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Articles

Carboxylates of Organotitanium Fluorides: Preparation of Cp− and Cp*−Fluorotitanium Trifluoroacetates and Pentafluorobenzoates

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The reactions of Cp^*TiF_3 and $CpTiF_3$ with $Me_3SiOCOCF_3$ and $Me_3SiOCOC_6F_5$, respectively lead under elimination of Me_3SiF in good yields to the dimers $(Cp^*TiF_2OCOCF_3)_2$ (**1**), $(Cp^*TiF_2OCOC_6F_5)_2$ (**2**), $(CpTiF_2OCOCF_3)_2$ (**3**), and $(Cp^*TiF(OCOCF_3)_2)_2$ (**4**). The structures of **1** and **2** have been determined by X-ray crystallography; both compounds crystallize in the triclinic space group $P\bar{1}$. These are the first examples of dimeric Cp− and Cp*−titanium carboxylates. The Ti atoms are bridged by two carboxylate groups and two F atoms which have nonequal distances to the Ti atoms. The dimeric structures exist also in solution. **1** and **2** show in the ^{19}F NMR the signals of magnetically nonequivalent bridging and terminal F atoms.

Introduction

For a long time there has been an interest in Cp− and Cp*−titanium compounds (Cp = H_5C_5, Cp* = Me_5C_5). They are important not only as catalysts for polymerization reactions[1] and organic syntheses[2] but in the last few years also as antitumor agents.[3] The chemistry of Cp− and Cp*−titanium fluorides was less known[4] until Me_3SnF was found as fluorinating reagent for a facile preparation of these compounds.[5] We were interested in the reactivity of $CpTiF_3$ and Cp^*TiF_3 with carboxylates as potentially bidentate ligands. Carboxylates of titanium alkoxides are used as reagents for cleavage of 2,3-epoxy alcohols.[6] Some titanium carboxylates containing the Cp or Cp* ligand are known, most of them based on Cp_2TiCl_2[7] and Cp^*TiMe_3[8] or compounds with carboxylates as a bridging group for titanium−chromium complexes.[9] All structurally characterized compounds were found to be monomeric; only a few contain halogen atoms like Br and Cl. We intended to prepare organotitanium carboxylates containing titanium−fluorine bonds.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen by employing either Schlenk line techniques or an inert atmosphere glovebox. Solvents were freshly distilled from sodium and degassed prior to use. $CDCl_3$ was distilled over calcium dihydride. Cp^*TiF_3, $CpTiF_3$,[5] $Me_3SiOCOCF_3$,[10] and $Me_3SiOCOC_6F_5$[11] were prepared according to published methods. ^1H and ^{19}F NMR spectra were recorded on a Bruker AM 250 instrument. Chemical shifts are reported relative to $SiMe_4$ for ^1H spectra and $CFCl_3$ for ^{19}F spectra. AA′ and XX′ stand for parts of a spectrum of an AA′XX′-spin system. Mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. IR spectra were obtained on a Bio-Rad FTS 7 spectrophotometer as Kel-F mulls between KBr plates in the range of 4000 to 1350 cm^{-1}. Elemental analyses were performed by Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen and by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Preparation of $(Cp^*TiF_2OCOCF_3)_2$ (1). Cp^*TiF_3 (1.50 g, 6.2 mmol) was dissolved in toluene (100 mL). A solution of $Me_3SiOCOCF_3$ (1.16 g, 6.2 mmol) in toluene (30 mL) was slowly added and the red solution stirred for 14 h. All volatile materials were removed under reduced pressure, and the remaining solid was washed with hexane to give **1** (1.91 g, 91%) as a red solid (mp 219 °C). Crystals for X-ray measurements were obtained by redissolving **1** in dimethoxyethane and cooling the solution to 5 °C for 5 days. ^1H NMR (C_6D_6): δ 1.81 (s, Cp*−H). ^{19}F NMR (C_6D_6): δ −74.62 (s, 6 F, CF_3), −20.19 (AA′; $^2J_{FF}$ = 118 Hz, $^2J_{FF}$ = 47 Hz, 2 F), 244.21 (XX′; $^2J_{FF}$ = 118 Hz, $^2J_{FF}$ = 47 Hz, 2 F). MS (EI): *m/e* (%) 514 [M − Cp* − F] (1), 409 $[Cp^*Ti(OCOCF_3)_2]$ (5), 315 [M/2 − F] (12), 221 [M/2 − $OCOCF_3$] (21), 135 [Cp*] (100). IR: 2916.3 (m), 2854.9 (m), 1642.8 (s), 1488.4 (m), 1462.3 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{30}F_{10}O_4Ti_2$ (668.28): C, 43.13; H, 4.52; F, 28.42. Found: C, 42.8; H, 4.6; F, 27.5.

