Reductive Coupling of $[(RO)_2Ti(L_2)_2]$ Complexes Containing a Chelating Bis(aryloxide) Ligand with Ketones (L_2 = bpy, dmbpy, or phen)

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The reactivity of $[(RO)_2Ti(L_2)_2]$ complexes (L_2 = bpy, dmbpy, or phen; $(RO)_2$ = DMSC or MBMP) with ketones was investigated (DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion; MBMP = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) dianion). The molecular structures of [(DMSC)Ti(bpy)$_2$] (**6a**) and [(DMSC)Ti(bpy)$_2$] (**7a**) were characterized by X-ray crystallography. Their structural data taken together with UV−visible and magnetic susceptibility data suggest some electron transfer into the LUMO (π^* orbital) of the diimine ligands. $[(RO)_2Ti(L_2)_2]$ complexes undergo light-assisted reaction with aromatic ketones in a reversible manner to afford Ti-η^2-ketone complexes $[(RO)_2Ti(\eta^2\text{-OCArR})(L_2)]$ (Ar = aryl while R = aryl or alkyl), which undergo further reaction with ketone to give the corresponding 2-aza-5-oxa-titanacyclopentene. Qualitatively, the efficacy of the formation of 2-aza-5-oxa-titanacyclopentene $[(RO)_2Ti(L_2)_2]$ complexes increased with increasing ketone concentration and in the order L_2 = bpy < dmbpy < phen. This order is best explained in terms of the dependence of the equilibrium between $[(RO)_2Ti(L_2)_2]$ and $[(RO)_2Ti(\eta^2\text{-OCArR})(L_2)]$ on relative abilities of the ketone and the diimine to accept π-electron density, as well as in terms of the order of the rate of reaction of $[(RO)_2Ti(\eta^2\text{-OCArR})(L_2)]$ with ketone.

Introduction

Low-valent titanium-mediated reductive coupling reactions of unsaturated organic substrates continues to grow in importance as a synthetic methodology.[1,2] However, better understanding of the synthesis, structure, and reactivity of reduced titanium complexes is needed in order to achieve greater mechanistic understanding and better control over selectivity of the reactions. Hence, increased effort has been focused on developing the synthesis and reactivity of well-characterized low-valent group 4 metal complexes.[3,4] Over the last several years, we have been developing the synthesis and reactivity of well-characterized Ti(II) synthons containing calix[4]arene-derived chelating bis(aryloxide) ligation.[4] Recently, we found that titanapinacolate complexes [(DMSC)Ti(OCAr$_2$CAr$_2$O)] (**1a**, Ar = *p*-MeC$_6$H$_4$; **1b**, Ar = Ph; DMSC = 1,2-alternate

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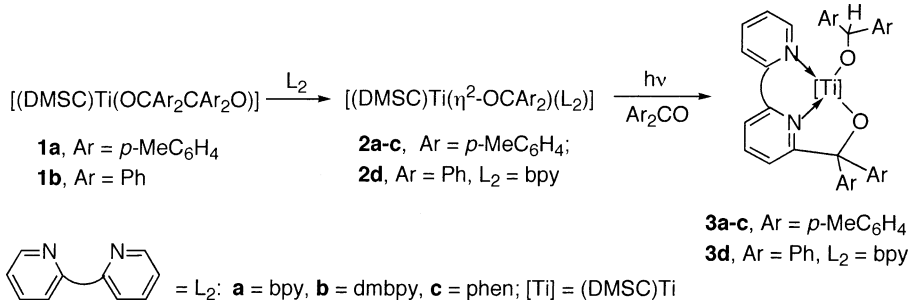
Scheme 1



dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion) react with aromatic diimines, such as 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-dipyridyl (dmbpy), or 1,10-phenanthroline (phen), to produce Ti-η^2-ketone complexes [(DMSC)Ti(η^2-OCAr$_2$)(L$_2$)] (**2a**−**d**, L$_2$ = bpy, dmbpy, or phen).[4b] The latter compounds undergo light-assisted reaction with 1 equiv of ketone to yield 2-aza-5-oxa-titanacyclopentenes **3a**−**d** (Scheme 1), in which C−H activation of the diimine ligand and hydride migration to a Ti-bound ketone to form an alkoxide group has occurred. Titanium-promoted reductive coupling of ketones with 2,2′-bipyridine or 1,10-phenanthroline is attractive because 6-(1-hydroxyalkyl)-2,2′-bipyridines and 2-(1-hydroxyalkyl)-1,10-phenanthrolines, especially chiral derivatives, are of interest as ligands for catalyst exploration.[5,6] Also, there is currently ample need of additional general methods for synthesis of this class of compounds.[5,7] Helquist and co-workers have recently reported SmI$_2$-promoted coupling of aliphatic ketones and aldehydes with 1,10-phenanthroline to produce 2-(1-hydroxyalkyl)-1,10-phenanthrolines, but aromatic ketones and aldehydes were not useful substrates.[7a,b]

Herein, we describe results from our studies of the reactions of ketones with titanium bis(diimine) complexes [(DMSC)Ti(L$_2$)$_2$] (**6a**−**c**) and [(MBMP)Ti(L$_2$)$_2$] (**7a** and **7b**, MBMP = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) dianion). We chose to study this class of compounds because aromatic diimines are redox-active π-acid ligands that have been shown to support electron-rich reduced titanium centers.[8] Furthermore, thermal or photochemical substitution of an aromatic diimine ligand can be used to open up coordination sites at metal centers.[9]

Experimental Section

General Details. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Solvents were dried and distilled by standard methods before use.[10] All solvents were stored in the glovebox over 4A molecular sieves that were dried in a vacuum oven at 150 °C for at least 48 h prior to use. Unless otherwise stated all reagents were purchased from Aldrich. Benzophenone, 1,10-phenanthroline, 4,4′-dimethylbenzophenone, 2,2′-bipyridine, and 4,4′-dimethyl-2,2′-dipyridyl were sublimed, while 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) was dried under vacuum for 24 h before use. [(DMSC)TiPh$_2$] (**4**), [(DMSC)Ti(bpy)$_2$] (**6a**), and [(DMSC)-Ti(dmbpy)$_2$] (**6b**) were prepared according to published procedures.[4d] [(MBMP)TiPh$_2$] (**5**)[11] was prepared via modification of the reported procedure (see Supporting Information). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at room temperature unless otherwise stated. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent peaks. Infrared spectra were recorded on a Nicolet Magna 560 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8453 series UV−visible spectroscopy system. GC-MS analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph with a Hewlett-Packard 5972 series mass selective detector at an ionizing potential of 70 eV or at University of Kentucky Mass Spectrometry Center on a Thermo Finnigan (San Jose, CA) Polaris Q (quadruple ion trap) or JEOL JMS-700T MStation spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

[(DMSC)Ti(phen)$_2$] (6c). To a toluene (15 mL) solution of [(DMSC)TiPh$_2$] (**4**) (1.55 g, 1.71 mmol) was added 1,10-phenanthroline (0.617 g, 3.42 mmol). The initially bright yellow solution immediately turned dark olive-green. After stirring for 2 min, pentane (30 mL) was added into the olive-green solution and the resulting mixture was cooled at −15 °C for 10 min. The olive-green solid isolated by filtration was washed with pentane (3 × 5 mL) and dried under vacuum.

