Synthesis, Characterization, and Reactivity of Group 4 Metalloporphyrin Diolate Complexes

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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 $(TTP)Hf[OCR_1R_2CR_1R_2O]$ ($R_1 = R_2 =$ 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 $(TTP)Ti[OCR_1R_2CR_1R_2O]$ ($R_1 = R_2 =$ 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 reaction, producing carbonyl compounds and oxometalloporphyrin species. For less substituted diolates **7** and **8**, an array of products including the enediolate complexes $(TTP)Ti[OC(Ar)C(Ar)O]$ (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.[1] 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.[2,3] Although chelating ligands containing phenolates are well known, especially in salen[4] chemistry, chelating bis(alkoxo) complexes are relatively less studied.[5]

A few group 4 metalloporphyrin complexes bearing alkoxide or aryloxide ligands have been reported. For example, $(TTP)Ti(OR)_2$ (R = Ph, Me, *tert*-butyl)[6] and $(OEP)Zr(OR)_2$ (R = *tert*-butyl, $SiMe_3$)[7] 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.[6,8] Metalloporphyrins bearing 1,3-dialkoxo chelating ligands, $(TTP)Zr[OC(^{t}Bu)CHC(R)(Me)O]$ (R = *tert*-butyl, *n*-hexyl)[9] and $(OEP)M[OC(R)CHC(R)O]$ (M = Zr, Hf; R = Me, Ph),[10] 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.[11] 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 $(TTP)MCl_2$[12] and imido complexes $(TTP)M=NAr^{iPr}$ (M = Ti, Hf)[13] (where Ar^{iPr} = 2,6-diisopropylphenyl) and $(TTP)Ti=N^{i}Pr$[14] were obtained as described in previous studies. Disodium pinacolate was pre-

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(4) 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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pared by reaction of the free pinacol with NaH in toluene. Hydrobenzoin (1:1 *dl*:meso mixture), 1,2-di(*p*-tolyl)ethylene glycol (1:1 *dl*:meso), and *dl*-2,3-diphenylbutane-2,3-diol were synthesized according to the literature procedures.[15]

^{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$_6$D$_5$H; 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.[36] 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)$_2$C(Me)$_2$O] (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$_6$D$_6$, 300 MHz): δ 9.23 (s, 8H, β-H), 8.38 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.95 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.29 (dd, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.40 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$), −0.98 (s, 12H, OC*Me*$_2$). ^{13}C NMR (C$_6$D$_6$, 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$_4$O$_2$Hf: 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$_6$D$_6$, 300 MHz): δ 9.27 (q, 8H, β-H), 8.32 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, *meso*-C$_6$H$_4$CH$_3$), 8.03 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, *meso*-C$_6$H$_4$CH$_3$), 7.28 (t, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.69 (m, 6H, *p*, *m*-C$_6$H$_5$), 5.79 (dd, 4H, *o*-C$_6$H$_5$), 2.41 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$), −1.36 (s, 6H, OC(C*H*$_3$)(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$_6$D$_6$, 300 MHz): δ 9.24 (s, 8H, β-H), 8.02 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 7.28 (m, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.50 (t, 4H, $^3J_{H-H}$ = 7.6 Hz, *p*-C$_6$H$_5$), 6.39 (t, 8H, $^3J_{H-H}$ = 7.6 Hz, *m*-C$_6$H$_5$), 5.06 (d, 8H, $^3J_{H-H}$ = 7.6 Hz, *o*-C$_6$H$_5$), 2.42 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 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), and the mixture was filtered to afford the purple-red diolate **4** (27.5 mg, 47%). Analytically pure samples were obtained by layering a CH$_2$Cl$_2$ 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$_6$D$_6$, 300 MHz): δ 9.09 (s, 8H, β-H), 8.43 (d, 4H, *meso*-C$_6$H$_5$), 8.00 (d, 4H, *meso*-C$_6$H$_5$), 7.50 (dd, 8H, *meso*-C$_6$H$_5$), 7.44 (d, 4H, *meso*-C$_6$H$_5$), −0.96 (s, 12H, OC*Me*$_2$). ^{13}C NMR (C$_6$D$_6$, 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$_4$O$_2$Zr: 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$_6$D$_6$, 400 MHz): δ 9.15 (s, 8H, β-H), 8.33 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 8.05 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.29 (br s, 8H, *meso*-C$_6$H$_4$CH$_3$), 2.39 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$), −1.25 (s, 12H, OC*Me*$_2$). ^{13}C NMR (C$_6$D$_6$, 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 similar to the above data, but the sample was contaminated with 15% (TTP)TiO.

