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Reductive Coupling Reactions of Carbonyl Compounds with a Low-Valent Titanium(II) Porphyrin Complex

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–c**, **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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Reductive Coupling Reactions of Carbonyl Compounds with a Low-Valent Titanium(II) Porphyrin Complex

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The reactions of a low-valent titanium(II) tetratolylporphyrin complex, (TTP)Ti(η^2 -PhC \equiv CPh) (**1**), with various aromatic aldehydes or aryl ketones afforded the reductive coupling products Ti(IV) diolato complexes (**2a–c**, **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.

Introduction

Low-valent titanium is used widely in metal-mediated organic synthesis.¹ Correspondingly, titanium-based pinacol coupling and McMurry reactions have been extensively investigated and elegantly employed in the syntheses of complex natural products.² Recent studies focused on the stereo- and enantiocontrol of pinacol coupling reactions under catalytic conditions. High diastereoselectivity has been achieved, although 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. CH₂Cl₂ was dried with P₂O₅, 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 through a pad of activated alumina. (TTP)Ti(η^2 -PhC \equiv CPh) (**1**)⁵ and (TTP)-TiCl⁸ were prepared according to literature procedures.

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 a proton solvent impurity (δ 7.15, C₆D₅H). 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*-ClC₆H₄)CH(*p*-ClC₆H₄)O] (2a**).** To a toluene solution of *p*-chlorobenzaldehyde (30 mg, 0.21 mmol) was added a solution of (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (91 mg, 0.10 mmol) in toluene (10 mL). The purple-red solution was stirred for ~40 min and filtered, and the solvent was

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removed in vacuo. The residue was taken up in toluene (2 mL), layered with hexane (6 mL), and placed in a freezer at $-25\text{ }^{\circ}\text{C}$ for ~ 18 h. Filtration, washing with hexane (2×2 mL), and drying under vacuum afforded a red-purple material, (TTP)-Ti[OCH(*p*-ClC₆H₄)CH(*p*-ClC₆H₄)O] (**2a**), which contained both *dl*- and *meso*-**2a** with a *dl*/*meso* ratio of 1.4 (63 mg, 63%). ¹H NMR (C₆D₆, 400 MHz): *dl*-**2a**, δ 9.13 (q, 8H, β -H), 8.10 (br, 4H, *meso*-C₆H₄CH₃), 7.94 (br, 4H, *meso*-C₆H₄CH₃), 7.25 (t, $J = 8.0$ Hz, 8H, *meso*-C₆H₄CH₃), 6.56 (d, $J = 8.0$ Hz, 4H, *m*-C₆H₄-Cl), 4.69 (d, $J = 8.0$ Hz, 4H, *o*-C₆H₄Cl), 2.59 (s, 2H, OCH), 2.37 (s, 12H, *meso*-C₆H₄CH₃); *meso*-**2a**, δ 9.16 (s, 8H, β -H), 6.30 (d, $J = 8.0$ Hz, 4H, *m*-C₆H₄Cl), 4.33 (d, $J = 8.0$ Hz, 4H, *o*-C₆H₄-Cl), 2.96 (s, 2H, OCH), 2.36 (s, 12H, *meso*-C₆H₄CH₃). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis (toluene): 553 (4.47), 427 (Soret, 5.48), 413 (5.52). The *dl* form of this complex has been reported previously.⁹

