Synthesis and Reactivity of [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] Complexes (DMSC = Dimethylsilyl-Bridged *p-tert*-Butylcalix[4]arene Dianion, Ar = Aryl Group, and L$_2$ = Delocalized Diimine)

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Reactions of titanapinacolate complexes [(DMSC)Ti(OCAr$_2$CAr$_2$O)] (**1**, Ar = Ph; **2**, Ar = *p*-MeC$_6$H$_4$; DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion) with 1 equiv of a delocalized diimine furnished titanium η^2-ketone complexes [(DMSC)Ti(η^2-OCAr$_2$)L$_2$)] **3**−**6** (L$_2$ = bpy, dmbpy, or phen). The ketone is weakly bound in **3**−**6**, and it is readily dissociated. The compounds dissolve in aromatic hydrocarbon solvents to give intense green solutions and undergo a photochemically assisted transformation into 1-aza-5-oxa-titanacyclopentene derivatives **8**−**11**, in which C−H activation of the heterocyclic diimine ligand and hydride migration to a Ti-bound ketone to form an alkoxide group has occurred. The reaction of **3**−**6** with one or more equivalents of appropriate ketone gave **8**−**11** in high yield. The compounds were characterized by NMR (^{1}H and ^{13}C) and microanalysis data, as well as by X-ray crystallography for [(DMSC)Ti{κ^3-OC(*p*-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}{OCH-(*p*-MeC$_6$H$_4$)$_2$}] (**9**). The ease of transformation of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}L$_2$] complexes (**4**, L$_2$ = bpy; **5**, L$_2$ = dmbpy; **6**, L$_2$ = phen) into **9**−**11** tracks the facility of metal to diimine ligand charge transfer (MLCT) transition and increased in the order **5** < **4** ≪ **6**. This transformation is suggested to occur by a mechanism that involves reversible coordination of ketone to titanium and a rate-limiting step that is dependent on ketone concentration.

Introduction

Transition metal-mediated reductive coupling reactions of unsaturated organic substrates, such as imines, alkynes, aldehydes, and ketones, are important to the fields of organic synthesis and organometallic chemistry.[1,2] In pinacol and McMurry reactions, metallapinacolate complexes have been implicated as intermediates.[2] We have recently reported the synthesis of well-characterized titanapinacolate complexes, [(DMSC)Ti-(OCAr$_2$CAr$_2$O)] (**1**, Ar = Ph; **2**, Ar = *p*-MeC$_6$H$_4$; DMSC = 1,2-alternate dimethylsilyl-bridged *p-tert*-butylcalix[4]arene dianion)[3] (Chart 1). Structural characterization of **1** by X-ray crystallography revealed that the unit cell contained two independent molecules and that the OCPh$_2$CPh$_2$O fragment of each molecule possessed an unusually long C−C bond [1.628(6) and 1.652(5) Å]. This led us to wonder whether titanapinacolates **1** and **2** would serve as useful synthons to (DMSC)Ti(OCAr$_2$) species. Thus, we decided to explore the synthesis of [(DMSC)Ti(OCAr$_2$)L$_2$] complexes in which L$_2$ is a delocalized diimine, such as 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-dipyridyl (dmbpy), or 1,10-phenanthroline (phen). Delocalized diimine ligands were chosen because they have been shown to support electron-rich low-valent titanium centers.[4]

Many aldehyde and ketone complexes of the transition metals are known, and metal-promoted reactivity of carbonyl compounds has been investigated.[5−8] Aldehyde and ketone complexes of the group 4 metals are usually bimolecular with bridging carbonyl functions.[8]

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(5) See for example the following and references therein: (a) Helberg, L. E.; Gunnoe, T. B.; Brooks, B. C.; Sabat, M.; Harman, W. D. *Organometallics* **1999**, *18*, 573. (b) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: New York, 1991; Vol. 1, Chapter 1.10.

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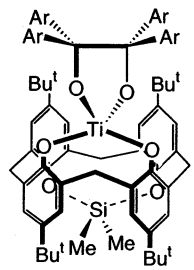
Chart 1



1, Ar = Ph; **2**, Ar = p-MeC$_6$H$_4$

Few well-characterized mononuclear group 4 metal-ketone complexes bearing alkyl or aryl substituents, such as η^2-ketone complexes [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(η^2-Ph$_2$-CO)(PMe$_3$)][7d,e] and [Hf(TC-3,5)(η^2-OC(CH$_2$Ph)$_2$)][7f] (TC-3,5 = tropocorand ligand), have been reported. Since the coordination of an organic functional group to a transition metal complex is undoubtedly central to achieving selectivity in transition metal-mediated reductive couplings of unsaturated organic substrates, increased knowledge of the structure and reactivity of organic carbonyl complexes of titanium would greatly facilitate the development of a greater control over titanium-mediated reductive coupling reactions. In this paper, we describe the synthesis, aspects of the structure, and reaction chemistry of titanium η^2-ketone complexes [(DMSC)Ti-(η^2-OCAr$_2$)L$_2$] supported by dimethylsilyl-bridged calix-[4]arene ligation.

Experimental Section

General Details. All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Solvents were dried and distilled by standard methods before use. Pentane was distilled twice from sodium benzophenone ketyl with addition of 1 mL/L of tetraethylene glycol dimethyl ether as a solubilizing agent. Benzene-d_6 was distilled from sodium benzophenone ketyl. 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. Ph$_2$^{13}CO, 1,10-phenanthroline, 4,4′-dimethylbenzophenone, and 2,2′-bipyridine were purchased from Aldrich and sublimed prior to use. [(DMSC)-Ti(OCPh$_2$CPh$_2$O)] (**1**) and [(DMSC)Ti{OC(p-MeC$_6$H$_4$)$_2$C(p-MeC$_6$H$_4$)$_2$O] (**2**) were prepared as previously reported.[3] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at ca. 22 °C. ^{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. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

[(DMSC)Ti(η^2-OCPh$_2$)(bpy)] (3). 2,2′-Bipyridine (30.0 mg, 0.192 mmol) was added into a 25 mL suspension of [(DMSC)-Ti(OCPh$_2$CPh$_2$O)] (**1**) (0.219 g, 0.197 mmol) in pentane. The reaction mixture was stirred for 30 min at room temperature, during which time orange solids started to precipitate. The resulting suspension was filtered, and the orange precipitate was washed with pentane (10 mL) and dried under vacuum. Yield: 0.213 g, 99%. ^{1}H NMR (C$_6$D$_6$): δ 8.64 (d, J = 5.0 Hz, 2H, arom CH), 7.73 (d, J = 1.6 Hz, 2H, arom CH), 7.69 (d, J = 1.4 Hz, 2H, arom CH), 7.62 (d, J = 2.2 Hz, 2H, arom CH), 7.47 (d, J = 2.6 Hz, 2H, arom CH), 7.12−6.64 (m, 14H, arom CH), 6.07 (m, 2H, arom CH), 4.76 (d, J = 15.6 Hz, 1H, calix-CH$_2$), 4.60 (d, J = 16.0 Hz, 2H, calix-CH$_2$), 4.33 (d, J = 16.4 Hz, 2H, calix-CH$_2$), 3.73 (d, J = 15 Hz, 1H, calix-CH$_2$), 3.19 (d, J = 14.2 Hz, 1H, calix-CH$_2$), 2.89 (d, J = 13.6 Hz, 1H, calix-CH$_2$), 1.50 (s, 18H, t-Bu), 1.29 (s, 18, t-Bu), 0.35 (s, 3H, *exo*-SiCH$_3$), −1.15 (s, 3H, *endo*-SiCH$_3$). ^{13}C NMR could not be recorded as the compound transforms to other species in solution. ^{13}C NMR (C$_6$D$_6$) for [(DMSC)Ti(η^2-O^{13}CPh$_2$)(bpy)] (**3b**): δ 117.9 (^{13}CPh$_2$). Anal. Calcd for C$_{68}$H$_{76}$O$_5$N$_2$SiTi: C, 75.81; H, 7.11. Found: C, 76.13; H, 7.32.

