Articles

Syntheses and Structures of 1,2,3-Substituted Cyclopentadienyl Titanium(IV) Complexes

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Cyclopentadiene compounds, 2-[CR'R(OMe)]-1,3-$Me_2C_5H_3$ (R, R' = 2,2'-biphenyl, **2**) and 2-[CR'R($OSiMe_3$)]-1,3-$Me_2C_5H_3$ (R, R' = 2,2'-biphenyl, **3**; R = ph, R' = ph, **4**; R = 2-naphthyl, R' = H, **5**) are readily synthesized from 2-bromo-3-methoxy-1,3-dimethylcyclopentene (**1**). Reaction of the cyclopentadienes with $Ti(NMe_2)_4$ in toluene results in clean formation of the cyclopentadienyl tris(dimethylamido)titanium complexes, which are transformed to the trichloride complexes, 2-[CR'R(OMe)]-1,3-$Me_2C_5H_2$}$TiCl_3$ (R, R' = 2,2'-biphenyl, **6**) and {2-[CR'R($OSiMe_3$)]-1,3-$Me_2C_5H_2$}$TiCl_3$ (R, R' = 2,2'-biphenyl, **7**; R = ph, R' = ph, **8**; R = 2-naphthyl, R' = H, **9**). Attempts to form C1-bridged Cp/oxido complexes by elimination of MeCl or Me_3SiCl were not successful. X-ray structures of **6**, **7** and an intermediate complex {2-[$Ph_2C(OSiMe_3)$]-1,3-$Me_2C_5H_2$}$TiCl_2(NMe_2)$ (**10**) were determined.

Key Words : Cyclopentadienyl, Titanium, X-ray structure

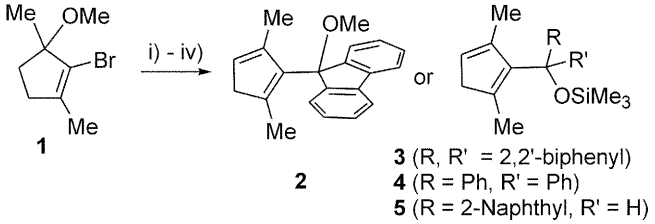
Introduction

The [Me_4Cp-Me_2Si-NR] based titanium and zirconium complexes developed by Dow and Exxon and know as CGC (constraint geometry catalyst) have drawn great interest in both academic and industrial fields.[1] The activated catalyst derived from the complex shows good comonomer incorporation in the ethylene/α-olefins copolymerization and provides very high molecular-weight polyethylene when activated with borate cocatalyst. Cp/phosphido,[2,3] Cp/amido,[4] and Cp/oxido complexes with various bridging moieties have been described. Recently, Erker attempted to prepare (sp^2-C_1)-bridged Cp/-oxido zirconium and titanium complexes by reacting [Cp-C(=CH_2)-O]$^{2-}$ with $Ti(NMe_2)_2Cl_2$ or $Zr(NEt_2)_2Cl_2(THF)_2$ but only obtained unbridged dinuclear complexes.[5] Cp/oxido titanium complexes with higher bridging moieties are frequently obtained by thermolysis of unbridged precursor complexes [RO-bridge-Cp]-$TiCl_3$ by elimination of RCl (R = Me or Me_3Si).[6-8] We have recently developed an efficient synthetic route for 1,4,6-substituted fulvenes.[9-11] An intermediates of the synthetic route is cyclopentadiene having methoxy group, 2-[CRR'(OMe)]-1,3-$Me_2C_5H_3$. We expected that the titanium trichloride complex derived from the cyclopentadiene or preferably more labile 2-[CRR'($OSiMe_3$)]-1,3-$Me_2C_5H_3$, which can be synthesized similarly, might afford the C_1-bridged Cp/-oxido titanium complexes by thermolysis. Even though we failed to obtain the desired C_1-bridged Cp/-oxido complexes, we report herein the preparation and molecular structures of the titanium trichloride complexes.

