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Synthesis and reactivity of titanocene and zirconocene triflates

Gerrit A. Luinstra *

Department of Chemistry, University of Konstanz, Postfach 5560 M738, D-78434 Konstanz, Germany

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Abstract

The synthesis of triflate derivatives of titanocene and zirconocene from the corresponding dimethyl complexes and triflic acid (HOTf) is described. Comproportionation of $Cp_2M(OTf)_2$ with Cp_2MX_2 gives $Cp_2M(OTf)X$ (M = Ti, X = Cl, F, Me; M = Zr, X = Cl, Me, BH_4). $Cp_2TiMe(OTf)$ reacts with ROH (R = Me, Me_3Si or $Me_2{}^tBuSi$) to give $Cp_2TiOR(OTf)$. $Cp_2TiMe(OTf)$ and $Cp_2TiOSiMe_3(OTf)$ react with H_2O to give the oxo-bridged dimer $(Cp_2TiOTf)_2(\mu\text{-}O)$. The triflate in $Cp_2TiX(OTf)$ (X = Cl, F, Me, $OSiMe_3$) is substituted by $^-OSiMe_3$ to give compounds $Cp_2TiX(OSiMe_3)$. $Cp_2Ti(OMe)OR$ (R = Me, $SiMe_3$) could not be obtained.

Keywords: Titanium; Zirconium; Triflate; Metallocenes; Alkyl; Alkoxide

1. Introduction

Tetravalent titanium and zirconium biscyclopentadienyl systems are utilized in many important stoichiometric and catalytic transformations [1–7]. The starting materials in the great majority of cases are metallocene dichlorides, which in general are not reactive catalysts. In Ziegler–Natta polymerization, (de)hydrogenation or hydrozirconation, the insertion of a substrate into a metal carbon or hydrogen bond is the key to the reaction. Metal hydrides and carbyls are generated by substitution of the chloride with hydrogen or carbon nucleophiles [1–7]. These are usually fast and clean. In contrast, reactions with oxygen or nitrogen centered nucleophiles occur with concomitant disproportionation, leading to mono-, tri- and tetracyclopentadienyl metal compounds [8]. Metallocene dialkoxides are therefore hard to synthesize. In Lewis acid catalyzed reactions, like Diels–Alder additions, a free coordination site is a prerequisite [9,10]. The active metallocene catalysts in these cases may be obtained by substitution of the chloride by a weakly or non-coordinating anion, usually through reaction with the corresponding silver salts [11–14].

Here, a convenient synthesis for and reactivity of a number of Group 4 metallocene triflates is described. Triflates are much weaker coordinating ligands than halides [15,16]. The advantages over metal chlorides lie in the enhanced polarity of the M–C bond and the tendency to generate cationic species, which are demonstrated to be exceedingly more reactive [17], and in the different solubilities of triflate derivatives, which may increase reaction rates and broaden the choice of solvents [18]. Similar results were obtained in organolanthanide chemistry [19,20]. They are useful as starting materials for the synthesis of derivatives with a titanium–oxygen bond.

2. Results and discussion

2.1. Synthesis of $Cp_2M(OTf)_2$ (M = Ti, Zr)

The synthesis of triflate (OTf) compounds of Ti and Zr has been described [11,12]. Typically, THF solutions of the metallocene dichlorides are treated with silver triflate to yield solutions of the metal triflate and insoluble silver chloride, which is filtered off. We found that it is essential to have the correct stoichiometry in such reactions. Removal of any excess of silver triflate or residual metallocene monochloride monotriflate results in much lower yields. In addition, the method requires a relative polar solvent to prevent precipitation of reactants and intermediates.

Alternatively, it is uncomplicated to prepare metallocene bistriflates from the easily accessible metal-

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* Corresponding author.

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locene dimethyl derivatives and triflic acid (Eq. (1)). Choice of solvent is not so crucial here, neither is stoichiometry: a small excess of triflic acid is simply removed by washing and drying in vacuum. Lewis base free products are formed if the reaction is carried out in a non-coordinating solvent [11]. The best results were obtained in toluene and diethyl ether where the product precipitates as a microcrystalline solid upon addition of the acid [21].