[(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(bpy)] (4). 2,2′-Bipyridine (53.2 mg, 0.34 mmol) was added into a 10 mL suspension of [(DMSC)Ti{OC(p-MeC$_6$H$_4$)$_2$C(p-MeC$_6$H$_4$)$_2$O] (**2**) (0.399 g, 0.341 mmol) in pentane. The reaction mixture was stirred for 15 min, during which time green solids started to precipitate. The green solid was filtered and washed with pentane (4 × 5 mL) and dried under vacuum. Yield: 0.279 g, 73%. ^{1}H NMR (C$_6$D$_6$): δ 8.68 (d, J = 4.8 Hz, 2H, arom CH), 7.64 (d, J = 2.2 Hz, 2H, arom CH), 7.46 (d, J = 2.6 Hz, 2H, arom CH), 7.25 (d, J = 2.2 Hz, 2H, arom CH), 7.00 (d, J = 2.6 Hz, 2H, arom CH), 6.81 (m, 6H, arom CH), 6.61 (m, 6H, arom CH), 6.07 (m, 2H, arom CH), 4.76 (d, J = 14.6 Hz, 1H, calix-CH$_2$), 4.65 (d, J = 16.2 Hz, 2H, calix-CH$_2$), 4.34 (d, J = 16 Hz, 2H, calix-CH$_2$), 3.74 (d, J = 15 Hz, 1H, calix-CH$_2$), 3.19 (d, J = 14 Hz, 1H, calix-CH$_2$), 2.89 (d, J = 13.8 Hz, 1H, calix-CH$_2$), 2.21 (s, 6H, Tol-CH$_3$), 1.52 (s, 18H, t-Bu), 1.29 (s, 18, t-Bu), 0.34 (s, 3H, *exo*-SiCH$_3$), −1.15 (s, 3H, *endo*-SiCH$_3$). ^{13}C NMR could not be recorded as the compound transforms to other species in solution. Anal. Calcd for C$_{71}$H$_{80}$N$_2$O$_5$SiTi: C, 76.32; H, 7.22; N, 2.51. Found: C, 76.38; H, 7.42; N, 2.41.

A sample of **4** was decomposed with H$_2$O in CH$_2$Cl$_2$. The suspension was allowed to stand for a few minutes, the solids were filtered off, and the filtrate was analyzed by GC−MS. The only products observed were 2,2′-bipyridine (m/z 156, M$^+$) and OC(p-MeC$_6$H$_4$)$_2$ (m/z 210, M$^+$).

[(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}(dmbpy)] (5). 4,4′-Dimethyl-2,2′-dipyridyl (62.8 mg, 0.341 mmol) was added into a 10 mL suspension of [(DMSC)Ti{OC(p-MeC$_6$H$_4$)$_2$C(p-MeC$_6$H$_4$)$_2$O] (**2**) (0.399 g, 0.341 mmol) in pentane. The reaction mixture was stirred for 15 min, during which time green solids started to precipitate. The green solid was filtered and washed with pentane (4 × 5 mL) and dried under vacuum. Yield: 0.350 g,

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89%. ^{1}H NMR (C_6D_6): δ 8.59 (d, J = 5.63 Hz, 2H, arom CH), 7.67 (d, J = 2.4 Hz, 2H, arom CH), 7.48 (d, J = 2.8 Hz, 2H, arom CH), 7.27 (d, J = 2.4 Hz, 2H, arom CH), 7.06 (d, J = 2.4 Hz, 2H, arom CH), 6.88 (s, 2H, arom CH), 6.75 (AB quartet, 8H, arom CH), 5.93 (d, J = 5.6 Hz, 4H, arom CH), 4.78 (d, J = 14.8 Hz, 1H, calix-CH_2), 4.68 (d, J = 16.4 Hz, 2H, calix-CH_2), 4.37 (d, J = 16.4 Hz, 2H, calix-CH_2), 3.75 (d, J = 15.2 Hz, 1H, calix-CH_2), 3.26 (d, J = 14 Hz, 1H, calix-CH_2), 3.01 (d, J = 13.6 Hz, 1H, calix-CH_2), 2.21 (s, 6H, Tol-CH_3), 1.65 (s, 6H, dmbpy-*Me*), 1.54 (s, 18H, t-Bu), 1.31 (s, 18, t-Bu), 0.35 (s, 3H, *exo*-SiCH_3), −1.12 (s, 3H, *endo*-SiCH_3). ^{13}C NMR (C_6D_6): δ 161.0, 151.1, 149.7, 148.6, 147.9, 143.6, 141.5, 140.8, 131.9, 131.0, 130.8, 129.9, 129.4, 128.2, 127.2, 127.0, 126.9, 125.6, 125.2, 123.5, 120.8, 118.2 (CPh_2), 41.2 (calix-CH_2), 39.2 (calix-CH_2), 38.4 (calix-CH_2), 34.7 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 21.3 (Tol-CH_3), 20.9 (dmbpy-*Me*), 3.6 (*exo*-SiCH_3), −1.7 (*endo*-SiCH_3). Anal. Calcd for $C_{73}H_{84}N_2O_5$-SiTi: C, 76.55; H, 7.39; N, 2.45. Found: C, 76.19; H, 7.47; N, 2.40.

Into a C_6D_6 solution of **5** in a NMR tube was added an excess of distilled isopropyl alcohol under N_2. The green color of the solution turned purple, then red, and finally pale yellow. A ^{1}H NMR spectrum of the pale yellow solution confirmed the presence of (DMSC)H_2, OC(p-MeC_6H_4)$_2$, and 4,4′-dimethyl-2,2′-bipyridine. The solution was hydrolyzed with D_2O and extracted with CH_2Cl_2. GC−MS analysis of the CH_2Cl_2 extract also revealed only 4,4′-dimethyl-2,2′-bipyridine (m/z 184, M^+) and OC(p-MeC_6H_4)$_2$ (m/z 210, M^+).

[(DMSC)Ti{η^2-OC(p-MeC_6H_4)$_2$}(phen)] (6). 1,10-Phenanthroline (74.3 mg, 0.412 mmol) was added into a 10 mL suspension of [(DMSC)Ti{OC(p-MeC_6H_4)$_2$C(p-MeC_6H_4)$_2$O] (**2**) (0.493 g, 0.421 mmol) in pentane. The reaction mixture was stirred for 15 min, during which time green solids started to precipitate. The precipitate was filtered and washed with pentane (4 × 5 mL) and dried under vacuum to give 0.403 g of a green powder. ^{1}H NMR showed the presence of a 50:50 mixture of **6** and **11**. ^{1}H NMR (unobstructed resonances of **6**) (C_6D_6): δ 4.79 (d, J = 11.6 Hz, 1H, calix-CH2), 4.75 (d, J = 13.2 Hz, 2H, calix-CH_2), 4.41 (d, J = 16.4 Hz, 2H, calix-CH_2), 3.75 (d, J = 14.8 Hz, 1H, calix-CH_2), 3.21 (d, J = 13.6, 1H, calix-CH_2), 2.14 (s, 6H, p-*Me*C_6H_4), 1.52 (s, 18H, t-Bu), 1.29 (s, 18H, t-Bu), 0.36 (s, 3H, *exo*-SiMe), −1.12 (s, 3H, *endo*-SiMe).

[(DMSC)Ti{κ^3-OCPh$_2$C$_{10}$H$_7$N$_2$}(OCHPh$_2$)] (8). Into a toluene (10 mL) solution of [(DMSC)Ti(η^2-OCPh$_2$)(bpy)] (**3**) (0.180 g, 0.166 mmol) was added benzophenone (32.0 mg, 0.176 mmol). The orange solution slowly turned to dark green within 30 min. The reaction mixture was stirred for 12 h at room temperature, during which time an orange solution resulted. This orange solution was stripped to dryness under vacuum. The gummy orange residue was washed with pentane (4 × 5 mL) and dried under vacuum to afford an orange powder. Yield: 0.180 g, 85%. ^{1}H NMR (C_6D_6): δ 8.11 (d, J = 7.2 Hz, 2H, arom CH), 7.57 (d, 7.2 Hz, 2H, arom CH), 7.32−7.17 (m, 7H, arom CH), 7.06−6.82 (m, 16H, arom CH), 6.59 (m, 2H, arom CH), 6.46−6.22 (m, 4H, arom CH), 6.38 (d, J = 15.2 Hz, 1H, calix-CH_2), 6.11 (d, J = 7.2 Hz, 2H, arom CH), 5.89 (s, 1H, OC*H*Ph$_2$, 4.81 (d, J = 16 Hz, 1H, calix-CH_2), 4.68 (d, J = 15.6 Hz, 1H, calix-CH_2), 4.26 (d, J = 16.4 Hz, 1H, calix-CH_2), 3.45 (d, J = 16 Hz, 1H, calix-CH_2), 3.20 (d, J = 16 Hz, 1H, calix-CH_2), 3.12 (d, J = 16.4 Hz, 1H, calix-CH_2), 2.73 (d, J = 13.6 Hz, 1H, calix-CH_2), 1.38 (s, 9H, t-Bu), 1.30 (s, 9H, t-Bu), 1.28 (s, 9H, t-Bu), 1.14 (s, 9H, t-Bu), 0.16 (s, 3H, *exo*-SiCH_3), −1.03 (s, 3H, *endo*-SiCH_3). ^{13}C NMR (C_6D_6): δ 172.0, 162.9, 162.7, 152.6, 151.8, 151.2, 149.9, 148.6, 147.4, 147.1, 146.2, 144.9, 143.7, 143.1, 141.9, 138.8, 138.7, 138.6, 136.6, 133.5, 131.6, 131.1, 129.7, 129.5, 129.3, 128.6, 128.1, 127.6, 127.5, 127.2, 126.7, 126.3, 126.0, 125.2, 124.6, 124.5, 119.7, 117.8, 99.3 (O*C*Ph$_2$C$_{10}$H$_7$N$_2$), 85.6 (O*C*HPh$_2$), 42.3 (calix-CH_2), 39.4 (calix-CH_2), 37.5 (calix-CH_2), 35.6 (calix-CH_2), 34.4 {$C(CH_3)_3$}, 34.3 {$C(CH_3)_3$}, 32.4 {$C(CH_3)_3$}, 32.3 {$C(CH_3)_3$, 32.3 {$C(CH_3)_3$}, 32.2 {$C(CH_3)_3$}, 3.5 (*exo*-SiCH_3), −0.81 (*endo*-SiCH_3). Anal. Calcd for $C_{68}H_{76}O_5N_2$SiTi: C, 75.81; H, 7.11. Found: C, 76.03; H, 7.37.