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Yield: 1.44 g, 75.8%. ^{1}H NMR (C_6D_6): δ 10.11 (d, J = 6.0 Hz, 2H, phen), 9.25 (d, J = 6.0 Hz, 2H, phen), 7.48 (d, J = 2.8 Hz, 2H, arom CH), 7.47 (d, J = 2.8 Hz, 2H, arom CH), 6.95 (d, J = 2.8 Hz, 2H, arom CH), 6.84 (s, 2H, phen), 6.78 (d, J = 7.2 Hz, 2H, phen), 6.75 (d, J = 2.8 Hz, 2H, arom CH), 6.49 (s, 2H, phen), 6.13 (d, J = 7.2 Hz, 2H, phen), 6.05 (dd, J = 7.2, 5.6 Hz, 2H, phen), 5.75 (dd, J = 7.2, 5.6 Hz, 2H, phen), 4.82 (d, J = 16.0 Hz, 2H, calix-CH_2), 4.57 (d, J = 15.2 Hz, 1H, calix-CH_2) 4.35 (d, J = 16.0) Hz, 2H, calix-CH_2) 3.92 (d, J = 13.6 Hz, 1H, calix-CH_2), 3.35 (d, J = 15.2 Hz, 1H, calix-CH_2), 3.22 (d, J = 13.6 Hz, 1H, calix-CH_2), 1.51 (s, 18 H, t-Bu), 0.88 (s, 18H, t-Bu), 0.32 (s, 3H, *exo*-SiMe), −0.74 (s, 3H, *endo*-SiMe). ^{13}C NMR (C_6D_6): δ 163.6 (Ti-O*C*), 152.2, 150.7, 145.4, 142.8, 142.1, 140.2, 135.6, 132.1, 131.5, 131.3, 131.2, 130.9, 130.1, 129.7, 129.4, 127.0, 126.9, 126.5, 126.2, 125.9, 123.1, 115.8, 115.3, 41.2 (calix-CH_2), 38.7 (calix-CH_2), 38.5 (calix-CH_2), 34.5 ($C(CH_3)_3$, 33.8 ($C(CH_3)_3$), 32.6 (C(CH_3)$_3$), 31.6 (C(CH_3)$_3$), 2.9 (*exo*-SiMe), −1.1 (*endo*-SiMe). Anal. Calcd for $C_{70}H_{74}N_4O_4SiTi$: C, 75.65; H, 6.71; N, 5.04. Found: C, 75.29; H, 6.57; N, 4.95.

[(MBMP)Ti(bpy)$_2$] (7a). To a solution of [(MBMP)TiPh_2] (**5**) (3.00 g, 5.60 mmol) in 15 mL of ether was added 2,2′-bipyridine (1.74 g, 11.2 mmol). The reaction mixture immediately turned dark blue and was stirred for 30 min. The solvent was removed under reduced pressure, and the dark blue residue was washed with pentane (3 × 10 mL) and dried under vacuum. Yield: 3.40 g, 86.9%. ^{1}H NMR at −20 °C (toluene-d_8): δ 10.69 (d, J = 5.2 Hz, 1H, bpy), 9.20 (d, J = 5.6 Hz, 1H, bpy), 8.41 (d, J = 5.6 Hz, 1H, bpy), 8.37 (d, J = 6.0 Hz, 1H, bpy), 7.67 (s, 1H, MBMP arom CH), 7.60 (s, 1H, MBMP arom CH), 7.32 (s, 1H, MBMP arom CH), 6.68 (d, J = 7.2 Hz, 2H, bpy), 5.89−6.00 (m, 4H, bpy), 5.85 (d, J = 12.4 Hz, 1H, MBMP-CH_2), 5.60−5.70 (m, 2H, bpy), 5.40 (t, 1H, bpy), 5.03 (t, 1H, bpy), 4.06 (d, J = 12.4 Hz, 1H, MBMP-CH_2), 2.47 (s, 3H, Me), 2.40 (s, 3H, Me), 1.37 (s, 9H, t-Bu), 0.70 (s, 9H, t-Bu). Anal. Calcd for $C_{43}H_{46}N_4O_2Ti$: C, 73.91; H, 6.63; N, 8.01. Found: C, 73.79; H, 6.37; N, 7.92. Single crystals of **7a** suitable for X-ray diffraction study were obtained by slow evaporation of a benzene solution.

[(MBMP)Ti(dmbpy)$_2$] (7b). To a solution of [(MBMP)-TiPh_2] (**5**) (0.250 g, 0.463 mmol) in 5 mL of toluene was added 4,4′-dimethyl-2,2′-dipyridyl (0.171 g, 0.930 mmol). The reaction mixture immediately turned dark blue-green and was stirred for 30 min. The solvent was removed under reduced pressure, and the dark blue residue was washed with pentane (3 × 5 mL) and dried under vacuum. Yield: 0.289 g, 82.7%. ^{1}H NMR at −75 °C (toluene-d_8): δ 10.92 (br s, 1H, dmbpy), 9.39 (br s, 1H, dmbpy), 8.85 (br m, 2H, dmbpy), 8.71 (br d, 1H, dmbpy), 8.56 (d, J = 4.8 Hz, 1H, dmbpy), 7.74 (br s, 1H, MBMP arom CH), 7.71 (br s, 1H, MBMP arom CH), 7.48 (br s, 1H, MBMP arom CH), 6.81 (br s, 1H MBMP arom CH), 6.59 (s, 1H, dmbpy) 6.46 (br d, J = 4.8 Hz, 1H, dmbpy), 6.14 (br d, 1H, MBMP-CH_2), 5.75 (br d, 1H, dmbpy), 5.68 (s, 1H, dmbpy), 5.24 (br d, 1H, dmbpy), 4.91 (br d, 1H, dmbpy), 4.21 (br d, 1H, MBMP-CH_2), 2.55 (br s, 3H, MBMP-Me) 2.43 (br s, 3H, MBMP-Me), 1.99 (br s, 3H, dmbpy-Me), 1.82 (s, 3H, dmbpy-Me), 1.68 (br s, 6H, 2 dmbpy-Me), 1.58 (br s, 9H, t-Bu), 0.86 (br s, 9H, t-Bu). Anal. Calcd for $C_{47}H_{54}N_4O_2Ti$: C, 74.78; H, 7.21, N, 7.42. Found: C, 74.62; H, 7.25; N, 7.34.

[(MBMP)Ti{κ^3-OCPh$_2$C$_{10}$H$_7$N$_2$}(OCHPh$_2$)] (8a). To a 10 mL ether solution of [(MBMP)TiPh_2] (**5**) (0.101 g, 0.187 mmol) in a glass pressure tube was added 2,2′-bipyridine (0.0613 g, 0.392 mmol). The resulting dark blue reaction mixture was stirred for 10 min and then charged with benzophenone (0.0910 g, 0.500 mmol). The reaction mixture was heated with stirring at 65 °C for 12 h. After cooling to ambient temperature, the mixture was filtered and the orange precipitate was washed with THF (2 × 3 mL) followed by toluene (2 × 3 mL) and dried under vacuum. Yield: 0.141 g, 83.2%. ^{1}H NMR (CD_2Cl_2): δ 8.69 (d, J = 5.2 Hz, 1H, arom CH), 8.18 (d, J = 8.4 Hz, 1H, arom CH), 7.89 (t, J = 7.6 Hz, 1H, arom CH), 7.80 (t, J = 7.6 Hz, 1H, arom CH), 7.69 (m, 2H arom CH), 7.62 (d, J = 8.0 Hz, 1H arom CH), 7.59 (d, J = 8.0 Hz, 1H arom CH), 7.41 (d, J = 8.0 Hz, 1H arom CH), 7.31 (br t, 1H, arom CH), 7.26−6.70 (m, 19 H, arom CH), 6.65 (s, 1H, MBMP arom CH), 6.48 (s, 1H, MBMP arom CH), 5.92 (d, 1H, J = 13.6 Hz, MBMP-CH_2), 5.56 (s, 1H, OC*H*Ph$_2$), 2.73 (d, 1H, d = 13.6 Hz, MBMP-CH_2), 2.19 (s, 3H, Me), 2.11 (s, 3H, Me), 1.50 (s, 9H, t-Bu), 0.38 (s, 9H, t-Bu). ^{13}C NMR (CD_2Cl_2): δ 170.4, 152.9, 151.3, 148.6, 147.05, 140.1, 139.6, 129.5, 128.7, 128.5, 128.4, 128.2, 127.9, 126.4, 126.3, 125.84, 125.7, 124.7, 121.9, 119.2, 99.5 (O*C*Ph$_2$C$_{10}$H$_5$Me$_2$N$_2$), 86.8 (Ti-O*C*HPh$_2$), 35.5 (MBMP-*C*H$_2$), 33.9($C(CH_3)_3$), 31.3 (C(CH_3)$_3$), 29.7 (C(CH_3)$_3$), 21.2 (dmbpy CH_3), 20.9 (dmbpy CH_3). MS (EI, 25 eV) *m/z*: 906 [M]$^+$, 724 [M − Ph_2CO]$^+$. Single crystals of **8a** suitable for X-ray diffraction study were obtained by slow evaporation of a dilute benzene solution.

