1)
C(26)	15997(3)	-1199(2)	5579(1)	40(1)
C(27)	15677(3)	-2385(2)	5372(1)	43(1)
C(28)	13880(3)	-2979(2)	5558(1)	45(1)
C(29)	12394(3)	-2384(2)	5943(1)	36(1)

Table II. (continued)

C(30)	10163(3)	-1192(2)	7155(1)	29(1)
N(1)	8789(3)	-733(2)	7582(1)	32(1)
N(2)	5178(3)	249(1)	8050(1)	31(1)
N(3)	6235(3)	2416(2)	7508(1)	37(1)
N(4)	9249(3)	1297(2)	6753(1)	38(1)

Table III. Bond lengths [Å] and angles [°] for $H_2[H(Ph)H(dach)_2]$ (**4a**).

C(1)-N(1)	1.460(2)	C(16)-N(3)	1.471(2)
C(1)-C(2)	1.520(3)	C(16)-C(17)	1.507(3)
C(1)-C(6)	1.534(2)	C(16)-C(21)	1.526(2)
C(2)-C(3)	1.528(2)	C(17)-C(18)	1.528(3)
C(3)-C(4)	1.522(2)	C(18)-C(19)	1.509(3)
C(4)-C(5)	1.521(3)	C(19)-C(20)	1.515(3)
C(5)-C(6)	1.528(2)	C(20)-C(21)	1.531(3)
C(6)-N(2)	1.463(2)	C(21)-N(4)	1.461(2)
C(7)-N(2)	1.306(2)	C(22)-N(4)	1.298(2)
C(7)-C(8)	1.414(3)	C(22)-C(23)	1.413(3)
C(8)-C(15)	1.399(2)	C(23)-C(30)	1.401(2)
C(8)-C(9)	1.476(2)	C(23)-C(24)	1.476(2)
C(9)-C(14)	1.394(3)	C(24)-C(25)	1.393(2)
C(9)-C(10)	1.403(2)	C(24)-C(29)	1.399(3)
C(10)-C(11)	1.379(2)	C(25)-C(26)	1.392(3)
C(11)-C(12)	1.376(3)	C(26)-C(27)	1.376(3)
C(12)-C(13)	1.383(3)	C(27)-C(28)	1.379(3)
C(13)-C(14)	1.384(3)	C(28)-C(29)	1.382(3)
C(15)-N(3)	1.306(2)	C(30)-N(1)	1.310(2)

N(1)-C(1)-C(2)	114.46(16)	C(15)-C(8)-C(7)	120.80(18)
N(1)-C(1)-C(6)	108.27(14)	C(15)-C(8)-C(9)	119.80(18)
C(2)-C(1)-C(6)	110.32(15)	C(7)-C(8)-C(9)	119.36(17)
C(1)-C(2)-C(3)	111.51(16)	C(14)-C(9)-C(10)	116.76(18)
C(4)-C(3)-C(2)	110.57(16)	C(14)-C(9)-C(8)	121.62(17)
C(3)-C(4)-C(5)	110.54(16)	C(10)-C(9)-C(8)	121.62(18)
C(4)-C(5)-C(6)	110.59(16)	C(11)-C(10)-C(9)	121.39(19)
N(2)-C(6)-C(5)	115.27(15)	C(12)-C(11)-C(10)	120.5(2)
N(2)-C(6)-C(1)	108.66(14)	C(11)-C(12)-C(13)	119.5(2)
C(5)-C(6)-C(1)	110.87(14)	C(12)-C(13)-C(14)	119.9(2)
N(2)-C(7)-C(8)	124.70(17)	C(13)-C(14)-C(9)	121.90(19)

Table III. (continued)

N(3)-C(15)-C(8)	125.6(2)	C(22)-C(23)-C(24)	119.15(17)
N(3)-C(16)-C(17)	114.78(16)	C(25)-C(24)-C(29)	117.10(19)
N(3)-C(16)-C(21)	108.07(15)	C(25)-C(24)-C(23)	121.71(19)
C(17)-C(16)-C(21)	111.09(16)	C(29)-C(24)-C(23)	121.19(17)
C(16)-C(17)-C(18)	110.77(17)	C(26)-C(25)-C(24)	121.4(2)
C(19)-C(18)-C(17)	110.35(18)	C(27)-C(26)-C(25)	120.13(19)
C(18)-C(19)-C(20)	111.10(18)	C(26)-C(27)-C(28)	119.6(2)
C(19)-C(20)-C(21)	111.68(17)	C(27)-C(28)-C(29)	120.4(2)
N(4)-C(21)-C(16)	108.70(15)	C(28)-C(29)-C(24)	121.4(2)
N(4)-C(21)-C(20)	114.25(16)	N(1)-C(30)-C(23)	124.83(19)
C(16)-C(21)-C(20)	110.18(16)	C(30)-N(1)-C(1)	125.65(18)
N(4)-C(22)-C(23)	125.04(18)	C(7)-N(2)-C(6)	123.87(16)
C(30)-C(23)-C(22)	121.61(17)	C(15)-N(3)-C(16)	123.55(19)
C(30)-C(23)-C(24)	119.23(18)	C(22)-N(4)-C(21)	123.41(17)

Table IV. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $H_2[H(Ph)H(dach)_2]$ (**4a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	33(1)	23(1)	31(1)	3(1)	8(1)	-4(1)
C(2)	33(1)	28(1)	44(1)	6(1)	11(1)	2(1)
C(3)	44(1)	31(1)	44(1)	12(1)	13(1)	1(1)
C(4)	40(1)	28(1)	48(1)	6(1)	16(1)	-6(1)
C(5)	33(1)	27(1)	40(1)	3(1)	13(1)	-2(1)
C(6)	29(1)	24(1)	30(1)	4(1)	8(1)	-1(1)
C(7)	27(1)	31(1)	33(1)	3(1)	9(1)	-5(1)
C(8)	31(1)	25(1)	31(1)	1(1)	8(1)	-1(1)
C(9)	29(1)	26(1)	27(1)	4(1)	7(1)	3(1)
C(10)	33(1)	27(1)	36(1)	3(1)	9(1)	0(1)
C(11)	30(1)	44(1)	39(1)	12(1)	11(1)	4(1)
C(12)	43(1)	41(1)	36(1)	6(1)	18(1)	13(1)
C(13)	50(1)	29(1)	44(1)	0(1)	16(1)	3(1)
C(14)	37(1)	28(1)	40(1)	1(1)	14(1)	-3(1)
C(15)	38(1)	25(1)	35(1)	0(1)	9(1)	-1(1)
C(16)	37(1)	27(1)	36(1)	4(1)	15(1)	-6(1)
C(17)	51(1)	29(1)	55(1)	2(1)	26(1)	-2(1)
C(18)	59(2)	29(1)	49(1)	4(1)	21(1)	-5(1)
C(19)	61(2)	34(1)	45(1)	6(1)	22(1)	-5(1)
C(20)	55(1)	38(1)	47(1)	6(1)	32(1)	1(1)
C(21)	43(1)	26(1)	33(1)	3(1)	16(1)	-3(1)
C(22)	35(1)	35(1)	32(1)	1(1)	10(1)	-6(1)
C(23)	27(1)	29(1)	31(1)	-1(1)	8(1)	-2(1)
C(24)	28(1)	34(1)	26(1)	3(1)	5(1)	0(1)
C(25)	32(1)	37(1)	32(1)	2(1)	6(1)	-5(1)
C(26)	30(1)	51(2)	40(1)	8(1)	11(1)	-4(1)
C(27)	37(1)	53(2)	43(1)	1(1)	18(1)	9(1)
C(28)	53(1)	34(1)	50(1)	-2(1)	19(1)	2(1)
C(29)	36(1)	36(1)	39(1)	2(1)	17(1)	-3(1)

Table IV. (continued)

C(30)	26(1)	29(1)	34(1)	0(1)	4(1)	1(1)
N(1)	32(1)	29(1)	38(1)	7(1)	14(1)	4(1)
N(2)	34(1)	23(1)	39(1)	0(1)	14(1)	0(1)
N(3)	45(1)	27(1)	44(1)	-2(1)	23(1)	-4(1)
N(4)	48(1)	31(1)	39(1)	6(1)	22(1)	3(1)

Table V. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for H_2[H(Ph)H(dach)$_2$] (**4a**).

	x	y	z	U(eq)
H(1)	8466	-1061	8686	35
H(2A)	9663	-2916	8257	41
H(2B)	7533	-3052	7667	41
H(3A)	7160	-4221	8765	47
H(3B)	7649	-3071	9307	47
H(4A)	3914	-3402	9121	45
H(4B)	3922	-3348	8209	45
H(5A)	2748	-1478	8646	39
H(5B)	4898	-1352	9228	39
H(6)	4758	-1397	7593	33
H(7)	2992	430	8737	36
H(10)	-121	1390	8808	38
H(11)	-2478	2338	9533	44
H(12)	-1748	4258	10021	46
H(13)	1450	5214	9808	48
H(14)	3876	4242	9118	41
H(15)	4698	3677	7970	39
H(16)	9052	3290	7556	39
H(17A)	6521	4841	7371	52
H(17B)	5686	4329	6537	52
H(18A)	8107	5932	6413	54
H(18B)	9923	5265	6977	54
H(19A)	10587	4941	5707	55
H(19B)	8218	4415	5492	55
H(20A)	11533	3296	6508	54
H(20B)	10625	2802	5677	54
H(21)	7272	2393	6094	40
H(22)	11266	1027	6023	40
H(25)	14761	214	6118	40
H(26)	17228	-784	5450	47

Table V. (continued)

H(27)	16687	-2792	5102	52
H(28)	13666	-3801	5423	54
H(29)	11151	-2801	6058	43
H(30)	10543	-2014	7234	36
H(1A)	8416	28	7499	38
H(2C)	5969	643	7756	38
H(3C)	6232	1634	7409	44
H(4C)	8743	996	7161	46

CHAPTER 6. SYNTHESIS AND CHARACTERIZATION OF CHIRAL TETRAAZA MACROCYCLIC NICKEL(II) AND PALLADIUM(II) COMPLEXES

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Abstract

Chiral tetraaza macrocyclic nickel(II) and palladium(II) complexes **2a-e**, containing one or two (*R,R*)-(–)-1,2-cyclohexanediyl bridges, were synthesized by template condensation reactions and characterized by ^{1}H, ^{13}C NMR, IR, UV-vis and mass spectrometry. The electrophilic reactivity of **2a** was explored. Crystal structures of Ni complex **2b** and metal-free ligand **5** were determined by single-crystal X-ray diffraction.