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 \equiv 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 a freezer at $-25\text{ }^{\circ}\text{C}$ 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%). ¹H NMR (C₆D₆, 300 MHz): *dl*-**2b**, δ 9.17 (q, 8H, β -H), 8.31 (br, 4H, *meso*-C₆H₄CH₃), 8.01 (br, 4H, *meso*-C₆H₄-CH₃), 7.25 (d, $J = 7.6$ Hz, 8H, *meso*-C₆H₄CH₃), 6.05 (s, 2H, C₆H₂(CH₃)₃), 5.77 (s, 2H, C₆H₂(CH₃)₃), 3.59 (s, 2H, OCHMes), 2.37 (s, 12H, *meso*-C₆H₄CH₃), 1.64 (s, 6H, C₆H₂(CH₃)₃), 0.52 (s, 12H, C₆H₂(CH₃)₃); *meso*-**2b**, δ 9.19 (s, 8H, β -H), 5.89 (s, 4H, C₆H₂(CH₃)₃), 3.34 (s, 2H, OCHMes), 2.36 (s, 12H, *meso*-C₆H₄CH₃). 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 \equiv CPh) with *p*-CH₃C₆H₄CHO. An NMR tube equipped with a Teflon stopcock was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (3.2 mg, 3.6 μ mol), *p*-CH₃C₆H₄-CHO (1.5 mg, 12 μ mol), Ph₃CH (1.7 mg, 7.0 μ mol, internal standard), and C₆D₆ (0.5 mL). Within 10 min, all of PhC \equiv CPh had been displaced and a diolate complex, (TTP)Ti[OCH(*p*-tolyl)CH(*p*-tolyl)O] (**2c**), was produced in 87% yield with a *dl*/*meso* ratio of 1.8. ¹H NMR (C₆D₆, 300 MHz): *dl* diolate, δ 9.17 (q, 8H, β -H), 8.15 (br s, 4H, *meso*-C₆H₄CH₃), 7.98 (br s, 4H, *meso*-C₆H₄CH₃), 7.26 (d, $J = 7.5$ Hz, 8H, *meso*-C₆H₄CH₃), 6.41 (d, $J = 7.5$ Hz, 4H, *m*-C₆H₄CH₃), 4.95 (d, $J = 7.5$ Hz, 4H, *o*-C₆H₄CH₃), 2.91 (s, 2H), 2.38 (s, 12H, *meso*-C₆H₄CH₃), 1.84 (s, 6H, C₆H₄CH₃); *meso* diolate, δ 9.21 (s, 8H, β -H), 6.17 (d, $J = 7.8$ Hz, 4H, *m*-C₆H₄CH₃), 4.61 (d, $J = 7.8$ Hz, 4H, *o*-C₆H₄-CH₃), 3.22 (s, 2H), 2.37 (s, 12H, *meso*-C₆H₄CH₃), 1.61 (s, 6H, C₆H₄CH₃). Other signals overlapped with the *dl* diolate in the aromatic region. UV-vis (toluene): 414 (5.26), 425 (5.38), 553 (4.36). These spectral data matched those for an authentic sample prepared by the reaction of (TTP)Ti=NⁱPr 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 \equiv 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%). ¹H NMR (C₆D₆, 300 MHz): *dl*-**3a**, δ 9.19 (s, 8H, β -H), 8.27 (br, 4H, *meso*-C₆H₄-CH₃), 8.05 (br, 4H, *meso*-C₆H₄CH₃), 7.27 (d, $J = 6.8$ Hz, 8H, *meso*-C₆H₄CH₃), 6.68 (m, 6H, *p*, *m*-C₆H₅), 5.55 (d, $J = 7.2$ Hz,