Typical Procedure for NMR Study of the Reaction between [(DMSC)Ti(L$_2$)$_2$] (6a−c) and 4,4′-Dimethylbenzophenone. A 0.094 mL portion of a 0.100 M stock solution of [(DMSC)Ti(bpy)$_2$] (**6a**) was added into a screw-capped NMR tube, followed by 0.180 mL of a 0.100 M stock solution of (p-MeC_6H_4)$_2$CO and finally 0. 518 mL of C_6D_6. This resulted in 0.800 mL of a 0.0117 M solution of **6a** and a 0.0225 M solution of (p-MeC_6H_4)$_2$CO. The tube was vigorously shaken and placed into the NMR spectrometer at 22 °C. The reaction was monitored by recording ^{1}H NMR spectra immediately after inserting the sample in the spectrometer and every 10 min thereafter. The dependence of the reaction on (p-MeC_6H_4)$_2$CO was obtained by varying the concentration of (p-MeC_6H_4)$_2$CO while conducting each experiment in C_6D_6 at the same temperature, using an identical amount of **6a** and the same total volume (0.800 mL). The dependence on the nature of the diimine was obtained by conducting analogous reactions for [(DMSC)Ti(dmbpy)$_2$] (**6b**) and [(DMSC)Ti(phen)$_2$] (**6c**).

Typical Procedure for Reaction of [(MBMP)Ti(bpy)$_2$] (7a) with Ketones. To an ether (10−15 mL) solution of [(MBMP)TiPh_2] (**5**) in a glass pressure tube was added 2,2′-bipyridine (2 equiv). The dark blue mixture was stirred for 2 min, and then the ketone (≥2 equiv) was added. The reaction mixture was heated at 65 °C for a period of time (18−72 h) during which the reaction progress was monitored via ^{1}H and GC-MS analysis of aliquots taken under N_2. After cooling the reaction mixture to ambient temperature, the orange suspension was filtered. The precipitate was washed twice with ether and then dissolved in a ∼2:1 mixture of CH_2Cl_2 and aqueous NH_4Cl. After stirring until the CH_2Cl_2 layer was yellow, the organic layer was separated and then subjected to chromatographic separation.

2,2′-Bipyridinyl-6-yl-diphenylmethanol (9a). From reaction of [(MBMP)TiPh_2] (**5**) (0.352 g, 0.653 mmol) with 2,2′-bipyridine (0.203 g, 1.30 mmol) and Ph_2CO (0.238 g, 1.30 mmol) for 18 h, 0.164 g (88% yield) of **9a** was isolated as an off-white solid after chromatographic purification on a silica column using 5:1 CH_2Cl_2/heptane as eluent. ^{1}H NMR ($CDCl_3$): δ 8.71−8.66 (m, 2H, bipyridyl), 8.45−8.37 (m, 3H, bipyridyl), 7.84−7.72 (m, 3H, arom CH), 7.42−7.26 (m, 8H, arom CH), 7.17 (dd, J = 7.6, 1.2 Hz, 1H, bipyridyl), 6.55 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$): δ 162.4, 155.3 154.2, 149.3, 146.3, 137.6, 137.0, 128.4, 128.1, 127.5, 124.1, 123.8, 123.3, 121.3, 120.0, 81.1 (*C*-OH). HRMS (EI, 25 eV): *m/z* calcd for $C_{23}H_{18}N_2O$ (M$^+$) 338.4066, found 338.1415.

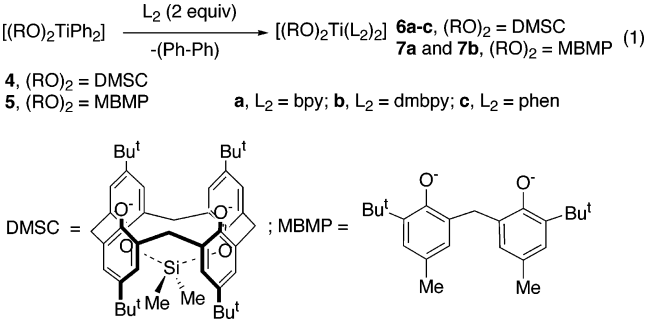
2,2′-Bipyridinyl-6-yl-1-phenylethanol (9b). From reaction of [(MBMP)TiPh_2] (**5**) (0.316 g, 0.585 mmol) with 2,2′-bipyridine (0.185 g, 1.18 mmol) and PhCOMe (0.141 g, 1.18 mmol) for 48 h, 0.0360 g (28% yield) of **9b** was isolated as a faint pink oil after two chromatographic purification steps on silica columns using 5:1 CH_2Cl_2/heptane and then followed by 7:1 acetone/heptane as eluent. ^{1}H NMR ($CDCl_3$): δ 8.71 (d, J = 4.4 Hz, 1H, bipyridyl), 8.46 (d, J = 8.0 Hz, 1H, bipyridyl), 8.34 (d, J = 8.0 Hz, 1H, bipyridyl), 7.87 (t, J = 8.0 Hz, 1H, bipyridyl), 7.81 (t, J = 7.6 Hz, 1H, bipyridyl), 7.56 (dd, J =

7.4, 1.2 Hz, 2H, arom CH), 7.40−7.22 (m, 5H, arom CH), 6.07 (s, 1H, O*H*), 2.00 (s, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 165.4, 155.9, 154.4, 148.1, 147.2, 139.3, 138.6, 128.6, 127.4, 126.4, 124.7, 122.1, 121.6, 120.2, 75.8 (*C*-OH), 29.6 (*C*H$_3$). HRMS (EI, 25 eV): *m/z* calcd for $C_{18}H_{16}N_2O$ (M^+) 276.3356, found 276.1257