Results and Discussion

Synthesis and Characterization. One-pot synthetic route for the cyclopentadiene compound, 2-[CR'R(OMe)]-1,3-$Me_2C_5H_3$ were developed previously (Scheme 1).[11] Thus, addition of *n*-BuLi to the bromo-compound **1**, which can be prepared in 80 g scale, in diethyl ether affords 2-lithio-3-methoxy-1,3-dimethylcyclopentene. Successive additions of 9-fluorenone and MeI to the lithium compound and aqueous acidic work-up provide cyclopentadiene compound **2** in overall 57% yield. Similarly trimethylsiloxy compounds **3-5** are obtained by the addition of Me_3SiCl instead of MeI in 59-76% yields (Scheme 1). The ^1H and ^{13}C NMR spectra are in agreement with the structure. Broad signals are observed for fluorenone-derived compounds **2** and **3** which might be attributed to the rotation barrier around C(Cp)-C(OR) bond.

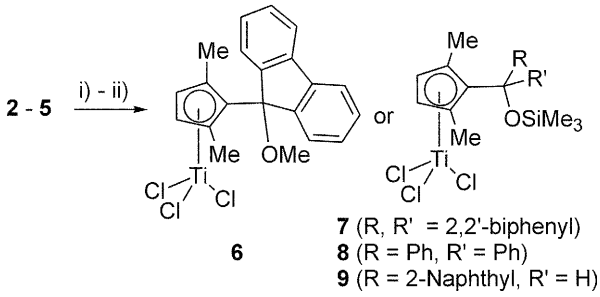
Reaction of the cyclopentadiene compounds **2-5** with $Ti(NMe_2)_4$ in toluene at 80 °C overnight under the weak stream of nitrogen gas furnishes the corresponding cyclopentadienyl tris(dimethylamido)titanium complexes which



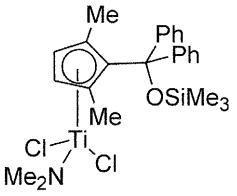
1 **2**

3 (R, R' = 2,2'-biphenyl)
4 (R = Ph, R' = Ph)
5 (R = 2-Naphthyl, R' = H)

Scheme 1[a]. [a]Legend: i) *n*-BuLi; ii) ketone or aldehyde; iii) MeI or Me_3SiCl; iv) HCl (2 N).



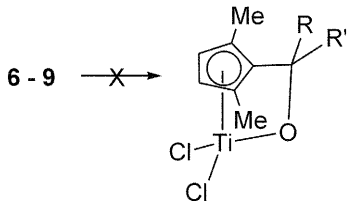
Scheme 2[a]. [a]Legend: i) $Ti(NMe_2)_4$; ii) Me_2SiCl_2.



is cleanly transformed to the trichloride complexes by treatment of 3 equivalents of Me_2SiCl_2 at 60 °C (Scheme 2). Clean complexes are obtained by trituration in pentane in overall 75%, 75% and 81% yield for **6**, **8**, and **9**, respectively or by recrystallization by vapor phase addition of pentane to a benzene solution in 44% yield for **7**. When the tris(dimethylamido) complex is reacted with Me_2SiCl_2 at room temperature, only two of the three dimethylamido ligands are substituted with the chloride ligand. A dichloro(dimethylamido) complex **10** was isolated as single crystals by layer addition of pentane to a C_6D_6 solution and its molecular structure is elucidated.