Preparation of $(Cp^*TiF_2OCOC_6F_5)_2$ (2). To a solution of Cp^*TiF_3 (1.50 g, 6.2 mmol) in toluene (80 mL) was slowly added a solution of $Me_3SiOCOC_6F_5$ (1.78 g, 6.2 mmol) in toluene (30 mL). The reaction mixture was stirred for 24 h, and volatile materials were removed under reduced pressure. The residue was washed with hexane to give **2** as a

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	4370(1)	8256(1)	6013(1)	17(1)
O(1)	2233(2)	9761(2)	6079(2)	22(1)
O(2)	6883(2)	7782(2)	5135(2)	23(1)
F(1)	5102(1)	10182(1)	6154(1)	19(1)
F(2)	3871(2)	7129(2)	4935(1)	26(1)
F(3)	9963(2)	6841(2)	5143(2)	72(1)
F(4)	9961(2)	7424(3)	2818(2)	67(1)
F(5)	10757(2)	9040(2)	3613(2)	50(1)
C(1)	2454(3)	7039(3)	8379(2)	24(1)
C(2)	3405(3)	7980(3)	8690(2)	24(1)
C(3)	5015(3)	7285(2)	8369(2)	24(1)
C(4)	5060(3)	5915(3)	7861(2)	23(1)
C(5)	3470(3)	5762(3)	7874(2)	22(1)
C(6)	7915(2)	8764(3)	4408(2)	21(1)
C(7)	9679(3)	800(3)	4009(3)	30(1)
C(1*)	662(3)	7268(3)	8642(3)	36(1)
C(2*)	2807(3)	9420(3)	9307(3)	35(1)
C(3*)	6415(3)	7858(3)	8585(3)	35(1)
C(4*)	6494(3)	4758(3)	7490(3)	32(1)
C(5*)	2955(3)	4495(3)	7427(3)	31(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

red solid (2.42 g, 90%), mp 196 °C. Crystals for X-ray measurements were obtained by redissolving **2** in dioxane at 50 °C and cooling the mixture slowly to room temperature. ^{1}H NMR ($CDCl_3$): δ 1.94, 2.13 (s, Cp*−H). ^{19}F NMR ($CDCl_3$): δ −161.6, −160.5 (t, $^3J_{FF} = 24$ Hz, 4 F, C_6F_5 m-F); −151.5, −150.4, (t, $^3J_{FF} = 24$ Hz, 2 F, C_6F_5 *p*-F); −139.9, −138.8 (d, $^3J_{FF} = 24$ Hz, 4 F, C_6F_5 o-F); −19.85 , −36.49 (AA′, $^2J_{FF} = 120$ Hz, $^2J_{FF} = 50$ Hz, 2 F); 201.04, 221.19 (XX′, $^2J_{FF} =$ 120 Hz, $^2J_{FF} = 50$ Hz, 2 F). ^{1}H NMR (70 °C, C_6D_6): δ 1.93, 2.10 (s). ^{19}F NMR (70 °C, C_6D_6): δ −163.2 −161.7, −160.9 (s); −152.0, −151.3, −148.8 (s); −140.1, −138.8, 137.5 (s); −38,6 (m); −24.7 (m); −17.9 (AA′); 151.3 (s); 240.2 (XX′); 245.6 (m); 254.1 (m). MS (EI): *m/e* (%) 605 [$Cp^*Ti(OCOC_6F_5)_2$] (7), 432 [M/2] (2), 413 [M/2 − F] (7), 135 [Cp*] (100). IR: 2962.5 (m), 2921.3 (m), 2857.8 (m), 1651.8 (s), 1596.2 (s), 1525.5 (m), 1491.6 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{30}F_{14}O_4Ti_2$ (864.38): C, 47.24; H, 3.50; F, 30.77. Found: C, 46.7; H, 3.7; F, 29.8.

