The Influence of Steric Congestion on the Catalytic Performance of Ti^{IV} Active Centers in the Epoxidation of Alkenes

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Abstract: Elucidation of the catalytic performance of Ti^{IV} centers in titanium-silica epoxidation catalysts has been probed by studying a range of soluble titanium-based silsesquioxane analogues. Several related and new Ti^{IV} complexes in which the Ti^{IV} is coordinated to only one or two siloxides of the silsesquioxane backbone have enabled us to modify, in a controlled fashion, the degree of steric congestion around the active site. It has been shown that the performance of these model catalysts is strongly influenced by the precise nature of the coordination environment about the Ti^{IV} active site, both in terms of steric crowding and in the likely occurrence of dative bonding.

Keywords: BINOL · catalysts · epoxidations · silsesquioxanes · titanium

Introduction

It has been established[1, 2] by in-situ X-ray absorption spectroscopic (XAS) studies that the atomic architecture of the active site in grafted (if not also framework-substituted) titanium–silica epoxidation catalysts is a Ti^{IV} ion tripodally bound to the silica matrix as schematized in Figure 1. These studies also reveal that a key feature of the active site is the coordination unsaturation of the tetrahedrally linked Ti^{IV} ion (during catalytic conversion, the coordination increases to six), and the magnitude of the catalytic activity was found[3] to be much influenced by the accessibility of the active site to the reactants (the alkene and the alkylhydroperoxide). These assignments have been corroborated by a range of other spectroscopic investigations such as FT-IR, UV/visible and photoluminescence spectroscopy.[4] Moreover, computational studies involving density functional theory calculations are consistent with these interpretations.[5]

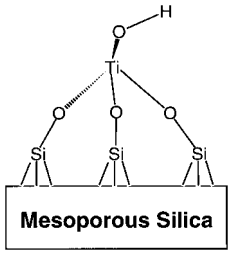

Figure 1. Ti^{IV} active center tripodally anchored to mesoporos silica (MCM-41).

In view of the considerable importance of Ti-centered epoxidations and related selective oxidations in the synthesis of bulk[6, 7] and fine[8, 9] chemicals (including stereoselective catalysis[10]), it is instructive to explore the role of steric hinderance at the active site upon the overall performance of such catalysts.

Results and Discussion

A wide range of soluble titanium silsesquioxane complexes of the type $Ti(L)R_7Si_7O_{12}$ (R = cyclohexyl[11], cyclopentyl[12] and L = alkyl,[13] aralkyl,[13] siloxy,[13] amido,[13] OH,[13] aryloxy,[13] alkoxy,[13, 14] Cp,[15] C_5Me_5,[16] or C_5Ph_5[17]), in which the Ti^{IV} center is coordinated to three siloxides of the silsesquioxane backbone, may be readily prepared and conveniently tested in