[(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (9). Into a toluene (10 mL) solution of [(DMSC)-Ti{η^2-OC(p-MeC_6H_4)$_2$}(bpy)] (**4**) (0.138 g, 0.123 mmol) was added 4,4′-dimethylbenzophenone (62.0 mg, 0.294 mmol). The resulting greenish brown solution was stirred for 12 h at room temperature, during which time an orange solution resulted. The orange solution was stripped to dryness under vacuum. The gummy orange residue was washed with cold pentane (2 × 5 mL) and dried under vacuum to afford an orange powder. Yield: 0.136 g, 83%. Single crystals were grown from a 60:40 toluene/pentane mixture at room temperature. ^{1}H NMR (C_6D_6): δ 8.09 (d, J = 8 Hz, 2H, arom CH), 7.56 (d, 7.8 Hz, 2H, arom CH), 7.33−7.17 (m, 6H, arom CH), 7.07−6.72 (m, 14H, arom CH), 6.60−6.45 (m, 2H, arom CH), 6.36−6.15 (m, 4H, arom CH), 6.30 (d, J = 14 Hz, 1H, calix-CH_2), 5.90 (s, 1H, OC*H*(p-MeC_6H_4)$_2$, 4.84 (d, J = 16 Hz, 1H, calix-CH_2), 4.70 (d, J = 15 Hz, 1H, calix-CH_2), 4.28 (d, J = 15.8 Hz, 1H, calix-CH_2), 3.46 (d, J = 15.8 Hz, 1H, calix-CH_2), 3.24 (d, J = 15.4 Hz, 1H, calix-CH_2), 3.12 (d, J = 16.4 Hz, 1H, calix-CH_2), 2.71 (d, J = 13.8 Hz, 1H, calix-CH_2), 2.14 (s, 3H, p-*Me*C_6H_4), 2.08 (s, 3H, p-*Me*C_6H_4), 1.99 (s, 3H, p-*Me*C_6H_4), 1.90 (s, 3H, p-*Me*C_6H_4), 1.38 (s, 9H, t-Bu), 1.32 (s, 9H, t-Bu), 1.30 (s, 9H, t-Bu), 1.17 (s, 9H, t-Bu), 0.18 (s, 3H, *exo*-SiCH_3), −1.02 (s, 3H, *endo*-SiCH_3). ^{13}C NMR (C_6D_6): δ 171.6, 162.2, 161.9, 151.9, 151.2, 150.6, 149.3, 148.0, 144.1, 143.7, 143.1, 142.4, 141.9, 140.9, 137.9, 137.7, 137.6, 136.6, 136.5, 136.2, 135.9, 135.0, 134.5, 132.8, 131.0, 130.4, 129.1, 128.8, 128.6, 128.4, 128.2, 127.6, 1227.4, 127.1, 126.9, 126.6, 126.5, 125.3, 125.2, 124.5, 123.9, 123.8, 118.9, 116.9, 98.5 {O*C*(p-MeC_6H_4)$_2$C$_{10}$H$_7$N$_2$}, 84.8 {O*C*H(p-MeC_6H_4)$_2$}, 41.7 (calix-CH_2), 38.7 (calix-CH_2), 36.8 (calix-CH_2), 35.1 (calix-CH_2), 33.8 {$C(CH_3)_3$}, 33.6 {$C(CH_3)_3$}, 31.8 {$C(CH_3)_3$}, 31.7 {$C(CH_3)_3$}, 31.6 {$C(CH_3)_3$}, 31.5 {$C(CH_3)_3$}, 20.9 (p-*Me*C_6H_4), 20.8 (p-*Me*C_6H_4), 20.7 (p-*Me*C_6H_4), 20.6 (p-*Me*C_6H_4), 2.9 (*exo*-SiCH_3), −1.46 (*endo*-SiCH_3). Anal. Calcd for $C_{86}H_{94}N_2O_6$SiTi: C, 77.81; H, 7.13; N, 2.11. Found: C, 77.54; H, 6.98; N, 1.99.

Compound **9** was hydrolyzed by exposure to water in air, and the residue was extracted with CH_2Cl_2. EI-GC−MS analysis of the CH_2Cl_2 extract revealed both (p-MeC_6H_4)$_2$-CHOH (m/z 212 M^+) and HOC(p-MeC_6H_4)$_2$C$_{10}$H$_7$N$_2$ (m/z 366 M^+) were present.

[(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_5$Me$_2$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (10). Into a toluene (10 mL) solution of [(DMSC)-Ti{η^2-OC(p-MeC_6H_4)$_2$}(dmbpy)] (**5**) (0.187 g, 0.163 mmol) was added 4,4′-dimethylbenzophenone (39.7 mg, 0.189 mmol). The resulting greenish brown solution was stirred for 24 h at room temperature, during which time an orange solution resulted. This orange solution was stripped to dryness under vacuum. The gummy orange residue was washed with cold pentane (4 × 5 mL) and dried under vacuum to afford an orange powder. Yield: 0.193 g, 88%. ^{1}H NMR (C_6D_6): δ 8.15 (d, J = 8 Hz, 2H, arom CH), 7.56 (d, 8 Hz, 2H, arom CH), 7.35−7.22 (m, 6H, arom CH), 7.07−6.74 (m, 14H, arom CH), 6.63 (d, J = 2.4 Hz, 1H, arom CH), 6.47 (s, 1H, arom CH), 6.40−6.30 (m, 4H, arom CH), 6.33 (d, J = 14 Hz, 1H, calix-CH_2), 5.89 (s, 1H, OC*H*(p-MeC_6H_4)$_2$, 4.83 (d, J = 15.6 Hz, 1H, calix-CH_2), 4.71 (d, J = 15.6 Hz, 1H, calix-CH_2), 4.29 (d, J = 16 Hz, 1H, calix-CH_2), 3.50 (pseudo-triplet, J = 16 Hz & 15.6 Hz, 2H, calix-CH_2), 3.24 (d, J = 16 Hz, 1H, calix-CH_2), 2.74 (d, J = 15.8 Hz, 1H, calix-CH_2), 2.11 (s, 3H, p-*Me*C_6H_4), 2.09 (s, 3H, p-*Me*C_6H_4), 2.08 (s, 3H, p-*Me*C_6H_4), 1.99 (s, 3H, p-*Me*C_6H_4), 1.87 (s, 3H, dmbpy-*Me*), 1.65 (s, 3H, dmbpy-*Me*), 1.39 (s, 9H, t-Bu), 1.31 (s, 9H, t-Bu), 1.26 (s, 9H, t-Bu), 1.18 (s, 9H, t-Bu), 0.19 (s, 3H, *exo*-SiCH_3), −0.99 (s, 3H, *endo*-SiCH_3). ^{13}C NMR (C_6D_6): δ 172.0, 162.9, 162.6, 152.9, 152.1, 151.3, 150.8, 149.9, 148.5, 147.4, 144.9, 144.4, 144.1, 143.4, 143.1, 141.4, 138.6, 138.3, 137.3, 137.1, 136.9, 135.2, 133.5, 132.4, 131.1, 129.9, 129.3, 129.2, 129.1, 128.8, 128.6, 128.0, 127.7, 127.5, 127.4, 127.1, 126.4,

