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# Some reactions of $Cp^*TiMe_2(OAr)$ and $Cp^*TiMe(CF_3SO_3)(OAr)$ with 5-hexen-1-ol and 3-buten-1-ol, structural analysis for $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ ($OAr = O\text{-}2,6\text{-}{}^iPr_2C_6H_3$)

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## Abstract

Reaction of $Cp^*TiMe(CF_3SO_3)(OAr)$ (**2**, $OAr = O\text{-}2,6\text{-}{}^iPr_2C_6H_3$) with 5-hexen-1-ol in *n*-hexane gave $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**) exclusively (94% yield). **3** was very stable upon heating, and the structural analysis has been made by X-ray crystallography. Reaction of $Cp^*TiMe_2(OAr)$ with both 5-hexen-1-ol and 3-buten-1-ol have also been explored.

*Keywords:* Titanium complex; Alken-1-ol; Half-titanocene; Olefin polymerization

## 1. Introduction

*Non-bridged* half-metallocene type group IV transition metal complexes of the type, $Cp'M(L)X_2$ ($Cp'$ = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, $NR_2$, $NPR_3$, $NCR_2$; X = halogen, alkyl) [1–15], have attracted considerable attention as the new type of olefin polymerization catalysts, because these types of complexes would exhibit unique characteristics as olefin polymerization catalysts that are different from both ordinary metallocene type and so-called 'constrained geometry' (hybrid 'half-metallocene') type catalysts. We reported that (cyclopentadienyl)(aryloxo)titanium(IV) complexes – MAO catalyst system exhibited unique characteristics especially for both ethylene/α-olefin and ethylene/styrene copolymerizations [3,16]. Concerning their mechanistic studies, we reported synthesis and structural analysis for $Cp^*TiMe(CF_3SO_3)(OAr)$ (**2**, $OAr = O\text{-}2,6\text{-}{}^iPr_2C_6H_3$), although we could not isolate the cationic methyl complex from the reaction of $Cp^*TiMe_2(OAr)$ (**1**) with $Ph_3CB(C_6F_5)_4$ [17].

Polymerization of non-conjugated diene attracts considerable attention not only because cyclopolymerization took place if ordinary metallocene type complexes [18] or a half-metallocene type complex [11c] were used as catalyst precursors, but also because functionalization of polyolefin would be attained by simple modification if one olefinic bond of the diene was remained as the side chain during polymerization. It has also been known that $Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ was isolated and the olefinic double bond was coordinated to the centered metal [19]. This result would be indicative for the above cyclopolymerization. In this paper, we wish to introduce some reactions of $Cp^*TiMe_2(OAr)$ (**1**) and $Cp^*TiMe(CF_3SO_3)(OAr)$ (**2**) with 5-hexen-1-ol and 3-buten-1-ol, and structural analysis for $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**).

## 2. Results and discussion

It was revealed that **2** prepared from **1** by treating with $CF_3SO_3H$ reacted with 1.0 equivalent of 5-hexen-1-

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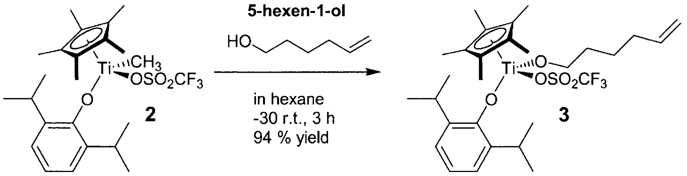

Scheme 1.

ol to give $Cp^{*}Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**) as red microcrystals in exclusive yield (94% isolated yield, Scheme 1). **3** was identified by $^{1}H$ and $^{13}C$ NMR as well as by elemental analysis. The reaction of **2** with 1.0 equivalent of 3-buten-1-ol gave the similar red microcrystals, and was also identified as $Cp^{*}Ti(CF_3SO_3)(OCH_2CH_2CH{=}CH_2)(OAr)$ (**4**) by $^{1}H$ and $^{13}C$ NMR as well as by elemental analysis. These complexes were stable at room temperature, and no decompositions would have occurred if the *n*-hexane solution was warmed to 50 °C for several hours.

The red prism microcrystals were grown from a concentrated hot *n*-hexane solution containing **3** upon standing, and the structure was determined by X-ray crystallography using a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The ortep drawing is shown in Fig. 1 and the selected bond lengths and bond angles are summarized in Table 1.