Introduction

The design and preparation of tetraaza macrocyclic ligands and their transition metal complexes has long been a field of extensive investigation. The initial interest in these compounds derived from their potential as small molecule analogues of the active sites of hemoproteins and metalloenzymes. The class of tetraaza macrocycles first reported by

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Jäger,[2] was well studied by changing the ring size, the peripheral substituents and the central metals.[3] Metal complexes of these ligands were investigated in catalytic electrochemical reduction of carbon dioxide[4] and for the activation of dioxygen.[5] Further work by Busch provided a new series of lacunar cyclidene complexes that showed remarkable dioxygen affinity.[6] Rational design and fine-tuning led to successful non-porphyrin oxygen carriers. These complexes were also used as oxygenation catalysts with molecular dioxygen[7] and as hosts for the formation of inclusion complexes.[8]

Chiral side chains have been introduced at the *meso* positions of this class of tetraaza macrocyclic complexes.[9] However, tetraaza macrocyclic complexes in this family bearing chiral bridges have not been reported. This is surprising, considering their possible application in asymmetric catalysis and the potentially strong analogy to the highly successful asymmetric tetradentate salen ligands developed and utilized by Jacobsen[10] and others.[11] We set out to incorporate chiral diamine bridges into new macrocyclic tetraazatetraene (TATE) ligands. Herein, we report the synthesis and characterization of a series of new chiral TATE Ni(II) and Pd(II) complexes, and reactivity towards electrophilic substitution.

Experimental Section

Materials and instrumentation. (*1R,2R'*)-[3,3'-[1,2-cyclohexane-diyl-bis(iminomethyl-idyne)]bis[2,4-pentanedionato](2-)-N,N',O^2,$O^{2'}$]nickel (**1a**) and [3,3'-[ethylenebis(iminomethyl-idyne)]bis[2,4-pentanedionato](2-)-N,N',O^2,$O^{2'}$]nickel (**1b**) were synthesized as reported.[12] (*R,R*)-(-)-1,2-diaminocyclohexane (dach) was resolved from a

commercial mixture by a published procedure of Jacobsen.[13] All other reagents were used as purchased.

^{1}H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts are referenced to proton solvent impurities (δ 7.24, $CDCl_3$; δ 1.94, CD_3CN). UV-vis data were recorded on a HP8453A diode array spectrophotometer and reported as λ_{max} in nm (log ε). Fourier Transform Infrared spectra were recorded on a FT-DL spectrometer. For mass spectra, a Finnegan TSQ 700 spectrometer equipped with EI or ESI ion sources was used. Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services.

Synthesis of Ni[cp-TATE(Ac)$_2$][14] (2a). A slurry of **1a** (1.02 g, 1.51 mmol) in 1,3-diaminopropane (ca. 8 mL) was refluxed under N_2 for 2 hours, in which period all the solid dissolved and the color changed from orange to red. Water (10 mL) was added after cooling. The resulting precipitate was collected by filtration, washed with water, methanol and diethyl ether and dried in air to give a pure, red product. Yield: 0.97 g (86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (s, 2H, vinyl-*H*), 3.64 (m, 2H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.56 (m, 2H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.64 (m, 2H, C$_6$*H*$_{10}$), 2.39 (s, 6H, C*H*$_3$), 2.25 (s, 6H, COC*H*$_3$), 2.21 (m, 2H, C$_6$*H*$_{10}$), 1.89 (m, 2H, C$_6$*H*$_{10}$), 1.78 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.29 (m, 2H, C$_6$*H*$_{10}$), 1.26 (m, 2H, C$_6$*H*$_{10}$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 194.2 (*C*OCH$_3$), 167.7 (vinyl-*C*), 152.1 (vinyl-*C*), 113.3 (vinyl-*C*), 70.1 (*c*-C$_6$H$_{10}$), 45.8 (NCH$_2$CH$_2$CH$_2$N), 29.5 (*c*-C$_6$H$_{10}$), 28.4 (COCH$_3$), 27.0 (NCH$_2$*C*H$_2$CH$_2$N), 25.4 (*c*-C$_6$H$_{10}$), 18.8 (*C*H$_3$). IR (KBr): 2926, 1629, 1578, 1511, 1395, 1293, 1275. UV-vis (CH_2Cl_2): 331 (4.75). MS (ESI): 429 (M^+). Anal. Found: C, 58.63; H, 7.26; N, 13.14. Calc. for $C_{21}H_{30}N_4O_2Ni$: C, 58.77; H, 7.05; N, 13.05%.

Synthesis of Ni[cc-TATE(Ac)$_2$] (2b). A mixture of **1a** (98.2 mg, 0.251 mmol) and (*R,R*)-1,2-diaminocyclohexane (ca. 1.0 g) was refluxed under N_2 for 6 hours, in which period all the solid dissolved and the color changed from orange to red. Water (ca. 3 mL) was added after cooling. The crude product was collected by filtration and purified by chromatography (EtOAc/silica gel, 1 cm × 25 cm column). The product was redissolved in CH_2Cl_2 (ca. 3 mL) and layered with Et_2O (ca. 3 mL) to produce dark red prisms. Yield: 47 mg (40%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (s, 2H, vinyl-*H*), 3.61 (m, 2H, C_6H_{10}), 2.73 (m, 2H, C_6H_{10}), 2.47 (s, 6H, CH_3), 2.43 (m, 2H, C_6H_{10}), 2.27 (m, 2H, C_6H_{10}), 2.22 (s, 6H, $COCH_3$), 1.86 (m, 2H, C_6H_{10}), 1.71 (m, 2H, C_6H_{10}), 1.31 (m, 8H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 193.7 ($COCH_3$), 170.8 (vinyl-*C*), 153.7 (vinyl-*C*), 114.7 (vinyl-*C*), 72.3 (*c*-C_6H_{10}), 69.2 (*c*-C_6H_{10}), 34.5 (*c*-C_6H_{10}), 29.9 (*c*-C_6H_{10}), 29.0 ($COCH_3$), 25.6 (*c*-C_6H_{10}), 25.1 (*c*-C_6H_{10}), 25.0 (CH_3). IR (KBr): 2935, 1577, 1560, 1296. UV-vis (CH_2Cl_2): 334 (4.55). MS (ESI): 469 (M^+). Anal. Found: C, 61.21; H, 7.09; N, 12.00. Calc. for $C_{24}H_{34}N_4O_2Ni$: C, 61.43; H, 7.30; N, 11.94%.

Synthesis of Ni[ec-TATE(Ac)$_2$] (2c). The procedure for **2a** was followed, starting from **1b** (3.18 g, 9.45 mmol) and excess (*R,R*)-1,2-diaminocyclohexane (ca. 16 mL). Recrystallization by layering a $CHCl_3$ (ca. 15 mL) solution with MeOH (ca. 10 mL) afforded an analytically pure purple product. Yield: 1.61 g (41%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (s, 2H, vinyl-*H*), 3.60 (m, 2H, C_6H_{10}), 3.26 (m, 2H, NCH_2CH_2N), 3.08 (m, 2H, NCH_2CH_2N), 2.46 (s, 6H, CH_3), 2.43 (m, 2H, C_6H_{10}), 2.22 (s, 6H, $COCH_3$), 1.72 (m, 2H, C_6H_{10}), 1.32 (m, 4H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 193.9 ($COCH_3$), 171.3 (vinyl-*C*), 157.9 (vinyl-*C*), 114.7 (vinyl-*C*), 72.8 (NCH_2CH_2N), 57.9 (*c*-C_6H_{10}), 34.8 (*c*-C_6H_{10}), 29.2 ($COCH_3$), 25.9 (*c*-C_6H_{10}), 25.5 (CH_3). IR (KBr): 2937, 2857, 1578, 1399, 1367, 1287. UV-

vis (CH_2Cl_2): 336 (4.62). MS (ESI): 415 (M^+). Anal. Found: C, 57.76; H, 6.81; N, 13.28. Calc. for $C_{20}H_{28}N_4O_2Ni$: C, 57.86; H, 6.80; N, 13.50%.

Synthesis of Pd[ce-TATE(Ac)$_2$] (2d). The precursor **1c** was synthesized in a manner similar to its nickel analogue, from free ligand (*1R,2R'*)-3,3'-[1,2-cyclohexane-diyl-bis(iminomethylidyne)]bis[2,4-pentanedione][12a] (104 mg, 0.311 mmol) and $Pd(OAc)_2$ (72 mg, 0.321 mmol) in a refluxing methanolic solution (ca. 6 mL). Yield: 90 mg (67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (s, 2H, C=C*H*N), 3.31 (m, 2H, NC*H*), 2.52 (s, 8 H, CH_3 and C$_6H_{10}$), 2.33 (s, 6H, CH_3), 1.93 (m, 2H, C$_6H_{10}$), 1.44 (m, 2H, C$_6H_{10}$), 1.35 (m, 2H, C$_6H_{10}$).

A slurry of **1c** (43 mg, 0.098 mmol) in ethylenediamine (ca. 1 mL) was refluxed under N_2 for 1 hour. Addition of 10 mL of water led to a yellow precipitate, which was collected and recrystallized by layering a CH_2Cl_2 (ca. 2 mL) solution with Et_2O (ca. 2 mL). Yield: 34 mg (74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (s, 2H, vinyl-*H*), 3.68 (m, 4H, NCH_2CH_2N), 3.34 (m, 2H, C$_6H_{10}$), 2.53 (m, 2H, C$_6H_{10}$), 2.40 (s, 6H, CH_3), 2.33 (s, 6H, COCH_3), 1.93 (m, 2H, C$_6H_{10}$), 1.41 (m, 4H, C$_6H_{10}$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 195.8 (*C*OCH_3), 165.0 (vinyl-*C*), 150.9 (vinyl-*C*), 113.2 (vinyl-*C*), 73.1 (*c*-C_6H_{10}), 56.3 (NCH_2CH_2N), 29.6 (COCH_3), 28.7 (*c*-C_6H_{10}), 25.1 (*c*-C_6H_{10}), 20.6 (*C*H_3). IR (KBr): 2932, 2857, 1576, 1559, 1332, 1272. UV-vis (CH_2Cl_2): 311 (4.35). MS (EI): 461 (M^+).