2,2′-Bipyridinyl-6-yl-1,2-diphenylethanol (9c). From reaction of [(MBMP)TiPh$_2$] (**5**) (0.201 g, 0.373 mmol) with 2,2′-bipyridine (0.116 g, 0.744 mmol) and PhCOCH$_2$Ph (0.225 g, 1.15 mmol) for 36 h, 19.0 mg (15% yield) of **9c** was isolated as an off-white solid after chromatographic purification on a silica column using 4:1 ethyl acetate/heptane as eluent. ^{1}H NMR ($CDCl_3$): δ 8.76 (d, J = 4.4 Hz, 1H, bipyridyl), 8.36 (d, J = 8.0 Hz, 1H, bipyridyl), 8.21 (d, J = 8.0 Hz, 1H, bipyridyl), 7.96 (t, J = 8.0 Hz, 1H, bipyridyl), 7.83 (t, J = 8.0 Hz, 1H, bipyridyl), 7.66 (dd, J = 8.0, 1.2 Hz, 2H, arom), 7.50 (d, J = 8.0 Hz, 1H, arom CH), 7.45 (t, J = 8.0 Hz, 1H, arom CH), 7.35 (t, J = 8.0 Hz, 2H, arom CH), 7.30−7.24 (m, 2H, arom CH), 7.16−7.08 (m, 3H, arom CH), 6.98−7.05 (m, 2H, arom CH), 5.38 (br s, 1H, O*H*), 3.80 (d, J = 13.6 Hz, 1H, C*H*$_2$Ph), 3.67 (d, J = 13.6 Hz, 1H, C*H*$_2$Ph). ^{13}C NMR ($CDCl_3$): δ 163.5, 154.0, 147.5, 145.9, 139.4, 138.4, 136.6, 131.1, 128.5, 128.0, 127.5, 126.6, 126.5, 124.6, 122.3, 120.2, 78.0 (*C*-OH), 47.5 (*C*H$_2$Ph). HRMS (EI, 25 eV): *m/z* calcd for $C_{24}H_{20}N_2O$ (M^+) 352.4320, found 352.1566.

Results and Discussion

Synthesis and Characterization of [(RO)$_2$Ti(L$_2$)$_2$] Compounds. We have previously reported that [(DMSC)Ti(bpy)$_2$] (**6a**) and [(DMSC)Ti(dmbpy)$_2$] (**6b**) are conveniently synthesized via bipyridine-induced reductive elimination of biphenyl from [(DMSC)TiPh$_2$] (**4**).[4d] [(DMSC)Ti(phen)$_2$] (**6c**), [(MBMP)Ti(bpy)$_2$] (**7a**), and [(MBMP)Ti(dmbpy)$_2$] (**7b**) are similarly obtained in high yield from reaction of the appropriate [(RO)$_2$TiPh$_2$] compound with 2 equiv of aromatic diimine (eq 1).[12] The



related deep blue-green complex [(2,6-Pr$^i_2$C$_6$H$_3$O)$_2$Ti(bpy)$_2$] was similarly prepared by Rothwell.[8a] Compounds **6a**,**b** and **7a**,**b** were isolated as deep dark blue solids, while **6c** was obtained as a dark olive-green powder. All of the compounds are stable in the solid state under N_2 atmosphere but are best stored for extended periods of time at low temperature (below −15 °C) and protected from light.[13] They are highly sensitive to hydrolysis and oxidation and immediately turn yellow or yellow-brown upon exposure to air in the solid state or in solution. [(DMSC)Ti(L$_2$)$_2$] compounds (**6a**−**c**) show higher solubility in organic solvents than [(MBMP)Ti(L$_2$)$_2$] compounds (**7a**,**b**). For instance, **6a**−**c** are highly soluble in THF and aromatic hydrocarbon solvents and moderately soluble in ether. In contrast, **7a**,**b** are highly soluble in THF but only moderately soluble in aromatic hydrocarbon solvents and ether. All of the compounds are insoluble in pentane. They react with polyhalogenated hydrocarbons, such as CH_2Cl_2 and $CHCl_3$, to yield a mixture of unidentified Ti(IV) products.

The formulation and structure of [(DMSC)Ti(phen)$_2$] (**6c**), [(MBMP)Ti(bpy)$_2$] (**7a**), and [(MBMP)Ti(dmbpy)$_2$] (**7b**) were characterized by microanalysis and spectroscopic data. ^{1}H and ^{13}C NMR data for **6c** displayed sharp resonances that are consistent with C_s-symmetry in solution at ca. 22 °C. The ^{1}H NMR spectrum of **6c** shows two singlets (integrating in 1:1 ratio) for the *tert*-butyl groups and six doublets for bridging methylene groups of the calixarene ligand. Two of the six doublets integrate as two protons each and represent the methylene protons that are reflected by the mirror plane, which contains the remaining four methylene protons. That the DMSC ligand exists in 1,2-alternate conformation is evidenced by the shift to high field (δ = −0.74 ppm) of the *endo*-Me of the bridging SiMe$_2$ group (located inside the calixarene cavity) compared to the *exo*-Me of the bridging SiMe$_2$ group (located outside the calixarene cavity), which shows at δ 0.32 ppm.[4]

At 25 °C, solution ^{1}H NMR spectra of [(MBMP)Ti(bpy)$_2$] (**7a**) and [(MBMP)Ti(dmbpy)$_2$] (**7b**) displayed mostly broad resonances, suggesting that the compounds are fluxional on the NMR time scale. Hence we conducted variable-temperature ^{1}H NMR studies of **7a** and **7b** in toluene-d_8 from 295 to 193 K. The peaks in the NMR spectrum for **7a** sharpened as the temperature was lowered, and the ^{1}H NMR data at 253 K are consistent with **7a** adopting C_1-symmetry in solution: each of the two *tert*-butyl groups, the two methyl groups, and the four aromatic protons of the MBMP ligand was observed as a singlet resonance. In addition, each proton of the bridging CH_2 unit of the MBMP ligand showed as a doublet resonance, and all of the bipyridine protons were inequivalent. While the peaks in the ^{1}H NMR spectrum of **7b** sharpened considerably as the temperature was lowered, they remained somewhat broad even at 193 K. Nonetheless, the ^{1}H data similarly established that **7b** is C_1-symmetric in solution (see Experimental Section). It is likely that **7a** and **7b** owe their stereochemical nonrigidity to isomerization via a twist mechanism; a number of such mechanisms have been reported for isomerization of M(chelate)$_3$ complexes.[14]

Molecular structures of [(DMSC)Ti(bpy)$_2$] (**6a**) and [(MBMP)Ti(bpy)$_2$] (**7a**) were also established by single-crystal X-ray diffraction studies. Crystallographic data and selected metrical parameters are given in Tables 1 and 2, respectively. The molecular structures of **6a** and **7a** (depicted in Figures 1 and 2, respectively) support their C_1-symmetry in solution as assigned by NMR spectroscopy. In **6a**, the geometry about Ti is twisted away from trigonal prismatic toward octahedral by ∼25°, whereas **7a** is distinctly octahedral, albeit distorted. These structures presumably reflect acute bite

(12) A dark purple precipitate is formed immediately from similar reaction of [(MBMP)TiPh$_2$] (**5**) with phen (2 equiv) in ether. This product is tentatively assigned as [(MBMP)Ti(phen)$_2$] on the basis of microanalysis data (Anal. Calcd for $C_{47}H_{46}N_4O_2Ti$: C, 75.60; H, 6.16; N, 7.50. Found: C, 75.92; H, 6.39; N, 7.29). The compound is moderately soluble in THF but only slightly soluble in aromatic solvents. Its poor solubility prevented structural characterization by spectroscopic methods and thwarted exploration of its reactivity with ketones.

(13) Compounds **6a**−**c** can be stored in the solid state at room temperature and exposed to light for 48 h without significant decomposition.