**3** folds tetrahedral geometry around the titanium and Ti—O(3) bond distance (2.006 Å) in $CF_3SO_3$ ligand was longer than those both in Ti—O(1) (1.806 Å, in aryloxo ligand) and Ti—O(2) (1.769 Å, in alkoxo ligand). The bond distance was also somewhat longer than that in **2** [1.978 Å, 17], but shorter than those for $[Cp^{*}TiF(\mu\text{-}F)(\mu\text{-}OSO_2\text{-}p\text{-}C_6H_4CH_3)]_2$ (2.070 and 2.094 Å) [20]. The result shows that $CF_3SO_3$ ligand coordinates relatively weak to titanium and the complex might thus possess a cationic character in some extent or would be 16e species. Ti—O(1) bond distance in the aryloxo ligand (1.806 Å) was somewhat longer than those in **2** (1.778 Å) and **1** (1.790 Å) as well as $Cp^{*}TiCl_2(OAr)$ (1.772 Å) [b,17]. Ti—O(2) bond distance (1.769 Å) is within the expected range [21].

It was also revealed that the bond angle of Ti—O—C (in phenyl, 165.0°) is still larger than those of other related complexes (162.3–163.1°) that consisted of different cyclopentadienyl or aryloxo groups [b,17], and somewhat smaller than those in **2** (166.2°), **1** (168.7°) and $Cp^{*}TiCl_2(OAr)$ (173.0°). The present result would thus also suggest that both Cp* and the aryloxo ligand containing two isopropyl groups in 2,6-position sterically forces the unique bond angle, which leads to more $O \rightarrow Ti\pi$ donation into the titanium.

It should be noted that the bond distance in the olefinic bond in alkoxo ligand [corresponded to C(27)—C(28)] was 1.21 Å, and the structure clearly shows that the olefinic bond does not coordinate to titanium. This result is a good agreement from resonances of olefinic protons in $^{1}H$ NMR spectrum that the NMR parameters of the vinyl groups for **3** and **4** were unchanged from the free olefin values. Although this is not an exact cationic species, the structure observed here should be an interesting contrast to $Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^{+}$ [19].

Since reactions of **2** with 5-hexen-1-ol and 3-buten-1-ol took place cleanly to afford **3** and **4** in exclusive yields, similar reactions with the dimethyl complex (**1**) were also explored. The reaction of **1** with 1.0 equivalent of 5-hexen-1-ol in *n*-hexane (at −30 °C to room temperature, 3 h) took place cleanly, affording yellow tan residue after removing solvent from the reaction mixture. The $^{1}H$ and $^{13}C$ NMR spectra showed that one methyl group consumed with OH group (confirmed by the decrease in protons at 0.81 ppm ascribed to Ti—Me), strongly suggesting the formation of $Cp^{*}TiMe[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**5**) exclusively. An attempt to isolate the pure microcrystals was not successful, but the $^{1}H$ NMR spectrum of the resultant tan residue after a standard purification procedure (passing through Celite pad after

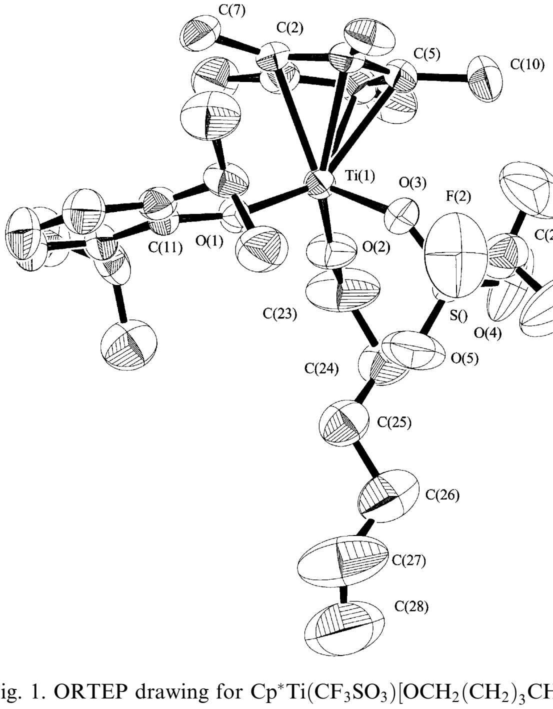

Fig. 1. ORTEP drawing for $Cp^{*}Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**). Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for Cp$^*$Ti(CF$_3$SO$_3$)[OCH$_2$(CH$_2$)$_3$CH=CH$_2$](OAr) (**3**)