Table 1. Crystallographic Data for $9\cdot(C_7H_8)_{0.5}(C_5H_{12})$

formula	$C_{94.5}H_{110}N_2O_6SiTi$
fw	1445.88
T, K	150.0(2)
cryst syst	monoclinic
space group	*Cc*
Z	8
a, Å	34.0940(14)
b, Å	22.0310(10)
c, Å	24.5200(10)
α, deg	90
β, deg	116.130(13)
γ, deg	90
V, Å^3	16535.2(12)
d_{calc}, g/cm^3	1.165
R indices [$I > 2\sigma(I)$]: R1, wR2	0.0965, 0.2057

125.5, 124.7, 124.1, 120.9, 118.8, 99.1 {O*C*(*p*-MeC$_6$H$_4$)$_2$C$_{10}$H$_5$-Me$_2$N$_2$}, 85.3 {O*C*H(*p*-MeC$_6$H$_4$)$_2$}, 42.3 (calix-*C*H$_2$), 39.6 (calix-*C*H$_2$), 37.6 (calix-*C*H$_2$), 35.8 (calix-*C*H$_2$), 34.5 {*C*(CH$_3$)$_3$}, 34.3 {*C*(CH$_3$)$_3$}, 32.5 {C(*C*H$_3$)$_3$}, 32.3 {C(*C*H$_3$)$_3$}, 32.2 {C(*C*H$_3$)$_3$}, 22.1 (dmbpy-*C*H$_3$), 21.5 (*p*-*M*eC$_6$H$_4$), 21.4 (*p*-*M*eC$_6$H$_4$), 21.3 (*p*-*M*eC$_6$H$_4$), 3.5 (*exo*-Si*C*H$_3$), −0.82 (*endo*-Si*C*H$_3$). Anal. Calcd for $C_{88}H_{98}N_2O_6SiTi$: C, 77.96; H, 7.29; N, 2.07. Found: C, 77.75; H, 7.38; N, 2.00.

[(DMSC)Ti{κ^3-OC(*p*-MeC$_6$H$_4$)$_2$C$_{12}$H$_7$N$_2$}{OCH(*p*-MeC$_6$H$_4$)$_2$}] (11). Into a toluene (10 mL) solution of the 50:50 mixture of [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}(phen)] (**6**) and [(DMSC)Ti{κ^3-OC(*p*-MeC$_6$H$_4$)$_2$C$_{12}$H$_7$N$_2$}{OCH(*p*-MeC$_6$H$_4$)$_2$}] (**11**) (0.322 g) was added 59.2 mg (0.281 mmol) of 4,4′-dimethylbenzophenone. The resulting greenish brown solution was stirred for 24 h at room temperature, during which time an orange solution resulted. The orange solution was stripped to dryness under vacuum. The gummy orange residue was washed with cold pentane (4 × 5 mL) and dried under vacuum to afford 0.298 g of orange powder. Yield: 73% based on **6** (0.161 g, 0.141 mmol). ^{1}H NMR (C$_6$D$_6$): *δ* 8.20 (d, *J* = 8.4 Hz, 2H, arom CH), 7.49 (br d, *J* = 6.8 Hz, arom CH), 7.42−7.19 (m, 9H, arom CH), 7.10−6.74 (m, 12H, arom CH), 6.60−6.51 (m, 1H, arom CH), 6.56 (d, *J* = 15.2 Hz, 1H, calix-CH$_2$), 6.19 (d, *J* = 2 Hz, 1H, arom CH), 5.90 (s, 1H, OC*H*(*p*-MeC$_6$H$_4$)$_2$, 5.85 (AB quartet, 4H, arom CH), 4.91 (d, *J* = 16 Hz, 1H, calix-CH$_2$), 4.72 (d, *J* = 15.6 Hz, 1H, calix-CH$_2$), 4.33 (d, *J* = 16 Hz, 1H, calix-CH$_2$), 3.51 (d, *J* = 15.6 Hz, 1H, calix-CH$_2$), 2.72 (m, 3H, calix-CH$_2$), 2.10 (s, 3H, *p*-*Me*C$_6$H$_4$), 2.09 (s, 3H, *p*-*M*eC$_6$H$_4$), 1.99 (s, 3H, *p*-*Me*C$_6$H$_4$), 1.66 (s, 3H, *p*-*Me*C$_6$H$_4$), 1.39 (s, 9H, t-Bu), 1.29 (s, 9H, t-Bu), 1.28 (s, 9H, t-Bu), 1.18 (s, 9H, t-Bu), 0.16 (s, 3H, *exo*-SiCH$_3$), −1.04 (s, 3H, *endo*-SiCH$_3$). ^{13}C NMR (C$_6$D$_6$): *δ* 171.7, 162.9, 162.5, 152.8, 151.7, 149.6, 149.3, 144.5, 143.9, 143.5, 143.4, 143.0, 142.0, 141.1, 138.6, 137.3, 136.9, 135.6, 135.0, 134.5, 131.2, 129.9, 129.6, 129.2, 128.9, 127.8, 127.5, 126.9, 125.9, 125.7, 124.8, 124.4, 123.9, 123.6, 99.9 {O*C*(*p*-MeC$_6$H$_4$)$_2$C$_{12}$H$_7$N$_2$}, 85.7 {O*C*H(*p*-MeC$_6$H$_4$)$_2$}, 42.5 (calix-*C*H$_2$), 39.4 (calix-*C*H$_2$), 37.3 (calix-*C*H$_2$), 35.6 (calix-*C*H$_2$), 34.5 {*C*(CH$_3$)$_3$}, 34.3 {*C*(CH$_3$)$_3$}, 32.5 {C(*C*H$_3$)$_3$}, 32.3 {C(*C*H$_3$)$_3$}, 32.2 {C(*C*H$_3$)$_3$}, 21.9 (*p*-*M*eC$_6$H$_4$), 21.6 (*p*-*M*eC$_6$H$_4$), 21.2 (*p*-*M*eC$_6$H$_4$), 21.0 (*p*-*M*eC$_6$H$_4$), 3.51 (*exo*-Si*C*H$_3$), −0.93 (*endo*-Si*C*H$_3$). Anal. Calcd for $C_{88}H_{98}N_2O_6SiTi$: C, 77.96; H, 7.29; N, 2.07. Found: C, 77.19; H, 6.88; N, 2.04.

Crystallographic Study. The crystal data for $9\cdot(C_7H_8)_{0.5}(C_5H_{12})$ are collected in Table 1. Further details of the crystallographic study are given in the Supporting Information.

Results and Discussion

Synthesis of [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] Complexes. The reaction in pentane of titanapinacolate complexes [(DMSC)Ti(OCAr$_2$CAr$_2$O)] (**1**, Ar = Ph; **2**, Ar = *p*-MeC$_6$H$_4$) with 1 equiv of a delocalized diimine (L$_2$ = bpy, dmbpy, or phen) produced titanium η^2-ketone complexes [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] (**3**−**6**, eq 1). All of the compounds

$$[(DMSC)Ti(OCAr_2CAr_2O)] \xrightarrow[\text{pentane}]{L_2} [(DMSC)Ti(\eta^2\text{-}OCAr_2)L_2] + Ar_2CO \quad (1)$$

1, Ar = Ph; **2**, Ar = *p*-MeC$_6$H$_4$

L$_2$	Ar		
bpy	Ph	(**3**)	99%
bpy	*p*-MeC$_6$H$_4$	(**4**)	73%
dmbpy	*p*-MeC$_6$H$_4$	(**5**)	83%
phen	*p*-MeC$_6$H$_4$	(**6**)	

bpy =2,2'-bipyridine; dmbpy = 4,4'-dimethyl-2,2'-dipyridyl; phen = 1,10-phenanthroline

were isolated in high yield with the exception of [(DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$}phen] (**6**), which was 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$_4$)$_2$}] (**11**)[9] (Scheme 2) as a 50:50 mixture. The reaction occurs essentially in the time of mixing, and **3**−**6** precipitate from solution as air- and moisture-sensitive orange (**3**) or green (**4**−**6**) solids. The compounds are best stored in the solid state at low temperature (below −15 °C) and protected from light. For example, [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}bpy] (**4**) slowly decomposed with release of (*p*-MeC$_6$H$_4$)$_2$CO when it was stored as a solid under nitrogen atmosphere (in a glovebox) at ambient temperature and unprotected from light. All of the compounds dissolve well in aromatic solvents but are only sparingly soluble in aliphatic solvents. They yield intense green solutions upon dissolution in benzene-*d*$_6$ or methylene chloride-*d*$_2$.[10]