Table 1. Crystallographic Data for 6a·($C_{10}H_8N_2$)$_{1.5}$, 7a, and 8a

	6a·($C_{10}H_8N_2$)$_{1.5}$	**7a**	**8a**
formula	$C_{81}H_{88}N_7O_4SiTi$	$C_{55}H_{58}N_4O_2Ti$	$C_{65}H_{64}N_2O_4Ti$
fw	1299.57	854.95	985.08
T, K	150.0(2)	90.0(2)	90.0(2)
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12$	$P2_1/c$
Z	2	4	4
a, Å	15.1753(13)	16.9420(6)	9.54100(10)
b, Å	15.2345(13)	17.5720(7)	26.3230(3)
c, Å	17.0936(15)	15.4750(9)	20.9570(3)
α, deg	99.096(2)	90	90
β, deg	113.247(2)	90.0000(17)	95.9410(5)
γ, deg	101.233(2)	90	90
V, Å^3	3438.2(5)	4607.0(4)	5235.03(11)
d_{calc}, g/cm^3	1.255	1.233	1.250
R indices [$I>2\sigma(I)$]: R1, wR2	0.0593, 0.1545	0.0621, 0.1156	0.0508, 0.1068
R1, wR2 (all data)	0.1040, 0.1742	0.0991, 0.1256	0.0958, 0.1224

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6a and 7a

6a		**7a**	
Ti(1)−O(1)	1.880(2)	Ti(1)−O(1)	1.882(3)
Ti(1)−O(2)	1.926(2)	Ti(1)−O(2)	1.908(3)
Ti(1)−N(2)	2.129(3)	Ti(1)−N(4)	2.070(4)
Ti(1)−N(3)	2.156(3)	Ti(1)−N(1)	2.165(4)
Ti(1)−N(1)	2.156(3)	Ti(1)−N(3)	2.174(4)
Ti(1)−N(4)	2.178(3)	Ti(1)−N(2)	2.216(4)
N(1)−C(1)	1.366(5)	N(1)−C(24)	1.359(6)
N(1)−C(5)	1.385(5)	N(1)−C(28)	1.361(6)
N(2)−C(10)	1.365(5)	N(2)−C(33)	1.351(6)
N(2)−C(6)	1.388(5)	N(2)−C(29)	1.374(6)
N(3)−C(11)	1.345(5)	N(3)−C(34)	1.348(6)
N(3)−C(15)	1.369(4)	N(3)−C(38)	1.369(6)
N(4)−C(20)	1.351(5)	N(4)−C(43)	1.363(6)
N(4)−C(16)	1.370(5)	N(4)−C(39)	1.407(6)
C(1)−C(2)	1.356(5)	C(24)−C(25)	1.373(7)
C(2)−C(3)	1.394(6)	C(25)−C(26)	1.389(7)
C(3)−C(4)	1.354(6)	C(26)−C(27)	1.377(7)
C(4)−C(5)	1.406(5)	C(27)−C(28)	1.407(7)
C(5)−C(6)	1.411(6)	C(28)−C(29)	1.454(7)
C(6)−C(7)	1.397(6)	C(29)−C(30)	1.386(7)
C(7)−C(8)	1.359(6)	C(30)−C(31)	1.380(7)
C(8)−C(9)	1.399(6)	C(31)−C(32)	1.376(7)
C(9)−C(10)	1.371(5)	C(32)−C(33)	1.363(7)
C(11)−C(12)	1.370(5)	C(34)−C(35)	1.353(7)
C(12)−C(13)	1.390(6)	C(35)−C(36)	1.399(7)
C(13)−C(14)	1.366(5)	C(36)−C(37)	1.360(7)
C(14)−C(15)	1.393(5)	C(37)−C(38)	1.415(7)
C(15)−C(16)	1.445(5)	C(38)−C(39)	1.426(7)
C(16)−C(17)	1.389(5)	C(39)−C(40)	1.408(7)
C(17)−C(18)	1.378(6)	C(40)−C(41)	1.369(7)
C(18)−C(19)	1.396(6)	C(41)−C(42)	1.404(7)
C(19)−C(20)	1.361(5)	C(42)−C(43)	1.355(7)
N(2)−Ti(1)−N(1)	72.30(12)	N(1)−Ti(1)−N(2)	72.52(16)
N(3)−Ti(1)−N(4)	71.36(11)	N(4)−Ti(1)−N(3)	75.36(17)

angles of the bidentate bipyridine ligands (which range from 71° to 75°, Table 2), as well as steric constraints imposed by the chelating bis(aryloxide) ligand. Ti−O and Ti−N bond distances of **6a** and **7a** essentially parallel those reported for [(2,6-Pr$^i_2$C$_6$H$_3$O)$_2$Ti(bpy)$_2$].[8a] However unlike in free bipyridine,[15] a small but systematic alternation of short and long C−C bond distances is apparent within pyridine units of the bipyridine ligands of **6a** and **7a** (Table 2).[16] In addition, the bridge C−C bonds of the bipyridine ligands are intermediate between single and double bonds (average bridge C−C = 1.428(6) and 1.440(7) Å for **6a** and **7a**, respectively). These data are indicative of some disruption of the aromaticity of the bipyridine ligands and suggest electron transfer into the LUMO (π^* orbital) of each bipyridine ligand. Comparable structural data and conclusions have been outlined for related bipyridine and biphosphinine complexes of Zr(II), [Zr(bpy)$_3$]$^{2-}$, and [Zr(P$_2$C$_{10}$H$_4$Me$_4$)$_3$]$^{2-}$,[8d] as well as for [Mo(OPr^i)$_2$(bpy)$_2$][15] and a bipyridine dianion.[17]

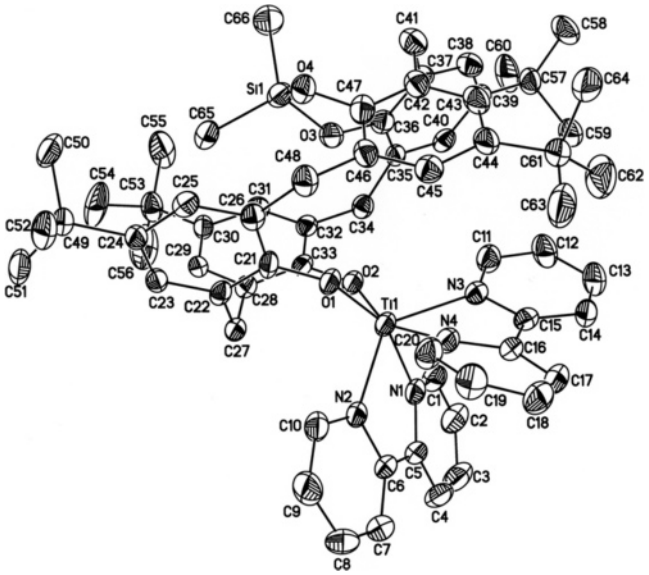


Figure 1. Molecular structure of [(DMSC)Ti(bpy)$_2$] (**6a**) (50% probability ellipsoids).

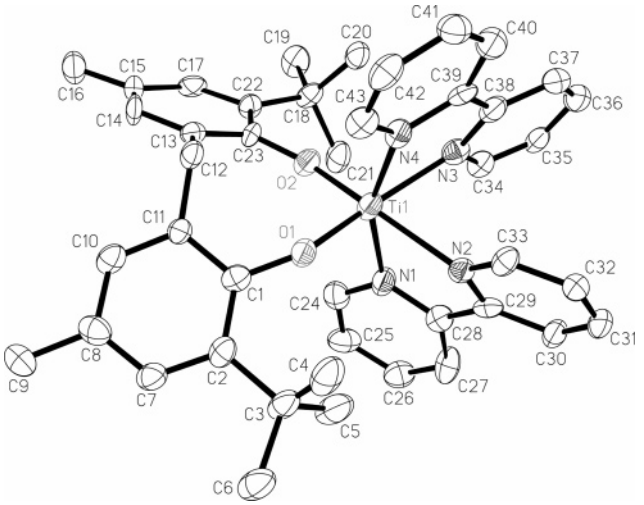


Figure 2. Molecular structure of [(MBMP)Ti(bpy)$_2$] (**7a**) (50% probability ellipsoids).