| | | | |
|---|---|---|---|
| | Bond distances in (Å) | | |
| Ti—C(1) in Cp$^*$ | 2.378(4) | Ti—C(2) in Cp$^*$ | 2.376(4) |
| Ti—C(3) in Cp$^*$ | 2.330(4) | Ti—O(1) in OAr | 1.806(3) |
| Ti—O(2) | 1.769(3) | Ti—O(3) in CF$_3$SO$_3$ | 2.006(3) |
| S—O(3) | 1.477(3) | S—O(4) in CF$_3$SO$_3$ | 1.413(4) |
| S—O(5) in CF$_3$SO$_3$ | 1.403(4) | S—C(29) in CF$_3$SO$_3$ | 1.828(7) |
| F(1)—C(29) | 1.262(7) | O(1)—C(11) in OAr | 1.369(4) |
| O(2)—C(23) | 1.433(6) | C(1)—C(2) in Cp$^*$ | 1.412(6) |
| C(2)—C(3) in Cp$^*$ | 1.418(6) | C(1)—C(6) in Cp$^*$ | 1.507(7) |
| C(2)—C(7) in Cp$^*$ | 1.509(6) | C(5)—C(10) in Cp$^*$ | 1.487(7) |
| C(23)—C(24) | 1.480(9) | C(24)—C(25) | 1.479(9) |
| C(26)—C(27) | 1.50(1) | C(27)—C(28) | 1.21(1) |
| | Bond angles in (°) | | |
| O(1)—Ti—O(2) | 103.8(1) | O(1)—Ti—O(3) | 101.7(1) |
| O(2)—Ti—O(3) | 101.3(2) | O(1)—Ti—C(1) | 107.9(1) |
| O(1)—Ti—C(2) | 88.4(2) | O(1)—Ti—C(3) | 104.0(1) |
| O(2)—Ti—C(1) | 145.5(1) | O(2)—Ti—C(2) | 136.0(2) |
| O(2)—Ti—C(3) | 101.2(2) | O(3)—Ti—C(1) | 85.4(1) |
| O(3)—Ti—C(2) | 117.6(1) | O(3)—Ti—C(3) | 140.4(1) |
| Ti—O(1)—C(11) | 165.0(2) | Ti—O(2)—C(23) | 166.7(3) |
| Ti—O(3)—S | 135.9(2) | O(3)—S—C(29) | 103.0(3) |
| Ti—C(1)—C(6) | 124.3(3) | O(2)—C(23)—C(24) | 111.3(6) |
| C(26)—C(27)—C(28) | 129(1) | | |

the reaction mixture, and was placed in vacuo) showed high purity of the expected product. No significant differences were observed in the $^1$H NMR spectra if the measurement was taken at low temperature (in toluene-d$_8$, −70, −50 and −30 °C). The reaction with 3-buten-1-ol was also explored, and the $^1$H and $^{13}$C NMR spectra also suggest that the reaction took place affording Cp$^*$TiMe[OCH$_2$CH$_2$CH=CH$_2$](OAr) (**6**) with exclusive yield. Although attempts to isolate these complexes as pure microcrystals were not successful (or these products may exist as liquid under these conditions), the resultant complexes were very stable at room temperature at least for several days, and no decomposed or other products were observed on $^1$H NMR spectra if the reaction mixture was warmed to 50 °C for several hours. In addition, we assume that these olefinic double bonds do not coordinate to the titanium metal, because no differences were observed in their $^1$H NMR spectra especially in olefinic regions for **3**–**6** (4.8–6.0 ppm, Fig. 2) in addition to the above experimental results. Although attempts to isolate the cationic analogue like Cp$^*$Ti[OCH$_2$CH$_2$CH=CH$_2$](OAr)$^+$ by removing methyl group from **5** or by a replacement of CF$_3$SO$_3$ from **3** were not successful at this moment, we believe that results observed here would be an interesting contrast to those performed by ordinary metallocene complexes. The observed results are also in good agreement with the result for polymerization of 1,5-hexadiene using Cp$^*$TiCl$_2$(OAr) – MAO catalyst system in which exclusive selectivity for cyclopolymerization observed in the polymerization using ordinary metallocene complexes was not seen [22].

