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# Synthesis and characterization of titanium complexes containing the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand

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## Abstract

A series of titanium complexes containing the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand $C_5Me_4CH_2CH_2CH{=}CH_2$ ($Cp^{=}$) have been synthesized and characterized. The dichloro complex $Cp^{=}{}_2TiCl_2$ was prepared by the reaction of $LiCp^{=}$ and $TiCl_3$ in dimethoxyethane, followed by oxidation using lead dichloride. $Cp^{=}{}_2TiCl_2$ was converted into the dimethyl derivative $Cp^{=}{}_2TiMe_2$, the molecular structure of which was confirmed by an X-ray structural analysis, which showed it to be a peralkyl titanocene complex containing the two pendent 3-butenyl side chains in the lateral positions of the bent metallocene unit. The reaction of $Cp^{=}{}_2TiMe_2$ with $B(C_6F_5)_3$ was monitored by NMR spectroscopy. $Cp^{=}TiCl_3$, which was used to synthesize $Cp^{=}CpTiCl_2$ by reacting with LiCp, was prepared from the reaction between $Cp^{=}SiMe_3$ and $TiCl_4$. $Cp^{=}CpTiCl_2$ was further converted into $Cp^{=}CpTiMe_2$ and $Cp^{=}CpTi(OTf)_2$. A significantly improved method for the preparation of 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene was developed.

*Keywords:* Titanium; Cyclopentadienyl; Group 4; Triflate; Metallocenes; Alkyl

## 1. Introduction

Homogeneous Ziegler–Natta catalysts based on metallocene complexes of Group 4 metals have greatly improved understanding on the molecular level of the chain initiation, growth and termination steps during olefin polymerization. Numerous synthetic [1], kinetic [2] and theoretical studies [3] have led to the general consensus that 14-electron cations of the general formula $[(C_5R_5)_2MR]^+$ (M = Ti, Zr or Hf; R = H, alkyl or growing polymer chain) are the active species responsible for the C–C bond formation by insertion of an olefinic substrate $H_2C{=}CHR$ into the metal–carbon bond. Although postulated already for the Cossee [4] mechanism and calculated by various computational methods [3], the crucial key intermediate prior to the insertion, namely the alkyl(olefin) complex of the $d^0$ metal center $[(C_5R_5)_2MR(H_2C{=}CHR)]^+$, has so far never been directly detected [5]. We report here our first attempts to generate olefin complexes of tetravalent titanium by utilizing the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($Cp^{=}$) [6]. This ligand was developed to allow the study of the intramolecular interaction of the C–C double bond with a transition metal center. The bifunctional bonding mode of the $Cp^{=}$ ligand as a result of the pronounced chelate effect has already been demonstrated in a number of cases [7].

## 2. Results and discussion

The original synthesis of 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene $C_5Me_4(CH_2CH_2CH{=}CH_2)H$ ($Cp^{=}H$) [6] by the reaction of 2,3,4,5-tetramethylcyclopentadienone-1 with the homoallyl Grignard reagent suffered from irreproducible yields as well as variable purity of the product, especially during large-scale preparations. As in the case of similarly highly alkylated cyclopentadienes such as tetramethylcyclopentadiene [8], systematic investigations revealed that the acid-induced dehydration of the intermediate carbinol $C_5Me_4H_2(OH)(CH_2CH_2CH{=}CH_2)$ is the critical step during this synthesis [8b]. Following an extensive search, we eventually discovered that the use of a strongly acidic ion-exchange resin such as Amberlite IR-120® results in smooth dehydration and in the isolation of highly pure $Cp^{=}H$ in excellent yields and with good reproducibility.

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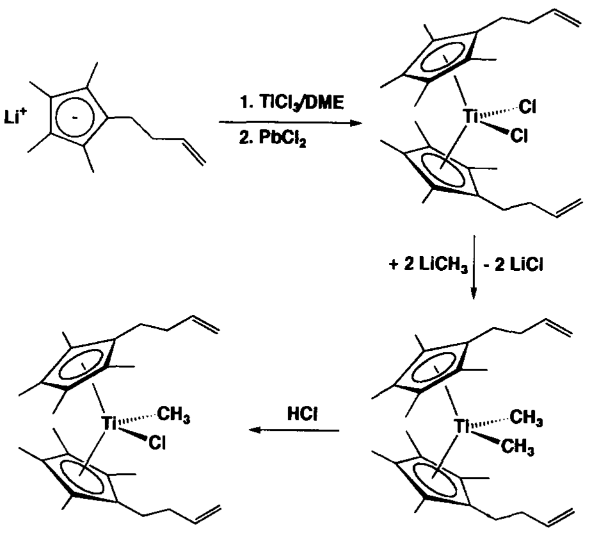


Scheme 1.

When two equivalents of lithium 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl (LiCp$^{=}$) are treated with titanium trichloride in dimethoxyethane for 24 h and the intermediate titanium(III) Cp$^{=}_{2}$TiCl complex is oxidized with lead dichloride [9], bis[1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium dichloride (Cp$^{=}_{2}$TiCl$_2$) can be isolated as pentane-soluble red crystals with good yields (Scheme 1). Owing to the higher solubility of LiCp$^{=}$ compared with LiCp$^{*}$ in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) [6], there is no indication that [1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]trichlorotitanium (Cp$^{=}$TiCl$_3$) (vide infra) forms in any substantial amount under these conditions. In contrast, the synthesis of Cp$^{*}_{2}$TiCl$_2$ (Cp$^{*}$ = pentamethylcyclopentadienyl) requires much harsher conditions, while at the same time Cp$^{*}$TiCl$_3$ is formed in considerable amounts [10]. However, as in the case of Cp$^{*}_{2}$TiCl$_2$, the use of DME as solvent is preferred to THF.

