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Reactivity of functionalised decamethyltitanocenes: Synthesis and structure of chiral monocyclopentadienyl titanium halogenides



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1. Introduction

There is a considerable interest in chiral metallocene complexes for various stoichiometric reactions and as well as catalysts for stereospecific polymerisations of prochiral olefins [1]. Thus, e.g., the half-sandwich titanium complexes in the catalytic systems Cp*TiCl₃/MAO or Cp*TiMe₃/MAO (Cp* = η^5 -C₅Me₅) display a high activity in the production of syndiotactic polystyrene [2]. In spite of the extensive investigations, less is known about reactive intermediates, and so there is a great interest in the synthesis and characterisation of new complexes of this type and their performance in catalytic reactions [3]. Recently we reported different C-C coupling reactions of decamethyltitanocene generated in the Cp*2TiCl2/Mg system with various disubstituted 1,3-butadivnes. The products of these reactions vary depending on the nature of the substituents of the diynes [4,5]. For Cp*₂TiCl₂, a reduction by Mg in the presence of the disubstituted butadiynes RC = C - C = CR'provides a new method for the generation of functionalised pentamethylcyclopentadienyl derivatives by the formation of different C-C coupling products of the butadiyne with the pentamethylcyclopentadienyl ligand. When using the decamethyltitanocene fragment, [Cp^{*}₂Ti], the reaction depends strongly on the substituents R and R' of the butadiynes and different products were isolated [5-7]. For R = R' = tBu, a coupling of the butadiyne with two methyl

ABSTRACT

The recently described unconventional substituted titanocene complex $[Cp^*Ti{\eta^5-C_5Me_3(CH_2-CH(tBu)-\eta^2-C_2-CH(tBu)-CH_2)}]$ (1) can be derivatised by simple means (Br₂, HX with X = Cl, Br) to generate the titanocene dihalogenides **2-Br**, **2-Cl**, which give in a subsequent reaction besides Cp*TiX₃ (**3-Br**: X = Br, **3-Cl**: X = Cl) the titanium complexes **4-Cl** resp. **4-Br** with one functionalised chiral cyclopentadienyl ligand. In the reaction of **1** with Et₃N·3HF an analogous isostructural titanocene dihalogenide **2-F** as well as the unusual dimeric anionic heptafluoride **5** are formed. All complexes have been characterised spectroscopically, and X-ray crystal structure determinations were performed for **4-Cl** and **2-F**.

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groups of one of the pentamethylcyclopentadienyl ring systems generates the complex [Cp*Ti{ $\eta^5-C_5Me_3(CH_2-CHR-\eta^2-C_2-CHR'-CH_2)$ }] (R = R' = tBu) (1) [5] (Scheme 1A).

A similar product has been obtained by using $tBuC \equiv C$ -C \equiv CSiMe₃ [5]. In these complexes one pentamethylcyclopentadienyl ligand is annellated with an eight-membered ring with a C-C triple bond, which is coordinated to the titanium centre. Activation of methyl groups of both pentamethylcyclopentadienyl ligands is observed for R = R' = Me, Ph (Scheme 1B), which displays besides the fulvene also a butadienyl-substituted pentamethylcyclopentadienyl ligand [5]. The reaction with Me₃SiC \equiv C-C \equiv CSiMe₃ yielded a titanacyclopropene [4] (Scheme 1C). Earlier we described simple derivatisation reactions of **1** by acidolysis with HCl or by hydrogenation to a titanacyclopropane and the subsequent reaction with Br₂ affording the correspondingly dihalogenated complexes, resp. [7].

Here we report further investigations of reactions of 1 with HX, e.g. full characterisation of all products and, in particular on the fluorination with Et_3N -3HF.