Formally, [(RO)$_2$Ti(L$_2$)$_2$] complexes **6a**−**c** and **7a**,**b** are Ti(II) complexes. In fact, the oxidation state of Ti in [(2,6-Pr$^i_2$C$_6$H$_3$O)$_2$Ti(bpy)$_2$] was assigned as +2 on the basis of electrochemical studies.[8a] However,

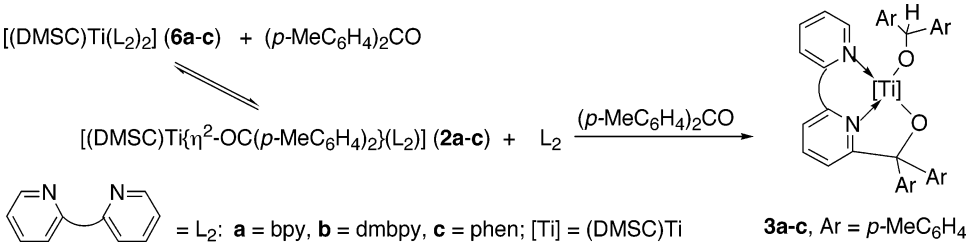
(14) (a) Serpone, N.; Bickley, D. G. In *Prog. Inorg. Chem.* **1972**, *17*, p 391. (b) Montgomery, C. D.; Shorrock, C. J. *Inorg. Chim. Acta* **2002**, *328*, 259. (c) Rodger, A.; Johnson, B. F. G. *Inorg. Chem.* **1988**, *27*, 3061.

(15) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945.

(16) The systematic nature of the alternation of short and long C−C bond distances is obvious, although the magnitude of the alternations is similar to accuracy limitations of the spherical atom scattering factor approximation (see, Coppens, P.; Sabine, T. M.; Delaplane, R. G.; Ibers, J. A. *Acta Crystallogr.* **1969**, *B25*, 2451).

(17) Bock, H.; Lehn, J.-M.; Pauls, J.; Holl, S.; Krenzel, V. *Angew. Chem., Int. Ed.* **1999**, *38*, 952.

Scheme 2



$[(RO)_2Ti(L_2)_2]$ complexes possess a delocalized electronic structure; hence redox properties of Ti will be strongly influenced by redox properties of the diimine ligands. In addition, excited electronic states may be thermally and/or photochemically accessible. For example, EPR and magnetic susceptibility studies of $[(\eta^5\text{-}C_5H_5)_2Ti(L_2)]$ (L_2 = bpy or phen) compounds have revealed that they possess a triplet excited state, which is thermally accessible from the ground-state singlet.[8b,c] The intense color of **6a**−**c** and **7a**,**b** is due to metal to (diimine) ligand charge-transfer (MLCT) transition.[4b,8] Hence electronic spectra of [(DMSC)Ti(dmbpy)$_2$] (**6b**) and [(DMSC)Ti(phen)$_2$] (**6c**) in toluene display strong bands below 400 nm. In the visible region, the absorbance maxima for **6b** and **6c** are observed at 640 and 712 nm, respectively. Bathochromic shift of the absorbance maximum of **6c** reflects the lower energy of the π^* state of 1,10-phenanthroline.[18] Magnetic susceptibility studies (by the Evans method)[19] of **6a** and **6c** over the 296 to 353 K temperature range revealed that the compounds are weakly paramagnetic.[20] For example, **6c** has a magnetic moment (μ_{eff}) of 0.6 μ_B at 296 K, similar to the magnetic moment (0.6−0.8 μ_B) reported for $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]$.[8f,g]

Reactivity of $[(RO)_2Ti(L_2)_2]$ with Ketones. [(DMSC)Ti(L$_2$)$_2$] (**6a**−**c**) undergo light-assisted reaction[21] with ≥2 equiv of $(p\text{-}MeC_6H_4)_2CO$ to cleanly yield corresponding 2-aza-5-oxa-titanacyclopentenes (**3a**−**c**).[4b] Dark blue or olive-green C_6D_6 solutions of **6a**−**c** turn deep dark green before eventually becoming orange at completion. ^{1}H NMR monitoring of the reaction mixtures revealed [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(L$_2$)] (**2a**−**c**)[4b] as intermediates (Scheme 2). However, reactions of **6a**−**c** with $(p\text{-}MeC_6H_4)_2CO$ proceed reversibly and the equilibrium between **6a**−**c** and **2a**−**c** depends on relative abilities of $(p\text{-}MeC_6H_4)_2CO$ and the diimine (L_2) to accept π-electron density.

Hence the equilibrium shifts increasingly toward **2a**−**c** with decreasing diimine π-acidity.[22] For example, reaction of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(dmbpy)] (**2b**) with 1 equiv of dmbpy in C_6D_6 furnished a ∼3:22:1 ratio of **6b**, **2b**, and **3b** after 2 h (by ^{1}H NMR). Conversely, similar reaction of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(bpy)] (**2a**) with 1 equiv of bpy in C_6D_6 for 2 h produced a ∼2:2:1 ratio of **6a**, **2a**, and **3a**. Reaction of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(phen)] (**2c**) with phen (1.4 equiv) in C_6D_6 was complete in 1 h, affording **6c** and **3c** in ∼1:1 ratio.[23] These results also imply that **2a**−**c** react faster with aromatic diimines than $(p\text{-}MeC_6H_4)_2CO$. Thus, the rate of formation of 2-aza-5-oxa-titanacyclopentenes **3a**−**c** from **6a**−**c** will show dependence on ketone concentration. Accordingly, only 95% of [(DMSC)Ti(bpy)$_2$] (**6a**) had reacted after 21 h in the presence of 2 equiv of $(p\text{-}MeC_6H_4)_2CO$ in C_6D_6 (by ^{1}H NMR), while complete consumption of **6a** occurred in ∼10.5 h with 3 equiv of $(p\text{-}MeC_6H_4)_2CO$. Moreover, quantitative formation of **3a** was observed in the latter reaction in ∼16 h, while the former reaction was only ∼90% complete even after 36 h.

Qualitatively, the rate of formation of **3a**−**c** from [(DMSC)Ti(L$_2$)$_2$] (**6a**−**c**) followed the order L$_2$ = bpy < dmbpy < phen. Thus, formation of **3b** was complete in 12 h when [(DMSC)Ti(dmbpy)$_2$] (**6b**) was reacted in C_6D_6 with 3 equiv of $(p\text{-}MeC_6H_4)_2CO$, while analogous reaction of [(DMSC)Ti(phen)$_2$] (**6c**) with $(p\text{-}MeC_6H_4)_2CO$ (3 equiv) yielded **3c** in 8 h. Interestingly, the rate of the reaction of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(L$_2$)] (**2a**−**c**) with $(p\text{-}MeC_6H_4)_2CO$ (1 equiv) in C_6D_6 was previously shown to increase in the order L$_2$ = dmbpy < bpy ≪ phen.[24] Consequently, the efficacy of the

(18) Reduction potentials for the diimine ligands are listed in the table below. The data suggest that the thermodynamic feasibility of one-electron transfer to the π^* orbital of the diimine ligand follows the order dmbpy < bpy < phen and reflects their ability to stabilize low-valent titanium.

compound	$E°$/V vs SCE	E_p^2/V[a] vs SCE
bpy	−2.13[b]	
dmbpy	−2.20[b]	
phen	−1.99[b]	
$(p\text{-}MeC_6H_4)_2CO$	−1.87[c]	−2.37[c]

[a] E_p^2 = peak potential for further reduction of the radical anion. [b] Krishnan, C. V.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1983**, *105*, 5617. [c] Grimshaw, J.; Hamilton, R. *J. Electroanal. Chem.* **1980**, *106*, 339.

(19) Evans, B. D. F. *J. Chem. Soc.* **1959**, 2003.