$$Cp_2MMe_2 + 2HOTf \rightarrow Cp_2M(OTf)_2 + 2MeH \qquad (1)$$

$$M = Ti, Zr; HOTf = HOSO_2CF_3$$

2.2. *Comproportionation reactions; synthesis of monotriflate derivatives*

$Cp_2Ti(OTf)_2$ reacts readily with one equivalent of $NaOSiMe_3$, MeLi or $HOMe/NEt_3$ to give the monosubstituted products $Cp_2TiX(OTf)$ ($X = OSiMe_3$, Me, OMe). However, separation from the triflate salts (Na, Li or NEt_3H) is difficult. The monotriflate complexes are not easily soluble in pentane, and extraction with more polar solvents (ether) does not yield pure products (by elemental analysis). These compounds are better prepared by comproportionation reactions and/or subsequent derivatization. Comproportionation of the bistriflate complexes with disubstituted metallocene derivatives is a convenient method to obtain monotriflate compounds $Cp_2M(OTf)X$ (M = Ti, X = Cl, F, Me; M = Zr, X = Cl, Me, BH_4) (Eq. (2)) [18]. These reactions are fast at room temperature and essentially quantitative (NMR), but reversible. This is indicated by the fact that extraction of solid $Cp_2TiCl(OTf)$ with, for example, ether results in mixtures of $Cp_2Ti(OTf)X$ and $Cp_2Ti(OTf)_2$. The better soluble Cp_2TiCl_2 is in this case purged from $Cp_2TiCl(OTf)$ through the back reaction of Eq. (2).

$$Cp_2M(OTf)_2 + Cp_2MX_2 \rightarrow 2Cp_2MX(OTf)_2 \qquad (2)$$

$$M = Ti, X = F, Cl, Me; M = Zr, X = Cl, Me, BH_4$$

The methyl triflate complex is about as soluble in benzene as the methyl chloride, $Cp_2TiMeCl$ (NMR), and is an ideal starting material for the preparation of monoalkoxide derivatives. The Ti–C bond in $Cp_2TiMe(OTf)$ is easily protolyzed by methanol, trimethyl- and dimethyl-tert-butylsilanol (Eq. (3)) to give derivatives $Cp_2TiOR(OTf)$ (R = Me, Me_3Si, $^tBuMe_2Si$ respectively). These reactions are clean and fast, complete within 5 min at room temperature. There is no tendency to form Cp redistribution products like $CpTi(OMe)_2OTf$. This acidolysis is much faster than that of the Ti–C bond in the chloride derivative $Cp_2TiMe(Cl)$, which is reported to react slowly even with water, or in Cp_2TiMe_2 [22]. The latter reacts with $HOSiMe_3$ to give $Cp_2TiMe(OSiMe_3)$, a process which takes about 4 h at 50°C in benzene-d_6. This is probably due to the decreased charge density at the metal in $Cp_2TiMe(OTf)$, resulting in more polar bonds. With water the oxo-bridged complex $(Cp_2TiOTf)_2(\mu\text{-}O)$ is formed, as confirmed by the independent synthesis of this compound through the reaction of two equivalents of AgOTf with $(Cp_2TiCl)_2(\mu\text{-}O)$. $Cp_2TiOSiMe_3(OTf)$ reacts likewise with water to give the oxo-bridged compound. The reactivity of the methyl triflates towards olefins and other unsaturated substrates is currently under investigation.

$$Cp_2TiMe(OTf) + ROH \rightarrow Cp_2TiOR(OTf) \qquad (3)$$

$$R = Me, SiMe_3, SiMe_2{}^tBu$$

Recently, we reported the synthesis of $Cp_2ZrH(OTf)$ from $Cp_2ZrBH_4(OTf)$, a soluble analog of Schwartz's reagent [18]. The corresponding titanium borohydride, $Cp_2TiBH_4(OTf)$, could not be obtained. Reaction of $Cp_2Ti(OTf)_2$ with one equivalent of $NaBH_4$ in THF gives, under gas evolution, the blue paramagnetic compound $Cp_2Ti(OTf)$ [23]. Reaction between $Cp_2TiCl(OTf)$ and $Cp_2ZrH(Cl)$ results in reduction as well (to Cp_2TiOTf, along with the formation of Cp_2ZrCl_2, Eq. (4)). This indicates that Cp_2TiH(triflate) is likewise not a stable species.

$$Cp_2TiCl(OTf) + Cp_2ZrH(Cl) \rightarrow Cp_2TiOTf + Cp_2ZrCl_2 + 0.5H_2 \qquad (4)$$

2.3. *Nucleophilic substitution reactions*

One of the objectives of this research has been the preparation of dialkoxide derivatives of titanocene, $Cp_2Ti(OR)_2$. These compounds are not easily accessible through salt metathesis reactions of Cp_2TiCl_2: as the result of Cp displacement and disproportionation processes, a complex mixture of products is formed from which the isolation of dialkoxides is hard to achieve, if at all [24]. It was therefore tested whether such dialkoxides can be prepared from $Cp_2Ti(OTf)_2$. It was expected that, by virtue of the weakly-coordinating triflates, the substitution mechanism might not run through the four-centered transition state, but rather through cationic intermediates, and thus lead to different Cp^-/anion (^-OTf, Cl^-) substitution ratios.