Reaction of Cp$^{=}_{2}$TiCl$_2$ with methyllithium in ether gives the dimethyl complex Cp$^{=}_{2}$TiMe$_2$ as somewhat air- and light-sensitive yellow cystals with excellent yields. As in the dichloro complex, NMR and IR spectroscopy data indicate that the 3-butenyl side chain in Cp$^{=}_{2}$TiMe$_2$ is not interacting with the titanium center. Interaction is not expected on the grounds of the electronic and steric saturation of the titanium center, even though an olefinic bond is present in the same molecule as a titanium–carbon $\sigma$ bond [5]. Thus in the $^{1}$H NMR spectrum the two equivalent methyl ligands at the tetravalent titanium center give rise to a signal at $\delta = -0.60$ ppm. The $^{13}$C NMR chemical shift of $\delta = 49.5$ ppm for the methyl group is comparable with that for the parent Cp$^{*}_{2}$TiMe$_2$ ($\delta = 48.8$ ppm) [11]. As a diagnostic feature of the intact Cp$^{=}$ ligand, the IR spectrum exhibits a band at 1639 cm$^{-1}$ of medium intensity. The thermal stability of Cp$^{=}_{2}$TiMe$_2$ is remarkable; no decomposition was observed after heating a benzene-$d^6$ solution for 24 h.

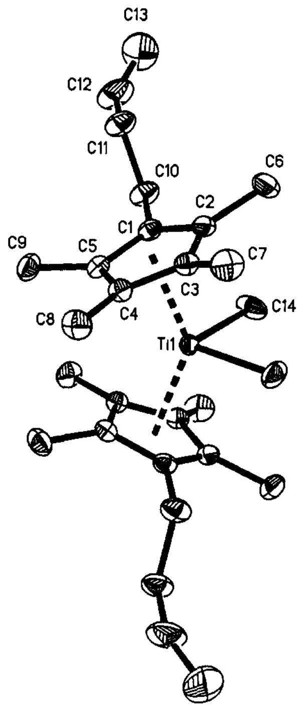


Fig. 1.

A single-crystal X-ray diffraction study established the expected bent titanocene structure for Cp$^{=}_{2}$TiMe$_2$. The molecular structure and atom numbering scheme are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The overall structure of Cp$^{=}_{2}$TiMe$_2$, containing a crystallographic $C_2$ axis, can be compared with that of decamethyltitanocene dichloride Cp$^{*}_{2}$TiCl$_2$, reported in the classic paper by Bercaw and coworkers [12]. The titanium-ring carbon bond lengths are in the range 2.440(2)–2.484(3) Å and the ring centroid–metal–ring centroid angle is 139°. As in Cp$^{*}_{2}$TiCl$_2$, the two five-membered rings are in a staggered conformation with the 3-butenyl substituents arranged in the lateral positions [13]. The titanium–methyl carbon bond length of 2.154(5) Å is similar to that found in the parent complex Cp$_2$TiMe$_2$ (2.170(2) and

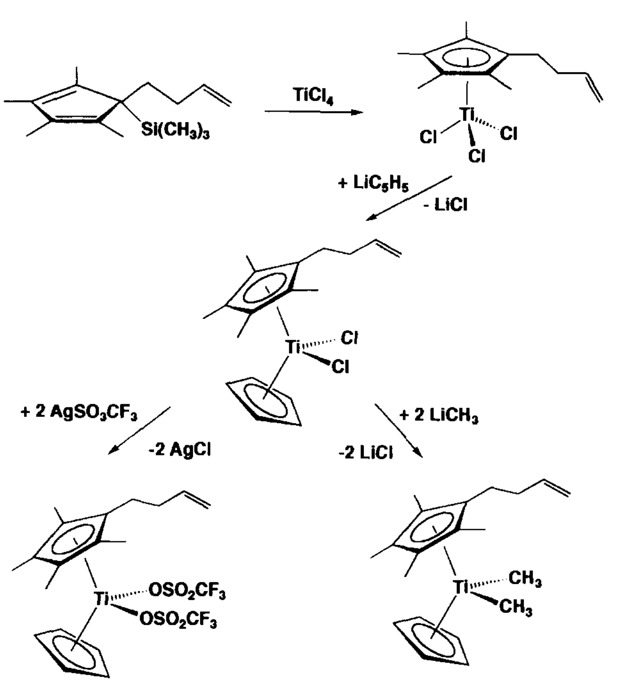
Table 1
Selected bond lengths (Å) and angles (°) for Cp$^{=}_{2}$TiMe$_2$

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Ti(1)–C(1) | 2.449(2) | Ti(1)–C(2) | 2.484(3) |
| Ti(1)–C(3) | 2.480(2) | Ti(1)–C(4) | 2.440(2) |
| Ti(1)–C(5) | 2.453(2) | Ti(1)–C(14) | 2.154(5) |
| C(1)–C(2) | 1.412(3) | C(2)–C(3) | 1.410(3) |
| C(3)–C(4) | 1.412(3) | C(4)–C(5) | 1.413(3) |
| C(1)–C(5) | 1.409(3) | | |
| *Bond angles* | | | |
| C(14)–Ti–C(14A) | 88.3(1) | C(5)–C(1)–C(2) | 108.6(2) |
| C(1)–C(2)–C(3) | 107.4(2) | C(2)–C(3)–C(4) | 108.4(2) |
| C(3)–C(4)–C(5) | 107.9(2) | | |

2.181(2) Å) [14a] as well as other examples such as $Me_2C(C_5H_4)_2TiMe_2$ (2.162(2) and 2.166(2) Å) [14b] ($\mu$-$\eta^5:\eta^5-C_{10}H_8$)$(CpTiMe_2)_2$ (2.158(6)–2.173(7) Å) [14c], $(Ind)_2TiMe_2$ (2.21(2) Å) [14d]. The Me–Ti–Me angle of 88.3° is also within the expected range. While the C–C double bond of the side-chain is outside the bonding range of the titanium atom, disorder in the pendent 3-butenyl group results in a less meaningful geometry for the vinyl group within the side chain [14e].