## 3. Experimental

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Anhydrous grade of *n*-hexane (Kanto Kagaku) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox under nitrogen flow. Syntheses of Cp$^*$TiMe$_2$ (O-2, 6-$^i$Pr$_2$C$_6$H$_3$) (**1**) and Cp$^*$TiMe(CF$_3$SO$_3$)(O-2, 6-$^i$Pr$_2$C$_6$H$_3$) (**2**) were according to our previous report [b,17]. All $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, $^1$H; 100.40 MHz, $^{13}$C). All chemical shifts are given in ppm and are referenced to tetramethylsilane, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves in the drybox.

### 3.1. Synthesis for Cp$^*$Ti(CF$_3$SO$_3$)[OCH$_2$(CH$_2$)$_3$CH=CH$_2$](OAr) (3)

Into a chilled *n*-hexane solution (ca. 25 ml) containing **2** (326 mg, 0.622 mmol), 5-hexen-1-ol (1.0 equivalent to **2**) diluted with *n*-hexane (5 ml) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 3 h. The reaction mixture was passed through Celite pad, and the filter cake was washed with hexane (10 ml). The combined filtrate and the wash were taken to dryness under reduced pressure to concentrate the total volume of 10 ml. The chilled

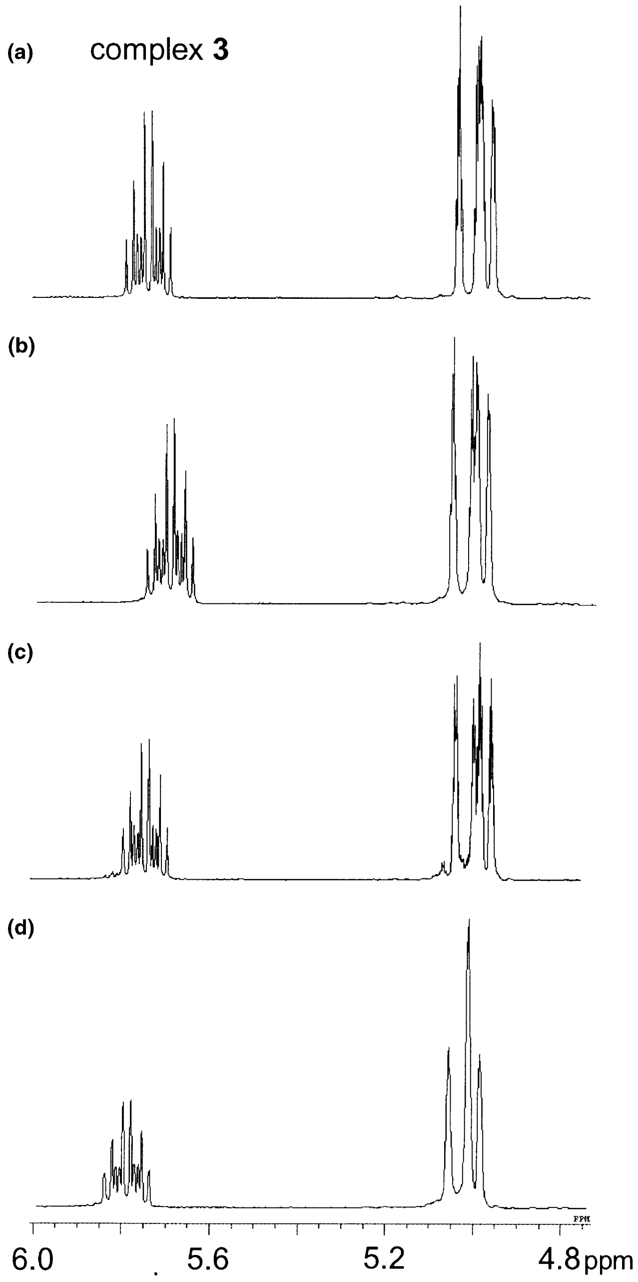

Fig. 2. $^1H$ NMR spectra (in $C_6D_6$, 4.8–6.0 ppm) for (a) $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**), (b) $Cp^*Ti(CF_3\ SO_3)[OCH_2CH_2CH{=}CH_2](OAr)$ (**4**), and for (c) the reaction product of **1** with 5-hexen-1-ol, and (d) the reaction product of **1** with 3-buten-1-ol.