Preparation of ($CpTiF_2OCOCF_3)_2$ (3). A solution of $Me_3SiOCOCF_3$ (0.56 g, 3.0 mmol) in toluene (15 mL) was added to $CpTiF_3$ (0.51 g, 3.0 mmol) in toluene (40 mL). The orange solution was stirred for 48 h, and the solvent was removed under reduced pressure (until 10 mL). Cooling of the residue at −50 °C for 3 days gave **3** as an orange solid (0.62 g, 78%), decomposing at 184 °C. ^{1}H NMR ($CDCl_3$): δ 6.77 (s, Cp-H). ^{19}F NMR ($CDCl_3$): δ −75.95 (s, 6 F, CF_3), −7.42 (t, $^2J_{FF} = 82$ Hz, 2 F) 240.42 (t, $^2J_{FF} = 82$ Hz, 2 F). MS (EI): m/e (%) 264 [M/2] (3), 245 [M/2 − F] (3), 151 [M/2 − $OCOCF_3$] (42), 65 [Cp] (100). IR: 3138.5 (m), 3134.6 (m), 2961.7 (m), 1642.8 (s), 1643.6 (s), 1439.0 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{10}F_{10}O_4Ti_2$ (528.02): C, 31.85; H, 1.91; F, 35.98. Found: C, 31.7; H, 1.9; F, 36.0.

Preparation of $Cp^*TiF(OCOCF_3)_2$ (4). Cp^*TiF_3 (0.50 g, 2.1 mmol) was dissolved in toluene (50 mL). A solution of $Me_3SiOCOCF_3$ (0.78 g, 4.2 mmol) in toluene (20 mL) was added, and the reaction mixture was stirred for 24 h. The solution was concentrated under reduced pressure to 5 mL. Filtration gave **4** as a violet solid (0.42 g, 47%), mp 295 °C. ^{1}H NMR ($CDCl_3$) δ 2.03 (s, Cp*−H). ^{19}F NMR ($CDCl_3$): δ −75.61 (s, 6 F, CF_3); −75.25 (s, 6 F, CF_3); −34.69 (s, 2 F). MS (EI): *m/z* (%) 608 [M − Cp* − $OCOCF_3$] (1), 533 [$(Cp^*TiF)_2O(OCOCF_3)$] (7), 409 [M/2 − F] (6), 135 [Cp*] (100). IR: 2926.8 (m) , 1733.7 (s) 1648.9 (s), 1470.1 (m), 1380.7 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{30}F_{14}O_8Ti_2$ (856.32): C, 39.27; H, 3.53; F, 31.06. Found: C, 39.1; H, 3.5; F, 31.7.

Crystal Structure Solution and Refinement. Diffraction data were collected on a Siemens-Stoe AED four-circle diffractometer at 153 K with Mo Kα radiation ($\lambda = 71.073$ pm). Both structures were solved by direct methods with SHELX-86[12] and refined by full-matrix least squares on F^2 (SHELXL-93[13]). Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted in calculated positions. Atomic coordinates of compounds **1** and **2** are given in Tables 1 and 2. Selected bond lengths (pm) and angles (deg) are given in Tables 3 and 4.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **2**