2. Experimental

2.1. General

All operations were carried out under argon with standard Schlenk techniques or in a glovebox. Prior to use nonhalogenated solvents (including benzene- d_6) were freshly distilled from sodium



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Scheme 1. Reactions of decamethyltitanocene generated in the Cp*2TiCl2/Mg system with various disubstituted 1,3-butadiynes.

tetraethylaluminate and stored under argon. Cp*2TiCl2 and tBu-C2-C₂-*t*Bu were purchased from MCAT (Metallocene Catalysts and Life Science Technologies, Konstanz, Germany) and Sigma Aldrich and used without further purification. The following instruments were used: NMR spectra: Bruker AV400 and AV300, respectively. The spectra were assigned with the help of DEPT and correlation experiments. Chemical shifts ¹H, ¹³C: relative to SiMe₄, referenced to the solvent signals: benzene- d_6 (δ_H 7.16, δ_C 128.0); ¹⁹F chemical shifts are given relative to CFCl₃ and ¹⁵N chemical shifts relative to nitromethane (Ξ = 10.136767 MHz). Detailed NMR data of complexes 4-Cl, 4-Br, 2-F and 5 as well as the assignment of all chemical shifts could be found in the Supporting Information. - MS: Finnigan MAT 95-XP from Thermo-Electron – Elemental analysis: Leco Tru Spec elemental analyzer - Melting points: Büchi 535 apparatus. Melting points are uncorrected and were measured in sealed capillaries under Argon. Compound **1** was prepared according to a published procedure [5].

2.2. Preparation of 3-Cl and 4-Cl

Complex **1** (0.666 g, 1.39 mmol), solved in 10–15 mL of toluene, was treated with 2 mL (8.0 mmol) of a 4 M solution of HCl in 1,4dioxane. The color of the mixture rapidly changed from yellow to red-brown and contained, as checked by NMR, almost pure complex **2-Cl** [7]. After heating (80 °C) for 10 days, the solution was cooled to r.t. and evaporated to dryness in vacuo. ¹H NMR spectrum of the raw material revealed the formation of **2-Cl** (13%), **3-Cl** (42%) and **4-Cl** (45%). After several recrystallisations from *n*-hexane 0.064 g of **3-Cl** and 0.055 g of **4-Cl** have been isolated.

2.2.1. Analytical data of compound 3-Cl

Red crystals. Yield: 0.064 g (0.22 mmol, 16% referred to Ti). M.p. 231–233 °C. Elemental *Anal*. Calc. for C₁₀H₁₅Cl₃Ti (289.45): C, 41.49; H, 5.22. Found: C, 41.19; H, 5.24%. ¹H NMR (benzene-*d*₆, 400 MHz, 297 K): δ = 1.91 (s, 15 H, Me-Cp) (see also Ref. [8]). ¹³C{¹H} NMR (benzene-*d*₆, 100 MHz, 297 K): δ = 14.01 (Me-Cp); 137.36 (Cq–Cp).

2.2.2. Analytical data of compound 4-Cl

Dark red crystals. Yield: 0.055 g (0.12 mmol, 8% referred to Ti). M.p: 196–197 °C. Elemental *Anal.* Calc. for $C_{22}H_{35}Cl_{3}Ti$ (453.74): C, 58.24; H, 7.77. Found: C, 58.03; H, 7.47%. ¹H NMR (benzene-*d*₆, 400 MHz, 297 K): δ = 0.91 (s, 9H, CMe₃); 0.92 (s, 9H, CMe₃); 1.88 (dt, ³*J* \approx 5/5/14 Hz, 1H, CH); 1.91 (s, 3H, Me–Cp); 2.02 (s, 3H, Me– Cp); 2.12 (s, 3H, Me–Cp); 2.44 (dd, ²*J* = 16.8 Hz, ³*J* = 12.8 Hz, 1H, CH₂); 3.07 (dd, ²*J* = 14.4 Hz, ³*J* = 5.3 Hz, 1H, CH₂); 3.38 (ddd, ³*J* \approx 4/9/13 Hz, CH); 3.54 (dd, ²*J* = 16.8 Hz, ³*J* = 4.4 Hz, 1H, CH₂); 3.63 (t, ²*J* \approx ³*J* \approx 14 Hz, 1H, CH₂); 5.26 (m, 1H, CH); 5.27 (m, 1H, CH). ¹³C{¹H} NMR (benzene- d_6 , 100 MHz, 297 K): δ = 13.75, 14.01, 14.29 (Me–Cp); 27.31, 27.87 (Me–tBu); 30.38, 32.02 (CH₂); 33.03, 35.16 (Cq–tBu); 44.34, 53.04, 129.75, 131.90 (CH); 137.19, 137.81, 138.52, 141.38, 141.84 (Cq–Cp). MS (70 eV, m/z): 452 [M]⁺ 417 [M–Cl]⁺, 382 [M–2Cl]⁺, 360 [M–Cl–tBu]⁺.