4H, *o*-C₆H₅), 2.40 (s, 12H, *meso*-C₆H₄CH₃), -1.57 (s, 6H, OC(Ph)CH₃); *meso*-**3a**, δ 6.35 (t, $J = 7.2$ Hz, 2H, *p*-C₆H₅), 6.29 (t, $J = 7.2$ Hz, 4H, *m*-C₆H₅), 4.48 (d, $J = 7.2$ Hz, 4H, *o*-C₆H₅), 2.40 (s, 12H, *meso*-C₆H₄CH₃), -0.73 (s, 6H, OC(Ph)CH₃). 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 \equiv 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 a freezer at $-25\text{ }^{\circ}\text{C}$ 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%). ¹H NMR (C₆D₆, 300 MHz): *dl*-**3b**, δ 9.21 (s, 8H, β -H), 8.29 (br, 4H, *meso*-C₆H₄CH₃), 8.06 (br, 4H, *meso*-C₆H₄CH₃), 7.26 (br, 8H, *meso*-C₆H₄CH₃), 6.32 (d, $J = 7.6$ Hz, 4H, *m*-C₆H₄OCH₃), 5.50 (d, $J = 7.6$ Hz, 4H, *o*-C₆H₄-OCH₃), 3.08 (s, 3H, C₆H₄OCH₃), 2.39 (s, 12H, *meso*-C₆H₄CH₃), -1.53 (s, 6H, OCCH₃); *meso*-**3b**, δ 5.96 (d, $J = 7.6$ Hz, 4H, *m*-C₆H₄OCH₃), 4.48 (d, $J = 7.6$ Hz, 4H, *o*-C₆H₄OCH₃), 2.94 (s, 3H, C₆H₄OCH₃), 2.39 (s, 12H, *meso*-C₆H₄CH₃), -0.72 (s, 6H, OCCH₃). 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 \equiv 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 a freezer at $-25\text{ }^{\circ}\text{C}$ 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%). ¹H NMR (C₆D₆, 300 MHz): *dl*-**3c**, δ 9.19 (q, 8H, β -H), 8.47 (br, 4H, *meso*-C₆H₄CH₃), 7.98 (br, 4H, *meso*-C₆H₄CH₃), 7.29 (m, 8H, *meso*-C₆H₄CH₃), 6.99 (t, $J = 7.2$ Hz, 2H, *m*-C₆H₅), 6.70 (t, $J = 7.2$ Hz, 2H, *p*-C₆H₅), 6.52 (t, $J = 7.2$ Hz, 2H, *m'*-C₆H₅), 5.75 (d, $J = 7.2$ Hz, 2H, *o'*-C₆H₅), 5.31 (d, $J = 7.2$ Hz, 2H, *o*-C₆H₅), 2.40 (s, 12H, *meso*-C₆H₄CH₃), -0.48 (m, 2H, CH₂CH₃), -0.93 (t, $J = 6.8$ Hz, 6H, CH₂CH₃), -2.27 (m, 2H, CH₂CH₃); *meso*-**3c**, δ 9.21 (s, 8H, β -H), 6.37 (t, $J = 7.2$ Hz, 2H, *p*-C₆H₅), 6.31 (t, $J = 7.2$ Hz, 4H, *m*-C₆H₅), 4.33 (d, $J = 7.2$ Hz, 4H, *o*-C₆H₅), 2.40 (s, 12H, *meso*-C₆H₄CH₃), 0.39 (m, 2H, CH₂CH₃), -0.56 (t, $J = 6.8$ Hz, 6H, CH₂CH₃), -1.18 (m, 2H, CH₂CH₃). 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 \equiv CPh) with Benzophenone. An NMR tube equipped with a Teflon stopcock was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (0.4 mg, 0.45 μ mol), benzophenone (0.5 mg, 2.7 μ mol), Ph₃CH (1.3 mg, 5.3 μ mol, internal standard), and C₆D₆ (0.5 mL). Within 10 min, all of the PhC \equiv CPh had been displaced and benzopinacolate (TTP)-Ti[OC(Ph)₂C(Ph)₂O] (**3d**) was produced in 84% yield. ¹H NMR (C₆D₆, 300 MHz): δ 9.16 (s, 8H, β -H), 8.04 (m, 4H, *meso*-C₆H₄-CH₃), 7.70 (m, 4H, *meso*-C₆H₄CH₃, obscured by benzophenone), 7.25 (m, 8H, *meso*-C₆H₄CH₃), 6.52 (t, 4H, $^3J_{\text{H-H}} = 7.5$ Hz, *p*-C₆H₅), 6.39 (t, 8H, $^3J_{\text{H-H}} = 7.5$ Hz, *m*-C₆H₅), 4.76 (d, 8H, $^3J_{\text{H-H}} = 7.5$ Hz, *o*-C₆H₅), 2.41 (s, 12H, *meso*-C₆H₄CH₃). The amount of **3d** diminished rapidly in solution, and only paramagnetic porphyrin species were observed after 3 h by ¹H NMR spectroscopy.