As mentioned above, the first substitution in $Cp_2Ti(OTf)_2$ with M'OR to give $Cp_2TiOR(OTf)$ is quantitative (NMR), as it is in Cp_2TiCl_2 [8]. It was expected that the second displacement might compete successfully with unwanted side reactions. This approach was only in part successful. The disiloxide, $Cp_2Ti(OSiMe_3)_2$ [8], could be prepared in high yields from two equivalents of $NaOSiMe_3$ and the bistriflate. Choice of solvent is essential in this reaction. Only decomposition was observed when the reaction was carried out in a non-polar solvent like benzene, whereas clean conversion to the disubstituted titanocene was found in dichloromethane. Separation from the reaction mixture is now easily achieved by extraction with pentane. $Cp_2Ti(OMe)_2$, however, could not be prepared by this procedure: reaction between $Cp_2Ti(OTf)_2$ and MOMe (M = Li, K) or between $Cp_2Ti(OTf)_2$ and $HOMe/NEt_3$ still leads to Cp redistribution products (NMR).

$NaOSiMe_3$ in general reacts cleanly with monotriflate compounds. In this way, a number of asymmetrically substituted derivatives, $Cp_2TiX(OSiMe_3)$ (X = Me, Cl, F, $OSiMe_3$), was prepared through simple salt metathesis reactions of $Cp_2Ti(X)OTf$ and $NaOSiMe_3$. Although reaction of $Cp_2TiF(OTf)$ and $NaOSiMe_3$ leads to $Cp_2TiF(OSiMe_3)$ (only product by NMR), it could not be isolated from NaOTf as an analytically pure compound. The compound is not stable in benzene solution, it slowly disproportionates to Cp_2TiF_2 and $Cp_2Ti(OSiMe_3)_2$. This is probably due to the differences in solubility of the disproportion products: the difluoride is only sparingly soluble and precipitates, thereby pulling Eq. (5) to the right-hand side. Direct synthesis of $Cp_2TiF(OSiMe_3)$ from Cp_2TiF_2 and $NaOSiMe_3$ results in unseparable mixtures of starting material, $Cp_2TiF(OSiMe_3)$ and $Cp_2Ti(OSiMe_3)_2$. Decomposition of $Cp_2TiF(OSiMe_3)$ to $FSiMe_3$ and Cp_2Ti oxides [25] was not observed. The chloride analog, $Cp_2TiCl(OSiMe_3)$, does not decompose by disproportionation to Cp_2TiCl_2 and $Cp_2Ti(OSiMe_3)_2$.

$$2Cp_2TiF(OSiMe_3) \rightarrow Cp_2Ti(OSiMe_3)_2 + Cp_2TiF_2 \downarrow \tag{5}$$

Reaction of $Cp_2TiOMe(OTf)$ with $NaOSiMe_3$ results in the formation of a mono Cp derivative, as indicated by the proton NMR (one half of the intensity of the Cp resonance is lost). Adversely, reaction of $Cp_2TiOSiMe_3(OTf)$ with NaOMe gives three products, none of which was identified. This suggests that with the methoxy nucleophile present, either in the complex or in the reagent, a change of salt substitution reaction pathway in titanocenes is induced, leading to Cp displacement. The reason for this is not clear at the moment.

Table 1
NMR data of $Cp_2MX_1X_2$ complexes in $CDCl_3$ (benzene-d_6 values in parentheses)