(−30 °C) solution gave red microcrystals (1st crop, 355 mg). Yield 94%. $^1H$ NMR ($C_6D_6$): $\delta$ 7.04 (d, 2H, $J = 7.0$ Hz, $C_6H_3$), 6.96 (t, 1H, $J = 7.7$ Hz, $C_6H_3$), 5.74 (m, 1H, $CH_2{=}CH{-}$), 5.00 (dd or *m*, 1H, $CH_2{=}CH{-}$), 4.97 (dd or m, 1H, $CH_2{=}CH{-}$), 4.56 and 4.36 (m, 2H, $-CH_2OTi$), 3.17 (m, 2H, $(CH_3)_2CH{-}$), 1.92 (m, 2H, $CH_2{=}CH{-}CH_2{-}$), 1.81 (s, 15H, $C_5Me_5$), 1.63 (m, 2H), 1.31 (m, 2H), 1.28 (d, 6H, $J = 7.0$ Hz, $(CH_3)_2CH{-}$), 1.20 (d, 6H, $J = 7.0$ Hz, $(CH_3)_2CH{-}$) ppm. $^{13}C$ NMR ($C_6D_6$): $\delta$ 11.2, 24.0, 24.1, 25.1, 26.8, 32.7, 33.7, 79.2, 114.8, 120.2 ($^2J_{C-F} = 319$ Hz), 123.0, 123.5, 129.0, 138.0, 138.7, 159.1 ppm. E.A. Calcd for $C_{29}H_{43}F_3O_5$ STi: C, 57.23%; H, 7.12%; N, 0%. Found: C, 57.36%; H, 7.25%; N, 0.02%. Red prism microcrystals were grown from a concentrated hot *n*-hexane solution upon standing, and the resultant microcrystals were used for the crystal structure analysis.

### 3.2. Synthesis for $Cp^*Ti(CF_3)(SO_3)(OCH_2CH_2CH{=}CH_2)(OAr)$ (4)

The synthetic procedure for **4** was the same as that for **3** except that **2** (352 mg, 0.671 mmol) and 3-buten-1-ol (1.0 equivalent of **2**) in place of 5-hexen-1-ol were used. The chilled (−30 °C) *n*-hexane solution gave red microcrystals (1st crop, 355 mg), and the chilled concentrated solution from the mother liquor gave the second crop (44 mg). Yield 90%. $^1H$ NMR ($C_6D_6$): $\delta$ 7.03 (d, 2H, $J = 7.3$ Hz, $C_6H_3$), 6.95 (t, 1H, $J = 7.7$ Hz, $C_6H_3$), 5.69 (m, 1H, $CH_2{=}CH{-}$), 5.02 (dd or m, 1H, $CH_2{=}CH{-}$), 5.00 (dd or m, 1H, $CH_2{=}CH{-}$), 4.62 and 4.40 (m, 2H, $-CH_2OTi$), 3.15 (m, 2H, $(CH_3)_2CH{-}$), 2.41 (m, 2H), 1.80 (s, 15H, $C_5Me_5$), 1.27 (d, 6H, $J = 6.6$ Hz, $(CH_3)_2CH{-}$), 1.19 (d, 6H, $J = 7.0$, $(CH_3)_2CH{-}$) ppm. $^{13}C$ NMR ($C_6D_6$): d 11.2, 24.0, 24.2, 28.8, 37.7, 117.3, 120.2 ($^2J_{C-F} = 318$ Hz), 123.1, 123.5, 129.3, 134.2, 138.1, 159.1 ppm. E.A. Calcd for $C_{27}H_{39}F_3O_5$ STi: C, 55.86%; H, 6.77%. Found (1): C, 55.94%; H, 6.91%. Found (2): C, 55.56%; H, 6.83%.

### 3.3. Reaction of 1 with 5-hexen-1-ol

Into a chilled *n*-hexane solution (ca. 25 ml) dissolved in **1** (384 mg, 0.984 mmol), 5-hexen-1-ol (1.0 equivalent to **1**) diluted with *n*-hexane (5 ml) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 3 h. The reaction mixture was passed through Celite pad, and the filter cake was washed with hexane (10 ml). The combined filtrate and the wash were taken to dryness under reduced pressure to afford yellow tan residue after removing low boiling point compounds (463 mg, estimated crude yield only by the weight was 99%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.11 (d, 2H, $J = 7.7$ Hz, $C_6H_3$), 6.97 (t, 1H, $J = 7.5$ Hz, $C_6H_3$), 5.76 (m, 1H, $CH_2{=}CH{-}$), 5.00 (dd or m, 1H, $CH_2{=}CH{-}$), 4.95 (dd or m, 1H, $CH_2{=}CH{-}$), 4.25 and 4.20 (m, 2H, $-CH_2OTi$), 3.32 (m, 2H, $(CH_3)_2CH{-}$), 1.95 (m, 2H, $CH_2{=}CH{-}CH_2{-}$), 1.83 (s, 15H, $C_5Me_5$), 1.52 (m, 2H), 1.37 (m, 2H), 1.31 (d, 6H, $J = 7.0$ Hz, $(CH_3)_2CH{-}$), 1.26 (d, 6H, $J = 6.6$ Hz, $(CH_3)_2CH{-}$), 0.81 (s, 3H, $Ti{-}Me$) ppm. $^{13}C$ NMR ($C_6D_6$): $\delta$ 10.9, 23.7, 24.0, 25.3, 26.3, 33.2, 33.6, 43.7, 74.2, 114.6, 120.5, 121.0, 123.0, 137.0, 138.7, 158.6 ppm.