2.3. Preparation of 3-Br and 4-Br

0.4 mL (2.4 mmol) of a 48% solution of HBr in water were added to a solution of **1** (0.283 g, 0.59 mmol) in 5 mL of toluene. The color of the mixture changed quickly from yellow to red-brown. After 2 h at room temperature the complexes **2-Br** and **4-Br** had formed in a ratio 6.7:1 (checked by ¹H NMR). After heating of the mixture (80 °C) for 2 days followed by evaporation to dryness in vacuo a crude mixture of the complexes **2-Br** (7%), **3-Br** (30%) and **4-Br** (63%) was isolated. Several recrystallisations from *n*-hexane gave 0.115 g of pure **4-Br**.

2.3.1. Analytical data of compound 3-Br

Red crystals. ¹H NMR (benzene- d_6 , 300 MHz, 297 K): δ = 1.96 (s, 15H, Me–Cp). ¹³C{¹H} NMR (benzene- d_6 , 75 MHz, 297 K): δ = 15.4 (Me–Cp); 138.1 (Cq–Cp).

2.3.2. Analytical data of compound 4-Br

Dark red crystals. Yield: 0.115 g (0.196 mmol, 33 % referred to Ti). M.p. 193–194 °C. Elemental *Anal.* Calc. for $C_{22}H_{35}Br_3Ti$ (587.09): C, 45.01; H, 6.01. Found: C, 44.63; H, 5.59%. ¹H NMR (benzene-*d*₆, 400 MHz, 297 K): $\delta = 0.91$ (s, 9H, CMe₃); 0.92 (s, 9H, CMe₃); 1.89 (dt, ²*J* ≈ 14 Hz, ³*J* ≈ 5 Hz, 1H, CH); 1.93 (s, 3H, Me-Cp); 2.12 (s, 3H, Me-Cp); 2.21 (s, 3H, Me-Cp); 2.45 (dd, ²*J* = 16.8 Hz, ³*J* = 12.8 Hz, 1H, CH₂); 3.12 (dd, ²*J* = 14.4 Hz, ³*J* = 5.2 Hz, 1H, CH₂); 3.41 (ddd, ³*J* = 8.6/12.8/4.4 Hz, 1H, CH); 3.57, (dd, ²*J* = 16.8 Hz, ³*J* = 4.4 Hz, 1H, CH₂); 3.77 (t, ²*J* ≈ ³*J* ≈ 14 Hz, 1H, CH₂); 5.26 (m, 1H, CH); 5.29 (m, 1H, CH). ¹³C{¹H} NMR (benzene-*d*₆, 100 MHz, 297 K): $\delta = 15.22$, 15.28, 15.87 (Me-Cp); 27.33, 27.88 (Me-*t*Bu); 31.85, 33.05 (CH₂); 33.05, 35.19 (Cq-*t*Bu); 44.26, 53.19, 129.74, 131.89 (CH); 137.63, 138.15, 139.71, 142.38, 143.02 (Cq-Cp).

2.4. Preparation of 2-F and 5

Complex **1** (0.917 g, 1.91 mmol) was dissolved in 20 mL of THF, and Et_3N ·3HF (0.21 mL, 1.29 mmol) was added to the yellow–green solution, which immediately became dark and then yellow. This yellow solution was concentrated in vacuo to 10 mL and allowed to stand at -78 °C. After 1 day the cold solution was filtered and evaporated to dryness under reduced pressure. The crude residue was a mixture of complexes **2-F** (85%) and **5** (15%) (checked by