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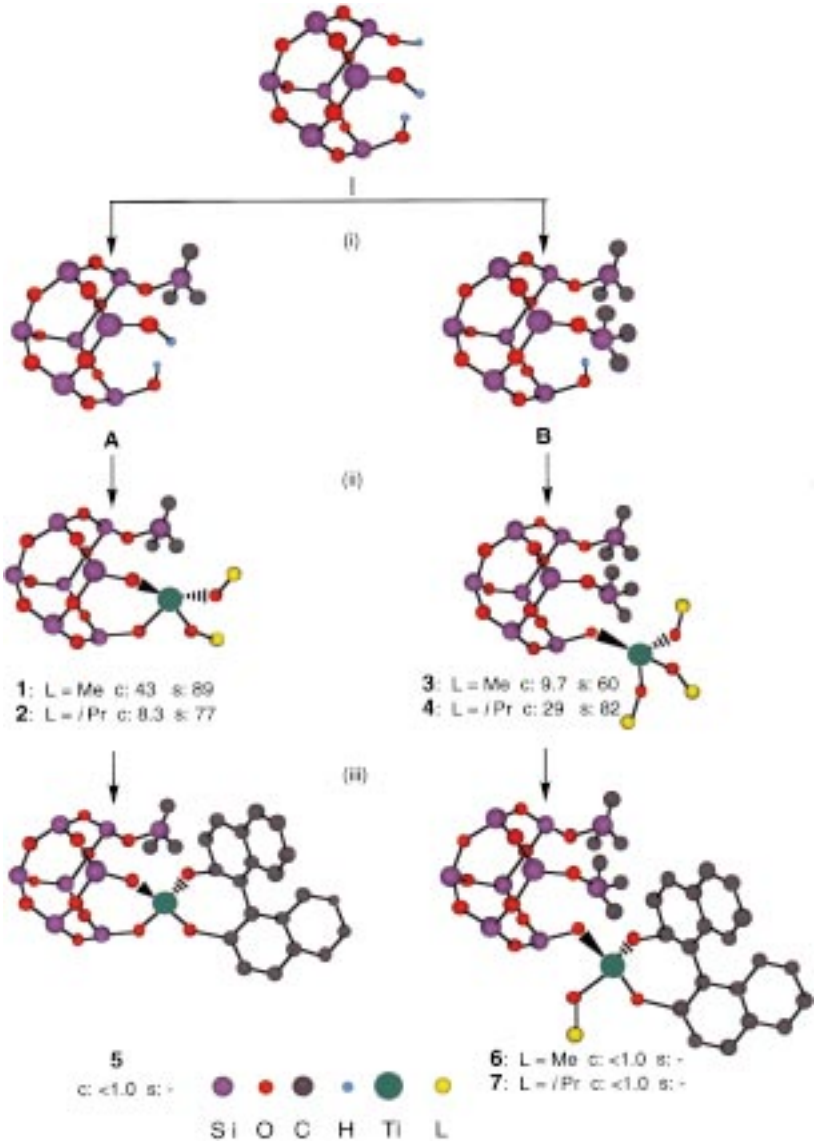
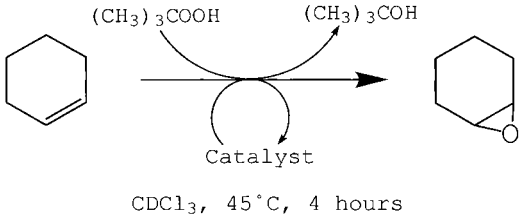
homogeneous solution. Moreover, their detailed structures may be determined, both by NMR (in solution and in the solid state) and single crystal X-ray crystallography.

By preparing a variety of related new Ti^{IV} complexes in which the Ti^{IV} is coordinated to only one or two siloxides of the silsesquioxane backbone, we have been able to modify, in a controlled fashion, the degree of steric congestion around the Ti^{IV} active site and thereby to assess the importance of this factor on the overall catalytic performance. In an analogous method to that used for $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ by Feher et al.[11, 18], the reaction of $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ with (TMS)Cl leads to the formation of the partially silylated precursor compounds **A** and **B.** Reaction of both compounds with $Ti(OL)_4$ (L = Me, *i*Pr) in THF leads to substitution of either two or one of the four titanium alkoxide ligands for each silsesquioxane to give complexes **1**, **2** (the cyclopentyl derivative of the complex previously synthesized by Crocker et al.[13]), **3** and **4**, with the subsequent elimination of LOH (see Scheme 1). On precipitation from solution by the use of MeCN and recrystallization from $CHCl_3$, it is possible to displace any coordinated THF molecules and obtain the compounds as predominantly Ti^{IV} tetrahedral species, as determined by UV/Vis spectroscopy ($\lambda_{max} < 250$ nm in all cases).



Scheme 1. Synthesis of partially silylated titanosilsesquioxane complexes. i) [TMS]Cl, NEt_3, THF, 25 °C; ii) $Ti(OL)_4$, THF, 24 h, reflux; iii) 1,1′-bi-2-naphthol, CH_2Cl_2, 25 °C; c = % conversion of TBHP; s = % selectivity to epoxide.