Synthesis of (TTP)Ti[OC(Me)(Ph)C(Me)(Ph)O] (6). A solution of (TTP)Ti=N^{i}Pr (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$_6$D$_6$, 300 MHz): δ 9.19 (s, 8H, β-H), 8.27 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 8.05 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.27 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.68 (m, 6H, *p*, *m*-C$_6$H$_5$), 5.55 (d, 4H, *o*-C$_6$H$_5$), 2.40 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$), −1.57 (s, 6H, OC(Ph)C*H*$_3$). 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$_6$D$_6$, 400 MHz): *dl*-diolate: δ 9.15 (q, 8H, *J* = 5.6 Hz, β-H), 8.14 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.98 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.26 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.61 (m, 6H, *p*, *m*-C$_6$H$_5$), 4.96 (d, 4H, $^3J_{H-H}$ = 6.6 Hz, *o*-C$_6$H$_5$), 2.90 (s, 2H, OC*H*), 2.39 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$); *meso*-diolate: δ 9.19 (s, 8H, β-H), 6.32 (m, 6H, *p*, *m*-C$_6$H$_5$), 4.62 (d, 4H, $^3J_{H-H}$ = 7.5 Hz, *o*-C$_6$H$_5$), 3.20 (s, 2H, OC*H*), 2.37 (s, 12H, *meso*-C$_6$H$_4$C*H*$_3$). 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

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was charged with (TTP)Ti[OCH(Ph)CH(Ph)O] (**7**) (2.0 mg, 2.17 μmol), Ph$_3$CH (1.02 mg, 4.17 μmol, internal standard), and C$_6$D$_6$ (~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$_6$H$_4$CH$_3$), 7.92 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.25 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.61 (m, 6H), 5.71 (d, 4H), 2.39 (s, 12H, *meso*-C$_6$H$_4$CH$_3$). Benzaldehyde (δ 9.61, −CHO, 12%), benzyl alcohol (δ 4.24, −CH$_2$OH, 12%), and stilbene oxide (δ 3.84, PhCH, 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$_3$CH (1.2 mg, 4.91 μmol, internal standard), and C$_6$D$_6$ (~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, −CHO, 75%), benzyl alcohol (δ 4.24, −CH$_2$OH, 4.6%), benzil (δ 7.90, *o*-C$_6$H$_5$, 20%), and H$_2$O (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)ethylene glycol (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$_6$D$_6$, 300 MHz): *dl*-diolate: δ 9.17 (q, 8H, β-H), 8.15 (br s, 4H, *meso*- C$_6$H$_4$CH$_3$), 7.98 (br s, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.26 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.41 (d, 4H, *m*-C$_6$H$_4$CH$_3$), 4.95 (d, 4H, *o*-C$_6$H$_4$CH$_3$), 2.91 (s, 2H, OCH), 2.38 (s, 12H, *meso*-C$_6$H$_4$CH$_3$), 1.84 (s, 6H, C$_6$H$_4$CH$_3$); *meso*-diolate: δ 9.21 (s, 8H, β-H), 6.17 (d, 4H, *m*-C$_6$H$_4$CH$_3$), 4.61 (d, 4H, *o*-C$_6$H$_4$CH$_3$), 3.22 (s, 2H, OCH), 2.37 (s, 12H, *meso*-C$_6$H$_4$CH$_3$), 1.61 (s, 6H, C$_6$H$_4$CH$_3$). 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$_3$CH (1.02 mg, 4.17 μmol, as internal standard), and C$_6$D$_6$ (~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$_6$H$_4$CH$_3$), 1.78 (s, 6H, C$_6$H$_4$CH$_3$). Other peaks were obscured in aromatic region. Tolualdehyde (δ 9.68, −CHO, 20%), *p*-methylbenzyl alcohol (δ 4.31, −CH$_2$OH, 15%), and 1,2-ditolylethylene epoxide (δ 3.91, tolyl-CH, 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

