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Guodong Du
Iowa State University

Arkady Ellern
Iowa State University, ellern@iastate.edu

L. Keith Woo
Iowa State University, kwoo@iastate.edu

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Reaction of Tin Porphyrins with Vicinal Diols

Abstract

Reactions of tin porphyrins with vicinal diols were investigated. Treatment of (TTP)Sn(C:CPh)₂ or (TTP)Sn(NHtoly)₂ with pinacol and 2,3-diphenylbutane-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)SnII and ketones. Reaction of (TTP)Sn(C:CPh)₂ with 1 equivalent of *o*-catechol generated (TTP)Sn(C:CPh)(OC₆H₄OH) (**3**), which subsequently transformed into (TTP)Sn(OC₆H₄O) (**4**). With excess catechol, disubstituted (TTP)Sn(OC₆H₄OH)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: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 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)(OC₆H₄OH) (**3**) was determined by X-ray crystallography.

Disciplines

Chemistry

Comments

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Reaction of Tin Porphyrins with Vicinal Diols

Guodong Du, Arkady Ellern, and L. Keith Woo*

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

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Reactions of tin porphyrins with vicinal diols were investigated. Treatment of (TTP)Sn(C≡CPh)₂ or (TTP)Sn(NHtoly)₂ with pinacol and 2,3-diphenylbutane-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≡CPh)₂ with 1 equivalent of *o*-catechol generated (TTP)Sn(C≡CPh)(OC₆H₄OH) (**3**), which subsequently transformed into (TTP)Sn(OC₆H₄O) (**4**). With excess catechol, disubstituted (TTP)Sn(OC₆H₄OH)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≡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 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)(OC₆H₄OH) (**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 the corresponding main group elements (group *n* + 10) were 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 metallocporphyrins³ as well as tin (group 14) porphyrins.⁴ Although some chemical similarities exist, significant differences are often observed. For example, treatment of (TTP)SnCl₂ with lithium phenylacetylide generated a σ -bond-

ed bisalkynyl complex, *trans*-(TTP)Sn(C≡CPh)₂.⁵ Quite surprisingly, the same reaction with (TTP)TiCl₂ 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 metallocporphyrin diolato complexes,⁷ efforts were extended to reactions of tin porphyrins with various diols. Although 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

* Author to whom correspondence should be addressed. E-mail: kwoo@iastate.edu.

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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. $(\text{TTP})\text{SnCl}_2$,⁹ $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})_2$,⁵ $(\text{TTP})\text{Sn}(\text{OH})_2$,¹⁰ and $(\text{TTP})\text{Sn}^{4b}$ 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

¹H and ¹³C 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 ($\text{C}_6\text{D}_5\text{H}$, 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 $(\text{TTP})\text{Sn}(\text{NHtoly})_2$. To a stirred solution of $(\text{TTP})\text{SnCl}_2$ (183 mg, 0.213 mmol) in 16 mL of toluene at -25 °C was added LiNHtoly (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%. ¹H NMR (CDCl_3 , 400 MHz): δ 8.97 (s, 8H, β -H), 8.03 (d, 8H, $J = 7.8$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.58 (d, 8H, $J = 7.8$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 5.40 (d, 4H, $J = 7.8$ Hz, *m*- $\text{NHC}_6\text{H}_4\text{CH}_3$) 2.72 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 1.81 (d, 4H, $J = 7.8$ Hz, *o*- $\text{NHC}_6\text{H}_4\text{CH}_3$), 1.69 (s, 6H, $\text{NHC}_6\text{H}_4\text{CH}_3$), -5.08 (s, 2H, $\text{NHC}_6\text{H}_4\text{CH}_3$). The ¹H NMR spectrum (C_6D_6) of $(\text{TTP})\text{Sn}(\text{NHtoly})_2$ prepared by an amine exchange reaction⁵ has been reported.