As Ti^{IV} alkoxy complexes of the ligand 1,1′-bi-2-naphthol (BINOL) are well-characterized species that have shown to be active catalysts for a number of reactions,[19] complexes **1**–**4** were further treated with BINOL at 25 °C to generate the orange BINOL-Ti^{IV}-silsesquioxane species by substitution of two alkoxide ligands, as depicted in Scheme 1. Each of the resulting complexes were tested as catalysts for the epoxidation of cyclohexene under the conditions given in Scheme 2, and their activity subsequently compared with that of other silsesquioxane based Ti^{IV} species[14] (Table 1).



Scheme 2. Catalytic epoxidation of cyclohexene.

Interestingly, the order of activity of complexes **1**–**7** does not follow in a straightforward fashion from that which would be expected by simple steric considerations. Complexes **3**, **4**, **6**, and **7** should be expected to be the most catalytically active, since the bulky silsesquioxane in each case acts as a monodentate ligand with respect to the Ti^{IV} center, whereas in complexes **1**, **2**, and **5** it is bidentate.

One explanation for the lower activity of complex **3** relative to **4** may arise from the likelihood of non-bonding interactions (see Figure 2) between the OTMS groups on the silsesquioxane backbone and the Ti^{IV} center, so blocking available coordination sites to the substrates. The relatively higher activity of complex **4** could result from the presence of the more sterically demanding *i*Pr moieties, which would prevent

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Table 1. Epoxidation of cyclohexene with TBHP-catalyzed titanosilsesquioxanes.[a]

Catalyst	Conversion[b] [%]	Selectivity[c] [%]
1	43	89
2	8.3	77
3	9.7	60
4	29	82
5	< 1.0	–
6	< 1.0	–
7	< 1.0	–
8	81	96
9	50	95
$[(c\text{-}C_5H_9)_7Si_7O_{12}(TiOMe)]$	> 98	> 98
$[(c\text{-}C_5H_9)_7Si_7O_{12}(TiO\mathit{i}Pr)]$	73	> 98

[a] Epoxidations were performed with equimolar amounts (15 mmol) of cyclohexene and *tert*-butyl hydroperoxide (TBHP) in $CDCl_3$ (0.4 mL) with tetramethylsilane (15 mmol) as an internal standard. Reactions were performed at 45 °C in sealed vials that were magnetically stirred for 4 h, with 1 equiv of pre-dried catalyst (100 °C, 10^{-4} Torr, 12 h) to 70 equiv of both peroxide and alkene. Data quoted are derived from at least two runs. Conversions and selectivities were determined by ^{1}H NMR spectroscopy. [b] Based on TBHP; [c] Based on the epoxide.

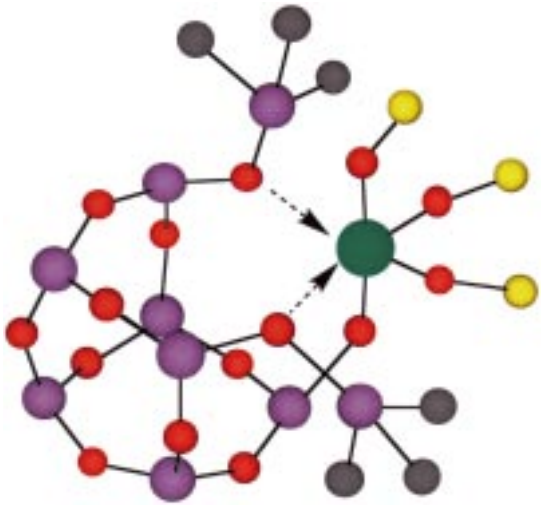
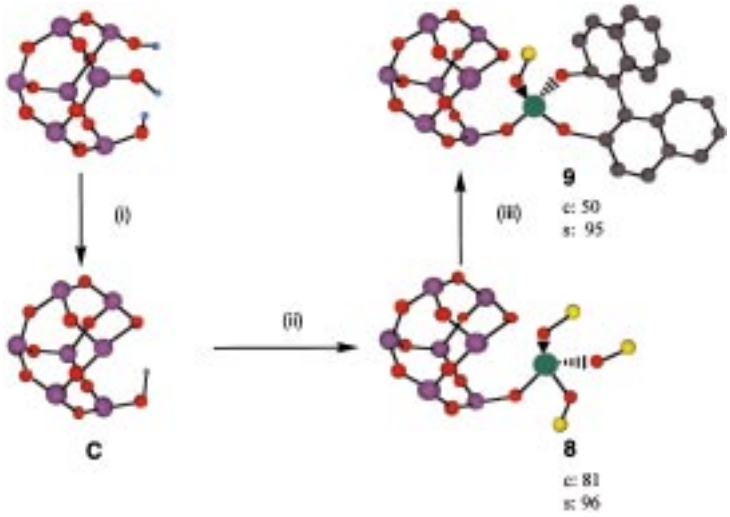