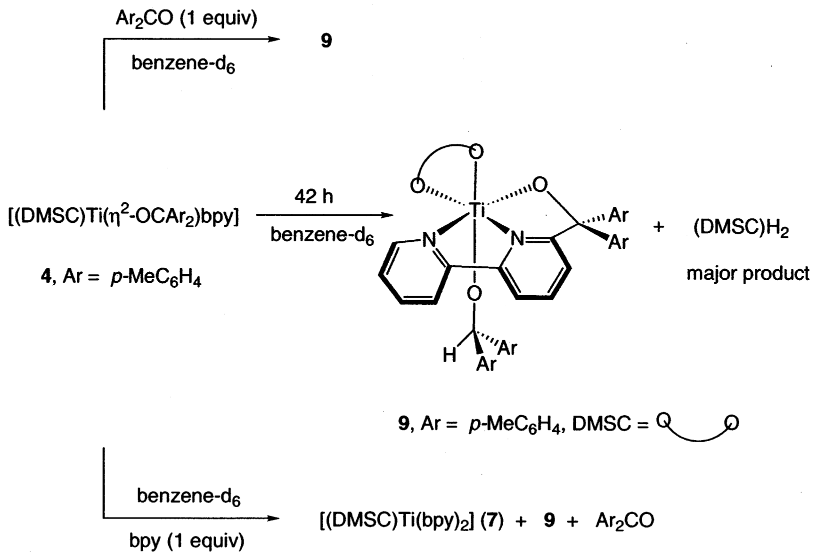
The formulation and structure of **3**−**6** were characterized by spectroscopic methods (^{1}H and ^{13}C NMR, IR), as well as by microanalysis for **3**−**5**. The ^{1}H NMR spectra of **3**−**6** displayed sharp resonances that are consistent with C_s-symmetry in solution and existence of the DMSC ligand in 1,2-alternate conformation. ^{1}H NMR resonances for the *endo*-Me (located inside the calixarene cavity) of the bridging SiMe$_2$ group are invariably strongly shielded compared to corresponding signals for the *exo*-SiMe (located outside the calixarene cavity).[11] For **3**−**6**, the *endo*-SiMe resonance is observed in the *δ* −1.12 to −1.16 ppm range, while the *exo*-SiMe resonance is found in the *δ* 0.34−0.36 ppm range (see Experimental Section). Their ^{1}H NMR spectra show two singlets (integrating in 1:1 ratio) for the Bu^t groups and four doublets and an AB system for the bridging methylene protons of the calixarene ligand. The AB

(9) An attempt to exclusively produce [(DMSC)Ti{η^2-OC(*p*-MeC$_6$H$_4$)$_2$}-phen] (**6**) by conducting the reaction of [(DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$C-(*p*-MeC$_6$H$_4$)$_2$O}] (**2**) with 1,10-phenanthroline (1 equiv) in pentane at low temperatures (−78 to 0 °C) was unsuccessful. No reaction was observed at −78 °C, and a mixture of products resulted as the reaction mixture was warmed.

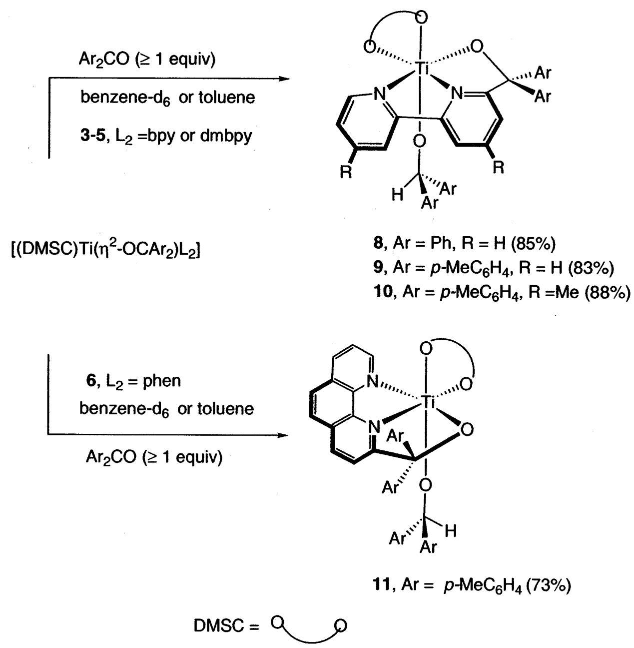
(10) [(DMSC)Ti(η^2-OCPh$_2$)bpy] (**3**) initially forms an orange suspension in benzene or toluene but dissolves gradually to give a green solution. Although a green color is usually observed within 5 min, it can take a few hours to completely dissolve all of **3**, during which time the formation of [(DMSC)Ti{κ^3-OCPh$_2$C$_{10}$H$_7$N$_2$}(OCHPh$_2$)] (**8**) occurs.

(11) See for example: (a) Ozerov, O. V.; Patrick, B. O.; Ladipo, F. T. *J. Am. Chem. Soc.* **2000**, *122*, 6423. (b) Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941. (c) Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216.

Scheme 1



Scheme 2



system integrates as four protons and represents the methylene groups not included in the mirror plane. A singlet resonance in the range of δ 2.14–2.20 ppm (integrating as six protons) is observed for the *p*-tolyl methyls of **4**–**6**, consistent with a mirror plane that contains the C–O unit of the ketone but bisects the *p*-tolyl substituents.

All of the compounds (**3**–**6**) are transformed into other species in solution. The transformations occur on a comparable or faster time-scale than that of the ^{13}C NMR experiment (vide infra), preventing acquisition of solution ^{13}C NMR data for every one of the compounds. For the same reason, all attempts to obtain single crystals of **3**–**6** suitable for an X-ray diffraction study have so far been unsuccessful. Solution ^{13}C NMR data could only be obtained for [(DMSC)Ti(η^2-O^{13}CPh$_2$)bpy] (**3b**), generated in-situ from reaction of [(DMSC)Ti(O^{13}CPh$_2$^{13}CPh$_2$O)] with 2,2′-bipyridine,[12] and for [(DMSC)Ti{OC(*p*-MeC$_6$H$_4$)$_2$}dmbpy] (**5**). Two coordination modes have been described for aldehyde and ketone complexes of transition metals: η^1-bound through oxygen (σ-complex)[6] and η^2-bound through both oxygen and carbon (π-complex).[7,8] Consistent with η^2-coordination of the ketone,[13]C NMR revealed a singlet resonance at δ 117.9 and 118.2 ppm for the Ar$_2$*C* carbon of **3b** and **5**, respectively. A singlet resonance at δ 91.4 ppm was reported for the Ph$_2$*C* carbon of the related complex [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(η^2-Ph$_2$CO)(PMe$_3$)],[7e] perhaps reflective of a greater degree of oxatitanacyclopropane character for the latter complex. Solid-state (Nujol mull) and solution-phase (CH$_2$Cl$_2$) measurements of the FTIR spectra for **3** showed no carbonyl stretch above 1060 cm^{-1}. Substitution of Ph$_2$^{13}CO for Ph$_2$CO resulted in only a small lowering of the IR bands at 1054 and 996 cm^{-1} for [(DMSC)Ti(η^2-OCPh$_2$)bpy] (**3**) to 1043 and 976 cm^{-1} for [(DMSC)Ti(η^2-O^{13}CPh$_2$)bpy] (**3b**).[13] The band at 1054 cm^{-1} has been assigned as the C–O stretch (ν_{C-O}) on the basis of the IR data for Ph$_2$CHOH[14] as well as related η^2-ketone and aldehyde complexes (ν_{C-O} range = 1000–1200 cm^{-1}).[7,8] Both the ^{13}C NMR and IR data indicate significant π-back-bonding into the π^* orbital of the ketone, consistent with a π-ligating mode for the ketone. These data parallel the trend reported for previously characterized η^2-aldehyde and ketone species.[7,8]

The intense green color of solutions of **3**–**6** presumably results from metal to ligand charge-transfer (MLCT) transitions.[4,15,16] For **3**–**6**, electron transfer from tita-

(12) A C$_6$D$_6$ solution of [(DMSC)Ti{1,2,4-(Me$_3$Si)$_3$C$_6$H$_3$}][11a] (18.0 mg, 17.2 mmol) and Ph$_2$^{13}CO (6.1 mg, 33.3 mmol) was heated at 65° C for 1 h. Next, 2.65 mg (16.9 mmol) of 2,2′-bipyridine was introduced into the solution. The reaction was monitored at 25 °C by ^{1}H and C NMR.

(13) A similar decrease in ν_{CO} from 1200 cm^{-1} for [Ta(η^5-C$_5$Me$_5$)(η^2-OCMe$_2$)Me$_2$] to 1180 cm^{-1} for [Ta(η^5-C$_5$Me$_5$)(η^2-O^{13}CMe$_2$)Me$_2$] was noted by Schrock. See: Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

(14) For IR data of Ph$_2$CHOH, see: Sommer, A.; Stamm, H.; Woderer, A. *Chem. Ber.* **1988**, *121*, 387.