In order to examine the possibilities of generating a titanocene methyl cation $[Cp^{=}{}_2TiMe]^+$, several experiments were performed in which it was attempted to remove one methyl ligand in $Cp^{=}{}_2TiMe_2$ either by protonolysis using $[PhNHMe_2]BPh_4$ or by Lewis-acid-mediated abstraction by $B(C_6F_5)_3$. In all the experiments, however, no tractable products could be isolated. Extensive low temperature NMR spectroscopy studies showed that, in a 1 : 1 reaction mixture of $Cp^{=}{}_2TiMe_2$ with $B(C_6F_5)_3$, mainly two new species are formed, each giving rise to eight distinct ring methyl singlets. From the complete disappearance of the butenyl olefinic signals it was concluded that both of the 3-butenyl groups had been completely consumed in these reactions, presumably by rapid intramolecular insertion into the reactive titanium methyl bond. These observations contrast to the resistance of coordinatively saturated titanium methyl complexes towards undergoing intramolecular C–C double bond insertion [5]. In this context it should also be noted that the use of similar peralkylated cyclopentadienyl ligands, as in $(C_5Me_4$-$^iPr)_2TiCl_2$, was reported to result in reduced activity towards ethylene polymerization when activated with methyl aluminoxane [15].

In another attempt at generating a methyl cation within the coordination sphere of the $Cp^{=}{}_2Ti$ fragment, the chloride abstraction of the methyl chloro complex $Cp^{=}{}_2TiMeCl$ by a suitable Lewis acid such as aluminum chloride was envisaged. This method, however, was hampered by the fact that $Cp^{=}{}_2TiMeCl$ could not be obtained in pure form, regardless of whether $Cp^{=}{}_2TiCl_2$ was carefully treated with one equivalent of LiMe or MeMgCl, or whether $Cp^{=}{}_2TiMe_2$ was reacted with one equivalent of HCl in ether [16]. In each experiment, an inseparable mixture of the dichloro, dimethyl and methyl chloro complex was obtained. At best, $Cp^{=}{}_2TiMeCl$ was isolated with 95% purity. $C_s$-symmetric $Cp^{=}{}_2TiMeCl$ can be easily recognized by the $^1H$ NMR resonance at $\delta = +0.25$ ppm for the titanium methyl group, as well as the doubled signals for the $Cp^{=}$ ligand, owing to the loss of enantiotopicity, and the appearance of the $Cp^{=}$ ligand signals at chemical shift positions sufficiently different from those of $Cp^{=}{}_2TiCl_2$ and $Cp^{=}{}_2TiMe_2$. In contrast with the decamethyl titanocene system $Cp^{*}{}_2TiMeCl$, described in the literature [17], ligand scrambling between $Cp^{=}{}_2TiCl_2$ and $Cp^{=}{}_2TiMe_2$ was observed. Thus, when a 1 : 1 mixture of pure $Cp^{=}{}_2TiCl_2$ and $Cp^{=}{}_2TiMe_2$ was heated to 65 °C in $C_6D_6$, a ratio of 3 : 3 : 2 was determined for the mixture containing $Cp^{=}{}_2TiCl_2$, $Cp^{=}{}_2TiMe_2$ and $Cp^{=}{}_2TiMeCl$ after 5 h.



Scheme 2.

In order to simplify the system, we subsequently turned to mono[1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium complexes. By reacting a suspension of $KCp^{=}$ in THF with chlorotrimethylsilane, trimethylsilyl-1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene ($Cp^{=}SiMe_3$) is formed and isolated as a distillable oil. Treating this compound with titanium tetrachloride in hexane affords the red crystalline trichloro complex $Cp^{=}TiCl_3$ with a good yield (Scheme 2). Variable-temperature $^1H$ and $^{13}C$ NMR as well as IR spectroscopy data show that a strong intramolecular interaction of the 3-butenyl side chain with the formally 12-electron titanium center is clearly absent [18].

The trichloro complex is converted into the mixed ligand titanocene dichloride $Cp^{=}CpTiCl_2$ by reaction with lithium cyclopentadienide and the product is isolated as red crystals. It should be noted that reacting $CpTiCl_3$ with $LiCp^{=}$ does not lead to $Cp^{=}CpTiCl_2$, since extensive reduction of the titanium occurs. $Cp^{=}CpTiCl_2$ can be straightforwardly converted into the highly air-sensitive pale-yellow dimethyl complex $Cp^{=}CpTiMe_2$ as well as the purple bis(triflate) ($Cp^{=}CpTi\ (OTf)_2$). However, as for the $Cp^{=}{}_2Ti$ systems described above, an interaction of the C–C double bond with the metal center with any of the mixed ring complexes could not be detected. The bis(triflate) complex was prepared in order to examine whether the pendent C–C double bond would displace the presumably weakly bonded triflato ligand. $Cp^{=}CpTi(OTf)_2$ was obtained by treatment of the dichloro complex $Cp^{=}CpTiCl_2$ with silver triflate in dichloromethane (similar reaction conditions in the case of $Cp^{=}{}_2TiCl_2$ leads to a mixture of $Cp^{=}{}_2Ti(OTf)_2$ and the mono(triflato) complex $Cp^{=}{}_2Ti(OTf)Cl$). However, there is no indication that the C–C double bond of the 3-butenyl side chain displaces the triflate ligand, although triflates are easily displaced by water, THF or acetonitrile to give dications of the type $[Cp_2Ti(L)_2]^{2+}(OTf^-)_2$ [19a]. Recently, it was reported that $CpTi(OTf)_2$ and $[Cp^*{}_2Ti(L)_2]^{2+}(OTf^-)_2$ act as homogeneous catalysts for Diels–Alder reactions [19b].