Figure 2. The catalytic performance of complexes **3** and **4** suggest (see text) that dative bonding is a key feature of their structures.

the OTMS groups from interacting with the Ti^{IV} center to the same extent as that found in complex **3**. This view is supported by evidence from UV/visible absorption studies, which show a broad absorption maximum occurring at a slightly higher wavelength in the case of **3** ($\lambda_{max} = 250$ nm) as compared with that for complex **4** ($\lambda_{max} = 237$ nm). This compares well with that found for other in solution predominantly tetrahedral Ti^{IV} complexes such as $Ti(OSiPh_3)_4$ ($\lambda_{max} = 233$ nm).[20] However, in both **1** and **2** ($\lambda_{max} = 233$ nm and $\lambda_{max} = 229$ nm respectively), the effect on the Ti^{IV} centers of any dative bonding arising from the *single* OTMS group appears to be negligible, compare with complex **3**, so that, for these complexes, the steric nature of the OL group plays no role in influencing any potential dative bonding. As there are only two alkoxy moieties bonded to each active site, it is probable that the less crowded coordination sphere in **1** allows better access to the Ti^{IV} center than in **2**, an effect which was observed previously in related titanosilsesquioxanes,[14] leading to its much better activity in terms of both conversion and selectivity. As the related work of others has shown,[13] these complexes are generally less active, under the same catalytic conditions, than their tripodally attached titanosilsesquioxane cousins, for example, complexes **2** and **3** are about one order of magnitude less active in terms of conversion than either $[(c\text{-}C_5H_9)_7Si_7O_{12}(TiO\mathit{i}Pr)]$ or $[(c\text{-}C_5H_9)_7Si_7O_{12}(TiOMe)]$ and show lower selectivities.

Curiously, complexes **5**–**7** were virtually inactive under these reaction conditions, and indeed, this is still the case with a variety of other alkenes (styrene, 1-octene, and trans-cinnamyl alcohol). This inactivity may be due to the steric demands of the BINOL group (in the case of **5**) as well as to the dative-bonding electronic effects arising from the OTMS groups (in the cases of **6** and **7**).

Hence, in order to test these hypotheses, we have synthesized related titanosilsesquioxane complexes that do not incorporate these OTMS groups on the silsesquioxane backbone. The dehydration of $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ under the same conditions employed for $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$[11] generates the monosilanol **C** (see Scheme 3), that can be



Scheme 3. Synthesis of partially dehydrated titanosilsesquioxane complexes. i) NEt_3, 4 Å molecular sieves, reflux 12 h; ii) $Ti(\mathit{i}OPr)_4$, THF, 24 h, reflux; iii) 1,1′-bi-2-naphthol, CH_2Cl_2, 25 °C; c = % conversion of TBHP; s = % selectivity to epoxide.

similarly treated with $Ti(O\mathit{i}Pr)_4$ to give complex **8**, which retains three *iso*-propoxide groups at the Ti^{IV} center. Again, precipitation from solution with the use of MeCN and recrystallization from $CHCl_3$ yields the predominantly Ti^{IV} tetrahedral species. Further derivatization with BINOL similarly substitutes two more *iso*-propoxide groups to yield the corresponding orange BINOL-Ti^{IV}-silsesquioxane complex (**9**), as shown in Scheme 3.