(15) See for example: (a) Loukova, G. V.; Strelets, V. V. *Collect. Czech. Chem. Commun.* **2001**, *66*, 185. (b) Vleck, A., Jr. *Coord. Chem. Rev.* **1998**, *177*, 219. (c) Flamini, A.; Giuliani, A. M. *Inorg. Chim. Acta* **1986**, *112*, L7. (d) Fischer, E. O.; Aumann, R. *J. Organomet. Chem.* **1967**, *9*, P15. (e) Calderazzo, F.; Salzmann, J. J.; Mosimann, P. *Inorg. Chim. Acta* **1967**, *1*, 65.

(16) (a) Covert, K. J.; Wolczanski, P. T. *Inorg. Chem.* **1989**, *28*, 4567. (b) Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66.

nium to either the diimine (Ti → L_2) or the ketone (Ti→ Ar_2CO) is possible since both ligands are π-acids. In this regard, thermally accessible singlet−triplet systems have been described for Cp_2TiL_2 systems (L_2 = 2,2′-bipyridyl or 1,10-phenanthroline derivatives) in which one unpaired electron occupies a molecular orbital that is localized on the Cp_2Ti unit, while the other unpaired electron resides in the lowest energy π^* orbital of the L_2 ligand.[4b,c] Second, Wolczanski and colleagues have characterized Ti(IV)-ketyl complexes, including [$(Bu^t{}_3SiO)_3Ti(OCPh_2{}^\bullet)$] and [$(Bu^t{}_3SiO)_3$Ti{ OC($p$-MeC$_6H_4$)$_2{}^\bullet$}], formed by electron transfer from Ti(III) to the ketone upon reaction with [$(Bu^t{}_3SiO)_3Ti$].[16] Preliminary data from room- and low-temperature (110 K) ESR studies of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}dmbpy] (**5**) in the solid state and in toluene indicate the presence of two radical species.[17] Although a precise determination of the nature of the radical species must await further ESR studies, among possible radical species that may be envisioned are Ti(III) and Ti(IV) radical species [(DMSC)-Ti{OC(p-MeC$_6$H$_4$)$_2{}^\bullet$}dmbpy] and [(DMSC)Ti{OC(p-MeC$_6$H$_4$)$_2{}^\bullet$}(dmbpy$^\bullet$)], respectively.[18]

Reactivity of [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] Complexes. As mentioned before, **3**−**6** undergo further transformation in solution. For instance, upon dissolving a pure sample of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}bpy] (**4**) in benzene-d_6 and allowing the dark green solution to stand under N_2, the solution slowly changed color to orange. ^{1}H NMR revealed that the orange solution contained three DMSC-based products after 42 h. The two main products were identified as (DMSC)H$_2$[11c] (major product) and [(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (**9**), in which C−H activation of the bipyridyl ligand and hydride migration to a Ti-bound ketone to form an alkoxide group had occurred (Scheme 1). The transformation of **4** to **9** is photochemically assisted and progresses much more slowly when the solution is protected from light.[19] We reasoned that a ketone molecule released by decomposition of **4** was probably incorporated to produce **9** since (DMSC)H$_2$ is a characteristic decomposition product in this system.

The substitution of the ketone in **3**−**6** is facile.[20] For example, when the reaction of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}bpy] (**4**) with 2,2′-bipyridine (1 equiv) in benzene-d_6 was monitored by ^{1}H NMR spectroscopy, release of (p-MeC$_6$H$_4$)$_2$CO and formation of [(DMSC)-Ti(bpy)$_2$] (**7**)[21] occurred immediately after mixing. Together with (p-MeC$_6$H$_4$)$_2$CO, a ∼2:2:1 ratio of **4**, **7**, and **9** was present in solution after 2 h (Scheme 1). This result indicates that substitution of the ketone moiety of **4** by 2,2′-bipyridine proceeds more efficiently than reaction of **4** with (p-MeC$_6$H$_4$)$_2$CO to produce **9**. Release of (p-MeC$_6$H$_4$)$_2$CO also occurred during hydrolysis of **4** with distilled water in air and protonolysis of [(DMSC)-Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}dmbpy] (**5**) with isopropyl alcohol under nitrogen atmosphere. Both ^{1}H NMR characterization of the reaction mixtures and GC−MS analysis of CH_2Cl_2 extracts revealed that (p-MeC$_6$H$_4$)$_2$CHOH was not produced in either reaction. In contrast, Ph$_2$CHOH was the product of the hydrolysis of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$-(η^2-Ph$_2$CO)(PMe$_3$)],[7e] probably reflecting the latter compound's lower coordination number and increased oxa-titanacyclopropane character.

The reaction between **4** and (p-MeC$_6$H$_4$)$_2$CO was examined in an effort to obtain **9** in high yield. In benzene-d_6, reaction of 1 equiv of (p-MeC$_6$H$_4$)$_2$CO with **4** occurred cleanly to form **9** (Scheme 1). The reaction was ∼66% complete after 2 h (by ^{1}H NMR), and complete conversion to **9** was observed after allowing the solution to stand overnight. The rate with which **3**−**6** react with ketone to give 1-aza-5-oxa-titanacyclopentene derivatives **8**−**11** (Scheme 2) depended on the concentration of the ketone. Thus, the reaction of **4** with 8 equiv of (p-MeC$_6$H$_4$)$_2$CO proceeded to ∼82% completion in 0.5 h, and quantitative formation of **9** was observed in less than 2 h. This result suggests involvement of a second ketone molecule in the rate-limiting step. Interestingly, when the reaction in benzene-d_6 of **4** with Ph$_2{}^{13}$CO (1 equiv) was monitored by ^{1}H NMR in an attempt to discern which ketone molecule is transformed into the alkoxide group, [(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}(O^{13}CHPh$_2$)] and [(DMSC)Ti(κ^3-O^{13}CPh$_2$C$_{10}$H$_7$N$_2$){OCH(p-MeC$_6$H$_4$)$_2$}] were observed in ∼1:1 ratio after 15 min.[22,23] This result is consistent with either (i) fast exchange of complexed and free ketone molecules or (ii) coordination of the second ketone (Ph$_2{}^{13}$CO) and little preference for which metal-bound ketone molecule {Ph$_2{}^{13}$CO or OC(p-MeC$_6$H$_4$)$_2$} is transformed into the alkoxide group. No incorporation of deuterium (from benzene-d_6) into the alkoxide group was observed by either ^{1}H or ^{13}C NMR, indicating that the OCHAr$_2$ moiety results exclusively from transfer of hydrogen from the nitrogen heterocycle to a complexed ketone molecule.

(17) Kingston, J. V.; Karapetyan, A.; Miller, A. F.; Ladipo, F. T. Unpublished results.

(18) Reduction potentials for the ketone and diimine ligands are listed in the table below. The data suggest that one electron transfer to ketone is thermodynamically favored over one electron transfer to diimine. However, further reduction of the resulting ketyl radical and electron transfer to diimine have comparable thermodynamic feasibility.

compound	$E°$/V vs SCE	$E_p{}^2$/V[a] vs SCE
bpy	−2.13[b]	
dmbpy	−2.20[b]	
phen	−1.99[b]	
Ph$_2$CO	−1.78[c]	−2.27[c]
(p-MeC$_6$H$_4$)$_2$CO	−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) The transformation of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}bpy] (**4**) into [(DMSC)Ti{κ^3-OC(p-MeC$_6$H$_4$)$_2$C$_{10}$H$_7$N$_2$}{OCH(p-MeC$_6$H$_4$)$_2$}] (**9**) was slowed considerably when a d_6-benzene solution of **4** (in a NMR tube) was protected from light and allowed to stand at ambient temperature under N$_2$ atmosphere. After 5 days, ^{1}H NMR revealed **4** and **9** in ∼1: 2 ratio, along with minor amounts of unidentified DMSC-containing products.

(20) More facile substitution of η^2-ketone complexes bearing alkyl or aryl moieties in comparison to η^2-aldehydes has been attributed to both steric crowding and the higher energy of the π^* orbital for ketones relative to the π^* orbital for aldehydes.[5a,7b,h,1]

(21) Ozerov, O. V.; Brock, C. P.; Carr, S.; Parkin, S.; Ladipo, F. T. *Organometallics* **2000**, *19*, 5016.

(22) Both a singlet resonance at δ 5.90 ppm and a doublet resonance centered at δ 5.90 ppm (in 1:1 ratio) were observed in the ^{1}H spectrum after 15 min. See the Experimental Section for ^{1}H and ^{13}C NMR chemical shift values for **8**−**11**.

(23) For typical ^{1}H and ^{13}C NMR chemical shift values for the Ti−OCHAr$_2$ group, see for example: Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329, and ref 16b.