Preparation of (TTP)Ti[OC(Ph)₂CH(Ph)O] (4a**).** A round-bottom flask was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (112 mg, 0.125 mmol), 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 a freezer at $-25\text{ }^{\circ}\text{C}$ for 12 h. Filtration, washing with hexane (2×2 mL), and drying under vacuum afforded a red-purple product, **4a** (73 mg, 58%). ^1H NMR (C_6D_6 , 400 MHz): δ 9.10 (dd, 8H, β -H), 8.07 (br m, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.96 (br m, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.28 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 6.71 (t, $J = 6.8$ Hz, 1H, *p*- C_6H_5), 6.64 (t, $J = 7.2$ Hz, 2H, *m*- C_6H_5), 6.48 (t, $J = 7.2$ Hz, 1H, *p*- C_6H_5), 6.34 (m, 5H, *m*, *p*- C_6H_5), 5.26 (d, $J = 7.2$ Hz, 2H, *o*- C_6H_5), 5.17 (d, $J = 6.8$ Hz, 2H, *o*- C_6H_5), 4.24 (d, $J = 7.2$ Hz, 2H, *o*- C_6H_5), 3.91 (s, 1H, OCH), 2.40 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$). ^{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 (OCH₂), 21.3 (*meso*- $\text{C}_6\text{H}_4\text{CH}_3$). UV-vis (toluene): 413 (5.29), 427 (5.21), 553 (4.22).

Preparation of (TTP)Ti[OC(Ph)₂C(Ph)(Me)O] (4b). A round-bottom flask was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (62 mg, 0.070 mmol), 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 a freezer at $-25\text{ }^{\circ}\text{C}$ for ~ 2 days. Filtration, washing with hexane (2×2 mL), and drying under vacuum afforded a red-purple product, **4b** (35 mg, 49%). ^1H NMR (C_6D_6 , 400 MHz): δ 9.14 (s, 8H, β -H), 8.21 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 8.01 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.27 (d, $J = 8.0$ Hz, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 6.72 (m, 3H, *m*, *p*- C_6H_5), 6.56 (m, 3H, *m*, *p*- C_6H_5), 6.45 (t, $J = 7.2$ Hz, 1H, *p*- C_6H_5), 6.32 (t, $J = 7.2$ Hz, 2H, *m*- C_6H_5), 5.80 (d, $J = 6.8$ Hz, 2H, *o*- C_6H_5), 5.75 (d, $J = 7.2$ Hz, 2H, *o*- C_6H_5), 4.76 (d, $J = 7.2$ Hz, 2H, *o*- C_6H_5), 2.40 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), -1.51 (s, 3H, OCH₃). UV-vis (toluene): 591 (3.81), 553 (4.29), 426 (5.52). Anal. Calcd for $\text{C}_{69}\text{H}_{54}\text{N}_4\text{O}_2\text{Ti}$: 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)₂C(Me)₂O] (4c). A round-bottom flask was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (66 mg, 0.073 mmol), 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 a freezer at $-25\text{ }^{\circ}\text{C}$ for ~ 2 days. Filtration, washing with hexane (1×2 mL), and drying under vacuum afforded a dark red product, **4c** (26 mg, 37%). ^1H NMR (C_6D_6 , 400 MHz): δ 9.13 (s, 8H, β -H), 8.12 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.98 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.29 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 6.69 (t, $J = 7.6$ Hz, 2H, *p*- C_6H_5), 6.60 (t, $J = 7.6$ Hz, 4H, *m*- C_6H_5), 5.18 (d, $J = 7.6$ Hz, 4H, *o*- C_6H_5), 2.40 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), -1.19 (s, 6H, C(CH₃)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 (OCH₂), 94.3 (OCMe₂), 26.0 (OCMe₂), 21.6 (*meso*- $\text{C}_6\text{H}_4\text{CH}_3$). UV-vis (toluene): 413 (5.33), 426 (5.41), 552 (4.22).