From the above results, it may be concluded that, for a C–C double bond to interact with a $d^0$ metal center, a substantially more Lewis-acidic–electrophilic metal fragment with a low coordination number is required [20]. On the contrary, reaction of $Cp^{=}CpTiMe_2$ with $B(C_6F_5)_3$ in $CD_2Cl_2$ led to the complete disappearance of the $^1H$ NMR signals corresponding to the the C–C double bond of the butenyl chain. At least two asymmetric, possibly diastereomeric species are formed, which can be identified in the $^1H$ NMR spectra by the Cp resonances at $\delta = 5.93$ and 6.67 ppm as well as by the heavily overlapping methyl singlets in the region of $\delta = 1.8$–2.1 ppm. Several multiplets due to the side chain can also be observed in this region. Attempts at isolating crystalline compounds are at present under way.

## 3. Experimental section

All operations were performed under a dry nitrogen atmosphere using standard Schlenk and glove-box techniques. 2,3,4,5-tetramethylcyclopent-2-enone was prepared from 2-butyl tiglate according to a published procedure [21]. Lithium cyclopentadienide was isolated from the reaction of cyclopentadiene and *n*-butyllithium in toluene. All other chemicals were commercially available. Solvents were purified by distillation over sodium benzophenone (diethyl ether, THF, toluene and pentane) and $CaH_2$ (dichloromethane). Anhydrous DME was obtained from Aldrich and used without further purification. Deuterated solvents were dried over sodium benzophenone ($C_6D_6$, toluene-$d_8$ and THF-$d_8$), $CaH_2$ ($CD_2Cl_2$), 4 Å molecular sieves ($CDCl_3$) and condensed under vacuum at −198 °C into storage flasks. NMR spectra were recorded on Varian XL-300i and Varian Gemini-300 spectrometers. $^1H$ and $^{13}C$ NMR chemical shifts were determined by reference to the residual deuterated solvent peaks. Elemental analyses were performed by Oneida Research Services in Whitesboro, New York. Mass spectra were determined on Varian 311 A spectrometer. IR spectra were recorded as KBr pellets with a Nicolet FT-5-DX instrument. Melting points were determined in sealed capillaries.

### 3.1. *Preparation of 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene ($Cp^{=}H$)*

4-Bromo-1-butene (36.53 g, 0.271 mol) in 60 ml of diethyl ether was added dropwise to magnesium turnings (7.18 g, 0.295 mol) in 100 ml of diethyl ether over a period of 1.5 h. The turbid gray reaction mixture was heated under reflux for a further 3.5 h. After cooling to room temperature, a solution of 2,3,4,5-tetramethylcyclopent-2-enone (33.61 g, 0.243 mol) in 50 ml of diethyl ether was added dropwise to the reaction mixture over a period of 45 min. The resulting reaction mixture was heated under reflux for a further 3 h. After it had cooled to room temperature, approximately 40 g of water and ice were added slowly. Then acidic ion-exchange resin (75 g of oven-dried Amberlite IR-120®) was added portionwise, followed by a further 40 ml of water. The mixture was stirred for 2.5 h during which the color changed from green to yellow–brown. The reaction mixture was decanted and extracted from the resin beads. The water layer was separated and removed, and the organic layer was dried over anhydrous magnesium sulfate; after addition of magnesium turnings, the solvent was removed on a rotary evaporator. The crude product was distilled under vacuum from magnesium turnings (40–45 °C, $10^{-2}$ Torr). The yield of the light-yellow product was 34.20 g (80%). Gas chromatography (GC)–Mass spectroscopy (MS) and $^1H$ NMR spectroscopy data were identical with those reported previously [6].

### 3.2. *Preparation of $Cp^{=}{}_2TiCl_2$*

Anhydrous 1,2-dimethoxyethane (80 ml) was condensed at −198 °C into a Schlenk flask, which had been charged with $Cp^{=}Li$ (3.07 g, 16.9 mmol) [6a] and $TiCl_3$ (1.30 g, 8.43 mmol). The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The dark-greenish reaction mixture was heated under reflux for 5–6 h and cooled to room temperature; dry lead dichloride (1.17 g, 4.22 mmol) was added, upon which the color changed immediately to red–brown. It was stirred for 30 min and then the solvent was evaporated off. The residue was washed twice with a small amount of pentane, which was removed by evaporation. The residue was then extracted with pentane and filtered through celite to remove LiCl and metallic lead. The solution was concentrated to afford red needles by recrystallization at −30 °C (yield, 2.38 g (60%); melting point (m.p.), 99 °C), $^1H$ NMR ($C_6D_6$): $\delta$ 1.86 (s, 6H, $CH_3$), 1.91 (s, 6H, $CH_3$), 1.97 (m, 2H, $CH_2$-2), 2.66 (m, $^3J$(H,H) = 7.9 Hz, 2H, $CH_2$-1), 4.92 (m, $^3J$(H,H) = 10.4 Hz, 1 H, $CH_2$-4(*E*)), 4.98

(m, $^{3}J$(H,H) = 17.1 Hz, 1 H, $CH_2$-4(*Z*)), 5.70 (m, $^{3}J$(H,H) = 6.7 Hz, 1 H, CH-3) ppm. $^{13}C\{^{1}H\}$ NMR ($C_6D_6$): $\delta$ 13.1 ($CH_3$), 13.2 ($CH_3$), 27.9 (C-1), 34.0 (C-2), 115.1 (C-4), 127.4, 128.4, 131.6 (ring C), 138.3 (C-3) ppm. IR (KBr): $\nu$ 3070 w, 2907 m, 2863 m, 1639 m ($\nu$(C=C)), 1435 m, 1376 ms, 1017 m, 995 m, 904 s, 793 w, 755 w, 653 w, 458 w $cm^{-1}$. Electron impact (EI) MS (80 °C): $m/z$ 468 (6) [$M^+$], 433 (88) ($M^+ - Cl$), 293 (100) [$M^+ - C_{13}H_{19}$], 258 (68) [$M^+ - Cl$, $C_{13}H_{19}$], 175 (60) [$C_{13}H_{19}^+$], 134 (60) [$C_{10}H_{14}^+$]. Anal. Found: C, 66.31; H, 8.24; Cl, 14.82. $C_{26}H_{38}Cl_2Ti$ Calc.: C, 66.53; H, 8.16; Cl, 15.11%.