The rate of the transformation of **3**−**6** into **8**−**11** also depended on the nature of the diimine ligand (L_2). Qualitatively, the rate of reaction between [(DMSC)Ti{OC(*p*-$MeC_6H_4)_2$}L_2] (**4**−**6**) and (*p*-$MeC_6H_4)_2CO$ (1 equiv) in benzene-d_6 increases in the order L_2 = dmbpy < bpy ≪ phen. The reaction between [(DMSC)Ti{OC(*p*-$MeC_6H_4)_2$}phen] (**6**) and (*p*-$MeC_6H_4)_2CO$ (1 equiv) to give **11** is essentially complete in the time of mixing. In an effort to eliminate transformation of **3**−**6**, via C−H activation of the heterocyclic nitrogen ligand, and obtain η^2-ketone complexes with improved stability, we examined reactions of [(DMSC)Ti{OC(*p*-$MeC_6H_4)_2C$(*p*-$MeC_6H_4)_2O$] (**2**) with PMe_3, 6,6′-dimethyl-2,2′-dipyridyl, and 2,2′-bithiophene. In none of these cases did we observe a reaction; only decomposition of **2** was observed when a benzene-d_6 solution of **2** and 6,6′-dimethyl-2,2′-dipyridyl was heated at 70 °C for 12 h. Presumably, **2** did not react with 6,6′-dimethyl-2,2′-dipyridyl or PMe_3 for steric reasons. On the other hand, 2,2′-bithiophene is a much poorer donor than the delocalized diimine compounds utilized in this study.

Characterization of 1-Aza-5-oxa-titanacyclopentene Derivatives 8−11. Compounds **8**−**11** were isolated in very good yield from reaction of **3**−**6** with the appropriate ketone in toluene (Scheme 2). Both microanalysis and solution NMR (^{1}H and ^{13}C) data for **8**−**11** are consistent with the proposed formulation. ^{1}H and ^{13}C NMR data for **8**−**11** are consistent with C_1-symmetry in solution and existence of the DMSC ligand in 1,2-alternate conformation. In their ^{1}H NMR spectra in benzene-d_6, the *endo*-Me resonance is observed at ∼δ −1.00 ppm, while the *exo*-SiMe resonance can be found at ∼δ 0.17 ppm (see Experimental Section). Four equally intense singlets are observed for the Bu^t groups, and eight equally intense doublets are seen for the bridging methylene protons of the calixarene ligand. For **9**−**11**, four singlet resonances in the range δ 1.65−2.14 ppm (each integrating as three protons) are observed for the four inequivalent *p*-tolyl methyl groups. The alkoxide group hydrogen (Ti−$OCHAr_2$) is observed as a singlet at ∼δ 5.9 ppm for **8**−**11**. The ^{13}C NMR resonance for the alkoxide-carbon (Ti−O−$CHAr_2$) of **8**−**11** is observed in the δ 84−86 ppm range.[23] That this signal belonged to a Ti−O−$CHAr_2$ fragment was established by both proton-coupled ^{13}C NMR and DEPT experiments. For example, a doublet centered at δ 85.6 ppm with J_{C-H} = 139 Hz was observed in the proton-coupled ^{13}C NMR spectrum of **8**. The resonance for the Ti−O−C carbon of the 1-aza-5-oxa-titanacyclopentene ring shows in the range of δ 98−100 ppm.[24] Four resonances were observed in the ^{13}C NMR spectra of **9**−**11** between δ 20.6 and 20.9 ppm for inequivalent *p*-tolyl methyl carbons.

X-ray analysis of single crystals of **9** confirmed the structure assigned by spectroscopy. In space group *Cc*,[27] the asymmetric unit contains two independent molecules of **9**, one toluene, and two pentanes to give the empirical formula **9**·$(C_7H_8)_{0.5}(C_5H_{12})$. Bond lengths and angles for the two molecules are very similar.[28] One of the molecules is shown in Figure 1, and selected metrical parameters are given in Table 2.[29] The compound adopts a distorted octahedral structure with a meridional tridentate bipyridyl-alkoxide, *cis*-calixarene, and alkoxide ligand environment. The distortion from idealized octahedral geometry arises from acute bite angles of the tridentate bipyridyl-alkoxide ligand [ca. 71° for N(2A)−Ti(2A)−N(1A) and ca. 74° for O(5A)−Ti-(2A)−N(1A)], as well as steric constraints imposed by

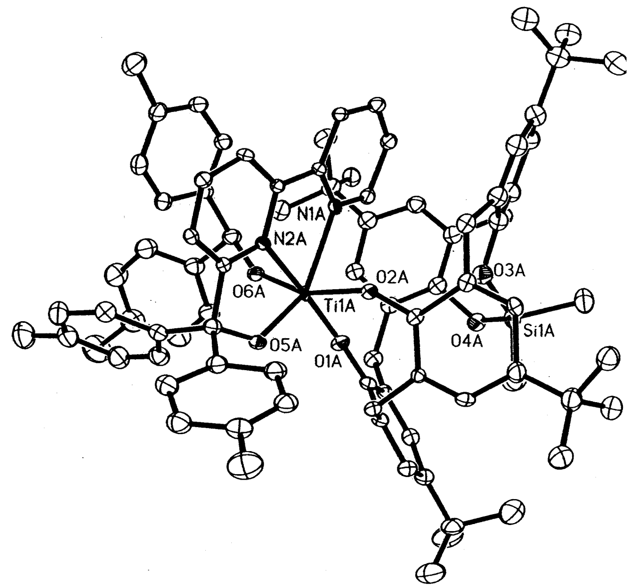


Figure 1. Molecular structure of [(DMSC)Ti{κ^3-OC(*p*-$MeC_6H_4)_2C_{10}H_7N_2$}{OCH(*p*-$MeC_6H_4)_2$}] (**9**) (50% probability ellipsoids).

Table 2. Selected Average Bond Distances (Å) and Angles (deg) for 9

Ti−O1	1.863(8)	O6−Ti−O2	159.5(4)
Ti−O2	1.928(8)	O1−Ti−O2	91.2(4)
Ti−O5	1.888(8)	O5−Ti−O2	99.5(4)
Ti−O6	1.820(8)	O6−Ti−N2	85.9(4)
Ti−N1	2.256(10)	O1−Ti−N2	173.5(4)
Ti−N2	2.178(10)	O2−Ti−N2	86.0(3)
O2−Ti−N1	77.3(3)	O6−Ti−N1	82.3(3)
N2−Ti−N1	71.0(4)	O5−Ti−N1	144.8(4)
O5−Ti−N2	73.8(4)	C25−O1−Ti	151.3(8)
O6−Ti−O1	94.9(4)	C26−O2−Ti	145.4(7)
O6−Ti−O5	98.4(4)	C55−O5−Ti	128.0(7)
O1−Ti−O5	101.1(3)	C70−O6−Ti	154.9(7)

(24) 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)[25] and ^{13}C NMR ($CDCl_3$): δ 107 ppm for [CpTi{κ^2-$OCR_2C_5H_4N$}Cl_2] (R = Pr^i or Ph)[26]

(25) Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16*, 3314.

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

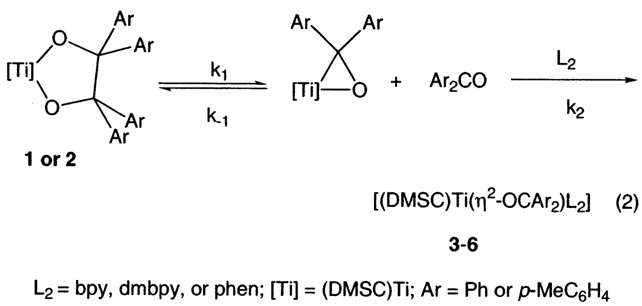
(27) Space group *Cc* was chosen in preference to *C*2/*c* for a number of reasons. No satisfactory structure solution could be obtained in *C*2/*c*. The two molecules per asymmetric unit in the Cc model could, however, be almost superimposed by rotation about an axis that was almost, but not exactly, parallel with the crystallographic *b* axis. Moreover, the superposition was far from perfect, resulting in many geometric clashes. The program PLATON was similarly unsuccessful in reducing the *Cc* model to a satisfactory model in *C*2/*c*. The solvent, which was partially disordered in the *Cc* model, would have been hopelessly disordered in *C*2/*c*. Furthermore, the data collection had to be performed at 150 K owing to a destructive phase transition on cooling to below 150 K. It is quite possible that the symmetry of the structure is indeed *C*2/*c* at room temperature, but owing to the unstable nature of both the crystals and the molecule itself and the general weakness of the diffraction pattern, data collection at room temperature was not feasible.

(28) Weak diffraction data were obtained due to the mediocre quality of the crystal utilized in the X-ray diffraction study. However, light atom positions in standard X-ray structure determinations are limited to about 0.02 Å, even for perfect data. See for example: (a) Coppens, P.; Sabine, T. M.; Delaplane, G.; Ibers, J. A. *Acta Crystallogr.* **1969**, *B25*, 2451. (b) Allen, F. H. *Acta Crystallogr.* **1986**, *B42*, 515.