Synthesis of Pd[cp-TATE(Ac)$_2$] (2e). A slurry of **1c** (45 mg, 0.103 mmol) in 1,3-diaminopropane (ca. 1 mL) was refluxed under N_2 for 1 hour. Addition of 10 mL of water led to a yellow precipitate, which was collected and recrystallized by layering a CH_2Cl_2 (ca. 2 mL) solution with Et_2O (ca. 2 mL). Yield: 36 mg (73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2H, vinyl-*H*), 3.40 (m, 2H, NCH_2CH_2CH_2N), 3.31 (m, 2H,), 3.23 (m, 2H, C$_6H_{10}$),

2.39 (s, 6H, CH_3), 2.31 (m, 2H, C$_6H_{10}$), 2.25 (s, 6H, COCH_3), 2.17 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.90 (m, 2H, C$_6H_{10}$), 1.42 (m, 2H, C$_6H_{10}$), 1.34 (m, 2H, C$_6H_{10}$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 194.8 (*C*OCH$_3$), 167.2 (vinyl-*C*), 152.0 (vinyl-*C*), 112.9 (vinyl-*C*), 72.3 (*c*-C$_6$H$_{10}$), 51.7 (NCH$_2$CH$_2$*C*H$_2$N), 33.2 (*c*-C$_6$H$_{10}$), 30.1 (NCH$_2$*C*H$_2$CH$_2$N), 28.8 (CO*C*H$_3$), 25.4 (*c*-C$_6$H$_{10}$), 21.8 (*C*H$_3$). IR (KBr): 2926, 2859, 1576, 1394, 1294, 1278. UV-vis (CH_2Cl_2): 315 (4.74) MS (ESI): 476 (M^+). Anal. Found: C, 51.29; H, 6.82; N, 11.39. Calc. for $C_{21}H_{30}N_4O_2Pd$: C, 52.89; H, 6.34; N, 11.75%.

Synthesis of Ni[cp-TATE(NO$_2$)$_2$] (3a). To a suspension of **2a** (202 mg, 0.472 mmol) in CH_3CN (ca. 10 mL) was added $NaNO_2$ (98 mg, 1.42 mmol) and CF_3COOH (180 mg, 1.58 mmol) at room temperature. The darkened mixture was stirred overnight and filtered. The solid was recrystallized by layering a $CHCl_3$ (ca. 4 mL) solution with Et_2O (ca. 4 mL) to provide red needles of **3a**. Yield: 153 mg (74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.20 (s, 2H, vinyl-*H*), 3.72 (m, 4H, NCH_2CH$_2$CH_2N), 2.69 (m, 2H, C$_6H_{10}$), 2.47 (s, 6H, CH_3), 2.28 (m, 2H, C$_6H_{10}$), 1.90 (m, 2H, C$_6H_{10}$), 1.84 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.44 (m, 2H, C$_6H_{10}$), 1.24 (m, 2H, C$_6H_{10}$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 165.2 (vinyl-*C*), 151.3 (vinyl-*C*), 129.6 (vinyl-*C*), 70.5 (*c*-C$_6$H$_{10}$), 46.4 (NCH$_2$CH$_2$*C*H$_2$N), 29.5 (*c*-C$_6$H$_{10}$), 26.4 (NCH$_2$*C*H$_2$CH$_2$N), 25.0 (*c*-C$_6$H$_{10}$), 18.6 (*C*H$_3$). IR (KBr): 2931, 2866, 1613, 1481, 1306, 1269, 1234, 1166. UV-vis (CH_2Cl_2): 413 (4.84). MS (EI): 434 (M^+). Anal. Found: C, 46.89; H, 5.70; N, 19.36. Calc. for $C_{17}H_{24}N_6O_4Ni$: C, 46.93; H, 5.56; N, 19.31%.

Synthesis of Ni[cp-TATE(Ac)(NO$_2$)] (3b). To a suspension of **2a** (103.2 mg, 0.240 mmol) in CH_3CN (ca. 5 mL) was added $NaNO_2$ (17.2 mg, 0.249 mmol) and CF_3COOH (27.5 mg, 0.241 mmol) at room temperature. The mixture was stirred for 4 h and filtered. The solid was recrystallized by layering a CH_2Cl_2 (ca. 3 mL) solution with Et_2O (ca. 3 mL) to

provide an orange product. Yield: 35 mg (40%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (s, 1H, vinyl-*H*), 7.42 (s, 1H, vinyl-*H*), 3.69 (m, 3H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.53 (m, 1H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.67 (m, 2H, C$_6$*H*$_{10}$), 2.45 (s, 3H, C*H*$_3$), 2.41 (s, 3H, C*H*$_3$), 2.26 (s, 3H, COC*H*$_3$), 2.21 (m, 2H, C$_6$*H*$_{10}$), 1.89 (m, 2H, C$_6$*H*$_{10}$), 1.82 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.40 (m, 2H, C$_6$*H*$_{10}$), 1.26 (m, 2H, C$_6$*H*$_{10}$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 194.4 (*C*OCH$_3$), 167.7 (vinyl-*C*), 164.9 (vinyl-*C*), 151.8 (vinyl-*C*), 151.2 (vinyl-*C*), 129.0 (vinyl-*C*), 113.3 (vinyl-*C*), 70.6 (*c*-C$_6$H$_{10}$), 69.7 (*c*-C$_6$H$_{10}$), 46.3 (NCH$_2$CH$_2$*C*H$_2$N), 45.5 (NCH$_2$CH$_2$*C*H$_2$N), 29.6 (*c*-C$_6$H$_{10}$), 29.1 (*c*-C$_6$H$_{10}$), 28.3 (NCH$_2$*C*H$_2$CH$_2$N), 26.4 (*c*-C$_6$H$_{10}$), 25.0 (*c*-C$_6$H$_{10}$), 18.53 (*C*H$_3$), 18.49 (*C*H$_3$),. IR (KBr): 2931, 1584, 1560, 1274, 1240, 1003. UV-vis (CH_2Cl_2): 403 (4.65). MS (EI): 431 (M^+).

Synthesis of Ni[cp-TATE(H)$_2$]·2HPF$_6$ (4). To a suspension of **2a** (206 mg, 0.480 mmol) in hot water (3 mL) was added 1 mL of HCl (*conc.*). After all the solid dissolved, NH_4PF_6 (158 mg, 0.971 mmol) was added to give a yellow precipitate **4**, which was filtered, washed with cold water and Et_2O, and air dried. Yield: 247 mg (89%). ^{1}H NMR (CD_3CN, 300 MHz): δ 4.37 (br s, 2H), 4.11 (br s, 2H), 3.77 (m, 4H), 3.21 (s, 2H), 2.17 (s, 2H), 2.07 (s, 6H), 1.97 (m, 2H), 1.81 (m, 2H), 1.33 (m, 4H). ^{13}C NMR (CD_3CN, 300 MHz): δ 179.8, 165.7, 119.8, 70.9, 48.4, 48.3, 30.6, 24.7, 24.0. IR (KBr): 2945, 2864, 1684, 1559, 1540, 1456, 837, 558. UV-vis (CD_3CN): 290 (3.32). MS (ESI): 491 (M^+-HPF$_6$), 345 (M^+-2HPF$_6$). Anal. Found: C, 31.51; H, 4.38; N, 8.58. Calc. for C$_{17}$H$_{28}$N$_4$P$_2$F$_{12}$Ni: C, 32.05; H, 4.43; N 8.79%.

Synthesis of H$_2$[cp-TATE]·2HPF$_6$ (5). Hydrogen chloride gas was bubbled through a solution of **4** (137.5 mg, 0.217 mmol) in absolute ethanol (5 mL) until it turned blue. Solvent was removed *in vacuo* and the residue dissolved in water (1 mL). After addition of

NH_4PF_6 (120 mg, 0.736 mmol), the mixture was cooled in a refrigerator to 0 °C for 6h. The colorless crystalline product **5** was filtered and washed by water and diethyl ether. Yield: 115.2 mg (91%). ^{1}H NMR (CD_3CN, 300 MHz): δ 7.85 (m, δ vinyl), 7.66 (m, δ vinyl), 7.44 (m, δ vinyl), 7.25 (br m, N*H*), 6.90 (br m, N*H*), 5.39 (d, J_{H-H}=12.3 Hz, γ vinyl), 5.19 (d, J_{H-H}=11.4 Hz, γ vinyl), 5.11 (d, J_{H-H}=12.0 Hz, γ vinyl), 4.95 (d, J_{H-H}=12.9 Hz, γ vinyl), 3.1-3.7 (m, NC*H* on C_6H_{12} and NCH_2) 2.32 (m, CH_3), 1.7-2.3 (m, C_6H_{12}), 1.2-1.6 (m, C_6H_{12} and $NCH_2CH_2CH_2N$). IR (KBr): 3386, 3363, 3226, 3.69, 2946, 1636, 841, 559. Anal. Found: C, 35.17; H, 5.44; N, 9.56. Calc. for $C_{17}H_{30}N_4P_2F_{12}$: C, 35.18; H, 5.21; N, 9.65%.

X-ray crystallography. Single-crystal intensity data collections for **2b** and **5** were performed on a BRUKER SMART 1000 CCD-based diffractometer with graphite monochromated, MoK_α radiation (0.71073 Å), using the full-sphere ω/2θ scan routine. The datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiply equivalent measurements.[15] Details about crystal data, data collection, and structure solution and refinement are summarized in Table 1. Selected bond distances and bond angels are collected in Tables 2 and 3 for compounds **2b** and **5**, respectively.

A black prism of **2b** was selected for X-ray analysis. The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$. The *E*-statistics strongly suggested the non-centrosymmetric space group yielding chemically reasonable and computationally stable results of refinement. The positions of Ni atoms were found by the Patterson method. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps and were refined in full-matrix

Table 1. Crystal data and structure refinement for **2b** and **5**.