The NMR signals of **8** and **9** are sharp and can be unequivocally assigned. In the ^{1}H NMR spectrum (toluene-d_8) of **8**, a Cp-H signal, a Cp-CH_3 signal and a $Si(CH_3)_3$ signal are observed as singlets at 5.93, 1.99, and 0.06 ppm, respectively. Complex **9** has a stereogenic center at the carbon attaching the oxygen consequently the two protons and methyls attached on Cp being diastereotopic, respectively. Separated two signals are observed at 6.06 and 5.81 ppm as doublets (J = 2.8 Hz) for Cp-H in the ^{1}H NMR spectra (C_6D_6). Cp-CH_3 signals are also separately observed at 2.74 and 1.88 ppm as singlets. The $Si(CH_3)_3$ and OCH signals are observed as singlets at 0.11 and 6.27 ppm, respectively. In the cases of **6** and **7**, very broad ^{1}H and ^{13}C NMR signals were observed. Only methoxy signal, trimethylsiloxy signal and a doublet signal derived from the fluorenyl moitiy are sharp and the rest signals are very broad. Two Cp-H and two Cp-CH_3 signals are separately observed. Because the complexes have no stereogenic center at all, it is odd to observe the two Cp-H and the two Cp-CH_3 signals. If the structures are correct, the ^{1}H NMR spectra can be tentatively explained by the rotation barrier around C(Cp)-C(OR) bond. If the rotation is prohibited, the fluorenyl plane and Cp planes are situated biased and consequently the two methyls and the two protons attached on Cp are diastereopotic, respectively. Single crystals of **6** and **7** suitable for X-ray crystallography were obtained by vapor phase addition of pentane to a benzene solution and their structures were confirmed unambiguously.

Attempts to prepare the C1-briged Cp/oxido complexes by elimination of MeCl or Me_3SiCl by heating in toluene (110 °C) or in decaline (190 °C) are not successful. Decomposition to unidentified complexes is observed. Addition of CsF in THF does not lead to clean formation of a single



(1)

complex either (eq. 1).

X-ray Structures of 6, 7, and 10. Structures of **6** and **7** determined by X-ray crystallography are shown in Figure 1 and Figure 2 with selected bond distances and angles. They show a typical distorted tetrahedral structure around titanium coordinated by three Cl ligand and a Cp.[12,13] The fluorenyl plane is almost perpendicular to the Cp plane (the angle between the two planes, 89.8(2)° and 81.0(4)° for **6** and **7**, respectively) and the oxygen atoms are situated laterally to the Cp plane (the dihedral angle of C2-C1-C8-O1, −168.2° for **6** and the corresponding angle for **7**, −13.7°). The Ti-O distances are too long to consider any bonding (4.078 and 4.228 Å, for **6** and **7**, respectively). One of the chloride ligands is directed opposite to the CRR'(OR") substituent in **6** (dihedral angle of C8-C1-Ti1-Cl3, 158.5°) and the other Cl is perfectly eclipsed with CH_3 (dihedral angle of C6-C2-Ti1-Cl1, −2.0°) while the remaining Cl is situated staggered with the other CH_3 (dihedral angle of C7-C5-Ti1-Cl2, 158.5°).

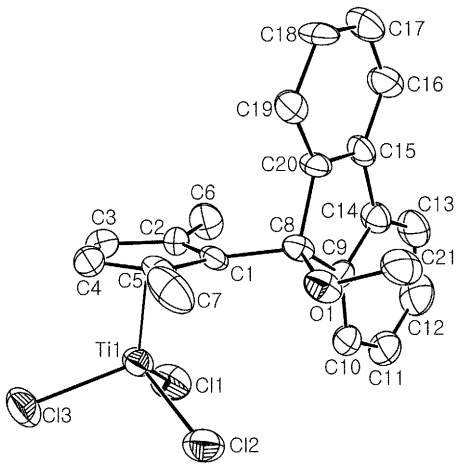


Figure 1. Thermal ellipsoid plot (30% probability level) of **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti(1)-Cl(1), 2.2037(17); Ti(1)-Cl(2), 2.2301(16); Ti(1)-Cl(3), 2.2312(15); Ti(1)-C(1), 2.434(4); Ti(1)-C(2), 2.411(5); Ti(1)-C(3), 2.290(5); Ti(1)-C(4), 2.279(5); Ti(1)-C(5), 2.391(5); Cp(c)-Ti(1), 2.031; Ti(1)-O(1), 4.078; Cl(1)-Ti(1)-Cl(2), 103.71(6); Cl(1)-Ti(1)-Cl(3), 101.86(7); Cl(2)-Ti(1)-Cl(3), 103.90(7); Cp(c)-C(2)-C(6), 176.37; Cp(c)-C(5)-C(7), 176.63; Cp(c)-C(1)-C(8), 170.58; C(2)-C(1)-C(8)-O(1), −168.2.