Compound	Assignment	^{1}H NMR [a]		^{13}C NMR		
		δ (ppm)	I (H)	δ (ppm)	m	^1J (Hz) [d]
$Cp_2Ti(OTf)_2$	Cp	6.93				
$Cp_2Zr(OTf)_2$	Cp	6.76		118.2	dtt	175
$Cp_2TiCl(OTf)$	Cp	6.57		121.5	d	179
$Cp_2TiF(OTf)$	Cp	6.65		121	dtt	177
$Cp_2TiMe(OTf)$	Cp	6.37	10	116.88	d	175
	Me	1.26	3	57.84	q	128
$Cp_2ZrCl(OTf)$	Cp	6.47		115.99	dtt	175
$Cp_2ZrMe(OTf)$	Cp	6.34	10	113.57	dtt	168
	Me	0.57	3	37.15	q	121
$Cp_2ZrBH_4(OTf)$	Cp	6.49 (5.73)	10	114.25	dtt	177
	BH_4	0.6–1.0 [b]	4			
$Cp_2TiOMe(OTf)$	Cp	6.4	10	117.57	dtt	177
	Me	4.5	3	72.12	q	143
$Cp_2TiOSiMe_3(OTf)$	Cp	5.85	10	118.4	dtt	177
	$SiMe_3$	0.13	9	1.77	q	118
$Cp_2TiOSi^tBuMe_2(OTf)$	Cp	6.44	10	118.4	dtt	170
	Me	0.14	6	−2.84	q	118
	$C\mathit{Me}_3$	0.94	9	19.28	s	
	$\mathit{C}Me_3$			26.0	q	127
$(Cp_2TiOTf)_2(\mu\text{-}O)$	Cp	6.45 (5.94)		118.5		
$Cp_2TiMe(OSiMe_3)$	Cp	5.92	10	112.58	dtt	172
	$SiMe_3$	−0.03	9	34.11	q	117
	Me	0.63	3	1.74	q	125
$Cp_2TiCl(OSiMe_3)$	Cp	6.26	10	117.15	dtt	178
	$SiMe_3$	0.062	9	1.51	q	119
$Cp_2TiF(OSiMe_3)$	Cp	6.24 [c]	10	116.77	dtt	177
	$SiMe_3$	0.09	9	2.11	q	118
$Cp_2Ti(OSiMe_3)_2$	Cp	6.07	10	115.11	dtt	173
	$SiMe_3$	0.029	18	2.22	q	117
$(Cp_2TiCl)_2O$	Cp	6.29	10			

[a] Singlets, except for [b] broad multiplet and [c] doublet due to coupling to F: $J(F–H) = 1.5$ Hz. [d] $^2J(C–H)$ and $^3J(C–H)$ to Cp carbons are 6–7 Hz.

In conclusion, triflate can be used as a substitute for chloride in salt metathesis reactions. Triflate complexes of Ti and Zr are easily accessible, comproportionations are much faster, and the alkyl triflates are much more reactive than their chloride counterparts. The comproportionation products are good starting materials for the synthesis of non-symmetrically substituted metallocenes. The synthesis of titanocene bismethoxide or monomethoxy monosiloxide was not achieved by application of triflate as a leaving group.

3. Experimental

3.1. General

All operations were performed in an inert atmosphere with rigorous exclusion of oxygen and moisture using Schlenk, vacuum-line or glove-box techniques. Solvents were thoroughly dried (ether and THF over Na/benzophenone, pentane over CaH_2, toluene over Na) and distilled prior to use. Benzene-d_6, and THF-d_8 were vacuum transferred from Na/K alloy, $CDCl_3$ was distilled from CaH_2. NEt_3 was dried over KOH and distilled. Cp_2TiCl_2, Cp_2ZrCl_2, HOTf, $LiBH_4$ were used as purchased. $Cp_2Zr(BH_4)_2$ was prepared as reported in Ref. [26], but was isolated by extraction of the reaction mixture with toluene after evaporation to dryness, rather than by sublimation. Scale 0.01 mol, yield 92%. $(Cp_2TiCl)_2(\mu\text{-}O)_2$ was prepared according to Ref. [22].

IR spectra were recorded on a Mattson Galaxy spectrometer as Nujol mulls between KBr disks. NMR spectra were recorded on Bruker WM250, AC250 and Jeol FX-90Q or JNM GX400 spectrometers. Chemical shifts are reported in Table 1 and referenced to residual protons in deuterated solvents ($CDCl_3$: $\delta = 7.24$ ppm; benzene-d_6: $\delta = 7.15$ ppm) for ^1H NMR and to the characteristic 1 : 1 : 1 triplets in the ^{13}C NMR spectrum ($CDCl_3$: $\delta = 77.00$ ppm; benzene-d_6: $\delta = 127.98$ ppm). The ^{11}B chemical shift is referenced to external $BF_3 \cdot OEt_2$. Elemental analyses were carried out at the Microanalytical Department of this University.