(20) Apparently, NMR spectra of **6a**−**c** are not significantly affected by any unpaired electron density. Sharp resonances were similarly observed in ^{1}H and ^{13}C NMR spectra of **2a**−**c** even though preliminary data from room- and low-temperature (110 K) ESR studies of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}dmbpy] (**2b**) in the solid state and in toluene indicate the presence of two radical species.[4b]

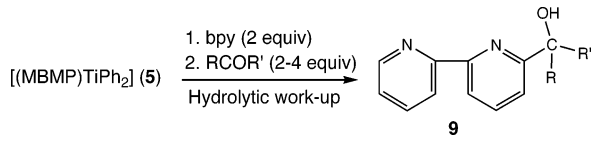
(21) Reactions of **6a**−**c** with $(p\text{-}MeC_6H_4)_2CO$ proceed at a much slower rate when their solutions are protected from light. For instance, the reaction of [(DMSC)Ti(dmbpy)$_2$] (**6b**) with 3 equiv of $(p\text{-}MeC_6H_4)_2CO$ in C_6D_6 to give [(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_5$Me$_2$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (**3b**) was complete in <7 h when a NMR tube containing the solution under N_2 was left exposed to ambient light. The reaction took much longer when an identical solution in a NMR tube was left spinning in the NMR probe (see Results and Discussion).

(22) Reference 18 lists reduction potentials for the diimine ligands and $(p\text{-}MeC_6H_4)_2CO$. It is apparent from the data that one-electron transfer to $(p\text{-}MeC_6H_4)_2CO$ is thermodynamically favored over one-electron transfer to diimine.

(23) [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(phen)] (**2c**) could only be isolated along with [(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{12}$H$_7$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (**3c**).[4b] Thus, reaction between 40 mg of a 1:4 molar mixture of **2c** (6.95 mg, 0.00622 mmol) and **3c** (33 mg, 0.0249 mmol) in C_6D_6 and 1.6 mg (0.0088 mmol) of 1,10-phenanthroline (∼1.4 equiv relative to **2c**) was followed by ^{1}H NMR spectroscopy. Formation of **3c** is irreversible and has no effect on the reaction, and the amount of **3c** initially present in solution was accounted for in our analysis.

(24) This reactivity order parallels the decrease in the energy gap between π and π^* states of the diimines. We believe that metal to diimine ligand charge transfer (MLCT) transitions and the resulting radical species play important roles in the transformation.[4b]

Table 3. Reductive Coupling of [(MBMP)Ti(bpy)$_2$] (7a) with Ketones



	RCOR′			
entry	R	R′	rxn time	% yield of **9**
1	Ph	Ph	18 h[a]	88[c] (**9a**)
2	Ph	Me	36 h[b]	28[c] (**9b**)
3	Ph	CH_2Ph	48 h[b]	15[c] (**9c**)
4	Ph	*i*-Bu	72 h[b]	trace[d]
5	$Me_2NC_6H_4$	$Me_2NC_6H_4$	72 h[b]	trace[d]
6	Et	Et	72 h[b]	trace[d]

[a] 2 equiv of Ph_2CO used. [b] 4 equiv of ketone used. [c] Unoptimized isolated yield. [d]Determined by GC-MS.

formation of 2-aza-5-oxa-titanacyclopentenes **3a**−**c** from [(DMSC)Ti(L$_2$)$_2$] (**6a**−**c**) must depend on the relative concentrations of **6a**−**c** and **2a**−**c** in solution (hence diimine π-acidity), as well as on the rate of reaction of **2a**−**c** with (*p*-$MeC_6H_4)_2CO$. For example, while reaction of [(DMSC)Ti{η^2-OC(*p*-$MeC_6H_4)_2$}(bpy)] (**2a**) with (*p*-$MeC_6H_4)_2CO$ is faster than reaction of [(DMSC)Ti{η^2-OC(*p*-$MeC_6H_4)_2$}(dmbpy)] (**2b**) with (*p*-$MeC_6H_4)_2CO$, the equilibrium between [(DMSC)Ti(L$_2$)$_2$] and [(DMSC)Ti{η^2-OC(*p*-$MeC_6H_4)_2$}(L$_2$)] lies further toward [(DMSC)Ti{η^2-OC(*p*-$MeC_6H_4)_2$}(L$_2$)] when L$_2$ = dmbpy than when L$_2$ = bpy (vide infra), and the net result is that complete conversion of **6b** into **3b** occurs faster than complete conversion of **6a** into **3a**.

MBMP is obtained from inexpensive 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol); hence the reactivity of [(MBMP)Ti(bpy)$_2$] (**7a**) with ketones was explored with the aim of developing a viable synthetic route to 6-(1-hydroxyalkyl)-2,2′-bipyridines.[25] We typically generated **7a** in a glass pressure tube by reaction of [(MBMP)TiPh$_2$] (**5**) with 2 equiv of bpy in ether. Next, 2−4 equiv of ketone is introduced into the resulting dark blue solution. The tube is then sealed with a Teflon screw cap and heated at 65 °C for a period of time during which the reaction progress was monitored via GC-MS analysis of aliquots. [(MBMP)Ti(κ^3-$OCPh_2C_{10}H_7N_2$)-($OCHPh_2$)] (**8a**) was isolated as an orange powder in good yield from reaction of **7a** with Ph_2CO (∼2.7 equiv) in ether at 65 °C for 12 h, while 6-(1-hydroxyalkyl)-2,2′-bipyridines (**9a**−**c**, Table 3) were isolated after hydrolysis and workup of corresponding reaction mixtures. The structure of **8a** was characterized by solution NMR data. Both the ^{1}H and ^{13}C NMR data are consistent with C_1-symmetry in solution. In its ^{1}H NMR spectrum, two singlets at δ 0.38 and 1.50 ppm, two singlets at δ 2.11 and 2.16 ppm, and two doublets at δ 2.73 and 5.92 ppm are observed for inequivalent *tert*-butyl groups, *p*-tolyl methyl groups, and bridging methylene protons of the MBMP ligand, respectively. The alkoxide proton (Ti-OCHPh$_2$) of **8a** is observed as a singlet at δ 5.56 ppm in the ^{1}H NMR spectrum and the alkoxide carbon (Ti-O*C*HPh$_2$) at δ 86.8 ppm in the ^{13}C NMR spectrum.[4b,26] The resonance for the Ti-O-C carbon of the 2-aza-5-oxa-titanacyclopentene ring shows at δ 99.5 ppm.[27] X-ray analysis of single crystals of **8a** confirmed the structure assigned by spectroscopy. Crystallographic data and selected metrical parameters are given in Tables 1 and 4, respectively. The molecular structure of **8a** shows that it has a distorted octahedral structure and a meridional tridentate alkoxy-bipyridyl ligand (Figure 3). The distortion from idealized octahedral geometry arises from acute bite angles of the tridentate alkoxy-bipyridyl ligand [ca. 74° for O(1)−Ti(1)−N(1) and 70° for N(1)−Ti(1)−N(2)], as well as steric constraints imposed by the MBMP chelate ligand. The Ti−N and Ti−O bond lengths are essentially identical to those of the related 2-aza-5-oxa-titanacylcopentene derivative [(DMSC)Ti{κ^3-OC(*p*-$MeC_6H_4)_2C_{10}H_7N_2$}{OCH(*p*-$MeC_6H_4)_2$}] (**3a**).[4b]