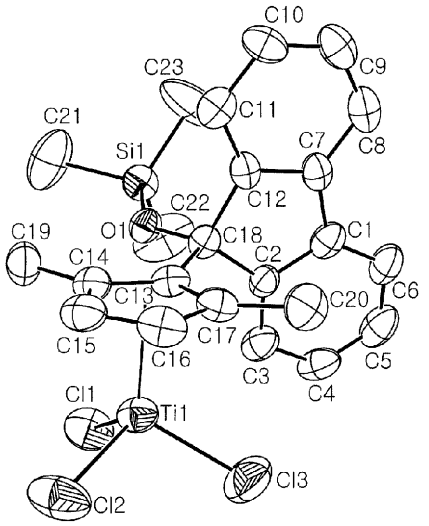


Figure 2. Thermal ellipsoid plot (30% probability level) of **7**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti(1)-Cl(1), 2.226(4); Ti(1)-Cl(2), 2.228(4); Ti(1)-Cl(3), 2.198(4); Ti(1)-C(13), 2.425(9); Ti(1)-C(14), 2.390(10); Ti(1)-C(15), 2.292(10); Ti(1)-C(16), 2.293(10); Ti(1)-C(17), 2.412(10); Cp(c)-Ti(1), 2.034; Ti(1)-O(1), 4.228; Cl(1)-Ti(1)-Cl(2), 101.05(15); Cl(3)-Ti(1)-Cl(2), 101.63(17); Cl(3)-Ti(1)-Cl(1), 105.41(16); Cp(c)-C(14)-C(19), 175.20; Cp(c)-C(17)-C(20), 176.23; Cp(c)-C(13)-C(18), 168.53; C(14)-C(13)-C(18)-O(1), −13.7.

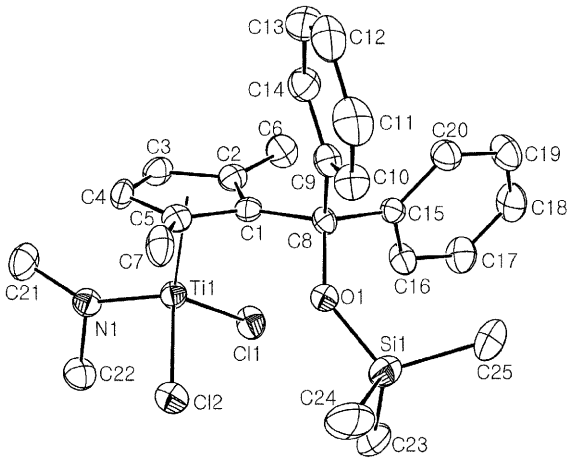


Figure 3. Thermal ellipsoid plot (30% probability level) of **10**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti(1)-Cl(1), 2.2861(17); Ti(1)-Cl(2), 2.285(2); Ti(1)-N(1), 1.861(4); Ti(1)-C(1), 2.446(5); Ti(1)-C(2), 2.439(7); Ti(1)-C(3), 2.316(6); Ti(1)-C(4), 2.310(6); Ti(1)-C(5), 2.396(5); Cp(c)-Ti(1), 2.059; Ti(1)-O(1), 3.685; Cl(2)-Ti(1)-Cl(1), 104.07(8); N(1)-Ti(1)-Cl(1), 103.22(15); N(1)-Ti(1)-Cl(2), 101.81(18); Cp(c)-C(2)-C(6), 173.90; Cp(c)-C(5)-C(7), 175.82; Cp(c)-C(1)-C(8), 170.73; C(2)-C(1)-C(8)-O(1), −136.4; C(21)-N(1)-C(22), 109.8(5); C(21)-N(1)-Ti(1), 140.5(4); C(22)-N(1)-Ti(1), 109.7(4); C(2)-C(1)-C(8)-O(1), −136.4.

