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Synthesis of $Cp^*_2Ti(OTf)$ and Its Reaction with Water

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$Cp^*_2Ti(OTf)$ (**2**) was prepared by oxidation of the known (alkyne)titanocene complex $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with $Fe(OTf)_3$. This reaction is highly selective; formation of $Cp^*_2Ti(OTf)_2$ by using an excess of the oxidizing agent was not observed. Complex **2** was treated with water to give $Cp^*_2Ti(OH)(OTf)$ (**5**) and hydrogen gas. This reaction was monitored by GC and volumetric analysis. Complexes **2** and **5** were characterized by X-ray crystallography and investigated by DFT analysis.

Introduction

Titanocene complexes in the oxidation state +3 have shown to be relevant for a wide range of organometallic stoichiometric and catalytic applications, e.g. epoxide ring opening[1] and polymerization reactions.[2] Several approaches for the preparation of Ti^{III} complexes are described in the literature; however, some of these have significant disadvantages. The reduction of Ti^{IV} compounds is accompanied by the formation of side products, which are formed by the incorporation of the reducing agent into the Ti species.[3] Moreover, direct transmetalation of Ti^{III} compounds with appropriate ligand(s) is possible, e.g. $[Cp_2TiCl]_2$ can be obtained from $TiCl_3$ and CpTl.[4] Further functionalizations of Ti^{III} complexes are possible by using halide exchange reactions. Teuben et al. have shown that Cp^*_2TiCl ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) is an excellent starting material for the synthesis of other compounds of the type Cp^*_2TiX (X = Br, I, BH_4, NMe_2, O*t*Bu, O_2CH) using the appropriate salt MX (M = Li, Na, K).[5] Recently, Thewalt and Berhalter described the reduction of $Cp_2Ti(OTf)_2$ with aluminum foil to give the Ti^{III} species $Cp_2Ti(OTf)\cdot THF$.[6] It is noteworthy that – similarly as observed for (alkyne)metallocene complexes[7] – the presence of an additional donor ligand is needed in this case. The corresponding permethylated complex is hitherto unknown. One obvious feature of titanocene(III) complexes is their general ability to undergo both, reduction reactions to give Ti^{II} species as well as oxidation reactions to yield Ti^{IV} compounds. This is interesting for investigations of redox processes, e.g. water reduction.

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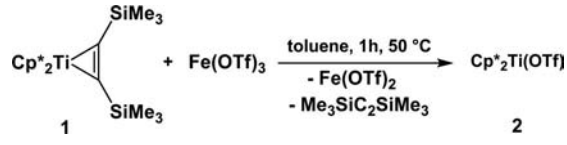
Results and Discussion

The (alkyne)titanocene complex **1** reacts with $Fe(OTf)_3$ in toluene to give the decamethyltitanocene(III) triflate **2**. The complex can be isolated as a dark-green crystalline solid in excellent yields (97%; Scheme 1). This complex can also be obtained from the reaction of **1** with $Yb(OTf)_3$; however, purification of the product is more difficult due to similar solubilities of the latter and the by-product $Yb(OTf)_2$.



Scheme 1. Formation of complex **2**.

Complex **2** was characterized by EPR spectroscopy. In the solid state an anisotropic signal with axial distortion[8] was found. The spectrum was simulated by using an axial *g* tensor with $g_\perp = 1.9881$ and $g_\parallel = 1.8552$ and a line width of $\Delta B_\perp = 28.6$ G and $\Delta B_\parallel = 33.1$ G (Figure 1).[9] In comparison to other Cp^*_2TiOR complexes,[10] this distortion is rather high, as reflected by the splitting of the *g* tensor components.

This can be due to the strongly electron-withdrawing triflate ligand in **2**, which might polarize the spin density more towards this ligand. To support this fact, DFT calculations were conducted for **2** and other Cp^*_2TiOR compounds with R = *t*Bu, Me and CF_3 in which the electronic impact relative to each other can be evaluated. The analysis of the Mulliken atomic spin densities located on the Ti centers shows a value of 1.092 in compound **2**, 1.116 for R = *t*Bu, 1.113 for R = Me and 1.105 for R = CF_3 (*t*Bu > Me > CF_3 > OTf), which is in accordance to the +I effect of the alkyl groups and the –I effect for CF_3 and OTf (see Supporting Information for details). Additionally, in mass