Cross-Coupling of Acetone with Acetophenone. An NMR tube equipped with a Teflon stopcock was charged with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) (1.4 mg, 1.6 μmol) and Ph₃CH (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)₂O] (**4d**), was produced in 85% yield. ^1H NMR data for **4d** (300 MHz, C_6D_6): δ

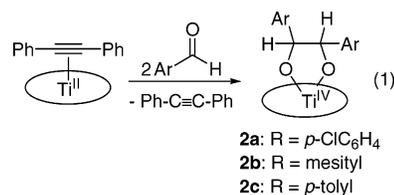
9.15 (s, 8H, β -H), 8.29 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 8.02 (br, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.27 (d, $J = 7.5$ Hz, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$, obscured), 6.65 (m, 3H, *p*, *m*- C_6H_5), 5.48 (d, $J = 7.2$ Hz, 2H, *o*- C_6H_5), 2.39 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), -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 $\sim 5\%$ 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 \equiv CPh) (**1**) (110 mg, 0.122 mmol) in 10 mL of toluene. The purple-red solution was stirred for 12 h and 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 a freezer at $-25\text{ }^{\circ}\text{C}$ for 24 h. Filtration, washing with hexane (2×2 mL), and drying under vacuum afforded a red-purple material, **5**. Yield: 76 mg (67%). ^1H NMR (C_6D_6 , 400 MHz): δ 9.04 (s, 8H), 8.19 (d, $J = 7.6$ Hz, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.91 (d, $J = 7.6$ Hz, 4H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 7.25 (d, $J = 7.6$ Hz, 8H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$), 6.62 (m, 6H, *m*- and *p*- C_6H_5), 5.71 (d, $J = 8.0$ Hz, 4H, *o*- C_6H_5), 2.39 (s, 12H, *meso*- $\text{C}_6\text{H}_4\text{CH}_3$). ^{13}C NMR: 150.6, 139.8, 137.2, 134.6 (*o*- $\text{C}_6\text{H}_4\text{CH}_3$), 134.5, 134.0 (*o*- $\text{C}_6\text{H}_4\text{CH}_3$), 132.7, 130.9 (β -pyrrole), 128.0 (*o*- C_6H_5), 127.7 (*m*- $\text{C}_6\text{H}_4\text{CH}_3$), 126.7 (*m*- C_6H_5), 125.3, 21.3 (*meso*- $\text{C}_6\text{H}_4\text{CH}_3$). UV-vis (toluene): 426 (5.43), 542 (4.34), 572 (3.75), 635 (3.29). Anal. Calcd for $\text{C}_{62}\text{H}_{46}\text{N}_4\text{O}_2\text{Ti} \cdot 0.2\text{CH}_2\text{Cl}_2$: 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), Ph₃CH (2.6 mg, 11 μmol), and C_6D_6 . The reaction was monitored by NMR spectroscopy. After 2 h, ^1H NMR analysis revealed the presence of (TTP)TiCl₂ 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 \equiv CPh) with Aldehydes. Aromatic aldehydes, ArCHO (Ar = *p*- $\text{CH}_3\text{C}_6\text{H}_4$, *p*-ClC₆H₄, mesityl), reacted cleanly and rapidly with (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) at ambient temperature to afford the reductive coupling products (TTP)Ti[OCH(Ar)CH(Ar)O] (**2a–c**) (eq 1). The identity of these diolato



complexes was confirmed by an independent synthesis from free diols and an imido titanium porphyrin complex.⁹ The isolated yields were 50–75%, although the conversions of these reactions determined by ^1H 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 1.4–2.2 and varied only slightly due to the electronic or steric properties of the aryl groups.