Synthesis of $(\text{TTP})\text{Sn}[\text{OC}(\text{Me})_2\text{C}(\text{Me})_2\text{O}]$ (1). To a solution of $(\text{TTP})\text{Sn}(\text{NHtoly})_2$ (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 a freezer at -25 °C for 6 d. The resulting dark red product was collected by filtration. Yield: 15 mg (53%). ¹H NMR (C_6D_6 , 400 MHz): δ 9.19 (s, 8H, β -H), 8.31 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.97 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.29 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 2.38 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), -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 ($(\text{TTP})\text{Sn}^+$). Anal. Found: C, 72.32; H, 5.90; N, 5.85. Calcd for $\text{C}_{54}\text{H}_{48}\text{N}_4\text{O}_2\text{Sn}$: C, 71.77; H, 5.35; N, 6.20.

Synthesis of $(\text{TTP})\text{Sn}[\text{OC}(\text{Me})(\text{Ph})\text{C}(\text{Me})(\text{Ph})\text{O}]$ (2). To a solution of $(\text{TTP})\text{Sn}(\text{NHtoly})_2$ (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 a freezer at -25 °C for 3 d. Filtration provided the desired product $(\text{TTP})\text{Sn}[\text{OC}(\text{Me})(\text{Ph})\text{C}(\text{Me})(\text{Ph})\text{O}]$. Yield: 16 mg (48%). ¹H NMR (C_6D_6 , 400 MHz): δ 9.24 (s, 8H, β -H), 8.25 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 8.05 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.26 (d, 8H, $J = 7.6$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 6.68 (m, 6H, *p,m*- C_6H_5), 5.88 (m, 4H, *o*- C_6H_5), 2.40 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), -1.69 (s, 6H, OCCH_3). UV–vis (toluene): 410 (sh), 430 (Soret), 490, 564, 604 nm. The presence of $(\text{TTP})\text{Sn}$ (~8%) was observed by its ¹H NMR β -H signal at 9.19 ppm.

Synthesis of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (3). A solution of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})_2$ (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 a freezer at -25 °C for 23 h. The dark green microcrystalline product **3** was collected by filtration and dried under vacuum. This compound could be stored with air over weeks. Yields: 24 mg (77%). ¹H NMR (C_6D_6 , 400 MHz): δ 9.18 (s, 8H, β -H), 8.02 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.25 (d, 8H, $J = 8.4$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 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, $\text{OC}_6\text{H}_4\text{OH}$), 5.71 (d, 1H, $J = 6.0$ Hz, $\text{OC}_6\text{H}_4\text{OH}$), 5.44 (m, 3H, *o*- C_6H_5 and $\text{OC}_6\text{H}_4\text{OH}$), 2.38 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 1.67 (d, 1H, $J = 7.2$ Hz, $\text{OC}_6\text{H}_4\text{OH}$), 0.57 (s, 1H, $\text{OC}_6\text{H}_4\text{OH}$). IR (KBr): 3440 (OH), 2129 ($\text{C}\equiv\text{C}$) 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 ($\text{M}^+ - \text{C}\equiv\text{CPh}$), 787 ($(\text{TTP})\text{Sn}^+$). The molecular structure of this complex was solved by X-ray crystallography (vide infra).

Generation of $(\text{TTP})\text{Sn}(\text{OC}_6\text{H}_4\text{O})$ (4) from **3.** An NMR tube equipped with a Teflon stopcock was charged with $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (**3**) (1.4 mg, 1.4 μmol) and C_6D_6 . After 12 d of heating in a sand bath (~ 120 °C), $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (**3**) was consumed, and a new species $(\text{TTP})\text{Sn}(\text{OC}_6\text{H}_4\text{O})$ (**4**) was observed by ¹H NMR spectroscopy. This species could be stored in air over months without noticeable change. ¹H NMR data for **4**: δ 9.15 (s, 8H, β -H), 8.02 (m, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.87 (m, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.25 (d, 8H, $J = 8.4$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 5.65 (m, 2H, $\text{OC}_6\text{H}_4\text{O}$), 5.38 (m, 2H, $\text{OC}_6\text{H}_4\text{O}$), 2.38 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$). UV–vis (CH_2Cl_2): 427 (Soret), 561, 602 nm. Free $\text{PhC}\equiv\text{CH}$ (1 equiv) was also observed.