### 3.3. Preparation of $Cp^{=}{}_2TiMe_2$

Methyllithium (10.0 ml of 1.4 M solution in diethyl ether, 14.06 mmol) was syringed into a solution of $Cp^{=}{}_2TiCl_2$ (3.000 g, 6.392 mmol) in diethyl ether (40 ml) at −78 °C. After warming to room temperature and stirring at room temperature for 3 h, the reaction mixture was cooled to −30 °C and 0.75 ml methanol was added. After warming to room temperature, all volatiles were evaporated. After rinsing the residue with pentane (2 × 5 ml), which was evaporated each time, the yellow product was extracted with pentane and filtered. The solution was concentrated and well-formed yellow crystals were obtained by slow cooling to −78 °C. The mother liquor yielded a further crop of crystals (yield, 2.22 g (81%); m.p., 72 °C). $^{1}H$ NMR ($C_6D_6$): $\delta$ −0.60 (s, 3H, $TiCH_3$), 1.73 (s, 6H, $CH_3$), 1.77 (s, 6H, $CH_3$), 2.24 (m, 2H, $CH_2$-2), 2.33 (m, $^{3}J$(H,H) = 7.8 Hz, 2H, $CH_2$-1), 4.98 (m, $^{3}J$(H,H) = 10.5 Hz, 1H, $CH_2$-4(*E*)), 5.08 (m, $^{3}J$(H,H) = 17.1 Hz, 1H, $CH_2$-4(*Z*)), 5.85 (m, $^{3}J$(H,H) = 6.5 Hz, 1 H, CH-3) ppm. $^{13}C$ NMR ($C_6D_6$): $\delta$ 12.1 (q, $J_{CH}$ = 126 Hz, $CH_3$), 27.3 (t, $J_{CH}$ = 126 Hz, C-1), 34.9 (t, $J_{CH}$ = 127 Hz, C-2), 49.5 (q, $J_{CH}$ = 123 Hz, $TiCH_3$), 114.8 (d, $J_{CH}$ = 152 Hz, C-4), 118.7, 120.0, 123.5 (s, ring C), 138.9 (d, $J_{CH}$ = 154 Hz, C-3) ppm. IR (KBr): $\nu$ 3074 w, 2977 m, 2935 m, 2722 w, 1639 m ($\nu$(C=C)), 1434 m, 1377 ms, 1019 w, 994 m, 904 s $cm^{-1}$. EI MS (80 °C): $m/z$ 413 (19) [$M^+ - CH_3$], 412 (28) [$M^+ - CH_4$], 398 (100) [$M^+ - 2CH_3$], 353 (60) [$M^+ - 2CH_4$, $-2H$, $C_3H_7^+$], 236 (17) ($TiC_{14}H_{20}^+$), 181 (28) [$TiC_{10}H_{13}^+$]. Anal. Found: C, 78.73; H, 10.60. $C_{28}H_{44}Ti$ Calc.: C, 78.47; H, 10.35%.

### 3.4. Preparation of $Cp^{=}{}_2TiMeCl$

Hydrogen chloride in diethyl ether (1 M, 1.217 mmol, 1.22 ml) was diluted by dissolving in 50 ml of diethyl ether. It was then added dropwise over 2 h to a solution of $Cp^{=}{}_2TiMe_2$ (1.400 mmol, 0.600 g) in diethyl ether (100 ml) at 0 °C. The color of the solution changed from light yellow to a transparent red. It was stirred at 0 °C for another 0.5 h and then stirred at room temperature for 1 h. The solvent was removed by evaporation; the residue was washed twice with pentane which was evaporated off each time. After drying, a red powder was obtained, which by NMR was shown to contain all three species; $Cp^{=}{}_2TiCl_2$, $Cp^{=}{}_2TiMe_2$ and $Cp^{=}{}_2TiMeCl$. This powder was then dissolved in pentane, and recrystallization at −30 °C overnight yielded well-formed orange platelets. This process completely removed $Cp^{=}{}_2TiMe_2$ to afford 0.41 g of orange crystals of $Cp^{=}{}_2TiMeCl$ with an approximately 76% yield, contaminated by approximately 5–10% of $Cp^{=}{}_2TiCl_2$ according to $^{1}H$ NMR. $^{1}H$ NMR ($C_6D_6$): $\delta$ 0.25 (s, 3H, $TiCH_3$), 1.78 (s, 6H, $CH_3$), 1.78 (s, 6H, $CH_3$), 1.82 (s, 12H, $CH_3$), 2.10 (m, 4H, $CH_2$-2), 2.47 (m, $^{3}J$(H,H) = 8.0 Hz, 4H, $CH_2$-1), 4.96 (m, $^{3}J$(H,H) = 10.1 Hz, 2H, $CH_2$-4(*E*)), 5.03 (m, $^{3}J$(H,H) = 17.1 Hz, 2H, $CH_2$-4(*Z*)), 5.78 (m, $^{3}J$(H,H) = 6.7 Hz, 2H, CH-3) ppm. $^{13}C\{^{1}H\}$ NMR ($C_6D_6$): $\delta$ 12.6 ($CH_3$), 27.6 (C-1), 34.5 (C-2), 54.5 ($TiCH_3$), 114.9 (C-4), 122.1, 122.3, 123.5, 123.8, 126.7 (ring C), 138.6 (C-3) ppm.