The eclipsed chloride is situated opposite to the oxygen atom and the Ti-Cl distance is relatively shorter (Ti1-Cl1, 2.2037(17) Å) than the other two Ti-Cl distances (Ti1-Cl2, 2.2301(16) Å; Ti1-Cl3, 2.2312(15) Å). Almost the same situation of the chloride ligands are observed for **7**. The Ti-C(Cp) distance increases in the order of Ti-CH, Ti-CCH_3, and Ti-CCO in both **6** and **7**.

Figure 3 shows the structure of **10** with the selected bond distances and angles. In this complex, the oxygen atom is not situated laterally to the Cp plane as is observed for **6** and **7** but C-O vector is rotated toward titanium (dihedral angle of C2-C1-C8-O1, −136.4°). The corresponding dihedral angle for **6** and **7** are −168.2° and −13.7°, respectively. This rotation places the oxygen atom to be closer to the titanium (Ti-O distance, 3.685 Å). The corresponding Ti-O distances are 4.087 and 4.228 Å for **6** or **7** respectively. The two Cl ligands are situated nearly eclipsed with the methyls (dihedral angles of C6-C2-Ti1-Cl1 and C7-C5-Ti1-Cl2, 13.9° and −13.4°, respectively) and the amido ligand is situated opposite to the $Ph_2(Me_3SiO)C$ substituent (dihedral angle of N1-Ti1-C1-C8, 169.9°). The nitrogen atom shows a perfect trigonal structure (sum of bonding angles, 360°) and the C21-N-C22 plane is almost perpendicular to the Cp plane (84.8(3)°). The Cp(c)-Ti distance (2.059 Å) is slight longer than those observed for **6** and **7** (2.031 and 2.034 Å, respectively).

Conclusion

Titanium trichloride complexes, 2-[CR'R(OMe)]-1,3-$Me_2C_5H_2$}$TiCl_3$ (R, R' = 2,2'-biphenyl, **6**) and {2-[CR'R-($OSiMe_3$)]-1,3-$Me_2C_5H_2$}$TiCl_3$ (R, R' = 2,2'-biphenyl, **7**; R = ph, R' = ph, **8**; R = 2-naphthyl, R' = H, **9**) are prepared and the molecular structures of **6**, **7** and an intermediate {2-[$Ph_2C(OSiMe_3)$]-1,3-$Me_2C_5H_2$}$TiCl_2(NMe_2)$ (**10**) are elucidated. The oxygen atoms are too far away from the titanium center to show any bonding with the titanium. Various attempts to prepare the corresponding C1-bridged Cp/oxido complexes by MeCl or Me_3SiCl elimination are not successful.

Experimentals

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from benzophenone ketyl. Me_3SiCl and Me_2SiCl_2 were purified by distillation over CaH_2. DMF was purified by vacuum distillation and subsequent contacting with molecular sieves. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury plus 400. Mass spectra were obtained on a Micromass VG Autospec. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University.

Compound 2. To a solution of compound **1** (1.00 g, 4.88 mmol) in diethyl ether (5 mL) was added *n*-BuLi (1.35 g, 4.88 mmol) at −30 °C. The cooling bath was removed and the solution was warmed to room temperature for 30 min. White solid precipitated. The slurry was cooled again to −78 °C and 9-fluorenone (0.703 g, 3.90 mmol, 0.8 eq.) in diethyl ether (8 mL) was added. After the solution was stirred for 4 hours at −78 °C, the solution was warmed to room