3.2. $Cp_2Ti(OTf)_2$

Cp_2TiCl_2 (2.5 g, 10 mmol) was suspended in 10 ml of toluene and 12.6 ml of 1.6 N (20 mmol) solution of MeLi in ether was added, yielding a yellow solution and a white precipitate. The solution was filtered, and 2.8 ml of triflic acid (30 mmol) was added. A red precipitate formed under violent gas evolution. After stirring for 1 h, the toluene was decanted off and the red solid washed extensively, first with toluene and then with pentane. Yield 4.07 g (8.5 mmol, 85%). IR (cm^{-1}): 3130 (m), 1240 (m), 1200 (vs), 1130 (w), 1080 (w), 1020 (s), 890 (m), 840 (s), 765 (w), 625 (s), 595 (m), 570 (w), 510 (m), 420 (m). Anal. Found: C, 29.50; H, 2.60. $C_{12}H_{10}F_6O_6S_2Ti$ Calc.: C, 30.22; H, 2.11%.

3.3. $Cp_2Zr(OTf)_2$

Cp_2ZrMe_2 (1.0 g, 4 mmol) was dissolved in 50 ml of ether, cooled to 0°C, and triflic acid (1.35 g, 9 mmol) was added dropwise. After the violent gas evolution had ceased the white precipitate was isolated on a frit and washed with 100 ml of ether. After drying in vacuum, 1.7 g of $Cp_2Zr(OTf)_2$ (3.26 mmol, 82%) remained. IR (cm^{-1}): 3160 (w), 1420 (s), 1412 (w), 1330 (s,d), 1195 (s), 1130 (w), 1030 (s), 905 (w), 850 (s), 625 (s, d), 595 (w), 540 (m). Anal. Found: C, 28.41; H, 2.06. $C_{12}H_{10}F_6O_6S_2Zr$ Calc.: C, 27.74; H, 1.94%.

3.4. $Cp_2TiCl(OTf)$

$Cp_2Ti(OTf)_2$ (476 mg, 1 mmol) and Cp_2TiCl_2 (248 mg, 1 mmol) were stirred in THF until all of the dichloride had dissolved. The solvent was removed, and the red residue was washed with 5 ml of pentane. Yield 689 mg (1.90 mmol, 95%). IR (cm^{-1}): 3125 (m), 3105 (m), 1685 (w), 1290 (w), 1240 (w), 1200 (s), 1130 (w), 1080 (w), 1020 (s), 1015 (s), 840 (s), 835 (s), 765 (w), 630 (s), 500 (m), 420 (m). Anal. Found: C, 35.41; H, 3.34. $C_{11}H_{10}ClF_3O_3STi$ Calc.: C, 34.90; H, 2.66%.

3.5. $Cp_2TiF(OTf)$

$Cp_2Ti(OTf)_2$ (476 mg, 1 mmol) and Cp_2TiF_2 (216 mg, 1 mmol) were dissolved in 10 ml of THF. After stirring for 20 min, the volatiles were removed in vacuum and the resulting orange solid isolated. Yield 597 mg (1.7 mmol, 86%). IR (cm^{-1}): 315 (m), 1340 (m), 1290 (w), 1205 (w), 1195 (s), 1180 (m), 1020 (s), 830 (s), 765 (w), 630 (s), 575 (m), 505 (m), 425 (w). Anal. Found: C, 36.22; H, 3.27. $C_{11}H_{10}F_4O_3STi$ Calc.: C, 36.48; H, 2.78%.

3.6. $Cp_2TiMe(OTf)$

Cp_2TiMe_2 (3 g, 13 mmol) was dissolved in 10 ml of toluene and added to $Cp_2Ti(OTf)_2$ (2.66 g, 5.6 mmol). The mixture was stirred for 2 h at 50°C during which $Cp_2Ti(OTf)_2$ slowly dissolved. The volatiles were removed in vacuum, and the residue was washed with pentane until colorless. After extraction with toluene, 2.3 g $Cp_2TiMe(OTf)$ (6.7 mmol, 60%) remained as a dark orange solid. IR (cm^{-1}): 3120 (m), 1330 (m), 1235 (w), 1205 (s), 1170 (w), 1070 (w), 1015 (s), 825 (s), 720 (s), 625 (s), 590 (w), 505 (m), 415 (m). Anal. Found: C, 40.46; H, 3.62. $C_{12}H_{13}F_3O_3STi$ Calc.: C, 42.13 H, 3.83%.