Synthesis of $(\text{TTP})\text{Sn}(\text{o-OC}_6\text{H}_4\text{OH})_2$ (5). A solution of $(\text{TTP})\text{Sn}(\text{NHtoly})_2$ (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 was reduced to 3 mL in vacuo. Then it was layered with hexane (2 mL) and placed in a freezer at -25 °C for 14 h. The brown-red product was collected by filtration and dried under vacuum. Yield: 18 mg (80%). ¹H NMR (CDCl_3 , 400 MHz): δ 9.14 (s, 8H, β -H), 8.07 (d, 8H, $J = 8.0$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.59 (d, 8H, $J = 7.6$ Hz, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 5.63 (td, 2H, $\text{OC}_6\text{H}_4\text{OH}$), 5.31 (dd, 2H, $\text{OC}_6\text{H}_4\text{OH}$), 5.16 (td, 2H, $\text{OC}_6\text{H}_4\text{OH}$), 2.72 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 1.37 (dd, 2H, $\text{OC}_6\text{H}_4\text{OH}$), 0.01 (s, 2H, $\text{OC}_6\text{H}_4\text{OH}$). IR (KBr): 3455 (OH). UV–vis (toluene): 426 (5.26), 523 (3.52), 563 (3.95), 603 (3.79).

Synthesis of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OCH}_2\text{CH}_2\text{OH})$ (6). A mixture of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})_2$ (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 a 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. ¹H NMR (C_6D_6 , 400 MHz): δ 9.18 (s, 8H, β -H), 8.03 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.24 (d, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 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*- $\text{C}_6\text{H}_4\text{CH}_3$), 0.61 (m, 2H, $\text{OCH}_2\text{CH}_2\text{OH}$), -1.65 (m, 1H, $\text{OCH}_2\text{CH}_2\text{OH}$), -1.95 (m, 2H, $\text{OCH}_2\text{CH}_2\text{OH}$). IR (KBr): 3432 (OH), 2123 ($\text{C}\equiv\text{C}$). UV–vis (toluene): 414 (4.59), 434 (5.56), 532 (3.47), 572 (4.08), 613 (4.12). MS (EI): m/z 888 ($\text{M}^+ - \text{OCH}_2\text{CH}_2\text{OH}$), 787 ($(\text{TTP})\text{Sn}^+$). Anal. Found: C, 70.87; H, 5.53; N, 5.37. Calcd. for $\text{C}_{58}\text{H}_{46}\text{N}_4\text{O}_2\text{Sn}\cdot\text{CH}_2\text{Cl}_2$: C, 70.92; H, 4.84; N, 5.61.