¹H NMR). After extraction with *n*-hexane (3×15 mL, 50 °C) an unsolved deposit of almost pure **5** (0.101 g) was obtained, which was dissolved in 15 mL of warm *n*-hexane (60 °C). After filtration of the warm solution and standing 1 day at room temperature light-yellow crystals had formed, which were separated from the mother liquor, washed with *n*-hexane and dried in vacuo to give 0.015 g of analytically pure **5**. The collected *n*-hexane solutions (extraction) were filtered, concentrated in vacuo (20-25 mL) and cooled to -78 °C. After 1 day at this temperature yellow crystals had formed which were separated from the mother liquor by decanting, washed with cold *n*-hexane and dried in vacuo to give yellow crystals rule yellow crystals for **2-F**.

2.4.1. Analytical data of compound 2-F

Yellow crystals: Yield: 0.610 g (1.17 mmol, 61% referred to Ti). M.p. 202–204 °C. Elemental *Anal.* Calc. for $C_{32}H_{50}F_2Ti$ (520.34): C, 73.83; H, 9.68. Found: C, 73.98; H, 9.85%. ¹H NMR (benzene- d_6 , 300 MHz, 297 K): $\delta = 1.00$ (s, 9H, CMe₃), 1.00 (s, 9H, CMe₃); 1.82 (s, 3H, Me–Cp); 1.89 (s, 15H, Me–Cp); 1.90 (s, 3H, Me–Cp); 1.92 (s, 3H, Me–Cp); 2.02 (dt, ²J = 13.8 Hz, ³J = 5 Hz, 1H, CH); 2.33 (dd, ²J = 16 Hz, ³J = 12.9 Hz, 1H, CH₂); 2.82 (dd, ²J = 14.2 Hz, ³J = 5.4 Hz, 1H, *CH*₂); 2.94 (dd, ²J = 16 Hz, ³J = 5.1 Hz, 1H, CH₂); 3.23 (t, ²J \approx ³J \approx 14 Hz, 1H, CH₂); 3.26 (m, ³J = 12.8/5.3 Hz, 1H, CH); 5.33 (m, 1H, CH); 5.35 (m, 1H, CH). ¹³C{¹H} NMR (benzene- d_6 , 75 MHz, 297 K): $\delta = 10.75$, 11.33, 11.33, 11.62 (Me–Cp); 26.90 (CH₂); 27.63, 28.20 (Me–tBu); 28.52 (CH₂); 33.22, 35.13 (Cq–tBu); 45.37, 52.75 (CH); 123.98, 124.30, 125.00, 126.82, 128.3, 129.39 (Cq–Cp); 130.33, 131.80 (CH). ¹⁹F NMR (benzene- d_6 , 284.4 MHz, 297 K): $\delta = 74.8$ (d, ²J_{FF} = 27 Hz); 73.7 (d, ²J_{FF} = 27 Hz). MS (70 eV, *m*/*z*): 501 [M–F]⁺, 385 [M–Cp⁺]⁺, 366 [M–Cp^{*}–F]⁺, 325 [M–Cp^{*}–tBu]⁺, 309 [M–Cp^{*}–tBu–F]⁺, 271 [M–Cp^{*}–tBu]⁺.