1: R$_1$=R$_2$=Me
2: R$_1$=Me, R$_2$=Ph
3: R$_1$=R$_2$=Ph
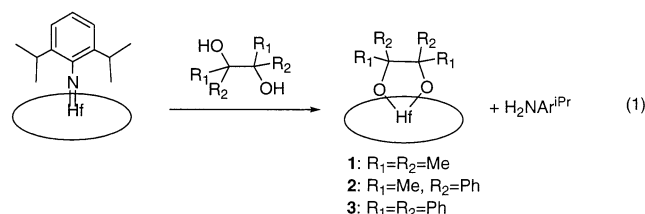
corresponding diolate complex (TTP)Hf[OC(Me)$_2$C-(Me)$_2$O] (**1**), as evidenced by ^{1}H NMR spectroscopy. This is in accord with the high oxophilicity of the group 4 transition metals. In a similar manner, (TTP)Hf[OC-(Me)(Ph)C(Me)(Ph)O] (**2**) and (TTP)Hf[OC(Ph)$_2$C(Ph)$_2$O] (**3**) were prepared in good yields. However, the reaction of (TTP)Hf=NAr^{iPr} with a less substituted diol, 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$_2$NAr^{iPr}. The ^{1}H NMR spectrum of this product[16] 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.

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
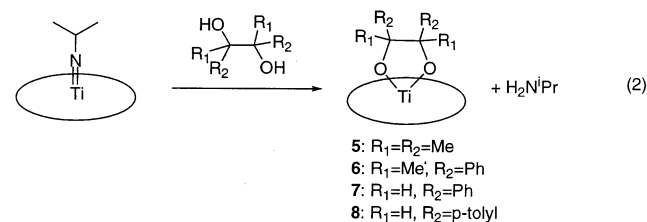
Alternatively, pinacolates could be prepared through salt elimination. Treatment of dichloro complexes, (TTP)MCl$_2$ (M = Ti, Hf), with disodium pinacolate in toluene afforded (TTP)M[OC(Me)$_2$C(Me)$_2$O] (M = Ti (**5**); Hf (**1**)) in high yields. This direct approach for preparing diolato metalloporphyrin complexes failed with benzopi-nacole, 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).[17] In a similar manner, (2,2′-biphenyldioxy)-(tetra-*tert*-butylphthalocyaninato)titanium(IV), (Pc)Ti-(BP), was synthesized by the reaction of (Pc)Ti=O with 2,2′-biphenol.[18] Thus, the possibility of using (TTP)-Ti=O as a starting material to prepare diolate complexes was explored and monitored by ^{1}H NMR spec-

(16) ^{1}H NMR of (TTP)Hf[OCH(Ph)CH(Ph)O] (C$_6$D$_6$): δ 9.25 (s, 8H, β-H), 8.18 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.94 (d, 4H, *meso*-C$_6$H$_4$CH$_3$), 7.25 (d, 8H, *meso*-C$_6$H$_4$CH$_3$), 6.72 (m, 6H, *p*, *m*-C$_6$H$_5$), 5.37 (br s, 4H, *o*-C$_6$H$_5$), 3.14 (s, 2H), 2.38 (s, 12H, *meso*-C$_6$H$_4$CH$_3$).
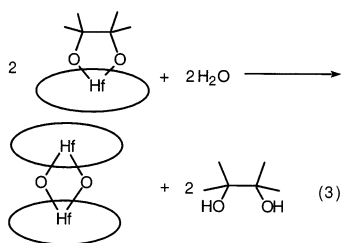(17) Deronzier, A.; Latour, J. M. *Nouv. J. Chim.* **1984**, *8*, 393.
(18) Kobayashi, N.; Muranaka, A.; Ishii, K. *Inorg. Chem.* **2000**, *39*, 2256.

troscopy. 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.[19] Similar line broadening was also observed in the cis-ligated tin porphyrin complexes (TTP)Sn(Me)$_2$[20] and (TPP)Sn(Ph)$_2$.[21]

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 on the basis of the similarity of its ^{1}H NMR spectrum with its zirconium analogue (eq 3).[9,22] The zirconium diolate **4** undergoes a similar

reaction with water. Diolate complexes **2** and **3** are seemingly inert toward 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)$_2$C(Me)$_2$O] (**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)$_2$C(Me)$_2$O] (**1**), was treated with benzopinacole (3.0 equiv) in C_6D_6, (TTP)Hf[OC(Ph)$_2$C(Ph)$_2$O] (**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)$_2$C(Me)$_2$O] (**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)$_2$C(Me)$_2$O] (**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)$_2$C(Ph)$_2$O] (**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 days. 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)$_2$C(Me)$_2$O] (**1**) thermalized to produce acetophenone and acetone, respectively (eq 4). Under N_2, these reactions proceeded to a