	2b	**5**
Formula	$C_{24}H_{34}N_4NiO_2$	$C_{17}H_{30}F_{12}N_4P_2$
Fw	469.26	580.39
Crystal size	0.3 x 0.2 x 0.2 mm^3	0.4 x 0.2 x 0.1 mm^3
Temperature	298(2) K	173(2) K
Crystal system	Triclinic	Orthorhombic
Space group	P1	C222(1)
a (Å)	9.9537(8)	13.3960(16)
b (Å)	10.9729(8)	14.9412(18)
c (Å)	11.8826(9)	12.0953(14)
α (°)	67.3100(10)	90
β (°)	75.226(2)	90
γ (°)	68.5490(10)	90
V ($Å^3$)	1104.59(15)	2420.9(5)
Z	2	4
D_{calc} (Mg/m^3)	1.411	1.592
Absorption coefficient	0.907 mm^{-1}	0.286 mm^{-1}
F(000)	500	1192
Theta range	2.11 to 28.25°	2.04 to 24.72°
Reflections collected	9155	6229
Independent reflections	6732 [R(int) = 0.0286]	2072 [R(int) = 0.0312]
Max. and min. transmission	1 and 0.71	0.81 and 0.75
Refinement method on F^2	Full-matrix least-squares	Full-matrix least-squares
Data / restraints / parameters	6732 / 3 / 568	2072 / 0 / 219
Goodness-of-fit on F^2	0.983	0.972
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0352, wR2 = 0.0837	R1 = 0.0335, wR2 = 0.0778
R indices (all data)	R1 = 0.0407, wR2 = 0.0860	R1 = 0.0428, wR2 = 0.0807

Table 2. Selected bond lengths [Å] and angles [°] for **2b**.

Ni(1A)-N(2A)	1.852(4)	N(3A)-Ni(1A)-N(2A)	85.44(16)
Ni(1A)-N(3A)	1.855(3)	N(3A)-Ni(1A)-N(4A)	92.13(15)
Ni(1A)-N(4A)	1.868(3)	N(2A)-Ni(1A)-N(1A)	93.81(15)
Ni(1A)-N(1A)	1.917(3)	N(4A)-Ni(1A)-N(1A)	89.11(15)
C(1A)-N(1A)	1.321(5)	N(2A)-Ni(1A)-N(4A)	173.75(14)
C(1A)-C(3A)	1.434(6)	N(3A)-Ni(1A)-N(1A)	174.84(16)
C(3A)-C(6A)	1.411(6)		
C(6A)-N(2A)	1.307(6)		
C(7A)-N(2A)	1.495(5)		
C(12A)-N(3A)	1.480(6)		

Table 3. Bond lengths [Å] and angles [°] for **5**.

C(1)-C(1)#1	1.518(5)	C(1)#1-C(1)-C(2)	112.3(2)
C(1)-C(2)	1.527(4)	C(3)-C(2)-C(1)	109.8(2)
C(2)-C(3)	1.521(3)	N(1)-C(3)-C(2)	114.0(2)
C(3)-N(1)	1.458(3)	N(1)-C(3)-C(3)#1	109.87(16)
C(3)-C(3)#1	1.548(5)	C(2)-C(3)-C(3)#1	109.53(18)
C(4)-N(1)	1.324(3)	N(1)-C(4)-C(5)	127.3(2)
C(4)-C(5)	1.365(4)	C(4)-C(5)-C(7)	121.1(2)
C(5)-C(7)	1.395(3)	N(2)-C(7)-C(5)	123.0(2)
C(6)-C(7)	1.499(4)	N(2)-C(7)-C(6)	114.8(2)
C(7)-N(2)	1.310(3)	C(5)-C(7)-C(6)	122.2(2)
C(8)-N(2)	1.455(3)	N(2)-C(8)-C(9)	111.2(2)
C(8)-C(9)	1.515(3)	C(8)-C(9)-C(8)#1	114.8(3)
C(9)-C(8)#1	1.515(3)	C(4)-N(1)-C(3)	121.6(2)
		C(7)-N(2)-C(8)	129.7(2)

Symmetry transformations used to generate equivalent atoms: #1 x,–y+1,-z+2.

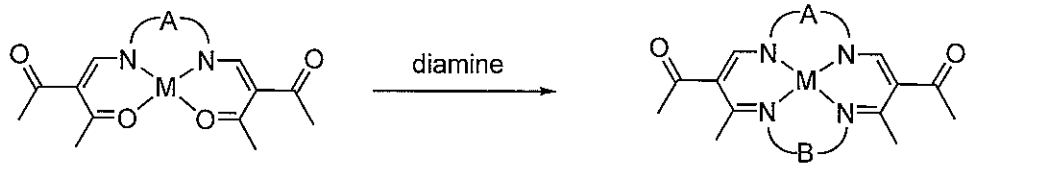
anisotropic approximation. All hydrogen atoms were placed at calculated positions and refined using a riding model. All attempts to transform the atomic coordinates to satisfy centrosymmetric space group $P\bar{1}$ gave a model with strong disorder in 6-membered rings and unreasonable thermal ellipsoids for the remaining atoms.

A thin colorless plate of **5** was used for X-ray analysis. The positions of all non-hydrogen atoms were found by direct methods and refined with a full-matrix anisotropic approximation. The hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps and were refined using a riding model.

Results and Discussion

Synthesis and characterization of macrocyclic complexes. Macrocyclic ligands can be synthesized by a wide variety of methods, among which template synthesis[16] is one of the most widely used strategies. Here, macrocyclic tetraazatetraene (TATE) complexes were prepared by template condensation of open chain complexes with appropriate neat diamines with good to high yields in an analogous manner to that previously reported. Thus, the reaction of **1a,b** with diamines yielded the corresponding macrocyclic tetraazatetraene complexes **2a-c** with one or two chiral cyclohexanediyl bridges incorporated (Scheme 1). The palladium complex **1c** also reacted readily with ethylenediamine or trimethylenediamine to afford **2d** and **2e**, respectively.

The reaction between **1a** and ethylenediamine led to the formation of double ethylene-bridged product, Ni[ee-TATE(Ac)$_2$], **2f**, presumably by a diamine exchange reaction. A similar exchange reaction was reported earlier.[3b] It was interesting to note that when the template cation Pd^{2+} was used under the same conditions, cyclization product



	M	A
1a	Ni	cyclohexanediyl
1b	Ni	ethylene
1c	Pd	cyclohexanediyl

	M	A	B
2a	Ni	cyclohexanediyl	propylene
2b	Ni	cyclohexanediyl	cyclohexanediyl
2c	Ni	ethylene	cyclohexanediyl
2d	Pd	cyclohexanediyl	ethylene
2e	Pd	cyclohexanediyl	propylene
2f	Ni	ethylene	ethylene

Scheme 1. Synthesis of macrocyclic complexes.

Pd[ce-TATE(Ac)$_2$], **2d** was formed without further amine exchange. Although the reaction of **1a** with (*R,R*)-dach went smoothly to afford Ni[cc-TATE(Ac)$_2$], **2b**, reaction of the palladium analogue **1c** with (*R,R*)-dach resulted in the decomposition of the ligand skeleton, and products were not further identified. Attempts to carry out the reaction in the presence of a solvent were unsuccessful.[17]

The identity and composition of the chiral macrocyclic tetraazatetraene Ni(II) and Pd(II) complexes were confirmed by elemental analyses as well as by electronic, infrared, NMR spectroscopies and mass spectrometry. The assignment of the ^{1}H and ^{13}C signals in these complexes is based upon ^{13}C APT and 2D COSY (^{1}H/^{1}H) and HETCOR (^{1}H/^{13}C) NMR experiments. These data are consistent with square planar coordination around nickel and palladium centers. Generally, the imine protons appear around 7.4-8.2 ppm as a singlet. The protons associated with α carbons on bridge A (Scheme 1) appear at 2.6-3.3 ppm, while on bridge B these protons appear at a lower field, 3.4-3.7 ppm. Also, on incorporation of the chiral cyclohexyldiamine, the α protons on the trimethylene bridge of **2a** become non-

equivalent. Four individual triplets were observed for these protons, although not completely baseline separated.

Structure of 2b. Two crystallographically non-equivalent molecules were found in the unit cell of **2b**. Both have very similar conformations (Fig. 1) with Ni atoms placed almost in the plane of four N atoms (RMS deviations are 0.071 and 0.085 Å for two crystallographically non-equivalent molecules respectively). However, the 14-membered ring system is significantly distorted from a planar conformation (RMS deviations are 0.190 and 0.208 respectively). Ni-N distances are of 1.845(4)–1.917(4) Å. N-C distances in 5- and 6-membered chelate rings range over 1.469(6)-1.498(6) and 1.285(6)-1.338(6) Å, respectively. Both molecules of **2b** in the asymmetric unit cell are almost parallel and form alternate layers in a crystal.

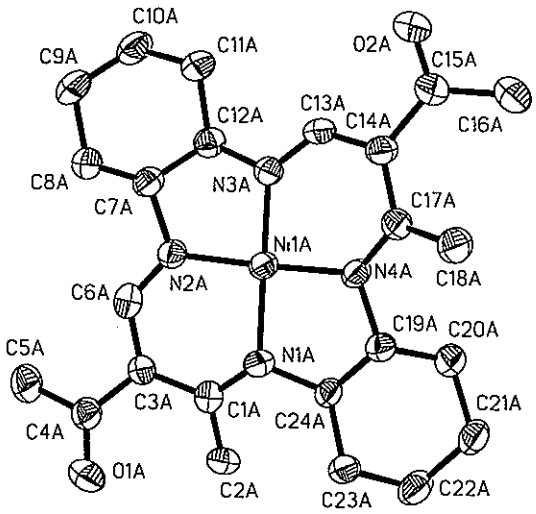
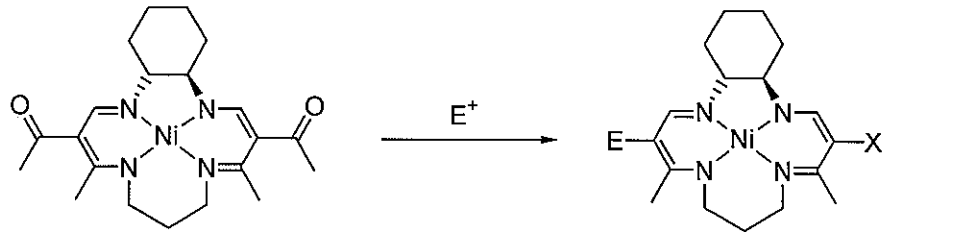


Figure 1. ORTEP of one of the two crystallographically independent molecules of **2b** at 50% probability level. Hydrogen atoms are omitted for clarity.