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	3893(1)	9673(1)	9411(1)	17(1)
O(1)	3622(2)	8849(2)	11393(2)	22(1)
O(2)	4695(2)	10899(2)	7807(2)	22(1)
F(1)	4161(2)	11079(2)	10168(1)	20(1)
F(2)	2172(2)	11005(2)	9295(2)	27(1)
C(1)	3576(3)	8989(3)	7643(3)	23(1)
C(2)	4873(3)	8064(3)	8119(3)	21(1)
C(3)	4637(3)	7271(3)	9398(3)	20(1)
C(4)	3194(3)	7704(3)	9695(3)	21(1)
C(5)	2536(3)	8738(3)	8607(3)	22(1)
C(1*)	3319(4)	10004(3)	6330(3)	33(1)
C(2*)	6246(3)	7901(3)	7376(3)	28(1)
C(3*)	5713(3)	6178(3)	10278(3)	25(1)
C(4*)	2474(3)	7070(3)	10915(3)	28(1)
C(5*)	1029(3)	9438(3)	8471(3)	33(1)
C(6)	4293(3)	8730(3)	12281(3)	20(1)
C(11)	3818(3)	8051(3)	13630(3)	21(1)
C(12)	2437(3)	8437(3)	14050(3)	26(1)
C(13)	1982(3)	7856(3)	15283(3)	30(1)
C(14)	2921(4)	6840(3)	16132(3)	30(1)
C(15)	4297(3)	6425(3)	15747(3)	30(1)
C(16)	4739(3)	7033(3)	14510(3)	25(1)
F(12)	1497(2)	9448(2)	13256(2)	38(1)
F(13)	650(2)	8301(2)	15674(2)	43(1)
F(14)	2498(2)	6259(2)	17333(2)	45(1)
F(15)	5216(2)	5424(2)	16575(2)	45(1)
F(16)	6088(2)	6575(2)	14175(2)	38(1)
O(21)	786(2)	4623(2)	11060(2)	39(1)
C(22)	681(4)	3584(3)	10568(3)	37(1)
C(23)	438(3)	4158(3)	9164(3)	34(1)
O(31)	9223(3)	4229(3)	4940(3)	65(1)
C(32)	10567(5)	3987(5)	4355(5)	65(1)
C(33)	9044(5)	4759(5)	5984(4)	61(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for **1**

Ti(1)−F(1a)	208.3(1)	Ti(1)−O(1)	210.1(2)
Ti(1)−F(1)	197.6(1)	Ti(1)−O(2)	210.8(2)
Ti(1)−F(2)	182.2(1)	O(2)−C(6)	125.0(2)
Ti(1)−Ti(1a)	327.6(1)	O(1a)−C(6)	124.7(3)
F(2)−Ti(1)−F(1)	151.36(6)	F(2)−Ti(1)−O(1)	92.35(6)
F(2)−Ti(1)−F(1a)	78.96(5)	F(2)−Ti(1)−O(2)	93.95(6)
O(1)−Ti(1)−O(2)	151.63(6)	Ti(1)−O(1)−C(6a)	128.2(1)
Ti(1)−F(1)−Ti(1a)	107.59(6)	Ti(1)−O(2)−C(6)	127.7(1)
F(1)−Ti(1)−F(1a)	72.41(6)	O(1a)−C(6)−O(2)	131.2(2)

Crystal Data for ($Cp^*TiF_2OCOCF_3)_2$: $C_{24}H_{30}F_{10}O_4Ti_2$, M = 668.28, space group triclinic $P\bar{1}$, $a = 878.4(2)$ pm, $b = 884.4(2)$ pm, $c = 960.9(2)$ pm, $\alpha = 72.64(2)°$, $\beta = 71.090(10)°$, $\gamma = 80.080(10)$, $V = 0.6717(3)$ nm^3, $Z = 1$, ρ(calcd) = 1.652 Mg/m^3, $\mu = 0.694$ mm^{-1}, $F(000) = 340$, crystal size (mm) 0.70 × 0.50 × 0.20, 4722 collected reflections, 2366 independent reflections, goodness of fit 1.059, refinement converged with R1 = 0.0375 and wR2 = 0.1006 [$I > 2\sigma(I)$], and for all data R1 = 0.0388 and wR2 = 0.1023 (maximum/minimum rest electron density +367/−576 $e \cdot nm^{-3}$).