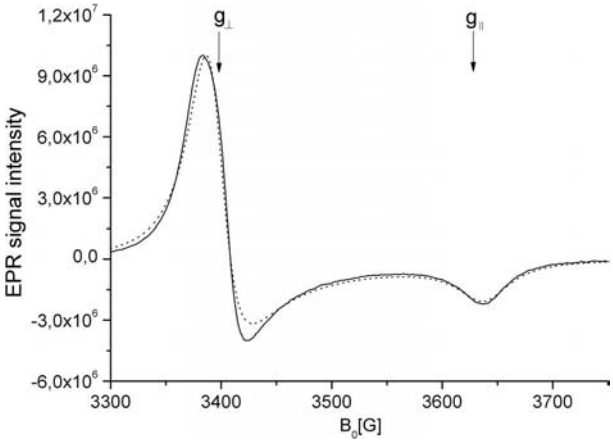


Figure 1. CW EPR spectrum of complex **2** (solid line: experimental; dotted line: simulated).

spectrometry a molecular ion peak was found at m/z = 467, revealing the presence of complex **2**.

The molecular structure of complex **2** is shown in Figure 2. The titanium center is coordinated by two Cp* ligands and a triflate group in a distorted trigonal-planar coordination geometry. Additional stabilizing ligands as seen before in the related complex $Cp_2Ti(OTf)\cdot THF$[6] are not needed due to the steric demand of the permethylated Cp ligands. The Ti1–O1 distance [2.078(1) Å] is longer than in other trivalent titanocene complexes, e.g. $Cp^*_2Ti(OSiPh_3)$ (1.919 Å)[10a] and $Cp^*_2Ti(OH)$ (1.889 Å).[10b]

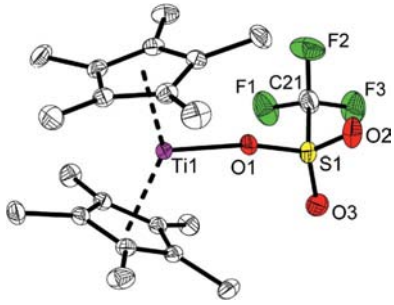
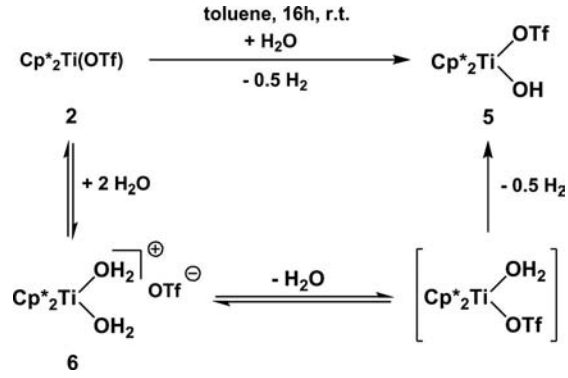


Figure 2. Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [°]: Ti1–O1 2.078(1), O1–S1 1.472(1), S1–O2 1.419(2), S1–O3 1.415(2), S1–C21 1.816(2); Ti1–O1–S1 169.0(1), O1–S1–O2 113.1(1), O1–S1–O3 114.1(1), O1–S1–C21 101.5(1), O2–S1–O3 117.6(1), O2–S1–C21 104.9(1).

Most remarkably, the formation of complex **2** from **1** is highly selective to yield exclusively complex **2**. A twofold oxidation to yield $Cp^*_2Ti(OTf)_2$ (**3**) was not observed. Nonetheless, DFT calculations revealed the presence of a minimum structure for complex **3**. Thus, it should in principle be possible to prepare this compound by using another method. The synthesis of $Cp_2Ti(OTf)_2$ was described by Luinstra, who used Cp_2TiMe_2 and HOTf.[11] A similar approach was used for the corresponding permethylated complex. However, from the reaction of $Cp^*_2TiMe_2$ with HOTf the dinuclear bridged species $[(Cp^*)Ti(\mu\text{-}OH)(OTf)(\mu\text{-}OTf)]_2$ (**4**) was isolated and investigated by X-ray analysis (see Supporting Information for details). This complex and its molecular structure were described before by Welch et al.[12] NMR spectroscopic data of this complex resemble those found in the literature. Investigations on the synthesis of **3** are ongoing and will be part of future publications.