Table 4. Selected Bond Distances (Å) and Angles (deg) for 8a

Ti(1)−O(2)	1.8502(17)
Ti(1)−O(1)	1.8651(17)
Ti(1)−O(4)	1.8850(17)
Ti(1)−O(3)	1.9075(17)
Ti(1)−N(2)	2.185(2)
Ti(1)−N(1)	2.277(2)
O(2)−Ti(1)−O(1)	99.09(7)
O(2)−Ti(1)−O(4)	91.09(7)
O(1)−Ti(1)−O(4)	97.71(8)
O(2)−Ti(1)−O(3)	94.00(7)
O(1)−Ti(1)−O(3)	98.66(7)
O(4)−Ti(1)−O(3)	161.86(8)
O(2)−Ti(1)−N(2)	172.25(8)
O(1)−Ti(1)−N(2)	74.68(7)
O(4)−Ti(1)−N(2)	85.26(8)
O(3)−Ti(1)−N(2)	91.55(7)
O(2)−Ti(1)−N(1)	115.73(8)
O(1)−Ti(1)−N(1)	145.16(8)
O(4)−Ti(1)−N(1)	81.55(7)
O(3)−Ti(1)−N(1)	80.56(7)
N(2)−Ti(1)−N(1)	70.54(8)

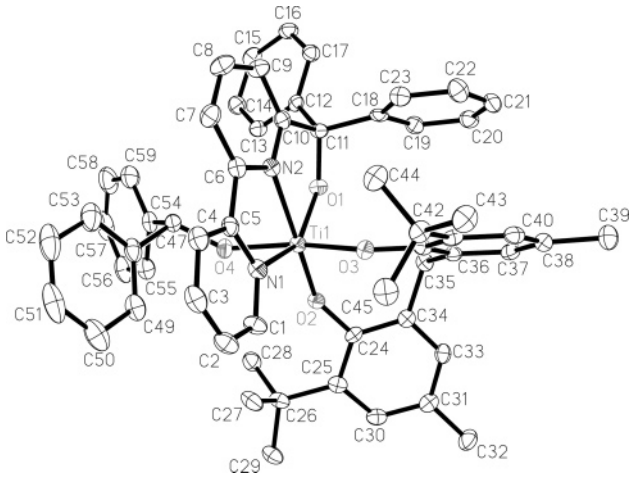


Figure 3. Molecular structure of [(MBMP)Ti{κ^3-$OCPh_2C_{10}H_7N_2$}($OCHPh_2$)] (**8a**) (50% probability ellipsoids).

(25) Our preliminary studies suggest that coordination of a chelating bis(aryloxide) ligand in [(RO)$_2$Ti(bpy)$_2$] compounds facilitates reductive coupling with ketones. Presumably, the chelating bis(aryloxide) ligand enforces *cis*-arrangement of diimine and ketone molecules. For example, Ti(OPr^i)$_4$/2Pr^{i}MgCl did not promote reductive coupling of bpy with Ph_2CO under a variety of conditions.

(26) For typical ^{1}H and ^{13}C NMR chemical shift values for the Ti-$OCHAr_2$ group, see also: (a) Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329. (b) Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66.

(27) Similar chemical shift values have been reported for related compounds. ^{13}C NMR (CD_2Cl_2): δ 93−97 ppm for [{κ^2-$OCAr_2C_5H_4N$}$_2$-Ti(NMe_2)$_2$] (Ar = various aryl groups)[28] and ^{13}C NMR ($CDCl_3$): δ 107 ppm for [CpTi{κ^2-$OCR_2C_5H_4N$}Cl_2] (R = Pr^i or Ph).[29]

Reactions that yield 2-aza-5-oxa-titanacyclopentenes invariably turn dark green before eventually becoming orange. The dark green color is identical to that for solutions of [(DMSC)Ti{η^2-OC(p-MeC_6H_4)$_2$}(L_2)] complexes (**2a**−**c**),[4b] implying [(MBMP)Ti(η^2-ketone)(bpy)] intermediates in the reaction. As in the formation of 2-aza-5-oxa-titanacyclopentenes **3a**−**c** from [(DMSC)-Ti(L_2)$_2$] (**6a**−**c**), the efficacy of reductive coupling reaction between [(MBMP)Ti(bpy)$_2$] (**7a**) and ketones is increased by increasing ketone concentration. Apparently, the formation of the 2-aza-5-oxa-titanacyclopentene product is increasingly inhibited by bipyridine released from **7a** as the reaction proceeds. The efficacy of the reaction also depends on the relative abilities of the ketone and the diimine to accept π-electron density, consistent with an equilibrium between **7a** and [(MBMP)Ti(η^2-ketone)(bpy)]. The yield of the 2-aza-5-oxa-titanacyclopentene product decreases with decreasing ketone π-acidity in the order Ph_2CO > PhCOR ≫ R_2CO (R = alkyl) ∼ (p-$Me_2NC_6H_4$)$_2$CO (Table 3). Aliphatic ketones and (p-$Me_2NC_6H_4$)$_2$CO probably react sluggishly with **7a** because formation of [(MBMP)Ti(η^2-ketone)(bpy)] species is thermodynamically unfavorable since aliphatic ketones and (p-Me_2N-C_6H_4)$_2$CO are weaker π-acids than bipyridine.[30] These results strongly support a mechanism that involves reversible dissociation of a diimine ligand (L_2) from [(RO)$_2$Ti(L_2)$_2$] and reversible coordination of a ketone to titanium prior to the rate-limiting step. Attempts to improve the efficiency of the reductive coupling of **7a** with ketones by conducting the reaction at higher temperatures in toluene or THF led to complicating side reactions, including formation of [(MBMP)$_2$Ti].[31,32]

Summary

Reactions of [(RO)$_2$Ti(L_2)$_2$] (L_2 = bpy, dmbpy, or phen; (RO)$_2$ = DMSC or MBMP) with ketones yield corresponding 2-aza-5-oxa-titanacyclopentenes. Efficacy of the formation of 2-aza-5-oxa-titanacyclopentenes **3a**−**c** from reductive coupling of [(DMSC)Ti(L_2)$_2$] (**6a**−**c**) with (p-MeC_6H_4)$_2$CO increased with increasing ketone concentration and in the order L_2 = bpy < dmbpy < phen. This order may be explained by reversible formation of [(DMSC)Ti{η^2-OC(p-MeC_6H_4)$_2$}(L_2)] (**2a**−**c**) intermediates and a rate-limiting step that is dependent on ketone concentration. In reactions of [(MBMP)Ti(bpy)$_2$] (**7a**) with ketones and aldehydes, the yield of 2-aza-5-oxa-titanacyclopentene (and hence 6-(1-hydroxyalkyl)-2,2′-bipyridine) decreased with decreasing ketone π-acidity in the order Ph_2CO > PhCOR ≫ R_2CO (R = H, Me, Et, Pr^i, Bu^t, Bu^i, or C_5H_9) ∼ (p-$Me_2NC_6H_4$)$_2$CO. We are continuing our investigations of the synthesis, electronic structure, and reactivity of reduced titanium complexes.

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Supporting Information Available: A summary of crystallographic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **6a**·($C_{10}H_8N_2$)$_{1.5}$, **7a**, and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Doherty, S.; Errington, R. J.; Jarvis, A. P.; Collins, S.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1998**, *17*, 3408.

(30) Mixtures of aliphatic ketones or (p-$Me_2NC_6H_4$)$_2$CO with [(MBMP)Ti(bpy)$_2$] (**7a**) in ether at 65 °C in a sealed tube slowly turn green. However, the reaction mixtures either remain green even after 7 days at 65 °C or exist as green solutions containing orange-green precipitate. This observation suggests that the equilibrium between **7a** and [(MBMP)Ti(η^2-ketone)bpy] lies decidedly toward **7a** and that conversion of [(MBMP)Ti(η^2-ketone)bpy] into 2-aza-5-oxa-titanacyclopentene is very slow in these cases.

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(32) ^{1}H NMR showed that [(MBMP)$_2$Ti] is formed from prolonged heating (at 70 °C) of **7a** in C_6D_6 under N_2 atmosphere.