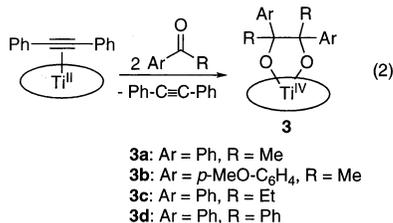
The ^1H NMR spectra of the diolato complexes **2a–c** displayed similar patterns. The β -pyrrole protons of the porphyrin with *dl* diolato ligands generally appear as an AB quartet, due to the presence of the stereogenic center in the diolato ligand. In contrast, the *meso* diolato complexes exhibit 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 ligand. In general, the NMR signals of aryl groups in *dl* diolates are usually less shifted than those of *meso* diolates. For example, the *o*-C₆H₄Cl protons in *dl*-(TTP)Ti[OCH(*p*-ClC₆H₄)CH(*p*-ClC₆H₄)O] (**2a**) appear at 4.69 ppm, while their *meso* counterparts appear at 4.33 ppm. On the other hand, the protons on the dioxatitanacyclopentane 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 toward reductive coupling (see mechanistic discussion). Treatment of Ph₂CHCHO with (TTP)Ti(η^2 -PhC≡CPh) (**1**) in C₆D₆ 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*-CH₃O-C₆H₄, R = Me), reacted cleanly and in a time span of minutes 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–d**) (eq 2). Both *dl* and *meso* diolato complexes were



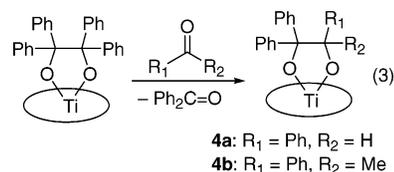
obtained and isolated in overall yields of 55–75%. The *dl* diolates were in excess with a *dl*/*meso* ratio of 5–6. This higher stereoselectivity displayed by aromatic ketones is presumably due to their lower activity and larger steric demands compared to aromatic aldehydes in these reactions.

The ¹H NMR spectra of the diolato complexes **3a–c** have patterns similar to those described above. An unusual phenomenon occurs for the diolato 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 ¹H NMR signals, corresponding to the five positions on the phenyl ring. In contrast, only three signals were observed for the phenyl protons in *meso*-**3c**. Apparently the rotation of the phenyl ring in the *dl* diolate is restricted on the NMR time scale, presumably due to the increased steric hindrance from the adjacent ethyl group. However, a variable-temperature NMR study of **3c** in CDCl₃ between –50 and 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 CH₂ unit by the porphyrin ring current.

Treatment of (TTP)Ti(η^2 -PhC≡CPh) (**1**) with benzophenone in C₆D₆ 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 was incorporated into a carbonyl coupling product, (TTP)Ti[OC(Ph)₂C(Ph)₂O] (**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 an 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 peroxy species, (TTP)Ti=O and (TTP)Ti(O₂), were generated as detected by NMR spectroscopy. The lability of the tetra-aryl-substituted diolato complexes is attributed, in part, to the unfavorably crowded arrangement of four aryl groups. An alternative attempt to prepare **3d** from benzopinacol and an imidotitanium porphyrin, (TTP)-Ti=N¹Pr, 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 to the reductive coupling reactions in this system. 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 Reactions of Carbonyl Compounds. The reactive complex (TTP)Ti[OC(Ph)₂C(Ph)₂O] (**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)₂C(Ph)(R)O] (R = H, **4a**; Me, **4b**) in near quantitative yields (eq 3). Only traces of the



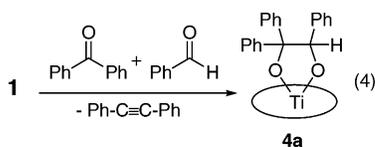
homo-coupling product (**3a**) were observed. Furthermore, it is surprising to note that treatment of **3d** with acetone, which itself is unreactive toward (TTP)Ti(η^2 -PhC≡CPh) (**1**), produced a coupling product, 1,1-dimethyl-2,2-diphenyl ethylenediolate, (TTP)Ti[OC(Ph)₂C(Me)₂O] (**4c**). Similarly, reaction of **1** with propionaldehyde yielded the cross-coupling product (TTP)Ti[OC(Ph)₂CH(Et)O].