Similar catalytic tests on these two complexes now show that *each* has significantly higher activity, both in terms of conversion and selectivity, than was the case for complexes **1**–**7**, despite the presence of the relatively bulky *i*Pr and BINOL groups (see Table 1). UV/visible studies on complex **8** also confirm its predominantly four coordinate structure in solution ($\lambda_{max} = 231$ nm) as compared with complex **4** (vide

infra). These observations further substantiate the view that the presence of the OTMS groups on the silsesquioxane backbone cause an increase in the average coordination number of the tetrahedral Ti^{IV} center and although this effect is slight, it is detrimental to catalytic performance.

Experimental Section

Unless otherwise stated, all experiments were performed under argon using solvents that were freshly distilled before use. UV/visible studies were carried out with 2 mg of pre-dried complex (100 °C, 10^{-4} Torr, 12 h) in distilled CH_2Cl_2 under argon. **A**, **B**, and **C** were synthesized in an analogous manner to that employed for $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$.[11, 18]

General synthetic method for the preparation of 1, 2, 3, 4, and 8: $Ti(OL)_4$ (L = Me or *i*Pr, 0.317 mmol) was added to a solution of **A**, **B**, or **C** (0.264 mmol) in THF (50 mL), and the resulting colorless solution was refluxed for 24 h. The solution was then filtered in air, the solvent removed in vacuo, and the remaining white solid redissolved in the minimum amount of CH_2Cl_2 (15 mL). MeCN was then added dropwise, until no further precipitation of the product was observed. Filtration in air yielded white powders, which were then redissolved in the minimum amount of $CHCl_3$ and allowed to stand in air at 25 °C. Slow evaporation of the solvent after 2 days yielded **1**, **2**, **3**, **4**, or **8** as white powders.

Compound 1: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.510$ (s, 3H; O*Me*), 3.493 (s, 3H; O*Me*), 1.727 (m, 20H; cyclopentyl-H), 1.567 (m, 36H; cyclopentyl-H), 0.938 (m, 7H; *ipso*-H), 0.157 (s, 9H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 63.76$ (s, CH_3; O*Me*), 27.91, 27.73, 27.62, 27.58, 27.55, 27.45, 27.42, 27.39, 27.29, 27.18 (s, CH_2; cyclopentyl-C, unassignable), 23.65, 23.11, 22.89, 22.40, 21.81 (1:2:2:1:1, s, CH; *ipso*-C), 1.70 (s, CH_3; Si*Me*$_3$); UV/Vis(CH_2Cl_2): λ (λ_{max}) = 210–320 nm (233); MS(FAB$^+$): *m/z*: 970 [$M^+ - Me - C_5H_9$], 915 [$M^+ - 2C_5H_9$]; $C_{40}H_{78}O_{14}Si_8Ti \cdot CHCl_3$ (1175.0) calcd C 41.9, H 6.7; found C 41.1, H 6.8.

Compound 2: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.023$ (br sept, 2H; OC*H*(CH_3)$_2$), 1.853 (m, 20H; cyclopentyl-H), 1.568 (m, 36H; cyclopentyl-H), 1.208 (d, 12H; OCH(C*H*$_3$)$_2$), 0.935 (m, 7H; *ipso*-H), 0.157 (s, 9H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 77.18$ (s, CH; OC*H*(CH_3)$_2$), 27.90, 27.75, 27.61, 27.46, 27.35, 27.05, 26.96 (s, CH_2; cyclopentyl-C, unassignable), 25.37 (s, CH_3; OCH(C*H*$_3$)$_2$), 24.32, 23.17, 22.99, 22.42, 22.31 (1:2:2:1:1, s, CH; *ipso*-C), 1.67 (s, CH_3; Si*Me*$_3$); UV/Vis(CH_2Cl_2): λ (λ_{max}) = 210–320 nm (229); MS(FAB$^+$): *m/z*: 1054 [M^+ – O*i*Pr], 915 [$M^+ - Ti(OiPr)_2 - H_2O - CH_3$], 863 [$M^+ - Ti(OiPr)_2 - H_2O - C_5H_9$], 739 [$M^+ - Ti(OiPr)_2 - 3C_5H_9$]; $C_{44}H_{86}O_{14}Si_8Ti \cdot CHCl_3$ (1231.1): calcd C 43.8, H 7.0; found C 42.5, H 6.9.