Some metrical correlations could be found in comparison with structures of (5,7,12,14-tetramethyldibenzo (b,i)-1,4,8,11-tetraaza-(14)-annulenato)-nickel(II), Ni(TMTAA), and (6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato-N,N′, N″, N‴) nickel(II), Ni[ee-TATE(Ac)$_2$]. Both crystallographically independent molecules in Ni(TMTAA) also have almost planar coordination of the Ni atoms.[18] However, the distortion of the 14-membered ring is much larger. The interplanar angle between these molecules is equal to 77.8°, forming a typical herringbone packing mode for the P2$_1$/c space group. One half of the molecule of Ni[ee-TATE(Ac)$_2$] was found in the asymmetric unit of a monoclinic cell with the Ni atom in the inversion center.[19] The symmetry requirements led to rigorously planar coordination of Ni. However, the 14-membered ring is slightly distorted from planarity (RMS deviations are 0.116 Å). All the molecules in the crystal of Ni[ee-TATE(Ac)$_2$] are parallel.

Reactivity towards electrophiles. The *meso* (or γ) positions of 15-membered macrocyclic complexes of this type can undergo electrophilic substitutions.[20] As shown in Scheme 2, the reaction of **2a** with hydrochloric acid afforded the deacylated macrocyclic complex **4** as a yellow crystalline product. Compound **4** was unreactive to air in the solid state but turned black within days in solution on exposure to normal room atmosphere. Compound **2a** also reacted with nitrogen electrophiles. Treatment of **2a** with sodium nitrite and trifluoroacetic acid under oxidizing conditions resulted in the formation of mono- and dinitro complex **3a** and **3b**, depending on the stoichiometry of the reaction.



2a

3a: E = X = NO2
3b: E = NO_2, X = COCH3
4•2HPF$_6$: E = X = H

Scheme 2. Reactivity of **2a**.

Demetallation of **4** by gaseous hydrogen chloride produced a colorless crystalline product. Sharp IR peaks around 3386 and 3363 cm^{-1} indicated the presence of N-H functional groups. Satisfactory elemental analysis confirmed its composition as a metal-free ligand salt, **5**. However, the ^1H NMR spectrum of **5** was complicated. For example, there were four doublets around the γ vinyl region (4.9-5.5 ppm) with approximately equal intensity. At higher temperature (50 °C), these peaks, as well as all others, were slightly broadened but the relative intensity of these four doublets showed little change. Upon addition of D_2O, however, the ratio of these peaks changed considerably and broad peaks at 6.9 and 7.25 ppm disappeared. This suggested that more than one tautomeric forms of the ligand salt existed in solution.[21] Due to this complexity, the ^{13}C NMR spectrum of **5** was not clearly interpretable. However, three peaks at 93.2, 92.7, and 89.7 ppm can be assigned to the carbon resonances associated with γ vinyl protons. Attempts to obtain the pure, neutral ligand by deprotonation with various bases such as sodium acetate and sodium ethoxide were not successful. Nevertheless, the structure of **5** was finally established by an X-ray crystallographic analysis.

Crystal structures of 5. The asymmetric unit of **5** consists of half of the centrosymmetric cation $[C_{17}H_{30}N_4]^{2+}$ (Fig. 2) and a PF_6^- anion. The conformation adopted by **5** differs significantly from neutral tetraazaannulene analogues. For example, the biscyclohexanediyl bridged TATE macrocycle maintains a square planar arrangement of the four donor nitrogens in the solid state.[22] However, **5** has all four donor atoms protonated. The extra charge strongly disfavors the square arrangement of nitrogens. Only one of two N atoms takes part in cation-anion intermolecular interactions in structure of **5**.

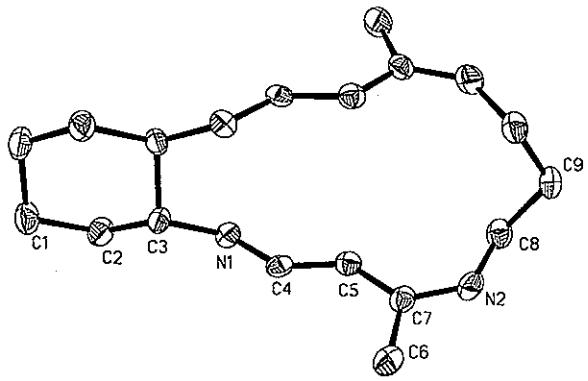


Figure 2. ORTEP of molecular structure of $[C_{17}H_{30}N_4]^{2+}$ cation in **5**. H-atoms are omitted for clarity.

Conclusion

In summary, we have shown that a series of chiral tetraaza macrocylic complexes can be readily prepared via template condensation reactions. The application of these chiral tetraaza macrocyclic ligands and their complexes in asymmetric catalysis are underway.

Acknowledgments. We thank the Research Corporation for partial financial support.

Supporting Information Available: Tables giving crystallographic data for compounds **2b** and **5** including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. ^{1}H NMR spectra for compounds **2a**, **2b**, **2c**, **3a**, and **5**. This information is available free of charge via the internet at http://pubs.acs.org.

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APPENDIX

Table I. Crystal data and structure refinement for Ni[cc-TATE(Ac)$_2$] (**2b**).

Empirical formula	C24 H34 N4 Ni O2	
Formula weight	469.26	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.9537(8) Å	α = 67.3100(10)°
	b = 10.9729(8) Å	β = 75.226(2)°
	c = 11.8826(9) Å	γ = 68.5490(10)°
Volume	1104.59(15) Å^3	
Z	2	
Density (calculated)	1.411 Mg/m^3	
Absorption coefficient	0.907 mm^{-1}	
F(000)	500	
Crystal size	0.3 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.11 to 28.25°	
Index ranges	-13<=h<=7, -14<=k<=14, -15<=l<=13	
Reflections collected	9155	
Independent reflections	6732 [R(int) = 0.0286]	
Completeness to theta = 28.25°	89.5 %	
Absorption correction	Empirical	
Max. and min. transmission	1 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6732 / 3 / 568	
Goodness-of-fit on F^2	0.983	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0837	
R indices (all data)	R1 = 0.0407, wR2 = 0.0860	
Absolute structure parameter	0.042(10)	
Extinction coefficient	0.0020(6)	
Largest diff. peak and hole	0.659 and -0.526 eÅ^{-3}	

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Ni[cc-TATE(Ac)$_2$] (**2b**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ni(1)	483(1)	6934(1)	182(1)	34(1)
Ni(2)	9517(1)	3068(1)	9818(1)	32(1)
C(1)	1137(4)	6410(4)	2579(3)	36(1)
C(2)	1341(5)	7082(4)	3414(4)	46(1)
C(3)	2138(4)	5053(4)	2634(4)	40(1)
C(4)	2804(4)	4134(4)	3733(4)	44(1)
C(5)	3981(5)	2779(5)	3709(5)	57(1)
C(6)	2495(5)	4599(4)	1591(4)	41(1)
C(7)	2514(4)	4675(4)	-466(4)	39(1)
C(8)	4021(5)	3639(4)	-485(4)	51(1)
C(9)	4386(5)	3208(5)	-1627(5)	63(1)
C(10)	4213(6)	4419(5)	-2806(4)	64(1)
C(11)	2701(5)	5486(5)	-2774(4)	58(1)
C(12)	2401(5)	5907(4)	-1631(4)	40(1)
C(13)	174(4)	7634(4)	-2316(4)	43(1)
C(14)	-1228(5)	8567(4)	-2234(4)	42(1)
C(15)	-1832(5)	9255(4)	-3404(4)	49(1)
C(16)	-3126(7)	10535(6)	-3647(5)	71(2)
C(17)	-1935(4)	8835(4)	-1108(4)	37(1)
C(18)	-3573(4)	9349(4)	-899(4)	49(1)
C(19)	-1918(4)	8935(3)	879(4)	35(1)
C(20)	-2554(5)	10507(4)	592(4)	44(1)
C(21)	-3439(5)	10831(4)	1761(4)	47(1)
C(22)	-2573(5)	10116(4)	2839(4)	52(1)
C(23)	-1803(4)	8580(4)	3012(4)	45(1)
C(24)	-852(5)	8458(4)	1810(4)	36(1)
C(25)	10942(5)	1772(4)	11958(4)	40(1)
C(26)	11946(4)	668(4)	11558(4)	36(1)

Table II. (continued)

C(27)	13051(5)	-321(4)	12346(4)	43(1)
C(28)	12831(7)	-460(6)	13691(5)	62(1)
C(29)	11892(4)	535(4)	10415(3)	33(1)
C(30)	12617(4)	-909(4)	10291(4)	40(1)
C(31)	11075(5)	1311(4)	8436(4)	34(1)
C(32)	12497(4)	758(4)	7622(3)	41(1)
C(33)	12053(5)	330(4)	6733(4)	53(1)
C(34)	10896(5)	1461(4)	5970(4)	50(1)
C(35)	9633(5)	2238(4)	6734(4)	47(1)
C(36)	10267(4)	2670(3)	7522(4)	36(1)
C(37)	8429(4)	4829(4)	7517(4)	36(1)
C(38)	8957(5)	5413(4)	6172(3)	49(1)
C(39)	7232(5)	5697(4)	8098(4)	36(1)
C(40)	6109(4)	6920(4)	7454(4)	44(1)
C(41)	5949(6)	7353(6)	6105(5)	63(2)
C(42)	6994(4)	5393(4)	9366(4)	37(1)
C(43)	7461(5)	4258(4)	11480(4)	39(1)
C(44)	6386(5)	5521(4)	11817(4)	51(1)
C(45)	6212(5)	5229(5)	13201(4)	55(1)
C(46)	7661(5)	4744(5)	13675(4)	58(1)
C(47)	8763(5)	3513(4)	13285(4)	50(1)
C(48)	8929(4)	3854(4)	11915(3)	38(1)
N(1)	204(3)	7079(3)	1784(3)	36(1)
N(2)	2012(4)	5287(3)	549(3)	36(1)
N(3)	933(4)	6875(3)	-1406(3)	38(1)
N(4)	-1176(3)	8465(3)	-184(3)	37(1)
N(5)	9879(4)	2747(3)	11375(3)	36(1)
N(6)	11147(3)	1550(3)	9556(3)	33(1)
N(7)	9188(4)	3580(3)	8197(3)	35(1)
N(8)	7845(3)	4419(3)	10149(3)	36(1)
O(1)	2457(4)	4359(3)	4719(3)	64(1)
O(2)	-1221(4)	8834(4)	-4298(3)	78(1)

Table II. (continued)

O(3)	14191(3)	-1081(3)	11972(3)	60(1)
O(4)	5163(3)	7645(3)	8021(3)	62(1)

Table III. Bond lengths [Å] and angles [°] for Ni[cc-TATE(Ac)$_2$] (**2b**).