It was also noted that the prior formation of (TTP)-Ti[OC(Ph)₂C(Ph)₂O] (**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

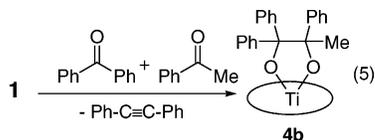
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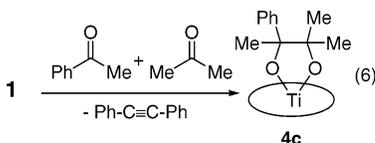
μmol) with a mixture of benzophenone (10 μmol) and benzaldehyde (15 μmol) afforded $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})_2\text{CH}(\text{Ph})\text{O}]$ (**4a**) in 95% yield (eq 4). Addition of a solution of



benzophenone (122 μmol) and acetone (121 μmol) to a solution of $(\text{TTP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ (1.9 μmol) resulted in the formation of diolate $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})_2\text{C}(\text{Me})_2\text{O}]$ (**4c**) in 61% yield (eq 5). Furthermore, other carbonyl com-



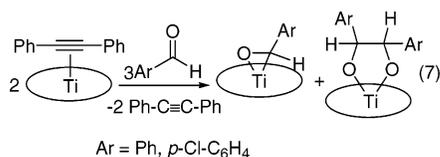
pounds other than benzophenone could be used as coupling partner to activate acetone in these coupling reactions. For example, treatment of $(\text{TTP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ with a mixture of acetophenone and acetone generated the cross-coupling product $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})(\text{Me})\text{C}(\text{Me})_2\text{O}]$ in 85% yield, as determined by NMR spectroscopy (eq 6). However, a complex mixture was



observed when $(\text{TTP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ 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 $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})_2\text{C}(\text{Ph})_2\text{O}]$ with a variety of other substrates, such as methyl benzoate, $^i\text{PrNCO}$, $\text{PhCH}=\text{NPh}$, or CS_2 , but no further reactions were observed.

Observation of η^2 -Carbonyl Complexes. Upon treatment of *p*-chlorobenzaldehyde with excess $(\text{TTP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ in C_6D_6 , a new diamagnetic species was observed, as a minor product, along with the coupling diolate product (eq 7). This species showed two



highly upfield shifted 2H doublets at 6.26 (*m*- $\text{C}_6\text{H}_4\text{Cl}$) and 3.69 ppm (*o*- $\text{C}_6\text{H}_4\text{Cl}$), a 1H singlet at -1.0 ppm (*CHO*), and an 8H β -pyrrole proton singlet at 9.02 ppm. A similar species was observed in the reaction of benzaldehyde with $(\text{TTP})\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})$ in hexane, featuring two upfield phenyl signals at 6.34 (*m*- C_6H_5) and 3.97 ppm (*o*- C_6H_5) and a one-proton singlet at -0.82 ppm (*CHO*). The proximity of the axial ligand to the porphyrin ring was indicated by the large upfield chemical shifts. These species are assigned as η^2 -carbonyl complexes (eq 7). Other group 4 zirconium and hafnium η^2 -carbonyl complexes have been prepared by

treatment of dialkyl¹² or alkyl hydride¹³ 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 $(\text{TTP})\text{Ti}(\eta^2\text{-OCHC}_6\text{H}_4\text{Cl})$), it has been reported that η^2 -carbonyl complexes possess a metalloxocyclopropyl-like ring due to the back-donation of electrons from the metal $d\pi$ orbital to the $\text{C}=\text{O}$ π^* orbital.¹⁵ Consequently, the ^1H NMR signal of aldehydic hydrogen in $\text{Cp}_2\text{Mo}(\eta^2\text{-PhCHO})$, for example, 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 $(\text{TTP})\text{Ti}(\eta^2\text{-OCHAr})$ species were labile and it was not possible to isolate or 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 metallapinacolato intermediates,¹⁶ some researchers prefer an alternative pathway involving a carbonyl insertion into the $\text{M}-\text{C}$ bond of a η^2 -carbonyl intermediate.¹⁷ The latter process is supported by DFT calculations.¹⁸ It seems reasonable 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 low reactivity of aliphatic carbonyl compounds with low-valent $\text{Ti}(\text{II})$ porphyrin complexes is consistent with this scheme. The lower π -acidity of aliphatic aldehydes would disfavor formation of an η^2 -complex. Moreover, the rapid formation of cross-coupling products from benzopinacolato complexes and carbonyl compounds indicates that an equilibrium exists between $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})_2\text{C}(\text{Ph})_2\text{O}]$ and an η^2 -carbonyl complex $(\text{TTP})\text{Ti}(\eta^2\text{-OCPh}_2)$. The reversibility between a pinacolato species and an η^2 -carbonyl compound has been demonstrated in other titanium-based systems recently.¹⁹ Furthermore, the enhanced reactivity of preformed $(\text{TTP})\text{Ti}[\text{OC}(\text{Ph})_2\text{C}(\text{Ph})_2\text{O}]$ toward acetone also agrees with a mechanism involving reversible cleavage of a $\text{C}-\text{C}$ bond and a carbonyl insertion pathway, since aryl ketones are better π -acid ligands and would enhance the formation of η^2 -carbonyl com-