### 3.4. Reaction of 1 with 3-buten-1-ol

The basic procedure was the same as that described above except that 478 mg (1.224 mmol) of **1**, and 3-buten-

1-ol in place of 5-hexen-1-ol were used. Yellow tan residue was obtained after the procedure described above. $^1H$ NMR ($C_6D_6$): d 7.11 (d, 2H, $J = 7.3$ Hz, $C_6H_3$), 6.97 (t, 1H, $J = 7.5$ Hz, $C_6H_3$), 5.79 (m, 1H, $CH_2{=}CH{-}$), 5.03 (dd or m, 1H, $CH_2{=}CH{-}$), 4.99 (dd or m, 1H, $CH_2{=}CH{-}$), 4.30 and 4.25 (m, 2H, $-CH_2OTi$), 3.30 (m, 2H, $(CH_3)_2CH-$), 2.27 (m, 2H), 1.82 (s, 15H, $C_5Me_5$), 1.30 (d, 6H, $J = 7.0$ Hz, $(CH_3)_2CH-$), 1.24 (d, 6H, $J = 7.0$ Hz, $(CH_3)_2CH-$), 0.82 (s, 3H, Ti—Me) ppm. $^{13}C$ NMR ($C_6D_6$): $\delta$ 10.9, 11.0, 23.9, 24.1, 26.4, 26.6, 38.6, 44.4, 44.6, 74.0, 74.1, 116.6, 120.7, 120.9, 121.4, 123.1, 123.3, 135.5, 137.3, 158.8 ppm.

### *3.5. Crystallographic analysis for* **3**

All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K$\alpha$ radiation. The selected crystal collection parameters are listed in Table 2, and the structure was solved by direct method and expanded using Fourier techniques [23]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan [24] crystallographic software package of Molecular Structure Corporation.

Table 2
Crystal and data collection parameters for $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$(**3**)[a]

| Complex | **3** |
|---|---|
| Formula; formula weight | $C_{29}H_{43}F_3O_5STi$; 608.61 |
| Habits; crystal size (mm) | Red, prism;<br>$0.80 \times 0.50 \times 0.45$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (No. 14) |
| *a* (Å); *b* (Å); *c* (Å) | 8.5325(6); 17.116(2);<br>22.332(2) |
| $\beta$ (deg); $V$ (Å$^3$) | 92.825(2); 3257.4(5) |
| *Z* value | 4 |
| $D_{calcd}$ (g/cm$^3$) | 1.241 g/cm$^3$ |
| $F_{000}$ | 1288.00 |
| Temp (K) | 243 |
| $\lambda$ (Mo-K$\alpha$) (Å) | 0.71069 |
| $2\theta$ range (°) | 3.0°–55.0° |
| No. of reflections measured: ($R_{int}$) | Total: 23172, unique:<br>7140 (0.100) |
| No. of observations ($I > -10.00\delta(I)$) | 7140 |
| No. of variables | 352 |
| Residuals: $R1$; $Rw$ | 0.079: 0.192 |
| GOF | 1.43 |
| Max (minimum) peak in final diff. map ($e-$/Å$^3$) | 0.83 (−0.87) |

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\sum \omega (F_o^2 - F_c^2)^2$. Least-square weights: $w = 1/\delta^2(F_o^2)$, $p$-factor 0.05.

## Supplementary material

X-ray structure report for $Cp^*Ti(CF_3SO_3)[OCH_2(CH_2)_3CH{=}CH_2](OAr)$ (**3**), and $^1H$ and $^{13}C$ NMR spectra for **5**–**6**.

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