Ni(1)-N(3)	1.846(3)	C(19)-N(4)	1.469(4)
Ni(1)-N(2)	1.868(3)	C(19)-C(20)	1.533(5)
Ni(1)-N(4)	1.874(3)	C(19)-C(24)	1.539(6)
Ni(1)-N(1)	1.913(3)	C(20)-C(21)	1.536(5)
Ni(2)-N(5)	1.849(3)	C(21)-C(22)	1.515(6)
Ni(2)-N(8)	1.853(3)	C(22)-C(23)	1.530(5)
Ni(2)-N(7)	1.867(3)	C(23)-C(24)	1.523(5)
Ni(2)-N(6)	1.916(3)	C(24)-N(1)	1.500(5)
C(1)-N(1)	1.307(5)	C(25)-N(5)	1.311(6)
C(1)-C(3)	1.444(5)	C(25)-C(26)	1.418(6)
C(1)-C(2)	1.531(5)	C(26)-C(29)	1.437(5)
C(3)-C(6)	1.426(6)	C(26)-C(27)	1.460(6)
C(3)-C(4)	1.449(6)	C(27)-O(3)	1.232(5)
C(4)-O(1)	1.227(5)	C(27)-C(28)	1.512(6)
C(4)-C(5)	1.525(5)	C(29)-N(6)	1.318(5)
C(6)-N(2)	1.285(6)	C(29)-C(30)	1.530(5)
C(7)-N(2)	1.493(4)	C(31)-N(6)	1.475(5)
C(7)-C(12)	1.510(6)	C(31)-C(36)	1.539(5)
C(7)-C(8)	1.516(5)	C(31)-C(32)	1.560(5)
C(8)-C(9)	1.521(6)	C(32)-C(33)	1.518(6)
C(9)-C(10)	1.509(7)	C(33)-C(34)	1.519(6)
C(10)-C(11)	1.534(6)	C(34)-C(35)	1.536(5)
C(11)-C(12)	1.524(6)	C(35)-C(36)	1.538(5)
C(12)-N(3)	1.490(5)	C(36)-N(7)	1.479(4)
C(13)-N(3)	1.302(5)	C(37)-N(7)	1.342(5)
C(13)-C(14)	1.403(6)	C(37)-C(39)	1.436(5)
C(14)-C(17)	1.430(6)	C(37)-C(38)	1.507(5)
C(14)-C(15)	1.466(6)	C(39)-C(42)	1.387(6)
C(15)-O(2)	1.246(5)	C(39)-C(40)	1.477(6)
C(15)-C(16)	1.506(6)	C(40)-O(4)	1.231(4)
C(17)-N(4)	1.340(5)	C(40)-C(41)	1.520(6)
C(17)-C(18)	1.506(5)	C(42)-N(8)	1.304(5)

Table III. (continued)

C(43)-N(8)	1.484(5)	C(45)-C(46)	1.517(7)
C(43)-C(48)	1.527(6)	C(46)-C(47)	1.545(5)
C(43)-C(44)	1.534(5)	C(47)-C(48)	1.501(5)
C(44)-C(45)	1.526(6)	C(48)-N(5)	1.495(4)
N(3)-Ni(1)-N(2)	85.61(15)	C(9)-C(10)-C(11)	112.3(4)
N(3)-Ni(1)-N(4)	92.97(15)	C(12)-C(11)-C(10)	108.9(4)
N(2)-Ni(1)-N(4)	173.51(15)	N(3)-C(12)-C(7)	104.0(3)
N(3)-Ni(1)-N(1)	173.29(15)	N(3)-C(12)-C(11)	116.3(4)
N(2)-Ni(1)-N(1)	93.21(14)	C(7)-C(12)-C(11)	112.0(3)
N(4)-Ni(1)-N(1)	88.92(14)	N(3)-C(13)-C(14)	125.6(4)
N(5)-Ni(2)-N(8)	85.45(14)	C(13)-C(14)-C(17)	121.4(4)
N(5)-Ni(2)-N(7)	173.71(13)	C(13)-C(14)-C(15)	113.6(4)
N(8)-Ni(2)-N(7)	92.19(14)	C(17)-C(14)-C(15)	124.9(4)
N(5)-Ni(2)-N(6)	93.94(14)	O(2)-C(15)-C(14)	120.2(4)
N(8)-Ni(2)-N(6)	174.69(14)	O(2)-C(15)-C(16)	115.7(4)
N(7)-Ni(2)-N(6)	88.94(14)	C(14)-C(15)-C(16)	124.0(4)
N(1)-C(1)-C(3)	122.1(4)	N(4)-C(17)-C(14)	120.8(4)
N(1)-C(1)-C(2)	121.7(3)	N(4)-C(17)-C(18)	119.7(4)
C(3)-C(1)-C(2)	116.0(4)	C(14)-C(17)-C(18)	119.0(4)
C(6)-C(3)-C(1)	120.0(4)	N(4)-C(19)-C(20)	115.7(3)
C(6)-C(3)-C(4)	118.7(4)	N(4)-C(19)-C(24)	110.3(3)
C(1)-C(3)-C(4)	121.2(4)	C(20)-C(19)-C(24)	105.4(3)
O(1)-C(4)-C(3)	123.9(4)	C(19)-C(20)-C(21)	109.6(3)
O(1)-C(4)-C(5)	116.4(4)	C(22)-C(21)-C(20)	112.2(3)
C(3)-C(4)-C(5)	119.7(4)	C(21)-C(22)-C(23)	112.7(3)
N(2)-C(6)-C(3)	126.5(4)	C(24)-C(23)-C(22)	108.1(3)
N(2)-C(7)-C(12)	104.6(3)	N(1)-C(24)-C(23)	119.1(3)
N(2)-C(7)-C(8)	117.2(3)	N(1)-C(24)-C(19)	108.5(3)
C(12)-C(7)-C(8)	110.9(3)	C(23)-C(24)-C(19)	105.5(3)
C(7)-C(8)-C(9)	109.8(4)	N(5)-C(25)-C(26)	125.7(4)
C(10)-C(9)-C(8)	113.2(4)	C(25)-C(26)-C(29)	121.4(4)

Table III. (continued)

C(25)-C(26)-C(27)	117.4(4)	C(46)-C(45)-C(44)	112.5(4)
C(29)-C(26)-C(27)	121.2(4)	C(45)-C(46)-C(47)	112.6(4)
O(3)-C(27)-C(26)	123.1(4)	C(48)-C(47)-C(46)	110.3(3)
O(3)-C(27)-C(28)	116.4(4)	N(5)-C(48)-C(47)	118.0(3)
C(26)-C(27)-C(28)	120.5(4)	N(5)-C(48)-C(43)	103.7(3)
N(6)-C(29)-C(26)	122.8(4)	C(47)-C(48)-C(43)	111.1(3)
N(6)-C(29)-C(30)	120.5(3)	C(1)-N(1)-C(24)	119.5(3)
C(26)-C(29)-C(30)	116.4(3)	C(1)-N(1)-Ni(1)	125.6(3)
N(6)-C(31)-C(36)	110.3(3)	C(24)-N(1)-Ni(1)	109.9(3)
N(6)-C(31)-C(32)	120.6(3)	C(6)-N(2)-C(7)	120.1(3)
C(36)-C(31)-C(32)	102.9(3)	C(6)-N(2)-Ni(1)	126.9(3)
C(33)-C(32)-C(31)	106.8(3)	C(7)-N(2)-Ni(1)	112.3(3)
C(32)-C(33)-C(34)	114.4(3)	C(13)-N(3)-C(12)	119.5(3)
C(33)-C(34)-C(35)	113.1(3)	C(13)-N(3)-Ni(1)	127.5(3)
C(34)-C(35)-C(36)	108.7(3)	C(12)-N(3)-Ni(1)	112.8(3)
N(7)-C(36)-C(35)	115.3(3)	C(17)-N(4)-C(19)	118.2(3)
N(7)-C(36)-C(31)	110.0(3)	C(17)-N(4)-Ni(1)	125.7(3)
C(35)-C(36)-C(31)	105.7(3)	C(19)-N(4)-Ni(1)	112.5(3)
N(7)-C(37)-C(39)	120.2(4)	C(25)-N(5)-C(48)	119.0(4)
N(7)-C(37)-C(38)	120.1(3)	C(25)-N(5)-Ni(2)	127.3(3)
C(39)-C(37)-C(38)	119.2(3)	C(48)-N(5)-Ni(2)	113.3(3)
C(42)-C(39)-C(37)	121.2(4)	C(29)-N(6)-C(31)	119.7(3)
C(42)-C(39)-C(40)	113.6(4)	C(29)-N(6)-Ni(2)	125.6(3)
C(37)-C(39)-C(40)	125.1(4)	C(31)-N(6)-Ni(2)	109.9(3)
O(4)-C(40)-C(39)	120.5(4)	C(37)-N(7)-C(36)	116.9(3)
O(4)-C(40)-C(41)	114.4(4)	C(37)-N(7)-Ni(2)	126.7(2)
C(39)-C(40)-C(41)	125.0(4)	C(36)-N(7)-Ni(2)	113.0(2)
N(8)-C(42)-C(39)	126.5(4)	C(42)-N(8)-C(43)	120.0(3)
N(8)-C(43)-C(48)	103.7(3)	C(42)-N(8)-Ni(2)	127.1(3)
N(8)-C(43)-C(44)	116.6(3)	C(43)-N(8)-Ni(2)	112.8(3)
C(48)-C(43)-C(44)	111.0(3)		
C(45)-C(44)-C(43)	110.0(4)		

Table IV. Crystal data and structure refinement for H_2[cp-TATE]·2HPF_6 (**5**).