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Synthesis of (TTP)Sn(OCH₂CH₂OH)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 CH₂Cl₂ (1 mL) solution with hexane (2 mL), allowing the mixture to stand at -25 °C, filtering, and drying the solid in vacuo. ¹H NMR (C₆D₆, 400 MHz): δ 9.16 (s, 8H, β-H), 8.03 (d, 8H, *J* = 8.0 Hz, *meso*-C₆H₄-CH₃), 7.25 (d, 8H, *J* = 8.0 Hz, *meso*-C₆H₄CH₃), 2.38 (s, 12H, *meso*-C₆H₄CH₃), 0.61 (m, 4H, OCH₂CH₂OH), -1.54 (m, 2H, OCH₂-CH₂OH), -1.95 (m, 4H, OCH₂CH₂OH). 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 C₅₂H₄₆N₄O₄Sn·0.25CH₂Cl₂: 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), Ph₃CH (1.2 mg, 4.9 μmol), and ~0.5 mL of C₆D₆. 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 (C₆D₆, 400 MHz): 9.15 (s, 8H, β-H), 8.06 (t, 8H, *J* = 9.2 Hz, *meso*-C₆H₄CH₃), 7.27 (t, 8H, *J* = 9.2 Hz, *meso*-C₆H₄CH₃), 6.46 (t, 1H, *J* = 7.6 Hz, *p*-C₆H₅), 6.42 (t, 1H, *J* = 7.2 Hz, *p*-C₆H₅), 6.33 (t, 2H, *J* = 7.6 Hz, *m*-C₆H₅), 6.12 (m, 3H, *m*-C₆H₅ and *p*-CCC₆H₅), 5.97 (t, 2H, *J* = 8.0 Hz, *m*-CCC₆H₅), 5.42 (d, 2H, *J* = 8.0 Hz, *o*-CCC₆H₅), 4.97 (d, 2H, *J* = 7.6 Hz, *o*-C₆H₅), 3.69 (d, 2H, *J* = 7.2 Hz, *o*-C₆H₅), 2.39 (s, 12H, *meso*-C₆H₄CH₃), 1.60 (m, CHPhOH), -1.11 (d, 1H, *J* = 6.8 Hz, CHPhOH), -1.88 (d, 1H, *J* = 3.2 Hz, OCHPh). 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 (C₆D₆, 400 MHz): 9.09 (s, 8H, β-H), 8.09 (d, 8H, *J* = 8.0 Hz, *meso*-C₆H₄CH₃), 7.30 (d, 8H, *J* = 7.6 Hz, *meso*-C₆H₄CH₃), 6.45 (m, 8H, *m,p*-C₆H₅), 6.17 (t, 4H, *J* = 7.2 Hz, *m*-C₆H₅), 5.22 (d, 4H, *J* = 7.6 Hz, *o*-C₆H₅), 3.95 (d, 4H, *J* = 7.2 Hz, *o*-C₆H₅), 2.42 (s, 12H, *meso*-C₆H₄CH₃), 1.64 (m, 2H, CHPhOH), -0.73 (d, 2H, CHPhOH), -1.62 (d, 2H, OCHPh). 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 %), Ph₃CH (2.5 mg, 10 μmol, internal standard), and C₆D₆ (~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 by 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 μmol), ethylene glycol (3.2 mg, 52 μmol), Ph₃CH (1.7 mg, 7.0 μmol), and ~0.6 mL of C₆D₆. 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(OCH₂CH₂OH)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), Ph₃CH

Table 1. Crystal Data and Structure Refinement for Complex 3

empirical formula	C ₆₂ H ₄₆ N ₄ O ₂ Sn
fw	997.72
temperature	173(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	P2 ₁ /c
<i>a</i>	10.594(3) Å
<i>b</i>	32.673(9) Å
<i>c</i>	15.814(4) Å
α	90°
β	98.477(5)°
γ	90°
volume	5414(2) Å ³
<i>Z</i>	4
density (calculated)	1.224 mg/m ³
absorption coefficient	0.517 mm ⁻¹
data/restraints/parameters	6589/0/622
goodness-of-fit on F ²	1.090
final R indices ^a [<i>I</i> > 2σ(<i>I</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 e ⁻ Å ⁻³

^aR1 = Σ||F_o| - |F_c||/Σ|F_o| and wR2 = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]}^{1/2}.

(2.4 mg, 9.8 μmol), and ~0.5 mL of C₆D₆. 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), Ph₃CH (2.4 mg, 9.8 μmol), and ~0.5 mL of C₆D₆. 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 (C₆D₆, 400 MHz): δ 6.17 (s, 1H, OH), 5.73 (t, 1H, *J* = 4.6 Hz, vinyl-H), 1.95 (t, 2H, COCH₂), 1.60 (q, 2H, CHCH₂), 1.22 (quintet, 2H, COCH₂CH₂). ¹H NMR in CDCl₃ (400 MHz): δ 6.13 (t, 1H, *J* = 4.6 Hz, vinyl-H), 5.95 (s, 1H, OH), 2.52 (t, 2H, COCH₂), 2.38 (q, 2H, CHCH₂), 1.99 (quintet, 2H, COCH₂CH₂).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 × 0.3 × 0.3 mm³ 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 Kα 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 measurements¹³ using SADABS software.¹⁴ Details of the X-ray structure determination are summarized in Table 1.

The systematic absences in the diffraction data were consistent for the monoclinic space group P2₁/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.

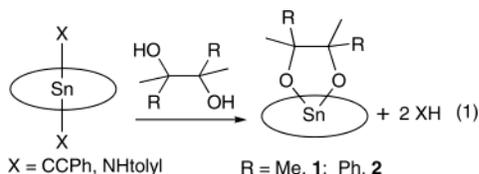
(12) Amon, C. M.; Banwell, M. G.; Gravatt, G. L. *J. Org. Chem.* **1987**, *52*, 4851.