temperature. All volatiles were removed by vacuum. Anhydrous DMF (5 mL) and NaH (0.117 g, 4.88 mmol) were added and the solution was stirred for 30 minutes at room temperature. MeI (1.39 g, 9.76 mmol) was added and the resulting mixture was stirred overnight. Water (10 mL) and hexane (10 mL) were added and the organic phase was collected, which is washed with brine (15 mL). Solvent was removed with rotary evaporator to give a residue which was dissolved in ethyl acetate (10 mL). Aqueous HCl (2 N, 10 mL) was added and the two-phase mixture was shaken vigorously for 2 minutes. Water phase was removed and the organic phase was washed with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried with anhydrous $MgSO_4$ and solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50 : 1). Overall yield was 57% (0.64 g). ^{1}H NMR ($CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 4 H, fluorenyl-H), 7.09 (td, J = 7.6, 1.2 Hz, 2 H, fluorenyl-H), 7.00 (td, J = 7.6, 1.2 Hz, fluorenyl-H), 5.61 (br s, 1H, vinyl-H), 2.76 (br s, 3H, CH_3), 2.71 (s, 3H, OCH_3), 2.6-2.8 (br, 2H, CH_2), 0.95 (br s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): 146.55 (br), 143.00 (br), 141.96 (br), 141.79 (br), 139.22 (sharp), 138.13 (br), 135.18 (sharp), 129.24 (br), 128.39 (sharp), 125.83 (sharp), 119.89 (sharp), 89.82 (br), 49.67 (sharp), 46.28 (br), 19.95 (br), 17.34 (br), 15.26 (br) ppm. HRMS-EI m/z = M^+ Calcd. ($C_{21}H_{20}O$): 288.1514. Found: 288.1515.

Compound 3. To a solution of compound **1** (1.00 g, 4.88 mmol) in diethyl ether (5 mL) was added *n*-BuLi (1.35 g, 4.88 mmol) at −30 °C. The cooling bath was removed and the solution was warmed to room temperature for 30 min. The slurry was cooled again to −78 °C and 9-fluorenone (0.703 g, 3.90 mmol, 0.8 eq.) in diethyl ether (8 mL) was added. After the solution was stirred for 2 hours at −78 °C, Me_3SiCl (0.80 g, 1.5 eq.) was added. The solution was warmed to room temperature and water (10 mL) was added. Volatile organics were removed by rotary evaporator and the organic compound was extracted with ethyl acetate (10 mL × 2). The combined ethyl acetate solution was shaken vigorously with aqueous HCl (2 N, 10 mL) for 2 minutes. The organic phase was washed with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried with anhydrous $MgSO_4$ and solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50 : 1). Overall yield was 60% (0.80 g). ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 4H, fluorenyl-H), 7.16 (td, J = 7.6, 1.2 Hz, 2H, fluorenyl-H), 7.05 (td, J = 7.6, 1.2 Hz, fluorenyl-H), 5.70 (br s, 1H, vinyl-H), 2.89 (s, 2H, CH_2), 2.74 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), −0.16 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): 149.82, 140.61, 129.20, 126.03, 125.61, 120.00, 46.24, 22.92, 15.14, 14.49, 1.75 ppm. Some signals were not observed by broadening in the ^{13}C NMR spectrum. HRMS-EI m/z = M^+ Calcd. ($C_{23}H_{26}OSi$): 346.1753. Found: 346.1752.

Compound 4. The compound was synthesized by the similar method and conditions for **4** except the addition of 1.0 equivalent of benzophenone. The compound was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50 : 1). Overall yield was 59 %. ^{1}H NMR (C_6D_6): δ 7.57-7.54 (m, 4H, Ph-H^o), 7.15-7.10 (m, 4H, Ph-H^m), 7.03 (tt, J = 6.4, 1.2 Hz, Ph-H^p), 5.85 (q, 2.0 Hz, 1H, vinyl-H), 2.70 (quintet, J = 2.0 Hz, 2H, CH_2), 1.88 (t, J = 2.0 Hz, 3H, CH_3), 1.50 (s, 3H, CH_3), 0.10 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 147.16, 145.52, 144.32, 139.70, 130.34, 128.16, 127.11, 126.14, 83.94, 46.16, 18.50, 17.55, 2.57 ppm. HRMS-EI m/z = M^+ Calcd. ($C_{23}H_{28}OSi$): 348.1909. Found: 348.1909.