Empirical formula	C17 H30 F12 N4 P2	
Formula weight	580.39	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C222(1)	
Unit cell dimensions	a = 13.3960(16) Å	α = 90°
	b = 14.9412(18) Å	β = 90°
	c = 12.0953(14) Å	γ = 90°
Volume	2420.9(5) $Å^3$	
Z	4	
Density (calculated)	1.592 Mg/m^3	
Absorption coefficient	0.286 mm^{-1}	
F(000)	1192	
Crystal size	0.4 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.04 to 24.72°	
Index ranges	-15<=h<=15, -12<=k<=17, -14<=l<=14	
Reflections collected	6229	
Independent reflections	2072 [R(int) = 0.0312]	
Completeness to theta = 24.72°	100.0 %	
Absorption correction	None	
Max. and min. transmission	1 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2072 / 0 / 219	
Goodness-of-fit on F^2	0.972	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0778	
R indices (all data)	R1 = 0.0428, wR2 = 0.0807	
Absolute structure parameter	-0.06(13)	
Largest diff. peak and hole	0.266 and -0.185 $eÅ^{-3}$	

Table V. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for H_2[cp-TATE]·2HPF_6 (**5**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	6998(1)	7805(1)	7680(1)	38(1)
F(1)	7857(2)	7133(1)	7360(2)	86(1)
F(3)	6179(1)	8517(1)	8054(2)	69(1)
F(4)	7709(2)	8619(1)	7361(2)	80(1)
F(2)	6290(2)	7034(1)	8026(2)	105(1)
F(6)	7434(2)	7847(2)	8910(2)	86(1)
F(5)	6596(2)	7792(2)	6469(2)	95(1)
C(1)	5081(2)	5277(2)	9474(2)	32(1)
C(2)	4138(2)	5135(2)	8788(2)	31(1)
C(3)	3220(2)	5317(2)	9494(2)	23(1)
C(4)	1524(2)	5787(2)	9084(2)	22(1)
C(5)	538(2)	5641(2)	8860(2)	24(1)
C(6)	79(2)	7226(2)	9409(3)	37(1)
C(7)	-185(2)	6278(2)	9127(2)	25(1)
C(8)	-1656(2)	5250(2)	8991(2)	30(1)
C(9)	-2265(2)	5000	10000	29(1)
N(1)	2279(1)	5235(2)	8898(2)	24(1)
N(2)	-1142(2)	6098(2)	9152(2)	30(1)

Table VI. Bond lengths [Å] and angles [°] for H_2[cp-TATE]·2HPF_6 (**5**).

P(1)-F(2)	1.550(2)	C(3)-C(3)#1	1.548(5)
P(1)-F(5)	1.561(2)	C(4)-N(1)	1.324(3)
P(1)-F(1)	1.5759(18)	C(4)-C(5)	1.365(4)
P(1)-F(4)	1.592(2)	C(5)-C(7)	1.395(3)
P(1)-F(3)	1.5939(18)	C(6)-C(7)	1.499(4)
P(1)-F(6)	1.599(2)	C(7)-N(2)	1.310(3)
C(1)-C(1)#1	1.518(5)	C(8)-N(2)	1.455(3)
C(1)-C(2)	1.527(4)	C(8)-C(9)	1.515(3)
C(2)-C(3)	1.521(3)	C(9)-C(8)#1	1.515(3)
C(3)-N(1)	1.458(3)		
F(2)-P(1)-F(5)	91.86(15)	C(1)#1-C(1)-C(2)	112.3(2)
F(2)-P(1)-F(1)	92.25(14)	C(3)-C(2)-C(1)	109.8(2)
F(5)-P(1)-F(1)	90.74(13)	N(1)-C(3)-C(2)	114.0(2)
F(2)-P(1)-F(4)	177.94(13)	N(1)-C(3)-C(3)#1	109.87(16)
F(5)-P(1)-F(4)	89.34(15)	C(2)-C(3)-C(3)#1	109.53(18)
F(1)-P(1)-F(4)	89.41(12)	N(1)-C(4)-C(5)	127.3(2)
F(2)-P(1)-F(3)	89.91(12)	C(4)-C(5)-C(7)	121.1(2)
F(5)-P(1)-F(3)	92.12(14)	N(2)-C(7)-C(5)	123.0(2)
F(1)-P(1)-F(3)	176.36(12)	N(2)-C(7)-C(6)	114.8(2)
F(4)-P(1)-F(3)	88.37(11)	C(5)-C(7)-C(6)	122.2(2)
F(2)-P(1)-F(6)	90.09(17)	N(2)-C(8)-C(9)	111.2(2)
F(5)-P(1)-F(6)	178.05(18)	C(8)-C(9)-C(8)#1	114.8(3)
F(1)-P(1)-F(6)	89.22(11)	C(4)-N(1)-C(3)	121.6(2)
F(4)-P(1)-F(6)	88.72(16)	C(7)-N(2)-C(8)	129.7(2)
F(3)-P(1)-F(6)	87.85(12)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,-z+2

CHAPTER 7. CATALYTIC EPOXIDATION OF METHYL LINOLEATE

A paper submitted to *J. Am. Oil Chem. Soc.*

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Abstract

The epoxidation of methyl linoleate was examined using transition metal complexes as catalysts. With a catalytic amount of methyltrioxorhenium and pyridine, methyl linoleate was completely epoxidized by aqueous H_2O_2 within 4 h. Longer reaction time was needed with lower catalyst loading. Manganese tetraphenylporphyrin chloride was found to catalyze the partial epoxidation of methyl linoleate. A monoepoxidized species was obtained as the major product after 20 h.

KEY WORDS: Catalytic epoxidation, epoxidized fatty acid methyl esters, iron porphyrin, manganese porphyrin, methyl linoleate, methyltrioxorhenium.

Bio-renewable materials such as fatty acid derivatives and carbohydrates have recently received increasing attention as a means of addressing environmental and economical concerns. Introduction of functional groups into these substances provides new materials that can replace petroleum-derived compounds, serve as valuable intermediates, or be utilized directly. For example, epoxidized fatty acids have use as plasticizers and stabilizers for halogen containing polymers such as polyvinyl chloride (1).

Traditionally, fatty acids and their derivatives are epoxidized by peracids that are generated *in situ* or preformed by the reaction of formic or acetic acid with hydrogen peroxide (2). However, these processes suffer from acid-catalyzed epoxy ring opening reactions. By using *in situ* generated peracids at low concentrations, unwanted epoxide ring opening can be minimized. Efforts for developing milder and more effective epoxidation of fatty acids and related derivatives are continuing. More recently, procedures using enzymatic peroxygenase to epoxidize fatty acids have appeared (3,4).

A number of efficient transition metal-based catalysts have been developed to effect the epoxidation of olefins, some with excellent regio-, stereo- and enantio- selectivities. For example, the Sharpless epoxidation catalysts based on titanium(IV) alkoxide complexes are highly effective at converting allylic alcohols to allylic epoxides (5). With the simple addition of tartrates, high enantioselectivity can be achieved.

Metalloporphyrins have been widely investigated due to their relevance to biological oxidation reactions. Particularly, manganese and iron porphyrins have shown great activity as olefin epoxidation catalysts, utilizing a variety of oxygen sources such as iodosylbenzene, alkyl hydroperoxide, aqueous sodium hypochlorite (NaOCl), persulfate, O_2 with a reducing cofactor, etc (6). Use of inexpensive NaOCl is especially attractive. Chiral salen-based

manganese complexes have given remarkable results in the asymmetric epoxidation of olefins (7).

Methyltrioxorhenium (MTO) is another effective catalyst for epoxidation of olefins (8,9). Further elaboration of this system revealed that addition of a large excess nitrogenous bases, particularly pyridine under biphasic conditions, is beneficial for both selectivity and lifetime of the catalyst (10). This system has been utilized successfully in the epoxidation of fish oils (11) and soybean oils (12).

Linoleic acid, bearing two non-conjugated C=C double bonds, is one of the major components in soybean oils. In this study, methyl linoleate was chosen as a model compound for fatty acid methyl esters and oils. We examined the utility of metalloporphyrins and MTO in the catalytic epoxidation of methyl linoleate using the readily available oxidants NaOCl and H_2O_2.

Experimental Procedures

Reagents. Methyl linoleate (containing 6.5 % methyl oleate) was prepared by urea fractionation of safflower oil (13). Methyl vernoleate (cis-12,13-epoxy octadec-9-enoate) was obtained by thin layer chromatography (TLC) purification of *Vernonia galamensis* seed lipid methyl esters. Methyltrioxorhenium (MTO), *meso*-tetraphenylporphyrin manganese(III) chloride (Mn(TPP)Cl), *meso*-tetraphenylporphyrin iron(III) chloride (Fe(TPP)Cl), *m*-chloroperoxybenzoic acid (mCPBA) and tetra-*n*-butylammonium bromide (*n*-Bu_4NBr) were obtained from Aldrich (Milwaukee, MI). Hydrogen peroxide (30%) and pyridine were obtained from Fisher Scientific (Fair Lawn, NJ). Aqueous NaOCl (6%) was

obtained from Clorax Co. (Oakland, CA). Chemicals obtained from commercial vendors were used as received.

Characterization methods. All ^{1}H NMR and ^{13}C NMR spectra were acquired on a 400 MHz Bruker DRX (Karlsruhe, Germany) or 300 MHz Varian VXR (Palo Alto, CA) spectrometers using $CDCl_3$ as a solvent. Chemical shifts were referenced to proton solvent impurities (δ 7.15 for ^{1}H, 77.5 for ^{13}C). GC-MS analyses were performed on a Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS). GC analyses were performed on a Hewlett-Parkard (Wilmington, DE) HP 5890II gas chromatograph equipped with a flame ionization detector and a DB-5 capillary column (30 m × 0.32 mm i.d.). TLC was performed using 500μm silicagel GF plates (Alltech Associates Inc., Deerfield, IL) and a solvent mixture of hexane/diethyl ether 75:25, vol/vol.

Epoxidation of methyl linoleate with mCPBA. To a stirred solution of methyl linoleate (87.6 mg, 0.297 mmol) in CH_2Cl_2 (5 mL), a solution of mCPBA (166.2 mg, 0.963 mmol) in CH_2Cl_2 (5 mL) was added portion-wise. The mixture was stirred for 6 h at room temperature, then washed with 5% $NaHCO_3$ (2×10 mL), water (3×10 mL) and dried over anhydrous Na_2SO_4. Removal of solvent under vacuum afforded a yellowish oil, 69.2 mg (72%). NMR showed it was diepoxide. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.64 (s, 3H, COOC*H*$_3$), 3.08 (m, 2H, 10, 12-C*H*), 2.95 (m, 2H, 9,13-C*H*), 2.28 (t, 2H, 2-C*H*$_2$), 1.72 (m, 2H, 11-C*H*$_2$), 1.59 (m, 2H, 3-C*H*$_2$), 1.48 (m, 8H), 1.30(m, 10H), 0.87 (t, 3H, 18-C*H*$_3$).