2.4.2. Analytical data of compound 5

Light yellow crystals. Yield: 0.101 (0.11 mmol, 12% referred to Ti). M.p. 227–229 °C. Elemental Anal. Calc. for C₅₀H₈₆F₇NTi₂ (929.9): C, 64.58; H, 9.32; N, 1.51. Found: C, 65.03; H, 9.11; N, 1.47%. ¹H NMR (benzene- d_6 , 300 MHz, 297 K): δ = 0.70 (t, 9H, Me-Et₃N); 1.13 (s, 18H, CMe₃); 1.15 (s, 18H, CMe₃); 1.19 (2H, CH); 2.17 (s, 6H, Me-Cp); 2.17 (s, 6H, Me-Cp); 2.30 (s, 6H, Me-Cp); 2.53 (2H, CH₂); 2.54 (m, 6H, CH₂-Et₃N); 3.07 (dd, ²*J* = 14.1 Hz, ³*J* = 4.9 Hz, 2H, CH₂); 3.49 (2H, CH₂); 3.50 (2H, CH); 3.67 (dd, ${}^{2}I$ = 16.1 Hz, ${}^{3}I$ = 4.8 Hz, 2H, CH₂); 5.48 (2H, CH), 5.51 (2H, CH); 8.5 (br, 1H, NH). ¹³C{¹H} NMR (benzene-d₆, 100 MHz, 297 K): δ = 8.18 (Me-Et₃N); 11.37, 11.88, 11.92 (Me-Cp); 27.67 (CH₂); 27.92, 28.38 (Me-tBu); 29.22 (CH₂); 33.33, 35.23 (Cq*t*Bu); 45.07 (CH); 45.20 (CH₂-Et₃N); 52.80 (CH); 130.30 (CH); 130.78 (Cq-Cp); 131.2 (br, Cq-Cp); 132.64 (CH); 132.9 (br, Cq-Cp); 134.35 (Cq–Cp). ¹⁹F NMR (benzene-*d*₆, 282.4 MHz, 297 K): $\delta \approx -42$ (br, 1F), ≈ -8 (br, 2F), ≈ 82 (br, 2F), 156.2 (2F). ¹⁵N NMR (benzene- d_6 , 30.4 MHz, 297 K): $\delta = -326.1$. MS (70 eV, m/z): 385 $[Cp'TiF_2]^+$, 328 $[Cp'TiF_2-tBu]^+$, 308 $[Cp'TiF-tBuH]^+$, 299 $[Cp']^+$, 271 [Cp'TiF₂-2*t*Bu]⁺, 101 [NEt₃]⁺.

2.5. Crystallographic details

Single crystals of **2-F** and **4-Cl** were obtained from *n*-hexane by fractional crystallisation. Data were collected on Bruker APEX II diffractometers using graphite-monochromated Mo K α radiation. The structures were solved by direct methods (SHELXS-97) [9] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97) [9]. Diamond was used for graphical representations [10].

Crystal data and details of the data collection and the structure refinement of complexes **2-F** and **4-Cl** are given in Table 1.

Table 1

Crystallographic	data	for	com	plexes	2-F	and	4-Cl.

	2-F	4-Cl
Chemical formula	C ₃₂ H ₅₀ F ₂ Ti	C ₂₂ H ₃₅ Cl ₃ Ti
$M (g \text{ mol}^{-1})$	520.62	453.75
Color	yellow	red
Crystal system	orthorhombic	triclinic
Space group	$P2_{1}2_{1}2_{1}$	$P\bar{1}$
a (Å)	10.3940(1)	9.3969(10)
b (Å)	15.2446(2)	11.5366(11)
<i>c</i> (Å)	18.0777(2)	11.951(2)
α (°)	90.00	103.627(5)
β(°)	90.00	97.146(5)
γ (°)	90.00	112.576(5)
V (Å ³)	2864.45(6)	1128.8(3)
Ζ	4	2
Density (g cm ⁻³)	1.210	1.335
μ (Mo K $lpha$) (mm $^{-1}$)	0.330	0.739
T (K)	150(2)	100(2)
Number of reflections (measured)	27898	9666
Number of reflections (independent)	6826	5378
Number of reflections (observed)	6473	4081
Parameters	330	244
Goodness-of-fit (GOF) on F ²	1.024	0.931
$R_1 (I > 2\sigma(I))$	0.0315	0.0359
wR_2 (all data)	0.0857	0.0921

3. Results and discussion

The reaction of **1** with HX (X = Cl, Br) leads in the first step to the formation of **2-Cl** resp. **2-Br** (Scheme 2). Complex **2-Br** has been synthesised earlier starting from **1** but using two synthetic steps [7].

Complexes **2-Cl** and **2-Br**, however, are unstable toward an excess of HX (X = Cl, Br), implying an acidolysis either of the Cp^{*} or the modified Cp^{*} ligand, and gives after several days besides Cp^{*}TiX₃ (**3-Cl**, **3-Br**) also the complexes **4-Cl** and **4-Br** with a chiral cyclopentadienyl ligand (Scheme 2). **4-Br** was obtained previously as a side product in the reaction of **2-Br** with an excess of bromine and was characterised only by X-ray crystallography [11].