### 3.5. Scrambling of $Cp^{=}{}_2TiMe_2$ and $Cp^{=}{}_2TiCl_2$

$Cp^{=}{}_2TiMe_2$ (0.035 mmol, 0.015g) and $Cp^{=}{}_2TiCl_2$ (0.032 mmol, 0.015g) were dissolved in 0.5 ml of $C_6D_6$ in an NMR tube. No $Cp^{=}{}_2TiMeCl$ was present in the $^{1}H$ NMR spectra of two independent $C_6D_6$ solutions containing $Cp^{=}{}_2TiMe_2$ and $Cp^{=}{}_2TiCl_2$ respectively. About 10 min after the mixing, the $^{1}H$ NMR of this mixture showed the presence of approximately 5% $Cp^{=}{}_2TiMeCl$. The solution was heated at 65 °C for 5 h, and its $^{1}H$ NMR spectrum was obtained. Integration of the cyclopentadienyl Me resonances showed the ratio of compounds $Cp^{=}{}_2TiMe_2 : Cp^{=}{}_2TiMeCl : Cp^{=}{}_2TiCl_2$ to be approximately 3 : 3 : 2.

### 3.6. Preparation of $Cp^{=}{}_2Ti(OTf)_2$

$Cp^{=}{}_2TiCl_2$ (0.469 g, 1.00 mmol) and silver triflate (0.514 g, 2.00 mmol) were dissolved in 50 ml of $CH_2Cl_2$ and stirred in the dark overnight. The purple reaction mixture containing a grey precipitate was filtered through Celite, and the solvent was removed to give a dark-purple oil, identified as an approximately 1 : 1 mixture of $Cp^{=}{}_2Ti(OTf)_2$ and $Cp^{=}{}_2TiCl(OTf)$. $Cp^{=}{}_2Ti(OTf)_2$ $^{1}H$ NMR ($CDCl_3$): $\delta$ 1.94 (m, 2H, $CH_2$-2), 2.12 (s, 6H, $CH_3$), 2.19 (s, 6H, $CH_3$), 2.87 (m, 2H, $CH_2$-1), 4.96 (m, 2H, $CH_2$-4), 5.73 (m, 1H, CH-3) ppm. $Cp^{=}{}_2TiCl(OTf)$ $^{1}H$ NMR ($CDCl_3$): $\delta$ 2.01 (s, 3H, $CH_3$), 2.03 (s, 3H, $CH_3$), 2.06 (s, 3H, $CH_3$), 2.08 (s, 3H, $CH_3$), 2.16 (m, 2H, $CH_2$-2), 2.69 (m, 2H, $CH_2$-1), 4.96 (m, 2H, $CH_2$-4), 5.73 (m, 1H, CH-3) ppm.

### 3.7. Preparation of $Cp^{=}SiMe_3$

At room temperature, 12.26 g (70 mmol) $Cp^{=}H$ in 20 ml of THF was added dropwise, over a period of 30 min, to a suspension of 2.90 g (72 mmol) potassium hydride in 75 ml of THF. The exothermic reaction was completed after heating under reflux for 1.5 h. After the resulting suspension was cooled to 0 °C, 10.5 ml of chlorotrimethylsilane (83 mmol) in 10 ml of THF was added dropwise. The reaction mixture was stirred for 16 h, the solvent removed in vacuo, and the residue extracted with 250 ml of pentane and filtered through a glass frit layered with kieselguhr. The solvent was removed under vacuum and the residue was distilled to afford the yellow main fraction distilling at 77–78°C and 0.01 Torr (Yield, 70%). $^1$H NMR ($C_6D_6$, +75 °C): $\delta$ −0.11 (s, 9H, $SiC\mathit{H}_3$), 1.63 (br, 2H, $CH_2$), 1.77 (s, 12H, $CH_3$), 2.48 (br, 2H, $CH_2$), 4.45 (d, $^3J$(H,H) = 14.2 Hz, 1H, $CH_2$-4(*E*)), 5.01 (d, $^3J$(H,H) = 17 Hz, 1H, $CH_2$-4(*Z*)), 5.63 (m, 1H, CH-3) ppm. IR (KBr): $\upsilon$ 3076 m, 2964 s, 2958 s, 2952 s, 2859 s, 1931 vs, 1640 m, 1454 s, 1447 sh, 1376 w, 1247 s, 1135 w, 1020 w, 991 w, 929 m, 836 vs, 755 mw, 683 w, 632 w cm$^{-1}$ GC–MS: *m/z* 248 (23) [$M^+$], 207 (29) [$M^+ - C_3H_5$], 133 (90) [$M^+ - SiMe_3$, $-C_3H_6$], 119 (27) [$M^+ -$ $SiMe_4$, $-C_3H_6$], 73 (100) [$SiMe_3^+$]. Anal. Found: C, 76.71; H, 11.45. $C_{16}H_{28}Si$ Calc.: C, 77.34; H, 11.36%.

### 3.8. Preparation of $Cp^{=}TiCl_3$

To a solution of 2.5 g (10 mmol) of $Cp^{=}SiMe_3$ in 30 ml of hexane was added dropwise 1.1 ml of titanium tetrachloride (1.90 g, 10 mmol). After heating at reflux for 1 h, 30 ml of hexane was added to the reaction mixture, and the solution was slowly cooled, whereby well-formed red crystals precipitated (yield, 2.2 g (67%); m.p., 78 °C). $^1$H NMR ($C_6D_6$): $\delta$ 1.83 (m, 2H, $CH_2$-2), 1.92 (s, 6H, $CH_3$), 1.97 (s, 6H, $CH_3$), 2.74 (t, $^3J$(H,H) = 7.3 Hz, 2H, $CH_2$-1), 4.84 (dt, $^3J$(H,H) = 16.8 Hz, $^4J$(H,H) = 1.2 Hz, 1H, $CH_2$-4(*E*)), 4.86 (d, $^3J$(H,H) = 11.6 Hz, 1H, $CH_2$-4(*Z*)), 5.51 (m, 1H, CH-3) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 14.0 ($CH_3$), 14.2 ($CH_3$), 28.9 (C-1), 34.0 (C-2), 115.9 (C-4), 137.1, 137.7, 140.4 (ring C), 136.9 (C-3) ppm. IR (KBr): $\nu$ 3078 w, 2952 m, 2911 m, 2924 m, 2863 m, 1641 m ($\nu$(C=C)), 1485 m, 1458 m, 1437 m, 1378 m, 1019 m, 992 m, 906 m, 613 s, 574 s, 543 s, 451 w, 402 w cm$^{-1}$ EI MS (80 °C): *m/z* 330 (4) [$M^+$], 293 (11) [$M^+ - Cl$], 287 (20) [$M^+ - C_3H_5$], 256 (11) [$M^+ - 2Cl$], 177 (13) [$M^+ - 3Cl - C_3H_6$], 133 (100) [$C_{10}H_{13}^+$]. Anal. Found: C, 47.36; H, 5.88; Cl, 31.67. $C_{13}H_{19}Cl_3Ti$: calc.: C, 47.38; H, 5.81; Cl, 32.27%.