Catalytic epoxidation of methyl linoleate using MTO/H_2O_2/pyridine. A round bottom flask was charged with methyltrioxorhenium (3.8 mg, 0.015 mmol) in CH_2Cl_2 (1.5 mL). A solution of pyridine (22.4 mg, 0.283 mmol) and methyl linoleate (109.3 mg, 0.371 mmol) in CH_2Cl_2 (1.5 mL) was added. The reaction was started by addition of 30% H_2O_2 (0.25 mL,

2.5 mmol). The mixture turned yellow immediately and remained yellow throughout the reaction. After completion of the reaction as detected by the disappearance of methyl linoleate by GC, the mixture was washed with water (2 x 10 mL) and aqueous $Na_2S_2O_3$ (10%, 5 mL), dried over anhydrous Na_2SO_4, and the solvent was removed by evaporation under vacuum. This provided a yellowish oil that was identified as methyl 9,10-12,13-diepoxy stearate in 88% yield (106 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.64 (s, 3H, COOC*H*$_3$), 3.08 (m, 2H, 10, 12-C*H*), 2.95 (m, 2H, 9,13-C*H*), 2.28 (t, 2H, 2-C*H*$_2$), 1.72 (m, 2H, 11-C*H*$_2$), 1.59 (m, 2H, 3-C*H*$_2$), 1.48 (m, 8H), 1.30(m, 10H), 0.87 (t, 3H, 18-C*H*$_3$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 174.5, 57.33, 57.29, 57.05, 57.00, 54.68, 54.67, 54.52, 51.76, 34.4, 32.0, 29.6, 29.5, 29.4, 28.23, 28.16, 27.6, 27.3, 26.9, 26.8, 26.6, 26.5, 25.2, 22.9, 14.3. EI-MS: m/z 327 (M^++H), 309 (M^+-17), 277, 253, 187, 165, 155, 147, 137, 109, 95, 81, 69, 55.

TLC separation of the reaction products above revealed the presence of ~7% cis-9,10-epoxy-stearate, resulting from epoxidation of methyl oleate, which was present (6.5%) in the starting material. ^{1}H NMR of cis-9,10-epoxy-stearate (300 MHz, CDCl3): δ 3.65 (s, 3H, COOC*H*$_3$), 2.88 (m, 2H, epoxy-C*H*), 2.29 (t, 2H, 2-C*H*$_2$), 1.60 (t, 2H), 1.47 (m, 6H), 1.20-1.45 (m, 20H), 0.86 (t, 3H).

Catalytic epoxidation of methyl linoleate using Mn(TPP)Cl/NaOCl/pyridine/ Bu_4NBr. A round bottom flask was charged with Mn(TPP)Cl (4.5 mg, 0.0064 mmol), pyridine (29.9 mg, 0.378 mmol), *n*-Bu_4NBr (37.1 mg, 0.115 mmol), methyl linoleate (100.5 mg, 0.341 mmol) and CH_2Cl_2 (8 mL). Aqueous NaOCl (Clorax, 6%, 1 mL) was added to the solution with stirring and after 8 h another 1 mL of NaOCl was added. After an additional 12 h of reaction time, GC analysis showed the total consumption of methyl linoleate. The reaction

mixture was washed with water (4 x 10 mL) and dried over anhydrous Na_2SO_4. Removal of solvent under vacuum afforded a yellow oil, 86.2 mg. ^1H NMR spectroscopy revealed that the major species was the mono-epoxidation product. ^1H NMR of mono-epoxide ($CDCl_3$, 400 MHz): δ 5.35-5.55 (m, 2H, vinyl-H), 3.64 (s, 3H, $COOCH_3$), 2.90 (m, 2H, epoxy-C*H*), 2.1-2.4 (m, 2H, 11-CH_2), 2.28 (t, 2H, 2- CH_2), 2.01 (m, 2H, adjacent to vinyl),1.2-1.6 (m, CH_2), 0.87 (m, 3H, 18-CH_3). The presence of diepoxide was observed with a mono:diepoxide ratio of 3.5:1. Minor peaks around 3.4 and 4.1 ppm were also observed. See text for assignments.

Results and Discussion

We examined the utility of metalloporphyrins for catalyzing the epoxidation of methyl linoleate. Mn(TPP)Cl (2 mol%) was employed as a catalyst using NaOCl (6%) as the oxidant in the presence of a phase transfer agent, *n*-Bu_4NBr. Pyridine was added to reduce the oxidative degradation of the catalyst. NaOCl was added in two portions (2.35 equiv each) over an 8-h interval. The reaction proceeded relatively slowly, taking ~20h to consume all the starting methyl linoleate. After workup, the ^1H NMR spectrum showed that mono-epoxide was the major product. Vinylic (5.35-5.55 ppm) and epoxy (2.9 ppm) proton signals were both observed as 2H multiplets. Its spectrum was also identical to that of an authentic sample of methyl vernoleate. The presence of diepoxide was also observed with a monoepoxide:diepoxide ratio of ~3.5 to 1. The level of overall epoxidation was about 61%, as determined by the disappearance of vinylic protons and the appearance of epoxy protons (2.8-3.1 ppm). Notably, very small peaks around 3.4 and 4.1 ppm were also observed,

indicating the presence of hydroxy groups, probably resulting from epoxide ring opening reactions or allylic oxidation (< 5%).

Fe(TPP)Cl was examined under similar conditions, using NaOCl (6%) as the oxidant in the presence of a phase transfer agent. However, the epoxidation reaction was significantly slower than the Mn(TPP)Cl-catalyzed process. Methyl linoleate was still present after 5 days of reaction even with a higher catalyst loading (~4 mol%) and a larger amount of oxidant (6.3 molar equiv). The degradation of Fe(TPP)Cl catalyst was quite fast as the characteristic dark brown color of the iron(III) porphyrin faded within 1 h.

MTO was found to be a highly effective catalyst for the epoxidation of methyl linoleate. With 4 mol% of MTO and 6.6 equivalents of H_2O_2, methyl linoleate was epoxidized within 4h in 88% isolated yield. The product obtained by this procedure has the identical NMR spectrum as that obtained from mCPBA epoxidation of methyl linolate. The complete disappearance of vinylic protons at 5.35 ppm and the appearance of epoxide protons at 3.07 and 2.95 ppm in the ^{1}H NMR spectrum indicated the total conversion of double bonds to epoxides. In accord with this, alkenic carbons were not observed in the ^{13}C NMR spectrum. Instead, seven peaks around 50-60 ppm were attributed to epoxide carbons. This also suggested that the product diepoxide was actually a mixture of diastereomers with an *anti:syn* ratio of approximately 1:1. The presence of hydroxy groups was not detected. The yellow color maintained throughout the reaction is characteristic of the catalytically active species responsible for epoxidation, indicating it is still active for catalysis (14).

The reaction course of the MTO-catalyzed epoxidation of methyl linoleate was further followed in $CDCl_3$ via NMR spectroscopy, using 1 mol% catalyst (Table 1). It is clear that the activity of this catalytic system decreased over time as the consumption of

methyl linoleate became slower with time and the accumulation of pyridine oxide was evident from ^{1}H NMR spectroscopy (14). Unlike the enzyme-catalyzed system (4), the formation of diepoxide occurred in the early stages of the reaction and well before the total consumption of methyl linoleate.

Table 1: Epoxidation of methyl linoleate catalyzed by MTO[a]

Time (h)	Methyl linoleate %	Monoepoxide %	Diepoxide %	Epoxidation[b] %
0.5	46.0	51.9	2.1	28.5
1.0	30.9	59.7	9.3	41.7
2.0	11.8	65.4	22.8	53.3
3.0	6.7	65.1	28.2	62.8
4.5	1.4	58.5	40.1	72.0
6.0	0	51.8	48.2	76.8

(a) Reaction condition: 1 mol% MTO, 24 mol% pyridine, 3.6 equiv H_2O_2. (b) Epoxidation was determined by the disappearance of vinyl proton signals by ^{1}H NMR spectroscopy.

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GENERAL CONCLUSIONS

Few transition metal 1,2-diolato complexes have been investigated previously. In this work, the first examples of group 4 metalloporphyrin 1,2-diolato complexes were prepared through a number of synthetic strategies. Chelating pinacolato complexes were prepared by metathesis of (TTP)MCl_2 (M = Ti, Zr, Hf) with disodium pinacolate. More generally, imido metalloporphyrin complexes, (TTP)M=NR, proved to be useful precursors to various diolato complexes, although the reactions also depended on the metal atoms and the steric bulk of imido ligands. For titanium porphyrins, diolato complexes could be obtained from reductive coupling reactions of organic carbonyl compounds with a readily available titanium(II) alkyne adduct. This route proved invaluable in the preparation of unsymmetrical diolato complexes via cross coupling of two different carbonyl compounds.

These group 4 metalloporphyrin diolato complexes undergo C-C cleavage reactions to produce organic carbonyl compounds. A catalytic cycle transforming vicianl diols to carbonyl compounds evolved from this reactivity, utilizing (TTP)Ti=O as a catalyst and atmospheric dioxygen as the oxidant. It was also found that (TTP)Ti=O was capable of catalyzing the oxidation of α-hydroxy ketones to α-diketones. Titanium porphyrin diolato and enediolato complexes were likely intermediates in these transformations. Furthermore, it appears to be quite general that high valent metalloporphyrin complexes can catalyze the diol oxidative cleavage and benzyl alcohol oxidation reactions with dioxygen.

Efforts were extended to reactions of vicinal diols with tin (group 14) porphyrins, where a greater structural diversity was exhibited. Mono-, bis-alkoxo, and chelating diolato complexes were obtained, depending on the diol and the stoichiometry employed. Like

titanium porphyrins, tin porphyrin complexes promoted the oxidative cleavage of vicinal diols and the oxidation of α-ketols to α-diketones in the presence of dioxygen.

In extending the chemistry of metalloporphyrins and analogous complexes, asymmetric catalysis was also investigated. Two iron(II) chiral porphyrins were found to be efficient catalysts for cyclopropanation of styrene with diazo reagents, though with modest enantio control. Closely related chiral tetraaza macrocyclic ligands were designed and synthesized. Some of them were examined as chiral ligands in iron(II) catalyzed cyclopropanations and showed promise for further investigation.

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