In the case of X = Cl after 10 days at 80 °C, a different percentage of the products in the mixture was detected: **2-Cl** (13%), **3-Cl** (42%) and **4-Cl** (45%). For X = Br after 2 days at the same temperature a mixture of **2-Br** (7%), **3-Br** (30%) and **4-Br** (63%) was isolated. The complexes **3-Cl**, **3-Br**, **4-Cl** and **4-Br** were isolated from the reaction mixtures and fully characterised by NMR spectroscopy.

NMR data of **4-Cl** and **4-Br** verify a titanium complex with one modified Cp* ligand. The presence of a noncoordinated double bond was confirmed by signals in both ¹H NMR (δ : **4-Cl**: 5.26, 5.27 ppm; **4-Br**: 5.26, 5.29 ppm) and ¹³C NMR spectra (δ : **4-Cl**: 129.75, 131.90 ppm; **4-Br**: 129.74, 131.89 ppm). It is a characteristic feature of this ligand system (also observed for the complexes **2**, **5** and others [5,7]) that the resonances of the two olefinic protons exhibit a very small chemical shift difference.

As described for the bromide congener **4-Br** [11], in the molecular structure of **4-Cl** (Fig. 1) the titanium centre is surrounded by three halogenide atoms which adopt with the η^5 -coordinated modified Cp* ligand a piano-stool like coordination geometry. The cyclooctene unit is oriented away from the metal centre and there is no hint for any interaction of its double bond (C8-C9 1.333(3) Å) with the metal. Complex **4-Cl** crystallises in the centrosymmetric space group $P\overline{1}$, therefore the *R*,*R*/*S*,*S* enantiomers are present in the crystal. As it was already described for other reactions of **1** the chirality (*R*,*R*/*S*,*S*) once defined for the starting complex **1** [5] is preserved.

The reaction of **1** with an excess of Et_3N ·3HF resulted in the formation of the difluoride **2-F** as well as a dimeric anionic heptafluoride complex **5** (Scheme 3).



Scheme 2. Reactions of 1 with an excess of HCl and HBr.



Fig. 1. Molecular structure of **4-Cl** with thermal ellipsoids set at 30% probability. All hydrogen atoms have been omitted for clarity. Important bond lengths [Å] and angles [°]: Ti–Cl1 2.2449(6), Ti–Cl2 2.2446(7), Ti–Cl3 2.2382(7), C1–C5 1.428(3), C5–C6 1.503(3), C6–C7 1.549(3), C7–C8 1.514(3), C8–C9 1.333(3), C9–C10 1.513(3), C10–C11 1.544(3), C1–C11 1.504(3), C11–Ti–Cl2 102.72(3), C11–Ti–Cl3 102.19(3), C5–C6–C7 116.0(2), C6–C7–C8 112.3(2), C7–C8–C9 129.2(2), C8–C9–C10 132.3(2), C9–C10–C11 113.6(2), C10–C11–C1 110.0 (2).

Yellow crystals of **2-F** suitable for an X-ray crystal structure analysis were isolated in 61% yield from *n*-hexane (Fig. 2).

The molecular structure of **2-F** shows a tetrahedral arrangement of one pentamethylcyclopentadienyl and one 3,4,5-trimethylcyclopentadienyl ligand anellated in 1,2 positions with a 3,6-di*tert*-butylcyclooct-4-ene ring and two fluorine ligands at the titanium centre. Altogether it is very similar to that of the congener **2-CI** and **2-Br** [7] as shown in the C–C double bond length of the cyclooctene ring (**2-F**: 1.329(2) Å, **2-CI**: 1.313(6), **2-Br**: 1.318(8) Å) and the bite angle between the functionalised and nonfunctionalised cyclopentadienyl ligands (**2-F**: 139°, **2-CI**: 138°, **2-Br**: 136°). Concerning the NMR data of the Cp* and the modified cyclopentadienyl ligand in **2-F** in comparison to **2-Br** and **2-CI** there were found also similar ¹H and ¹³C resonances. ¹⁹F NMR show two doublets (74.8 and 73.7 with ²*J*_{F,F} = 27 Hz) close to the value found for related titanocene fluoride complexes [12–15].