Compound 5. The compound was synthesized by the similar method and conditions for **4** except the addition of 1.0 equivalent of 2-naphthaldehye. The compound was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50 : 1). Overall yield was 76%. ^{1}H NMR ($CDCl_3$): δ 8.14 (s, 1H, naphthyl-H^1), 7.69 (d, J = 8.0 Hz, naphthyl-H$^{3 \text{ or } 4}$), 7.70 (AA'BB', 1H, naphthyl-H$^{5 \text{ or } 8}$), 7.64 (AA'BB', 1H, naphthyl-H$^{5 \text{ or } 8}$), 7.56 (dd, J = 8.0 Hz, 2.4 Hz, naphthyl-H$^{3 \text{ or } 4}$), 7.24 (AA'BB', 2H, naphthyl-H$^{6 \text{ and } 7}$), 6.05 (s, 1H, OCH), 5.78 (s, vinyl-H), 2.72-2.68 (m, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.91 (q, J = 1.6 Hz, 3H, CH_3), 0.21 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 127.89, 127.41, 127.36, 125.58, 125.17, 124.59, 124.37, 123.82, 69.33, 44.13, 15.45, 14.29, 0.18 ppm. HRMS-EI m/z = M^+ Calcd. ($C_{21}H_{26}OSi$): 322.1753. Found: 322.1754.

Complex 6. Compound **2** (0.340 g, 1.18 mmol) and $Ti(NMe_2)_4$ (0.268 g, 1.18 mmol) were dissolved in toluene

Table 1. Crystallographic Parameters of **6**, **7**, and **10**[a]

	6	**7**	**10**
formula	$C_{21}H_{19}Cl_3OTi$	$C_{23}H_{25}Cl_3OSiTi$	$C_{25}H_{33}Cl_2NOSiTi$
Fw	441.61	499.77	510.41
size, mm^3	0.30 × 0.20 × 0.20	0.30 × 0.15 × 0.15	0.25 × 0.25 × 0.10
a, Å	7.3025(2)	15.289(2)	16.9230(10)
b, Å	11.8706(4)	10.634(3)	9.1000(10)
c, Å	23.8534(11)	16.929(4)	17.490(2)
α, deg	90	90	90
β, deg	82.7931(16)	116.489(12)	103.022(5)
γ, deg	90	90	90
V, Å^3	2051.40(13)	2463.4(10)	2624.2(4)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$	$P2_1/c$
D(calc), gcm^{-1}	1.430	1.348	1.292
Z	4	4	4
μ, mm^{-1}	0.815	0.733	0.592
no. of data collected	10842	9085	10697
no. of unique data	3876	2899	3961
no. of variables	239	268	287
R(%)	0.0487	0.0900	0.0706
R_w(%)	0.0893	0.1854	0.1033
Goodness of fit	0.820	1.155	1.017

[a]Data collected at (273(2) K with Mo-Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

(8 mL) and the solution was heated at 80 °C overnight under the weak stream of nitrogen gas. All volatiles were removed under vacuum to give a red residue. The residue was dissolved in toluene (8 mL) and Me_2SiCl_2 (0.457 g, 3.54 mmol) was added. The solution was heated at 60 °C overnight. The volatiles were removed to give a residue which is triturated in pentane. Red solid was obtained (0.39 g, 75%). Single crystals were obtained by vapor phase addition of pentane to a benzene solution. ^{1}H NMR (C_6D_6): δ 8.0 (very broad, 1H, fluorenyl-H), 7.31 (d, J = 8.0 Hz, 2H, fluorenyl-H$^{4 \text{ and } 5}$), 7.09 (t, J = 7.6 Hz, 2H), 7.25-6.86 (very broad, 3H), 6.3 (very braod, 1H, Cp-H), 5.5 (very braod, 1H, Cp-H), 2.77 (very broad, 3H, CH_3), 2.64 (s, 3H, OCH_3), 1.3 (very broad, 3H, CH_3). ^{13}C NMR signals were too broad to be analyzed. Anal. Calcd. for $C_{21}H_{19}Cl_3OTi$: C, 57.1; H, 4.34. Found: C, 57.5; H, 4.25.