3.7. $Cp_2ZrCl(OTf)$

$Cp_2Zr(OTf)_2$ (520 mg, 1 mmol) and Cp_2ZrCl_2 (292 mg, 1 mmol) were dissolved in 10 ml of CCl_2H_2. The reaction mixture was stirred for 1 h and evaporated to dryness to give a grayish powder. Yield 629 mg (1.55 mmol, 77%). IR (cm^{-1}): 3105 (m), 1335 (s), 1320 (w), 1260 (s), 1235 (s), 1210 (s), 1175 (w), 1025 (s), 830 (w), 810 (s), 725 (w), 630 (m), 590 (w), 515 (m). Anal. Found: C, 33.25; H, 2.95. $C_{11}H_{10}ClF_3O_3SZr$ Calc.: C, 32.55; H, 2.48%.

3.8. $Cp_2ZrMe(OTf)$

$Cp_2Zr(OTf)_2$ (410 mg, 0.79 mmol) and Cp_2ZrMe_2 (200 mg, 0.80 mmol) were dissolved in 10 ml of CCl_2H_2. The mixture was stirred for 10 min, evaporated to dryness, and extracted with toluene. After removal of the solvent in vacuum, an off-white product was isolated. Yield 356 mg (0.92 mmol, 58%). IR (cm^{-1}): 3110 (m), 1340 (s), 1205 (vs, m), 1125 (w), 1070 (w), 1020 (s), 810 (s), 740 (s), 690 (m), 625 (s), 590 (w), 570 (w), 525 (w), 505 (m), 460 (m). Anal. Found: C, 36.52; H, 3.07. $C_{12}H_{13}F_3O_3SZr$ Calc.: C, 37.39; H, 3.40%.

3.9. $Cp_2ZrBH_4(OTf)$

$Cp_2Zr(BH_4)_2$ (1 g, 4 mmol) and $Cp_2Zr(OTf)_2$ (2.1 g, 4 mmol) were suspended in diethyl ether and stirred for 1 h, during which the solution slowly became clearer. The solution was filtered and evaporated to dryness. Yield 2.7 g (7 mmol, 87%). ^{11}B NMR (C_6D_6, 70°C): −2.3 ppm (quintet, $J(B-H) = 87$ Hz). IR (cm^{-1}): 3115 (m), 2465 (s), 2410 (s), 2240 (w), 2130 (m), 2095 (w), 2040 (w), 1940 (m), 1340 (m), 1240 (w), 1190 (s), 1125 (m), 1005 (s), 835 (s), 765 (w), 830 (s), 585 (m), 562 (w), 525 (w), 505 (m), 430 (m). Anal. Found: C, 35.27; H, 3.78. $C_{11}H_{14}BF_3O_3SZr$ Calc.: C, 34.28; H, 3.66%.

3.10. $Cp_2TiOMe(OTf)$

$Cp_2TiMe(OTf)$ (341 mg, 0.99 mmol) was suspended in 5 ml of toluene and MeOH (41 μl, 1 mmol) was added. The mixture was stirred for 1 h. The volatiles were removed in vacuum, yielding an orange oil which slowly crystallized. Yield 260 mg (0.72 mmol, 73%). IR (cm^{-1}): 3120 (m), 1325 (s), 1235 (m), 1210 (m), 1180 (m), 1090 (w), 1025 (s), 820 (s), 725 (s), 630 (s), 630 (s), 590 (w), 540 (m), 510 (w). Anal. Found: C, 39.45; H, 3.77. $C_{12}H_{13}F_3O_4STi$ Calc.: C, 40.24; H, 3.66%.

3.11. $Cp_2TiOSiMe_3(OTf)$

THF (10 ml) was added to a mixture of $Cp_2Ti(OTf)_2$ (476 mg, 1 mmol) and $NaOSiMe_3$ (110 mg, 1 mmol) at liquid N_2 temperature. The vessel was slowly warmed to room temperature. The volatiles were removed in vacuum and the resulting orange solid was washed with pentane and then extracted with ether. Evaporation to dryness gave $Cp_2TiOSiMe_3(OTf)$ (234 mg, 0.6 mmol, 58%). IR (cm^{-1}): 3120 (m), 1325 (s), 1300 (w), 1240 (w), 1215 (s), 1185 (m), 1040 (s), 935 (s), 820 (s), 730 (s), 630 (s), 590 (m), 510 (w).