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(14) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library. Sheldrick, G., Bruker Analytical X-ray Systems, Madison, WI.

Results

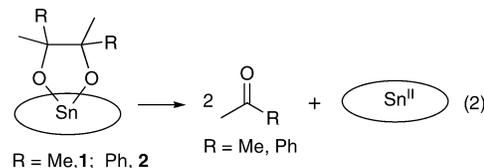
Synthesis of Tin Porphyrin Diolato Complexes. Tin porphyrins have high affinity for oxygen donor ligands.¹⁵ This is reflected in the reactions of MeOH with (TTP)Sn(C≡CPh)₂ that sequentially afforded (TTP)Sn(C≡CPh)(OMe) and then (TTP)Sn(OMe)₂.⁵ Replacement of MeOH with vicinal diols in these reactions 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 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)₂C(Me)₂O] (**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)₂C(Me)₂OH] (**1a**) and (TTP)Sn[OC(Me)₂C(Me)₂OH]₂ (**1b**), as monitored by ¹H NMR spectroscopy. However, attempts to isolate either **1a** or **1b** under a variety of conditions proved unsuccessful. Treatment of (TTP)Sn(C≡CPh)₂ with benzopinacol at ambient temperature in C₆D₆ 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)SnCl₂ 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)₂C(Me)₂O] (**1**) and (TTP)Sn[OC(Me)(Ph)C(Me)(Ph)O] (**2**) share similar ¹H 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 C₆D₆, 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)₂C(Me)₂O] (**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 ¹H NMR spectrum,¹⁰ although the signal for the OH group was not observed.

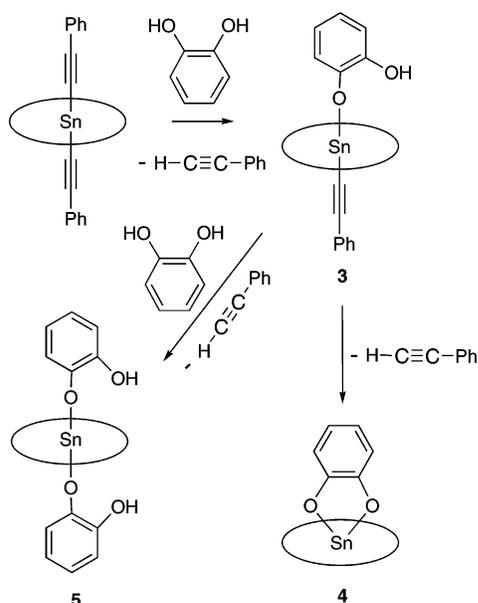
Reaction of Tin Porphyrins with *o*-Catechol. (TTP)Sn(C≡CPh)₂ and (TTP)Sn(NHtolyl)₂ react readily with excess *o*-catechol, resulting in the formation of a bis catecholato complex, (TTP)Sn(OC₆H₄OH)₂ (**5**), with two pendant -OH groups. This complex is sparingly soluble in nonpolar solvents such as C₆D₆, but readily soluble in polar CDCl₃. 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 ¹H 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*-C₆H₄(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)(OC₆H₄OH) (**3**). In the ¹H 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 C₆D₆ (~120 °C), this complex slowly transformed to a new species, as monitored by ¹H NMR spectroscopy. The β-H signal for (TTP)Sn(C≡CPh)(OC₆H₄OH) (**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(OC₆H₄O) (**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

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Scheme 1



OH functional groups. Unlike $(\text{TTP})\text{Sn}[\text{OC}(\text{Me})_2\text{C}(\text{Me})_2\text{O}]$ (**1**) and $(\text{TTP})\text{Sn}[\text{OC}(\text{Ph})(\text{Me})\text{C}(\text{Ph})(\text{Me})\text{O}]$ (**2**), this species was very inert to heating at 120 °C. Alternative routes to **4** were attempted. Reaction of $(\text{TTP})\text{SnCl}_2$ with the dilithium salt of catechol did not afford the expected diolato complex. Treatment of $(\text{TTP})\text{Sn}(\text{NHtoly})_2$ with 1 equiv of catechol in toluene resulted in no reaction; whereas with more than 2 equiv of catechol, the disubstituted product $(\text{TTP})\text{Sn}(\text{OC}_6\text{H}_4\text{OH})_2$ (**5**) was obtained.