Crystal Data for ($Cp^*TiF_2OCOC_6F_5)_2 \cdot 2$ Dioxane: $C_{42}H_{46}F_{14}O_8Ti_2$, M = 1040.59, space group triclinic $P\bar{1}$, $a = 1059.8(3)$ pm, $b = 1077.1(3)$ pm, $c = 1097.9(3)$ pm, $\alpha = 71.23(2)°$, $\beta = 79.280(10)°$, $\gamma = 67.210(10)$, $V = 1.0913(5)$ nm^3, $Z = 1$, ρ(calcd) = 1.583 Mg/m^3, $\mu = 0.478$ mm^{-1}, $F(000) = 532$, crystal size (mm) 0.50 × 0.50 × 0.30,

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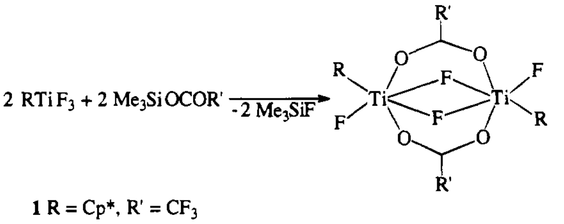
Table 4. Selected Bond Lengths (pm) and Angles (deg) for **2**

Ti(1)−F(1)	207.2(2)	Ti(1)−O(1)	208.0(2)
Ti(1)−F(1a)	198.5(2)	Ti(1)−O(2)	209.3(2)
Ti(1)−F(2)	182.9(2)	O(1)−C(6)	125.6(3)
O(2a)−C(6)	126.1(4)	Ti(1)−Ti(1a)	326.6(1)
F(2)−Ti(1)−F(1)	79.83(7)	F(2)−Ti(1)−O(1)	93.75(8)
F(2)−Ti(1)−F(1a)	152.62(7)	F(2)−Ti(1)−O(2)	92.73(8)
O(1)−Ti(1)−O(2)	151.36(8)	Ti(1)−O(1)−C(6)	129.6(2)
Ti(1)−F(1)−Ti(1a)	107.18(7)	Ti(1)−O(2)−C(6a)	128.8(2)
F(1)−Ti(1)−F(1a)	72.82(7)	O(1)−C(6)−O(2a)	128.5(3)

4163 collected reflections, 2852 independent reflections, goodness of fit 1.033, refinement converged with R1 = 0.0423 and wR2 = 0.1116 [$I > 2\sigma(I)$], and for all data R1 = 0.0448 and wR2 = 0.1163 (maximum/minimum rest electron density +429/-624 e·nm^{-3}).

Results and Discussion

Treatment of Cp^*TiF_3 and $CpTiF_3$ with the trimethylsilyl esters of fluorinated acids in the ratio of 1:1 in toluene gives the dimers $(Cp^*TiF_2OCOCF_3)_2$ (**1**), $(Cp^*TiF_2OCOC_6F_5)_2$ (**2**), and $(CpTiF_2OCOCF_3)_2$ (**3**) (eq 1). The X-ray structures of **1** and **2** and the ^{19}F NMR spectra show the dimeric nature of the molecules with bridging and terminal F atoms. Compounds **1** and **2** show the signals of an AA′XX′-system with the two bridging F atoms and the terminal F atoms, but from the expected 20 signals, only 12 are observed.[14] The F atoms are not magnetically equivalent in solution, consistent with a structure having unsymmetrically bridging fluorine atoms comparable to the solid state structure. The ^1H and ^{19}F NMR spectra of **2** show twice the number of signals necessary for a dimeric species. An explanation is the existence of an equilibrium of isomers of **2** in solution, having bridging (**2a**) and bidentate carboxylate groups on both Ti atoms (**2b**) (eq 2). The bidentate carboxylate bonding mode of **2b** is known in $Cp^*Ti(OCOC_6H_5)_3$.[8]

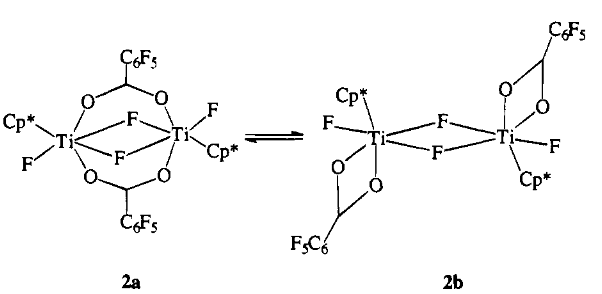


(1)

1 R = Cp*, R' = CF$_3$

2 R = Cp*, R' = C$_6$F$_5$

3 R = Cp, R' = CF$_3$



(2)

2a **2b**

However, even at 70 °C the NMR spectra of **2** in solution are not showing a temperature depending equilibrium. Obviously the two isomers are stable under those conditions due to the strong Ti−O bonds in **2a** and **2b**.