Complex **2** can be treated with water to give the Ti^{IV} complex **5**, which can be obtained from toluene as a brown crystalline solid in moderate yields (66%; Scheme 2). In addition, a light-blue by-product is formed; unfortunately the exact constitution of this species could not be identified. However, EPR and NMR spectroscopic measurements suggest the existence of a paramagnetic Ti^{III} complex; results from elemental analysis imply the presence of the complex $[Cp^*_2Ti(H_2O)_2](OTf)$ (**6**). Interestingly, if the hydrolysis of complex **2** is performed at lower temperatures (T = 5 °C) or with an excess of water this blue, toluene-insoluble compound is formed exclusively, whereas a reaction temperature of T = 80 °C results in the exclusive formation of complex **5**. Heating of a suspension of the paramagnetic species **6** in toluene to 80 °C yields the complex **5** and hydrogen (detected by GC). Thus, $[Cp^*_2Ti(H_2O)_2](OTf)$ (**6**) could be referred to as an intermediate for the formation of **5** from **2**.



Scheme 2. Hydrolysis of complex **2**.

^{1}H NMR investigations of complex **5** have shown a singlet for the Cp* protons (δ = 1.74 ppm) as well as a singlet in the downfield region for the OH proton at δ = 10.41 ppm. The molecular ion could not be found in mass spectrometry; however, fragments due to the loss of the OH group and the OTf group were identified at m/z = 467 and 335, respectively.

The molecular structure of complex **5** is depicted in Figure 3 and shows the metal center in a distorted tetrahedral coordination environment. The Ti1–O4 bond length is as expected [1.884(2) Å] and the same as found before in the dihydroxido complex $Cp^*_2Ti(OH)_2$ [1.892(3) and 1.891(3) Å].[13] The Ti1–O1 distance is longer [2.107(2) Å], which can be attributed to the electron-withdrawing nature of the Tf fragment. Moreover, this bond appears to be slightly weaker than in complex **2**.

Besides the calculation of spin densities to understand the EPR spectra, a DFT study concerning the geometry in complexes **2** and **5** was performed. Moreover, as mentioned before, a search for a minimum structure for the hypotheti-

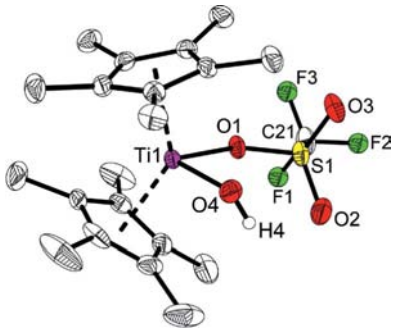


Figure 3. Molecular structure of complex **5**. Hydrogen atoms (except H4) are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [°]: Ti1–O1 2.107(2), Ti1–O4 1.884(2), O1–S1 1.477(2), O2–S1 1.419(2), O3–S1 1.421(2), C21–S1 1.823(3); O1–Ti1–O4 91.64(7), Ti1–O1–S1 136.1(1), O1–S1–O2 114.3(1), O1–S1–O3 114.3(1), O1–S1–C21 99.5(1), O2–S1–O3 117.1(1), O2–S1–C21 104.8(1).

cal complex $Cp^*_2Ti(OTf)_2$ was carried out. For all three compounds the hybrid functional B3LYP[14] as implemented in the Gaussian 09 suite[15] was used. For all non-metal atoms the 6-31G(d) basis set and for Ti the LANL2DZ[16] basis set with a pseudo-potential were used. Analytical gradient calculations were performed on the found stationary-point structures proving a minimum. Furthermore, for compounds **2** and **5** minimum structures were calculated by a more sophisticated method using the M06 hybrid functional from Truhlar and Zhao.[17] This functional has shown to give accurate results with molecules in which dispersion effects occur as is the case in π-bonded aromatic systems to metal atoms. The triple-ζ basis set TZVP from Ahlrichs and co-workers[18] was used and all electrons were taken into account even for the Ti centers. The calculated bond parameters are in reasonable agreement with the data obtained by X-ray crystallography; except for the O–H bond length in complex **5**, which is drastically overestimated (see Supporting Information for details).

The gaseous reaction product was analyzed by gas chromatography and found to be exclusively hydrogen. This result is of interest since the transition-metal-catalyzed generation of hydrogen from water is a hot topic in organometallic chemistry.[19] However, in most cases the overall catalytic cycles and the elemental steps are not understood very well.[20] Stoichiometric reactions of water with transition metal fragments such as shown in this contribution could help to model the catalytic cycle and to understand the mechanism of the overall reaction.