Reaction of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})_2$ with Other Diols. As observed in the reaction of catechol, $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})_2$ 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, $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OCHRCHROH})$ ($\text{R} = \text{H}$, **6**; $\text{R} = \text{Ph}$, **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 $(\text{TTP})\text{Sn}(\text{OCHRCHROH})_2$ ($\text{R} = \text{H}$, **7**; $\text{R} = \text{Ph}$, **9**) can be obtained cleanly.

The ^1H NMR spectra of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OCH}_2\text{CH}_2\text{OH})$ (**6**) and $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})[\text{OCH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}]$ (**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 ^1H NMR signals of alkoxo ligands in complexes **7** and **9** are shifted downfield. In addition, it is observed that in $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OCH}_2\text{CH}_2\text{OH})$ (**6**), the alkoxo ligand is more labile than $-\text{C}\equiv\text{CPh}$ toward water, as $\text{HOCH}_2\text{CH}_2\text{OH}$ was detected within days upon exposure with air, while the acetylide ligand remained bound.

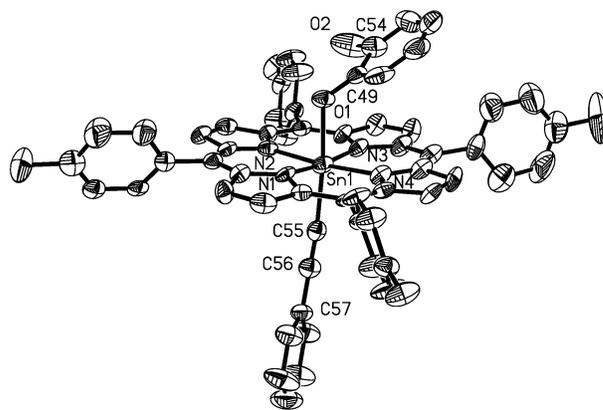
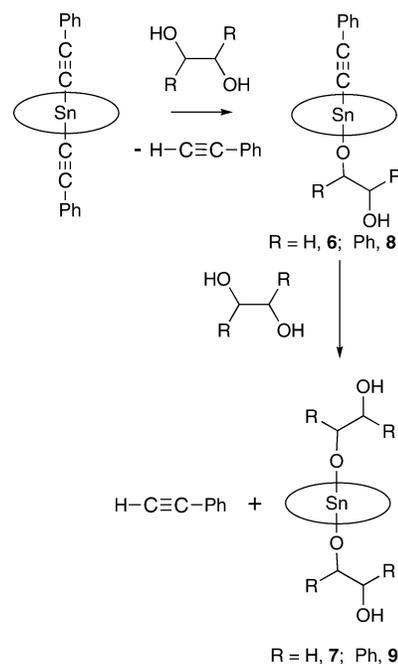


Figure 1. ORTEP representation of the structure of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (**3**).

Scheme 2



When pure $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OCH}_2\text{CH}_2\text{OH})$ (**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 $(\text{TTP})\text{Sn}(\beta\text{-H}: 9.19 \text{ ppm})$ was observed as well as other unidentifiable species.

Structure of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (3**).** The molecular structure of $(\text{TTP})\text{Sn}(\text{C}\equiv\text{CPh})(\text{OC}_6\text{H}_4\text{OH})$ (**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 ligands 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 toward 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 $(\text{TTP})\text{Sn}$ –

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)

(C≡CPh)₂,⁵ 2.212(4) and 2.196(4) Å in *trans*-(TTP)SnPh₂(CH₂-Cl₂), 2.210(7) and 2.193(7) Å in *cis*-(TBPP)SnPh₂¹⁶) 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)(OC₆H₄OH) is large voids of 218.4 Å³ found in the lattice that could capture organic solvents with up to 9 non-hydrogen atoms. However, the SQUEEZE routine from the PLATON package¹⁸ found only three “unaccounted” electrons per cell. The negative and positive residuals are almost equal (1.348 and -1.359 eÅ⁻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 C₆D₆ solution of 2,3-diphenylbutane-2,3-diol and 5.7 mol % (TTP)Sn(C≡CPh)₂ in a sealed NMR tube resulted in the conversion of diol to acetophenone in modest yield (55%, entry 1). Benzopinacol 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

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

^a For reaction conditions, see Experimental Section. ^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%).