### 3.9. Preparation of $Cp^{=}CpTiCl_2$

Cyclopentadienyllithium (325 mg, 4.5 mmol) was dissolved in THF (50 ml) and solid $Cp^{=}TiCl_3$ (1.52 g, 4.6 mmol) was added portionwise over a period of 1 h, yielding a deep-red mixture. The solvent was removed under vacuum and the product was extracted with 60 ml of pentane and 5 ml of $CH_2Cl_2$. LiCl was removed by filtration and was washed with pentane (3 × 5 ml). The solvent was concentrated to 40 ml, and the product was obtained as bright red crystals by recrystallization at −30 °C (yield, 0.82 g (49%); m.p., 76 °C). $^1$H NMR ($C_6D_6$): $\delta$ 1.76 (s, 6H, $CH_3$), 1.81 (s, 6H, $CH_3$), 1.90 (m, 2H, $CH_2$-2), 2.45 (t, $^3J$(H,H) = 7.9 Hz, 2H, $CH_2$-1), 4.92 (m, $^3J$(H,H) = 10.2 Hz, 1H, $CH_2$-4(*E*)), 4.95 (m, $^3J$(H,H) = 17.0 Hz, 1H, $CH_2$-4(*Z*)), 5.65 (m, $^3J$(H,H) = 6.8 Hz, 1H, CH-3), 5.99 (s, 5H, $C_5\mathit{H}_5$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 13.3 ($CH_3$), 13.4 ($CH_3$), 28.3 (C-1), 33.9 (C-2), 115.4 (C-4), 119.6 ($C_5H_5$), 128.8, 130.0, 131.9 (ring C), 137.8 (C-3) ppm. IR (KBr): $\nu$ 3127 w, 3085 w, 2988 m, 1641 m ($\nu$(C=C)), 1453 m, 1435 m, 1378 ms, 1017 m, 1000 m, 816 s ppm. EI MS (80 °C): *m/z* 358 (9) [$M^+$], 323 (9) [$M^+ - Cl$], 293 (75) [$M^+ - C_5H_5$], 175 (100) [$C_{13}H_{19}^+$], 134 (87) [$C_{10}H_{14}^+$], 119 [$C_9H_{11}^+$]. Anal. Found: C, 60.27; H, 6.60. $C_{18}H_{24}Cl_2Ti$: Calc.: C, 60.19; H, 6.73%.

### 3.10. Preparation of $Cp^{=}CpTiMe_2$

$Cp^{=}CpTiMe_2$ was synthesized from $Cp^{=}CpTiCl_2$ (0.40 g, 1.11 mmol) and MeLi in a manner analogous to that described to prepare $Cp^{=}{}_2TiMe_2$ and isolated as extremely light- and air-sensitive light-yellow crystals (yield 0.142 g (40%); m.p., 35 °C), $^1$H NMR ($C_6D_6$): $\delta$ −0.24 (s, 3H, $TiCH_3$), 1.62 (s, 6H, $CH_3$), 1.63 (s, 6H, $CH_3$), 2.10 (2 overlapping multiplets, 4H, $CH_2$-1 and $CH_2$-2), 4.97 (m, $^3J$(H,H) = 10.2 Hz, 1H, $CH_2$-4(*E*)), 5.03 (m, $^3J$(H,H) = 17.1 Hz, 1 H, $CH_2$-4(*Z*)), 5.72 (s, 5H, $C_5H_5$), 5.79 (m, $^3J$(H,H) = 7.0 Hz, 1H, CH-3) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 12.1 ($CH_3$), 12.2 ($CH_3$), 27.5 (C-1), 34.8 (C-2), 46.6 ($TiCH_3$), 114.0 ($C_5H_5$), 114.9 (C-4), 119.1, 120.5, 123.2 (ring C), 138.6 (C-3) ppm. IR (KBr): $\nu$ = 3080 w, 2957 m, 2934 m, 1641 m ($\nu$(C=C)), 1450 m, 1377 ms, 1018 w, 990 m, 815 s ppm. EI MS (80 °C): *m/z* 301 (100) [$M^+ - CH_3$, 2H], 288 (97) [$M^+ - 2CH_3$], 247 (52) [$M^+ - C_3H_5$, $2CH_3$], 243 (36) [$M^+ - 5CH_3$]. Anal. Found: C, 69.32; H, 9.02. $C_{20}H_{30}Ti$: Calc.: C, 75.45; H, 9.50%.

### 3.11. Preparation of $Cp^{=}CpTi(OTf)_2$

$Cp^{=}CpTiCl_2$ (0.100 g, 0.278 mmol) and silver triflate (0.613 mmol) were dissolved in 10 ml of $CH_2Cl_2$ and stirred in the dark overnight. The purple reaction mixture containing a grey precipitate was filtered through kieselguhr, and the solvent was removed to give a purple solid. Recrystallization from diethyl ether at −30 °C afforded purple crystals (yield, 0.100 g (61%); m.p., 123 °C). $^1$H NMR ($C_6D_6$): $\delta$ 1.61 (s, 6H, $CH_3$), 1.66 (s, 6H, $CH_3$), 1.68 (m, 2H, $CH_2$-2), 2.36 (m, $^3J$(H,H) = 7.8 Hz, 2H, $CH_2$-1), 4.86 (m, $^3J$(H,H) = 16.5 Hz, 1H, $CH_2$-4(*Z*)), 4.90 (m, $^3J$(H,H) = 10.6 Hz, 1H, $CH_2$-4(*E*)), 5.50 (m, $^3J$(H,H) = 6.7 Hz, 1H, CH-3),