Compound 3: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.584$ (s, 9H; O*Me*), 1.735 (m, 20H; cyclopentyl-H), 1.568 (m, 36H; cyclopentyl-H), 0.963 (m, 7H; *ipso*-H), 0.133 (s, 18H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 64.42$ (s, CH_3; O*Me*), 27.93, 27.70, 27.62, 27.52, 27.40, 27.29, 27.19, 27.06, 26.96, 26.89, 26.85 (s, CH_2; cyclopentyl-C, unassignable), 24.51, 23.79, 23.26, 22.66, 22.38 (1:2:2:1:1, s, CH; *ipso*-C), 1.82 (s, CH_3; Si*Me*$_3$); UV/Vis(CH_2Cl_2): λ (λ_{max}) = 210–320 nm (250); MS(FAB$^+$): *m/z*: 1158 [M^+], 1085 [$M^+ - SiMe_3$], 1019 [$M^+ - Ti(OMe)_3$]; $C_{44}H_{90}O_{15}Si_9Ti \cdot 3CHCl_3$ (1518.0): calcd C 37.2, H 6.1; found C 36.0, H 6.7.

Compound 4: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.019 - 3.842$ (br sept, 3H; OC*H*(CH_3)$_2$), 1.736 (m, 20H; cyclopentyl-H), 1.566 (m, 36H; cyclopentyl-H), 1.254 (d, 18H; OCH(C*H*$_3$)$_2$), 0.964 (m, 7H; *ipso*-H), 0.133 (s, 18H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 77.20$ (s, CH; OC*H*(CH_3)$_2$), 27.93, 27.55, 27.43, 27.40, 27.33, 27.27, 27.23, 27.09, 27.01, 26.99 (s, CH_2; cyclopentyl-C, unassignable), 25.11 (s, CH_3; OCH(C*H*$_3$)$_2$), 23.60, 22.76, 22.42, 22.33, 22.20 (1:2:2:1:1, s; CH, *ipso*-C), 1.66 (s, CH_3; Si*Me*$_3$); UV/Vis(CH_2Cl_2): λ (λ_{max}) = 210–320 nm (237); MS(FAB$^+$): *m/z*: 831 [$M^+ - C_5H_9 - 3OiPr$], 789 [$M^+ - Ti(OiPr)_3$]; $C_{50}H_{102}O_{15}Si_9Ti \cdot 3CHCl_3$ (1602.1): calcd C 39.7, H 6.5; found C 39.2, H 6.3.

Compound 8: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.022$ (br sept, 3H; OC*H*(CH_3)$_2$), 1.758 (m, 20H; cyclopentyl-H), 1.586 (m, 36H; cyclopentyl-H), 1.242 (d, 18H; OCH(C*H*$_3$)$_2$), 0.967 (m, 7H, *ipso*-H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 77.22$ (s, CH; OC*H*(CH_3)$_2$), 27.38, 27.26, 27.20, 27.14, 27.00, 26.96, 26.91, 26.87 (s, CH_2; cyclopentyl-C, unassignable), 25.37 (s, CH_3; OCH(C*H*$_3$)$_2$), 22.31, 22.19, 22.17, 22.04, 21.50 (2:1:1:2:1, s; CH, *ipso*-C); UV/Vis(CH_2Cl_2): λ (λ_{max}) = 210–320 nm (231); MS(FAB$^+$): *m/z*: 831 [$M^+ - C_5H_9 - 3OiPr$], 789 [$M^+ - Ti(OiPr)_3$]; $C_{44}H_{84}O_{14}Si_7Ti \cdot 2CHCl_3$ (1320.4): calcd C 41.8, H 6.5; found C 42.1, H 6.8.