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

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(20) Chen, J.; Woo, L. K. *Inorg. Chem.* **1998**, *37*, 3269.
(21) Dawson, D. Y.; Sangalang, J. C.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 6082.
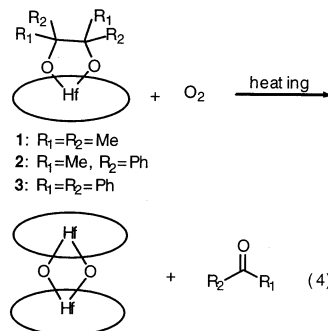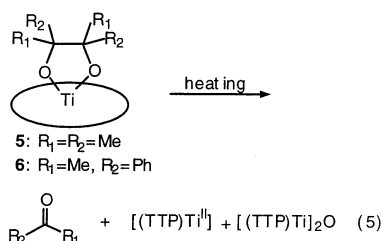(22) (a) Ryu, S.; Kim, J.; Yeo, H.; Kim. K. *Inorg. Chim. Acta* **1995**, *228*, 233. (b) Kim, H.-J.; Whang, Y.; Do, Y.; Kim, K. *Chem. Lett.* **1993**, 807.

much lower extent, producing only small amounts of

ketones and dimeric species, with starting diolates largely unchanged after extended heating in toluene-d_8 after 14 days. 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)$_2$C(Me)$_2$O] (**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).[23] One

5: R$_1$=R$_2$=Me
6: R$_1$=Me, R$_2$=Ph

$$ \underset{R_2}{\overset{O}{\|}}\underset{}{C}R_1 \ +\ [(TTP)Ti^{II}]\ +\ [(TTP)Ti]_2O \quad (5) $$

paramagnetic species could be only 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.[24] The other unreactive species was probably a Ti(III) μ-oxo complex, [(TTP)Ti]$_2$O,[25] 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.[26] 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, and imido complexes, have been prepared by the metathetical reaction of (por)MCl or (por)MCl$_2$ with various anion sources.[27] 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.[6] Diols such as benzopinacole tend to decompose to free radicals under strongly basic conditions[28] 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.[13,14] 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.[6,8,20] 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 analogue, 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 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)$_2$C(Me)$_2$O] 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.[5a] Under thermal conditions, extrusion of alkenes from diolate complexes has been reported.[5d,29] 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.[30] However, photochemical conditions do promote oxidative C–C cleavage of diolates as shown for Pt(II)[31] and Rh(III)[5a] complexes. In addition, transition metal diolate complexes have been postulated as possible intermediates in catalytic diol C–C cleavage reactions.[32] The metalloporphyrin com-

(23) The low yield of acetone may come from an inadequate pulse delay in ^{1}H NMR spectroscopy. See: Merkley, N.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 942–949.

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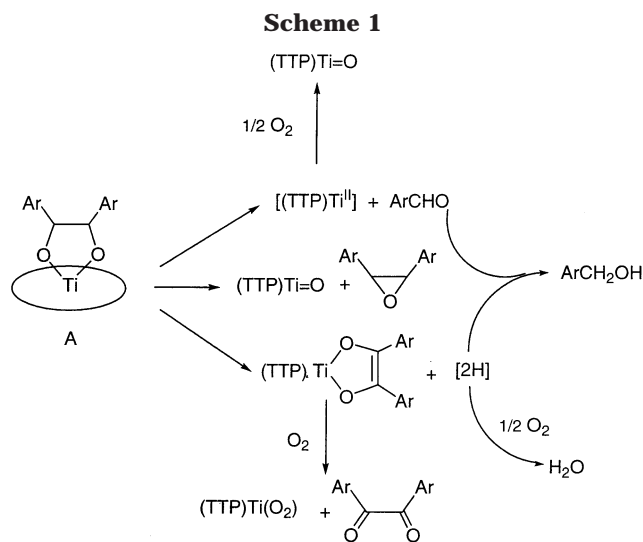(28) Holm, T. *Acta Chem. Scand. B* **1988**, *42*, 685.

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Scheme 1

plexes described here provide additional insight into thermal diolate cleavage reactions. Although the metalloporphyrin diolate complexes described here are 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 and zirconium cases. 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.[33] Enediolate complexes of early transition metals are also common, mainly obtained by treatment of dialkyl precursors with CO[34] or by oxidation of low-valent precursors with α-dicarbonyl compounds.[5c,35] However, the observation of dehydrogenation in diolate ligands to give

enediolates is unprecedented to the best of our knowledge. Bergman[5a] 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 the (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 analogues 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 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.[26] 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$_2$O was also observed as a byproduct when O$_2$ is present.

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