From $Cp_2TiMe(OTf)$: $Cp_2TiMe(OTf)$ (171 mg, 0.5 mmol) was dissolved in 5 ml of toluene and Me_3SiOH (100 μl) was added. The mixture was stirred for 0.5 h during which the color became yellow–orange. The volatiles were removed in vacuum and residue to yield an orange solid (130 mg, 0.31 mmol, 62%). Anal. Found: C, 39.80; H, 4.34. $C_{14}H_{19}F_3O_4SSiTi$ Calc.: C, 40.39; H, 4.60%.

3.12. $Cp_2TiOSiMe_2{}^tBu(OTf)$

$Cp_2TiMe(OTf)$ (320 mg, 0.94 mmol) was dissolved in 6 ml of CCl_2H_2 and $Me_2{}^tBuSiOH$ (150 μl, 0.96 mmol) was added. The mixture was stirred for 4 h, during which the color became yellow–orange. The volatiles were removed in vacuum and the residue was washed with pentane (20 ml). After drying an orange solid was obtained. Yield 247 mg (0.54 mmol, 57%). IR (cm^{-1}): 3115 (m), 1325 (s), 1230 (w), 1210 (s), 1190 (m), 1025 (s), 920 (s), 820 (s), 770 (m), 730 (w), 675 (m), 630 (s), 590 (w). Anal Found: C, 44.02; H, 5.43. $C_{17}H_{25}F_3O_4SSiTi$ Calc.: C, 44.55; H, 5.50%.

3.13. Reaction between Cp_2TiMe_2 and $HOSiMe_3$

The reaction between Cp_2TiMe_2 and excess trimethylsilanol (4 equiv.) in benzene-d_6 was monitored by NMR spectroscopy. At room temperature no reaction was observed for 2 h. Heating to 50°C led to a smooth reaction to yield the monosubstitution product $Cp_2TiMe(OSiMe_3)$ and methane. At this temperature no further alcoholysis was observed. Raising the temperature to 85°C resulted in disproportionation processes leading to mixtures, not, however, containing the disubstituted product $Cp_2Ti(OSiMe_3)_2$.

3.14. Synthesis of $Cp_2TiMe(OSiMe_3)$

5 ml of THF and 2 g of $HOSiMe_3$ (22 mmol) were added to $Cp_2TiMe(OSiMe_3)$ (4.3 g, 20.6 mmol). The mixture was stirred at 50°C and periodically a sample was analyzed by proton NMR. When the signals due to Cp_2TiMe_2 had disappeared, the mixture was evaporated to dryness. A yellow, viscous oil resulted, containing a small amount of orange solid. The oil was filtered, yielding 3.3 g of $Cp_2TiMe(OSiMe_3)$ (by NMR, 12 mmol, 58%).

3.15. $(Cp_2TiOTf)_2(\mu\text{-}O)_2$

$(Cp_2TiCl)_2(\mu\text{-}O)_2$ (100 mg, 0.221 mmol) and AgOTf (150 mg, 0.44 mmol) were dissolved in 5 ml of THF, stirred for 1 h and filtered. The volatiles were removed in vacuum and the residue was washed with 5 ml of ether. Yield 117 mg (0.174 mmol, 79%) of an orange solid. IR (cm^{-1}): 3130 (m), 1325 (s), 1235 (w), 1210 (s), 1165 (w), 1080 (w), 1020 (s), 930 (w), 815 (s), 730 (s), 630 (m), 590 (m), 510 (w), 410 (m). Anal. Found: C, 39.72; H, 3.28. $C_{22}H_20S_2O_7F_6Ti_2$ Calc.: C, 39.42; H, 3.01%.

NMR experiment: $Cp_2TiMe(OTf)$ (6 mg) was dissolved in benzene-d_6 (0.5 ml) and 2 μl of H_2O was added. Immediately an orange solid formed. The NMR spectrum of the remaining solution showed the presence of $(Cp_2TiOTf)_2(\mu\text{-}O)_2$ as the only component.

3.16. Reaction of $Cp_2Ti(OTf)_2$ and $NaBH_4$

$Cp_2Ti(OTf)_2$ (1.9 g, 4 mmol) and $NaBH_4$ (150 mg, 4.4 mmol) were suspended in 40 ml of THF. The mixture was stirred for 6 h, during which the color slowly became turquoise under gas evolution. The mixture was evaporated to dryness, and the residue extracted with toluene to yield sky-blue crystals on cooling. Yield 910 mg (2.78 mmol, 70%) $Cp_2Ti(OTf)$. IR(cm^{-1}): 3110 (w), 3095 (w), 1315 (s), 1245 (s), 1220 (s), 1195 (s), 1180 (w), 1040 (s), 1010 (m), 805 (s), 620 (s), 585 (w), 510 (m), 410 (m). Anal. Found: C, 40.79; H, 3.20. $C_{11}H_{10}F_3O_3SiTi$ Calc.: C, 40.39; H, 3.08%.