(29) In light of the similarity of the two molecules in the asymmetric unit, bond lengths and angles are given as the average over both molecules.

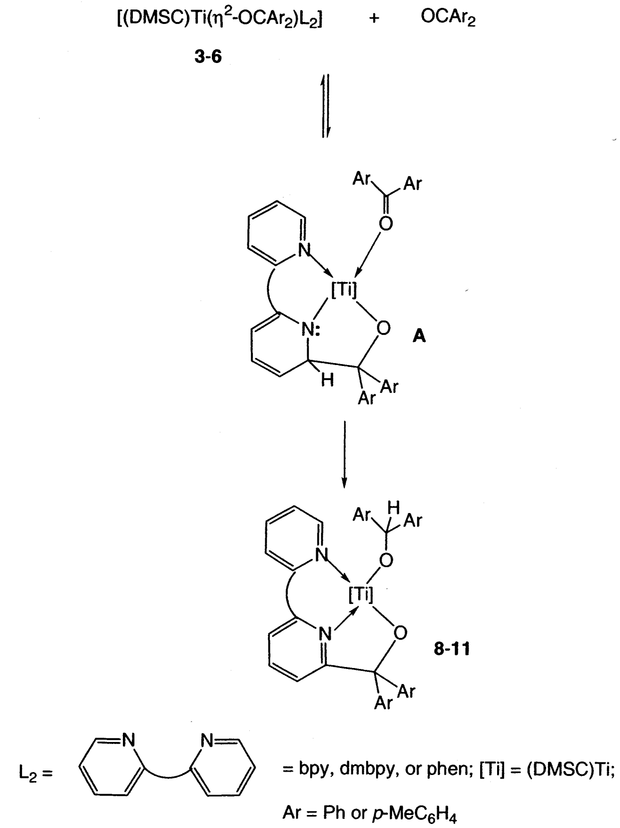
the bidentate DMSC ligand. All of the Ti−O bond distances {average = 1.886(8) Å}[30] are shorter than the Ti−O σ-bond distance predicted on the basis of covalent radii (ca. 1.99−2.05 Å),[25] perhaps reflective of partial Ti−O π-bonding. The Ti−O bond distance of the Ti−OCH(p-MeC$_6$H$_4$)$_2$ unit (average for the two molecules 1.820(8) Å) is especially short and may reflect a greater degree of partial Ti−O π-bonding. Orange (or orange-red) solids **8**−**11** are moisture-sensitive but moderately air-stable. The rate of their decomposition in air is noticeably slower than that of four-coordinate (DMSC)-Ti-based complexes with Ti−C bonds but similar to that of six-coordinate [(DMSC)Ti(η^2-RC≡CH)L$_2$] (R = Bu^t or SiMe$_3$; L$_2$ = bpy or dmbpy) complexes,[21] probably reflecting steric saturation of the coordination sphere. Thus, **8** is stable in air as a solid for several days, and even solutions of **8** are stable in air for hours. All of the compounds are insoluble in pentane but quite soluble in aromatic solvents. The compounds are thermally stable in C$_6$D$_6$ and do not undergo any observable decomposition at 22 °C for several days.

Mechanistic Considerations. We have recently demonstrated that the mechanism of the reaction of [(DMSC)Ti(OCAr$_2$CAr$_2$O)] (**1**, Ar = Ph; **2**, Ar = p-MeC$_6$H$_4$) with alkynes involves reversible dissociation of the titanapinacolate complexes into (DMSC)Ti(η^2-OCAr$_2$) species and Ar$_2$CO, followed by rate-limiting reaction of the (DMSC)Ti(η^2-OCAr$_2$) species with alkyne.[3b] It is therefore reasonable to conclude that [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] complexes (**3**−**6**) are produced via trapping of (DMSC)Ti(η^2-OCAr$_2$) species with appropriate diimine (eq 2). We found that titanium-η^2-ketones **3**−**6**



undergo a photochemically assisted transformation to yield 1-aza-5-oxa-titanacyclopentene derivatives **8**−**11**. In addition, the rate of formation of **8**−**11** increased with an increase in ketone concentration. This result strongly supports a mechanism that involves reversible coordination of ketone to titanium and a rate-limiting step that is dependent on ketone concentration. A plausible pathway for formation of **8**−**11** involves the intermediacy of 1-aza-5-oxa-titanacyclopentane species **A**[31] (Scheme 3). Subsequent hydride migration to a metal-bound ketone affords the alkoxide moiety and restores aromaticity to the nitrogen heterocycle. The photodependence of the reaction leads us to believe that metal to diimine charge transfer and the resulting radical species play important roles in the transformation. A lowering of the energy of the $\pi-\pi^*$ state results with increased conjugation in delocalized systems.[33] Thus,

Scheme 3



the $\pi-\pi^*$ state energy gap is lowest for 1,10-phenanthroline and the energy of metal to diimine charge transfer (Ti → L$_2$) transition is lowest for [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}phen] (**6**).[34] In this regard, it is noteworthy that the rate of transformation of [(DMSC)-Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}L$_2$] complexes (**4**, L$_2$ = bpy; **5**, L$_2$ = dmbpy; **6** L$_2$ = phen) into 1-aza-5-oxa-titanacyclopentene derivatives **9**−**11** followed the order **5** < **4** ≪ **6**, which parallels the decrease in $\pi-\pi^*$ state energy gap for the diimines.

Conclusions

The titanium-η^2-ketone complexes [(DMSC)Ti(η^2-OCAr$_2$)L$_2$)] **3**−**6** (L$_2$ = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-dipyridyl, or 1,10-phenanthroline) were obtained in good yield from reaction of [(DMSC)Ti(OCAr$_2$CAr$_2$O)] (**1**, Ar

(30) Average Ti−O bond distances of ~1.910(4) Å were reported for the related octahedral Ti(IV) complexes, [{κ^2-OCAr$_2$C$_5$H$_4$N}$_2$Ti(NMe$_2$)$_2$] (CAr$_2$ = 9-fluorenyl and Ar = 4-NEt$_2$−C$_6$H$_4$).[25]

(31) 1-Aza-5-oxa-titanacyclopentane species **A** may be formed from [(DMSC)Ti(η^2-OCAr$_2$)L$_2$] via nucleophilic aromatic substitution of a pyridyl ring at the 2-position[32] and ketone complexation. Alternatively, **A** may result from Ti(III) and Ti(IV) radical species such as [(DMSC)-Ti(OCAr$_2$•)L$_2$] and [(DMSC)Ti(OCAr$_2$•)(L$_2$•)].

(32) A nucleophilic aromatic substitution step is involved in the generally accepted mechanism for the Chichibabin reaction, through which heterocyclic nitrogen compounds can be aminated with alkali metal amides. See for example: (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*; John Wiley & Sons: New York, 2001; p 873. (b) Vobruggen, H. *Adv. Heterocycl. Chem.* **1990**, *49*, 117.

(33) See for example: (a) Wu, F.; Thummel, R. P. *Inorg. Chim. Acta* **2002**, *327*, 26. (b) Kaizu, Y.; Yazaki, T.; Torii, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2068.

(34) In the electronic spectra of [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}-dmbpy] (**5**) and [(DMSC)Ti{η^2-OC(p-MeC$_6$H$_4$)$_2$}phen] (**6**) in methylene chloride, strong bands are observed below 400 nm. In the visible region, the absorbance maximum for **5** and **6** are observed at 427 and 467 nm, respectively. The bathochromic shift of the absorbance maximum of **6** reflects the lower energy of the π^* state of the 1,10-phenanthroline ligand.

= Ph; **2**, Ar = *p*-MeC_6H_4) with the appropriate delocalized diimine compound in pentane. The η^2-ketone moiety of **3**−**6** is readily dissociated. Hence slow decomposition of **3**−**6** by release of a ketone was observed, and the decomposition was found to be photochemically assisted. Titanium η^2-ketone complexes **3**−**6** undergo facile reaction with a second ketone molecule to produce 1-aza-5-oxa-titanacyclopentene derivatives **8**−**11**, via C−H activation of the nitrogen heterocycle and hydride migration to a Ti-bound ketone molecule. The transformation is suggested to proceed by a mechanism involving a photochemically assisted electron transfer from titanium to diimine ligand. We are continuing our investigations of synthesis and reactivity of titanium η^2-ketone complexes with emphasis on isolating more stable complexes, as well as elucidating details of the mechanism for the transformation of **3**−**6** into **8**−**11**. We are also investigating applications of **3**−**6** and related complexes to prepare substituted diimine compounds.

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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 **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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