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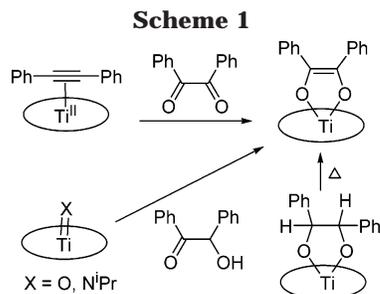
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plexes. Such a pathway is also consistent with our investigation of (TTP)Ti=O-catalyzed diol cleavage reaction, where a radical pathway appears to be less likely.²⁰

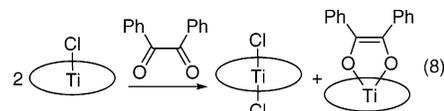
Reaction of (TTP)Ti(η^2 -PhC \equiv CPh) with Diketone. The reaction of (TTP)Ti(η^2 -PhC \equiv CPh) (**1**) with a vicinal diketone, benzil, in toluene yielded a new complex with a 6H multiplet at 6.62 ppm (*m,p*-C₆H₅) and a 4H doublet of doublets at 5.71 ppm (*o*-C₆H₅), as well as an 8H β -pyrrolic proton 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)Ti=O 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 porphyrin enediolato complex was also detected upon treatment of dialkylmetalloporphyrin complex [(OEP)TaMe₂]BPh₄ 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 titanium porphyrin (TTP)Ti(O₂). 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*-ClC₆H₄)CH(*p*-ClC₆H₄)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 N₂, diolato complexes **3a–c** decomposed to free ketones and paramagnetic porphyrin species with broad NMR signals at 2.40 and/or 2.50 ppm. Trapping with a large excess of pyridine generated a well-defined bispyridine adduct, (TTP)Ti(py)₂,^{6c} in low yield, 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 N₂ afforded a complex mixture of products, including (TTP)Ti=O,

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 pinacol coupling reactions.²³ CpTiCl₂ reacts with R₂CO to form dimeric coupling complexes.²⁴ We also found that (TTP)TiCl reacts with aryl azides to afford imido Ti(IV) porphyrin complexes.²⁵ To extend the scope of chemistry described in previous sections, the investigation of reactions of (TTP)TiCl with carbonyl compounds was conducted. Treatment of (TTP)TiCl with excess benzil in C₆D₆ produced equal amounts of (TTP)TiCl₂ and the enediolate (TTP)Ti[OCPhCPhO] within 2 h (eq 8). However, no coupling



reaction was observed when (TTP)TiCl was treated with benzaldehyde or *p*-tolualdehyde in C₆D₆. Interestingly, transformation of (TTP)TiCl to (TTP)Ti=O and (TTP)TiCl₂ 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 1,2-di(*p*-tolyl)-ethane-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 \equiv 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 \equiv CPh). This is a novel reductive coupling system in that both the low-valent metal reagent and the ensuing diolate complexes can be isolated and observed as well-defined compounds. 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.²⁰

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Supporting Information Available: ¹H NMR spectra for compounds **2b**, **3a**, **3b**, **4a**, and **4c**. This information is available free of charge via the Internet at <http://pubs.acs.org>. OM049686K

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