3.17. $Cp_2Ti(OSiMe_3)_2$

$Cp_2Ti(OTf)_2$ (0.857 g, 1.86 mmol) was dissolved in 15 ml of dichloromethane and cooled to −20°C. At that temperature, 7.7 ml of a 0.48 M dichloromethane solution of $NaOSiMe_3$ (3.7 mmol) was added, and the reaction mixture was allowed to warm to room temperature. The solution became bright yellow during this process. The solvent was exchanged for pentane, and after filtration and crystallization at −80°C, 201 mg (0.56 mmol, 30%) of a bright yellow solid was obtained. IR (cm^{-1}): 3095 (w), 1306 (w), 1245 (s), 980 (m), 925 (s), 835 (s), 790 (m), 745 (m), 675 (m), 600 (w), 440 (m). Anal. Found: C, 54.19; H, 8.07. $C_{16}H_{28}O_2Si_2Ti$ Calc.: C, 53.91; H, 7.92%.

3.18. $Cp_2TiCl(OSiMe_3)$

Cp_2TiCl_2 (940 mg, 3.8 mmol) was suspended in 20 ml of CCl_2H_2 and $NaOSiMe_3$ (423 mg, 3.8 mmol) was added at 0°C. The mixture was stirred for 3 h, during which it became yellow–orange. The volatiles were removed in vacuum and the residue was extracted with 150 ml of pentane. After evaporation, a yellow solid remained which was isolated. Yield 787 mg (0.26 mmol, 64%). IR (cm^{-1}): 3093 (m), 1245 (s), 1020 (m), 945 (vs), 845 (w), 810 (vs), 745 (s), 580 (w), 445 (m). Anal. Found: C, 51.96; H, 6.26. $C_{13}H_{19}ClOSiTi$ Calc.: C, 51.58; H, 6.33%.

NMR reaction: $Cp_2TiCl(OTf)$ (10 mg, 0.03 mmol) and $NaOSiMe_3$ (3 mg, 0.03 mmol) were suspended in 0.5 ml of $CDCl_3$. The color slowly became orange. The ^1H NMR spectrum showed that only $Cp_2TiCl(OSiMe_3)$ had formed, with no indication of the formation of $Cp_2Ti(OSiMe_3)_2$.

3.19. $Cp_2TiF(OSiMe_3)$

$Cp_2TiF(OTf)$ (346 mg, 1 mmol) and $NaOSiMe_3$ (112 mg, 1 mmol) were cooled in a liquid nitrogen bath, and 10 ml of THF was added. The mixture was allowed to warm to room temperature. The color became a brighter yellow. The THF was removed in vacuum, and the residue was extracted with ether. The ether was removed and the resulting oil was solidified by stirring in pentane. Yield 178 mg (0.62 mmol, 62%) of a yellow powder. IR (cm^{-1}): 3120 (w), 1280 (s), 1246 (s), 1170 (m), 1045 (s), 1020 (w), 945 (s), 805 (s), 735 (m), 520 (w). Anal. Found: C, 45.59; H, 5.06. $C_{13}H_{19}FOSiTi$ Calc.: C, 54.54; H, 6.69%. The compound could not be obtained in a pure form.

3.20. Reaction between $Cp_2TiMe(OTf)$ and $NaOSiMe_3$

$Cp_2TiMe(OTf)$ (171 mg, 0.5 mmol) and $NaOSiMe_3$ (56 mg, 0.5 mmol) were cooled to liquid N_2 temperature and 5 ml of THF was added. The mixture was allowed to warm to room temperature. The solvent was exchanged for pentane and after filtration 33 mg of an orange compound was isolated with an ^1H NMR spectrum identical to the above compound, apart from an impurity identified as $Cp_2Ti(OSiMe_3)_2$.

3.21. Reaction between $Cp_2TiOSiMe_3(OTf)$ and $NaOSiMe_3$

4 mg of $Cp_2TiOSiMe_3(OTf)$ and 1 mg of $NaOSiMe_3$ were dissolved in 0.5 ml of $CDCl_3$. The ^1H NMR spectrum provided evidence for the clean formation of $Cp_2Ti(OSiMe_3)_2$.

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