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(OC₆H₁₀OH)₂ was observed without the formation of oxidation products.

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)SnCl₂, which possesses robust Sn–Cl bonds, the cleavage of benzopinacol to benzophenone was observed, although it was substantially slower compared to reactions with other tin porphyrins (entry 9).

Given the ability of (TTP)Ti=O to catalyze the oxidation of α-ketols to α-diketones, we further examined the utility of tin porphyrin complexes in this transformation. Heating an aerobic C₆D₆ 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 benzaldehyde (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 ¹H NMR spectroscopy.

Discussion

Reaction of Tin Porphyrins with Diols. The structure and coordination geometry of metal diolato complexes have

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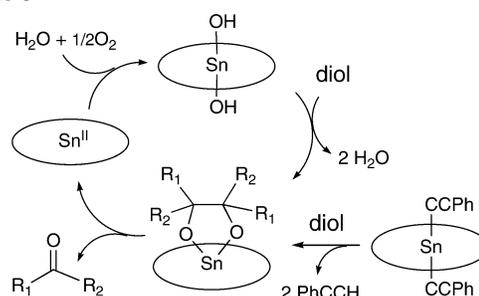
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been shown to be influenced greatly by the type of diolato moiety.²² Although chelated diolato complexes were invariably obtained for Ti porphyrins,⁷ the outcome of reactions between (TTP)Sn(C≡CPh)₂ or (TTP)Sn(NHtolyl)₂ and vicinal diols was dependent on the diols employed. Highly substituted vicinal diols tended to yield diolato chelate complexes, whereas less substituted diols preferred to form mono- and bisalkoxo complexes. With pinacol and 2,3-diphenylbutane-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 temperatures 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. On the other hand, it is possible to produce the diolato complex (TTP)Sn(OC₆H₄O) (**4**) by heating a C₆D₆ solution of (TTP)Sn(C≡CPh)(OC₆H₄OH) (**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≡CPh)(OCH₂CH₂OH) (**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≡CPh)₂ with pinacol and 2,3-diphenylbutane-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(OC₆H₄O) (**4**) from (TTP)Sn(C≡CPh)(OC₆H₄OH) (**3**). Moreover, protic acids do not seem to catalyze the conversion of a bisalkoxo species into a chelated diolato complex. For example, heating a solution of (TTP)Sn(OC₆H₄OH)₂ (**5**) in the presence of 5% acetic acid did not result in the formation of diolato complex **4**. 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. On the basis of analogous studies with (TTP)Ti=O-mediated oxidations,²¹ a probable

Scheme 3



catalytic cycle for the tin porphyrin-mediated diol cleavage is shown in Scheme 3. Sn(IV) complexes, such as (TTP)Sn(C≡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 N₂. 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-diphenylbutane-2,3-diol in the presence of (TTP)Sn^{II}. Under N₂, no acetophenone production was observed, whereas 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≡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(OCH₂CH₂OH)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≡CPh)₂ under N₂ was monitored by ¹H 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. This behavior contrasts with the related oxotitanium porphyrin-mediated reaction, where an enediolato species (TTP)Ti[OC(Ph)=C(Ph)O] was readily observed.²¹ We have also shown that titanium(II) porphyrins react with benzil to afford the enediolato complex (TTP)Ti[OC(Ph)=C(Ph)O]. Treatment of (TTP)Sn(II) with benzil does not produce the analogous tin(IV) product. Although the generation of such tin(IV) porphyrin species has been elusive, non-porphyrin tin enediolato complexes are known.²⁵ Thus, by analogy with the (TTP)Ti=O-mediated reaction, we believe an enediolato

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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 cannot be oxidized under the same conditions.

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the National Science Foundation for financial support of this work.

Supporting Information Available: Tables of crystallographic data for **3** including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters; and proton NMR spectra for **1** and **6**. Crystallographic information files for the studied complexes (cif). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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