Conclusions

We have shown that oxidation of the (alkyne)titanocene complex **1** with $Fe(OTf)_3$ is a highly selective method for the formation of the decamethyltitanocene(III) triflate **2**. The reaction of this complex with water to give complex **5** and hydrogen gas can serve as a model reaction for water splitting. The general applicability and the scope of the preparation method for the oxidation of metallocenes (e.g. use of FeF_3 to give metallocene fluorides) is currently studied in our group; the results will be published in due course.

Experimental Section

General: All operations were carried out under argon with standard Schlenk techniques or in a glovebox. Prior to use, non-halogenated solvents (including [D_6]benzene) were freshly distilled from sodium tetraethylaluminate and stored under argon. $Fe(OTf)_3$ and $Yb(OTf)_3$ were purchased from Sigma Aldrich and used as received; $Cp^*_2TiCl_2$ was purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. Complex **1** was synthesized according to published procedures.[21] The following spectrometers were used: Mass spectra: MAT 95-XP. NMR spectra: Bruker AV 300; chemical shifts (^1H, ^{13}C) are given in ppm relative to $SiMe_4$ and are referenced to signals of the solvent used ([D_6]benzene: δ_H = 7.16, δ_C = 128.0). X-band EPR spectra were conducted with a CW-Bruker EMX micro spectrometer by using an ER 4119HS-WI high-sensitivity optical resonator with the following settings: microwave power = 7.197 mW, frequency = 9.446 GHz, modulation frequency = 100 kHz, and amplitude = 0.2 G. Gas chromatography: Agilent Technologies 7890A, column: 60/80 Carboxen 1000 (Supelco), detection: TCD. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 2 from $Fe(OTf)_3$: A mixture of complex **1** (2.191 g, 4.48 mmol) and $Fe(OTf)_3$ (2.270 g, 4.51 mmol) was suspended in toluene (40 mL) and stirred at 50 °C for 1 h. The color of the reaction mixture changed from brown to dark-green. The mixture was cooled to room temperature and filtered to give a dark-green solution from which all volatiles were removed in vacuo. The dark-green residue was washed with cold *n*-hexane and dried in vacuo. Yield: 2.037 g (97%). M.p. 179–182 °C (dec., under Ar). $C_{21}H_{30}F_3O_3STi$ (467.39): calcd. C 53.96, H 6.47, S 6.86; found C 54.10, H 6.53, S 7.08. EPR: $g_\perp$ = 1.9881, $g_\parallel$ = 1.8552; $\Delta B_\perp$ = 28.6 G, $\Delta B_\parallel$ = 33.1 G. MS (CI, isobutane): m/z = 467 $[M]^+$. Crystals suitable for X-ray analysis were obtained from a toluene solution at –78 °C.

Preparation of Complex 2 from $Yb(OTf)_3$: A mixture of complex **1** (0.245 g, 0.50 mmol) and $Yb(OTf)_3$ (0.620 g, 1.00 mmol) was suspended in toluene (20 mL) and stirred at 60 °C for 3 d. The colour of the reaction mixture slowly changed from brown to dark-green. The mixture was cooled to room temperature and filtered to give a dark-green solution from which all volatiles were removed in vacuo. The dark-green residue was washed with cold *n*-pentane and dried in vacuo. Yield: 0.227 g (98%). M.p. 192–205 °C (dec., under Ar). $C_{21}H_{30}F_3O_3STi$ (467.39): calcd. C 53.96, H 6.47, S 6.86; found C 49.12, H 6.11, S 7.49. The product contains considerable amounts of Yb salts, which could not be separated. MS (EI, 70 eV): m/z = 467 $[M]^+$, 335 $[Cp^*_2TiO + H]^+$, 318 $[Cp^*_2Ti]^+$.

Preparation of Complex 5: To a stirred solution of complex **2** (0.528 g, 1.13 mmol) in toluene (40 mL) was added degassed water (41 μL). The reaction mixture was stirred at room temperature overnight; during this time, the color changed from dark green to reddish-brown, and a blue precipitate formed. The mixture was filtered, and the filtrate was concentrated to dryness in vacuo to give a brown crystalline solid, which was washed with cold *n*-hexane. Yield: 0.360 g (66%). M.p. > 300 °C (under Ar). NMR ([D_6]-benzene, 300 MHz, 296 K): ^1H: δ = 1.74 (s, 30 H, Cp*), 10.41 (s, 1 H, OH). ^{13}C: δ = 11.7 (C_5Me_5), 127.0 (C_5Me_5). $C_{21}H_{31}F_3O_4STi$

(484.40): calcd. C 52.07, H 6.45, S 6.62; found C 48.55, H 6.29, S 7.05. Despite repeated recrystallization no better results could be obtained. MS (CI, isobutane): m/z = 467 $[Cp^*_2Ti(OTf)]^+$, 335 $[Cp^*_2Ti(OH)]^+$. Crystals suitable for X-ray analysis were obtained from a saturated toluene solution at room temperature.