Table 2
Summary of crystallographic data for $Cp^{=}_2TiMe_2$

| | |
|---|---|
| Temperature (K) | 298 |
| Cryst system | Monoclinic |
| Space group | $C2/c$ |
| $a$ (Å) | 12.077(2) |
| $b$ (Å) | 12.706(3) |
| $c$ (Å) | 16.706(5) |
| $\beta$ (°) | 90.22(2) |
| $V$ (Å$^3$) | 2563.5(10) |
| Formula | $C_{28}H_{44}Ti$ |
| Formula weight | 428.5 |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.110 |
| $F(000)$ | 936 |
| Crystal dimensions (mm) | 0.50×0.80×0.80 |
| Scan rate (° min$^{-1}$) | 4–20 |
| Scan type | $\theta - 2\theta$ |
| Scan width (°) | $2\theta(K\alpha_1) = -1.0$ to $2\theta(K\alpha_2) = +1.0$ |
| $2\theta$ range (°) | 3–55 |
| Background measurement | Stationary crystal, stationary counter, at the beginning and end of each scan, each for 25% the time taken for the scan |
| Number of total reflections collected | 3332 |
| Number of unique reflections | 2979 |
| Number of independent reflections | 2259 ($\lvert F_o \rvert \geq 6\sigma \lvert F_o \rvert$) |
| Absorption coefficient (cm$^{-1}$) | 3.4 |
| Absorption correction | Not applied |
| $R = \Sigma[\lvert F_o \rvert - \lvert F_c \rvert / \Sigma \lvert F_o \rvert]$ | 0.0476 |
| $R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g = 0.0002$ | 0.0494 |
| Goodness of fit $= [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(N_O - N_V)]^{1/2}$, where $N_O$ is the number of observations and $N_V$ is the number of variables | 2.39 |

Table 3
Atomic coordinates and equivalent isotropic displacement parameters

| | $x$ (×10$^{-4}$) | $y$ (×10$^{-4}$) | $z$ (×10$^{-4}$) | $U_{eq}$ [a] (×10$^{-3}$ Å$^{-2}$) |
|---|---|---|---|---|
| Ti(1) | 0 | 1111(1) | 2500 | 39(1) |
| C(1) | 1466(2) | 596(2) | 1569(1) | 48(1) |
| C(2) | 862(2) | 1392(2) | 1170(1) | 50(1) |
| C(3) | −211(2) | 998(2) | 1025(1) | 49(1) |
| C(4) | −274(2) | −30(2) | 1342(1) | 47(1) |
| C(5) | 775(2) | −290(2) | 1661(1) | 46(1) |
| C(6) | 1289(3) | 2418(3) | 851(2) | 74(1) |
| C(7) | −1067(3) | 1489(4) | 496(2) | 79(1) |
| C(8) | −1220(3) | −771(3) | 1178(2) | 69(1) |
| C(9) | 1170(3) | −1375(3) | 1863(2) | 69(1) |
| C(10) | 2683(3) | 636(3) | 1757(2) | 68(1) |
| C(11) | 3407(3) | 273(3) | 1066(2) | 76(1) |
| C(12) | 4599(3) | 314(4) | 1270(3) | 117(2) |
| C(13) | 5358(4) | 780(4) | 1058(4) | 148(3) |
| C(14) | 1175(4) | 2328(3) | 2795(2) | 87(1) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

6.34 (s, 5H, $C_5H_5$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 12.5 ($CH_3$), 12.8 ($CH_3$), 27.3 (C-1), 33.3 (C-2), 116.2 (C-4), 119.1, 120.0 (q, $^1J$(CF) = 315 Hz, $CF_3$), 122.8 ($C_5H_5$), 135.0 (ring C), 136.6, 136.8 (ring C, C-3), 137.4 (ring C) ppm. Anal. Found: C, 41.04; H, 4.15. $C_{20}H_{24}F_6O_6S_2Ti$ Calc.: C, 40.96; H, 4.13%.

### 3.12. Reactions of $B(C_6F_5)_3$ with $Cp^{=}_2TiMe_2$ and $Cp^{=}CpTiMe_2$

$Cp^{=}_2TiMe_2$ or $Cp^{=}CpTiMe_2$ (0.12 mmol) and $B(C_6F_5)_3$ (0.12 mmol, 61.4 mg), each dissolved in 0.4 ml of $CD_2Cl_2$, were cooled to −70 °C and added together in a NMR tube. An immediate reaction with an accompanying color change to dark red was observed in both cases. $^1H$ NMR spectra were measured at intervals not greater than 20 °C, between −70 °C and +25 °C.

### 3.13. X-ray crystallographic structure analysis of $Cp^{=}_2TiMe_2$

Single crystals of $Cp^{=}_2TiMe_2$ were obtained by recrystallization from pentane at −35 °C. A well-shaped prism was mounted on the end of a glass fiber and covered with epoxy. Intensity data were measured on a Nicolet (Siemens) R3m four-circle diffractometer equipped with a graphite monochromator, using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 298 K. Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption [22]. The solution of the structure was accomplished via Patterson methods and full-matrix least-squares refinement utilized the SHELXTL PLUS package of programs. The titanium atom is situated on the crystallographic twofold axis (Wyckoff notation *e* for space group $C2/c$). Neutral atomic scattering factors were used throughout the analysis [23]. Anomalous dispersion [24] was applied to all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps in the latter stages of the refinement and refined isotropically with the exception of the three vinylic hydrogen atoms, the positions of which were calculated geometrically, fixed at a C–H distance of 0.96 Å, and not refined. Crystallographic data are summarized in Table 2. Final atomic coordinates are given in Table 3. Further crystallographic details can be obtained from the authors.

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