Fig. 2. Molecular structure of **2-F** with thermal ellipsoids set at 30% probability. All hydrogen atoms have been omitted for clarity. Important bond lengths [Å] and angles [°]: Ti-F1 1.8596(12), Ti-F2 1.8561(11), C1-C2 1.417(2), C2-C3 1.510(2), C3-C4 1.540(2), C4-C5 1.516(2), C5-C6 1.329(2), C6-C7 1.511(2), C7-C8 1.537(2), C1-C8 1.506(2), F1-Ti-F2 96.81(8), C4-C5-C6 131.30(13) C5-C6-C7 130-31(13), C6-C7-C8 108.80(12).

From the reaction of **1** with an excess of Et₃N·3HF the second product **5** was isolated in 11% yield (Scheme 3). Detailed NMR investigations of **5** were performed and revealed the formation of a dimeric titanium species $[Et_3NH]^+$ [({ $\eta^5-C_5Me_3$ (-CH₂CH(*t*Bu)CH = CHCH(*t*Bu)CH₂-)}Ti)₂F₇]⁻ (**5**) where two Cp'TiF₂ units (Cp' = modified Cp* ligand) are connected by three fluorine bridges. NMR spectra of **5** shows signals of the cation Et₃NH⁺ (¹H NMR: δ 0.70, 2.54, 8.5 ppm; ¹⁵N NMR: δ -326.1 ppm rel. to nitromethane) and of one functionalised cyclopentadienyl ligand, with resonances in good accordance with **2-F**. Moreover ¹⁹F NMR spectroscopy gave additional information about fluorine coordination environment – four different signals were detected: δ -42 (br, 1F), -8 (br, 2F), 82 (br, 2F), 156.2 (2F) which can be assigned to four



Scheme 3. Reaction of 1 with an excess of Et₃N-3HF.

(2 different) terminal and three bridging fluorine atoms (cis/trans position). The broadening of the ¹⁹F NMR resonances at r.t. can be explained by dynamic processes, e.g. by exchange of fluoride ions between bridging and terminal positions or e.g. by assuming a F···H-N hydrogen bond flopping process among various fluorine atoms, which is fast enough to average the multiplet structure of fluorine resonances. Such fluorine bridges are also obtained for the anion in $[Hdmpy]^+$ $[(Cp^*Ti)_2F_7]^-$, which was achieved by the reaction of Cp^*TiF_3 with dmpy 2HF (dmpy = 2,6-dimethylpyridine) [13]. It was characterised by X-ray structural analysis and ¹⁹F NMR investigations, which were performed at different temperatures and revealed similar effects [13-15], as for complex 5. Since the $Ti(n^{5}$ -cyclopentadienyl) moiety is chiral, formation of diastereomers should occur upon dimerisation to 5. This is, however, not perceptible from ¹H and ¹³C NMR spectra but might be obscured by the described dynamic processes.

4. Conclusions

Altogether, reactions of **1** with an excess of HX (X = Cl, Br), resp., Et₃N·3HF follow the same course: the first step is the formation of a titanocene dihalogenide **2** which is unstable towards an excess of the reagent and implying an acidolysis of the Cp* resp. the modified cyclopentadienyl ligand and the complexes **3-Br** and **4-Br**, respectively, **3-Cl** and **4-Cl** were formed. For X = F a complex like **4-F** was not isolated and a stabilisation by fluoride bridges resulted in a dimeric anion (**5**). The formation and cleavage of such fluorine titanium complexes [15–18] were widely investigated with regard to their catalytic performance and in this context, complex **5** exhibits besides the fluorine bridges also a chiral modified cyclopentadienyl ligand – both are interesting features for catalytic applications. Further work is in progress.

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Appendix A. Supplementary material

CCDC 915021 and 915022 contains the supplementary crystallographic data for **2-F** and **4-CI**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03.025.

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