Preparation of Compound 6: To a solution of complex **2** (0.203 g, 0.43 mmol) in toluene (20 mL) was added an excess of degassed water (1 mL, 55 mmol). While the emulsion brightened up to light-green, it was stirred at ambient temperature for 10 min and subsequently concentrated to dryness in vacuo. The light-blue residue was washed with toluene (20 mL) and dried in vacuo. Yield: 0.211 g (98%). M.p. 136 °C (dec., under Ar). $C_{21}H_{34}F_3O_5STi$ (503.42): calcd. C 50.10, H 6.81, S 6.37; found C 49.80, H 6.48, S 6.37.

Formation of Complex 5 and H_2 from Complex 6: A suspension of compound **6** (0.129 g, 0.25 mmol) in toluene (20 mL) was heated to 80 °C, resulting in the initial formation of a green solution. The mixture was stirred overnight, giving a dark-brown solution. A gas sample was taken and analyzed by gas chromatography indicating the presence of hydrogen as the only gaseous reaction product. The solution was filtered and concentrated to dryness. NMR analysis in [D_6]benzene revealed the presence of complex **5** (see above).

Crystallographic Details: Diffraction data were collected with a STOE-IPDS II diffractometer by using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-97[22]) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[22]). DIAMOND was used for graphical representations.[23]

Complex 2: $C_{21}H_{30}F_3O_3STi$, M_r = 467.41, dark-green crystal, 0.50 × 0.50 × 0.26 mm, monoclinic, space group $P2_1/c$, a = 14.7812(3) Å, b = 10.5697(3) Å, c = 14.6305(3) Å, β = 107.619(2)°, V = 2178.54(9) Å^3, Z = 4, $\rho_{calcd.}$ = 1.425 g cm^{-3}, T = 200(2) K, μ = 0.533 mm^{-1}, numerical absorption correction (max., min. transmission: 0.9049, 0.7627), 41478 reflections collected, 5872 independent reflections (R_{int} = 0.0319), 4763 reflections observed [$I > 2\sigma(I)$], 272 refined parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0378, wR_2 = 0.1077, R indices (all data): R_1 = 0.0469, wR_2 = 0.1114.

Complex 4: $C_{30}H_{38}F_{12}O_{14}S_4Ti_2$, M_r = 1074.64, dark brown crystal, 0.55 × 0.55 × 0.30 mm, monoclinic, space group $C2/c$, a = 18.2889(8) Å, b = 10.5774(3) Å, c = 21.673(1) Å, β = 91.420(4)°, V = 4191.3(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.703 g cm^{-3}, T = 150(2) K, μ = 0.696 mm^{-1}, numerical absorption correction (max., min. transmission: 0.7962, 0.6935), 30435 reflections collected, 4821 independent reflections (R_{int} = 0.0599), 4010 reflections observed [$I > 2\sigma(I)$], 286 refined parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0467, wR_2 = 0.1273, R indices (all data): R_1 = 0.0549, wR_2 = 0.1303.

Complex 5: $C_{21}H_{31}F_3O_4STi$, M_r = 484.42, red crystal, 0.50 × 0.32 × 0.13 mm, monoclinic, space group $P2_1/n$, a = 10.4879(3) Å, b = 19.9095(7) Å, c = 11.1274(4) Å, β = 106.578(3)°, V = 2226.92(13) Å^3, Z = 4, $\rho_{calcd.}$ = 1.445 g cm^{-3}, T = 200(2) K, μ = 0.528 mm^{-1}, numerical absorption correction (max., min. transmission: 0.9226, 0.7903), 35647 reflections collected, 5117 independent reflections (R_{int} = 0.0435), 3427 reflections observed [$I > 2\sigma(I)$], 285 refined parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0387, wR_2 = 0.0892, R indices (all data): R_1 = 0.0642, wR_2 = 0.0947.

CCDC-799902 (for **2**), -799903 (for **5**) and -799904 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the DFT calculations, including plots showing the spin densities of complex **2** and $Cp^*_2Ti(OMe)$, $Cp^*_2Ti(OtBu)$ and $Cp^*_2Ti(OCF_3)$.

Acknowledgments

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