General synthetic method for the preparation of 5, 6, 7, and 9: 1,1′-Bi-2-naphthol (15 mg, 0.052 mmol) was added to a colorless solution of **1**, **2**, **3**, **4**, or **8** (0.041 mmol) in CH_2Cl_2 (10 mL). The resulting orange solution was stirred at 25 °C for 12 h, the solvent removed in vacuo, and the resulting orange solid stirred in an excess of acetone (20 mL) for 4 h. Filtration yielded **5**, **6**, **7**, or **9** as orange powders.

Compound 5: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.981$ (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.894 (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.402 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.384 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.315 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.154 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 1.730 (m, 20H; cyclopentyl-H), 1.555 (m, 36H; cyclopentyl-H), 0.899 (m, 7H; *ipso*-H), 0.162 (s, 9H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 152.77$ (s, C; $C_{20}H_{12}O_2$), 133.42 (s, C; $C_{20}H_{12}O_2$), 131.47 (s, CH; $C_{20}H_{12}O_2$), 129.49 (s, C; $C_{20}H_{12}O_2$), 128.44 (s, CH; $C_{20}H_{12}O_2$), 127.51 (s, CH; $C_{20}H_{12}O_2$), 124.22 (s, CH; $C_{20}H_{12}O_2$), 124.07 (s, CH; $C_{20}H_{12}O_2$), 117.77 (s, CH; $C_{20}H_{12}O_2$), 110.82 (s, C; $C_{20}H_{12}O_2$), 29.71, 29.38, 27.76, 27.62, 27.50, 27.46, 27.36, 27.18, 27.11, 27.06 (s, CH_2; cyclopentyl-C, unassignable), 24.32, 23.46, 23.09, 22.71, 22.43 (1:2:2:1:1, s; CH, *ipso*-C), 1.67 (s, CH_3; Si*Me*$_3$); MS(FAB$^+$): *m/z*: 993 [$M^+ - C_{20}H_{12}O_2$], 947 [$M^+ - C_{20}H_{12}O_2Ti$]; $C_{58}H_{84}O_{14}Si_8Ti$ (1277.9): calcd C 54.5, H 6.6; found C 55.8, H 7.4.

Compound 6: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.971$ (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.897 (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.392 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.386 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.303 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.149 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 5.585 (s, 1H; O*Me*), 1.736 (m, 20H; cyclopentyl-H), 1.568 (m, 36H; cyclopentyl-H), 0.934 (m, 7H; *ipso*-H), 0.133 (s, 18H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 152.78$ (s, C; $C_{20}H_{12}O_2$), 133.42 (s, C; $C_{20}H_{12}O_2$), 131.47 (s, CH; $C_{20}H_{12}O_2$), 129.48 (s, C; $C_{20}H_{12}O_2$), 128.44 (s, CH; $C_{20}H_{12}O_2$), 127.51 (s, CH; $C_{20}H_{12}O_2$), 124.23 (s, CH; $C_{20}H_{12}O_2$), 124.07 (s, CH; $C_{20}H_{12}O_2$), 117.79 (s, CH; $C_{20}H_{12}O_2$), 110.84 (s, C; $C_{20}H_{12}O_2$), 62.40 (s, CH_3; O*Me*), 27.69, 27.67, 27.62, 27.54, 27.44, 27.41, 27.36, 27.29, 27.18, 27.06, 26.99, 26.97 (s, CH_2; cyclopentyl-C, unassignable), 24.51, 23.78, 23.26, 22.65, 22.40 (1:2:2:1:1, s, CH; *ipso*-C), 1.82 (s, CH_3; Si*Me*$_3$); MS(FAB$^+$): *m/z*: 1380 [M^+], 1086 [$M^+ - C_{20}H_{12}O_2 - Me$], 1019 [$M^+ - C_{20}H_{12}O_2Ti(OMe)$]; $C_{62}H_{96}O_{15}Si_9Ti$ (1382.1): calcd C 53.9, H 7.0; found C 54.0, H 6.3.