Complex 7. The compound was synthesized by the same method and conditions for **6** by using **3**. Single crystals were obtained by vapor phase addition of pentane to a benzene solution (44%). ^{1}H NMR (C_6D_6): δ 8.08 (br s, 1H, fluorenyl-H), 7.27 (d, J = 7.2 Hz, 2H, fluorenyl-H$^{4 \text{ and } 5}$), 7.06 (br s, 2H, fluorenyl-H), 6.98 (br s, 2H, fluorenyl-H), 6.92 (br s, 1H, fluorenyl-H), 6.36 (br s, 1H, Cp-H), 5.48 (br s, 1H, Cp-H), 2.85 (br s, 3H, CH_3), 1.22 (br s, 3H, CH_3), −0.22 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR (C_6D_6): δ 148.45 (br), 145.71 (br), 142.71 (sharp), 140.55 (br), 140.10 (br), 139.51 (br), 136.65 (br), 130.30 (br), 129.81 (br), 128.55 (sharp), 126.13 (br), 125.13 (br), 124.83 (br), 120.02 (br), 85.83 (sharp), 20.60 (br), 16.83 (br), 1.58 (sharp) ppm. Anal. Calcd. for $C_{23}H_{25}Cl_3OSiTi$: C, 55.3; H, 5.04. Found: C, 55.2; H, 4.95.

Complex 8. The compound was synthesized by the same method and conditions for **6** by using **4**. The complex was purified by trituration in pentane (75%). ^{1}H NMR (toluene-d_8): δ 7.33 (dt, J = 6.4, 2.0 Hz, 4H, Ph-H^o), 7.07-6.99 (m, 6 H, Ph-H$^{m \text{ and } p}$), 5.93 (s, 2H, Cp-H), 1.99 (s, 6H, CH_3), 0.06 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR (toluene-d_8): δ 147.27, 143.03, 138.62, 137.16, 128.87, 128.26, 125.41, 84.96, 18.83, 2.59 ppm. Anal. Calcd. for $C_{23}H_{27}Cl_3OSiTi$: C, 55.1; H, 5.42. Found: C, 49.8; H, 5.15.

Complex 9. The compound was synthesized by the same method and conditions for **6** by using **5**. The complex was purified by trituration in pentane (81%). ^{1}H NMR (C_6D_6): δ 7.64 (s, 1H, naphtyl-H^1), 7.61 (d, J = 8.0 Hz, 1H, naphtyl-H$^{3 \text{ or } 4}$), 7.55 (d, J = 8.0 Hz, 1H, naphtyl-H$^{5 \text{ and } 8}$), 7.31 (d, J = 8.0 Hz, 1H, naphtyl-H$^{3 \text{ or } 4}$), 7.25 (t, J = 8.0 Hz, 2H, naphtyl-H$^{6 \text{ and } 7}$), 6.27 (s, 1H, OCH), 6.06 (d, J = 2.8 Hz, 1H, Cp-H), 5.81 (d, J = 2.8 Hz, 1H, Cp-H), 2.74 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 0.11 (s, 9H, $SiMe_3$) ppm. ^{13}C NMR (C_6D_6): δ 140.81, 140.22, 137.84, 137.62, 133.48, 433.45, 129.12, 126.82, 126.76, 126.19, 125.79, 124.85, 122.93, 75.47, 18.93, 17.13, 0.57 ppm. Anal. Calcd. for $C_{21}H_{25}Cl_3OSiTi$: C, 53.0; H, 5.30. Found: C, 53.3; H, 5.25.

Crystallographic Studies. Crystals of **6, 7** and **10** coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97)[14] and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 1.

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Supplementary material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (**6**: CCDC no. 244662, **7**: CCDC no. 244663, and **10**: 244664). Copies of this information may be obtained free of charge form The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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