Compound 7: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.989$ (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.894 (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.393 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.380 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.303 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.145 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 4.063 (br sept, 1H; OC*H*(CH_3)$_2$), 1.736 (m, 20H; cyclopentyl-H), 1.566 (m, 36H; cyclopentyl-H), 1.245 (d, 6H; OCH(C*H*$_3$)$_2$), 0.963 (m, 7H; *ipso*-H), 0.135 (s, 18H; Si*Me*$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 152.78$ (s, C; $C_{20}H_{12}O_2$), 133.42 (s, C; $C_{20}H_{12}O_2$), 131.47 (s, CH; $C_{20}H_{12}O_2$), 129.48 (s, C; $C_{20}H_{12}O_2$), 128.44 (s, CH; $C_{20}H_{12}O_2$), 127.51 (s, CH; $C_{20}H_{12}O_2$), 124.23 (s, CH; $C_{20}H_{12}O_2$), 124.07 (s, CH; $C_{20}H_{12}O_2$), 117.79 (s, CH; $C_{20}H_{12}O_2$), 110.84 (s, C; $C_{20}H_{12}O_2$), 77.19 (s, CH; OC*H*(CH_3)$_2$), 29.72 (s, CH_3; OCH(C*H*$_3$)$_2$), 27.55, 27.42, 27.40, 27.33, 27.27, 27.24, 27.11, 27.03, 26.92 (s, CH_2; cyclopentyl-C, unassignable), 23.59, 22.76, 22.42, 22.33, 22.22 (1:2:2:1:1, s; CH, *ipso*-C), 1.66 (s, CH_3; Si*Me*$_3$); MS(FAB$^+$): *m/z*: 1375 [$M^+ - CH_3 - H_2O$], 860 [$M^+ - C_{20}H_{12}O_2Ti(OiPr) - 2C_5H_9 - H_2O$]; $C_{64}H_{100}O_{15}Si_9Ti$ (1410.1): calcd C 54.5, H 7.1; found C 53.8, H 6.7.

Compound 9: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.993$ (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.904 (d, ^2J(H,H) = 5.3 Hz, 2H; $C_{20}H_{12}O_2$), 7.393 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.389 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.305 (t, ^3J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 7.147 (d, ^2J(H,H) = 4.9 Hz, 2H; $C_{20}H_{12}O_2$), 4.153 (br sept, 1H; OC*H*(CH_3)$_2$), 1.742 (m, 20H; cyclopentyl-H), 1.574 (m, 36H; cyclopentyl-H), 1.246 (d, 6H; OCH(C*H*$_3$)$_2$), 0.967 (m, 7H, *ipso*-H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 152.76$ (s, C; $C_{20}H_{12}O_2$), 133.42 (s, C; $C_{20}H_{12}O_2$), 131.48 (s, CH; $C_{20}H_{12}O_2$), 129.48 (s, C; $C_{20}H_{12}O_2$), 128.44 (s, CH; $C_{20}H_{12}O_2$), 127.51 (s, CH; $C_{20}H_{12}O_2$), 124.22 (s, CH; $C_{20}H_{12}O_2$), 124.07 (s, CH; $C_{20}H_{12}O_2$), 117.78 (s, CH; $C_{20}H_{12}O_2$), 110.83 (s, C; $C_{20}H_{12}O_2$), 77.23 (s, CH; OC*H*(CH_3)$_2$), 28.90 (s, CH_3; OCH(C*H*$_3$)$_2$), 27.38, 27.25, 27.20, 27.14, 27.02, 26.96, 26.91, 26.87 (s,

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CH_2; cyclopentyl-C, unassignable), 22.60, 22.28, 22.17, 22.04, 21.53 (2:1:1:2:1, s; CH, *ipso*-C); MS(FAB$^+$): *m/z*: 919 [$M^+ - C_{20}H_{12}O_2 - i$Pr], 789 [$M^+ - C_5H_9 - C_{20}H_{12}O_2$Ti(O*i*Pr)]; $C_{58}H_{82}O_{14}Si_7Ti$ (1247.8): calcd C 55.9, H 6.6; found C 54.9, H 5.9.

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