On the other hand compound **3** gives only two triplets in the ^{19}F NMR spectrum for the titaninium bonded F atoms. This different behaviour can be explained by symmetrically bridging F atoms in solution at room temperature. Due to the ^{19}F NMR spectrum the structure of **3** is probably similar to those found in **1** and **2**.

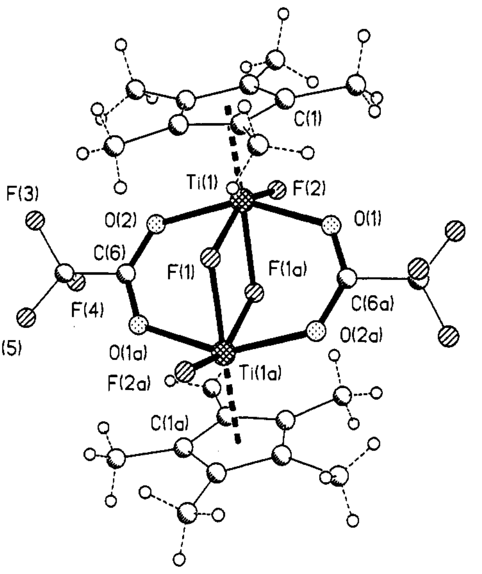
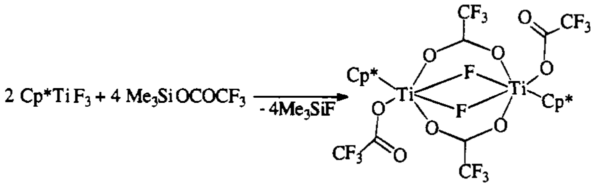


Figure 1. Molecular structure of $(Cp^*TiF_2OCOCF_3)_2$ (**1**).

Treatment of Cp^*TiF_3 with 2 equiv of trimethylsilyl trifluoroacetate gives $(Cp^*TiF(OCOCF_3)_2)_2$ (**4**). The ^{19}F NMR spectrum shows only one singlet for the titanium bonded F atoms and two singlets for the CF_3 groups indicating two different carboxylate ligands. The IR spectrum of **4** gives the asymmetrical carboxylate vibrations (ν_{asym}) at 1734 cm^{-1} and 1649 cm^{-1} and the symmetrical vibration (ν_{sym}) at 1381 cm^{-1}, respectively. The ν_{asym} vibration (1734 cm^{-1}) and the separation between ν_{asym} and ν_{sym} (357 cm^{-1}) are in the range of unidentate trifluoroacetates. The second ν_{asym} (1649 cm^{-1}) is in the range found for bridging carboxylates.[15] For **1**, having only bridging trifluoroacetate groups, ν_{asym} is found at 1643 cm^{-1}. Compound **4** contains bridging and unidentate carboxylate groups, a proposal for the structure is given in eq 3.



(3)

4

X-ray structure of 1 and 2. Compounds **1** and **2** crystallize in the triclinic space group $P\bar{1}$. In contrast to most structurally known Cp− and Cp*−titanium carboxylates **1** and **2** are dimers of two molecules of Cp^*TiF_2OCOR bridged by two F atoms and the two carboxylate groups.

The unit cell of **2** contains 2 molecules of dioxane; Figure 2 shows **2** without these solvent molecules. Each of the Ti atoms has a sixfold coordination sphere. The C−O distances are equal for both O atoms of the carboxylate groups with O−C−O angles of 131.1(2)° for **1** and 128.5(3)° for **2**, respectively. The Ti−O distances are in the range of the monomeric $Cp^*Ti(OCOC_6H_5)_3$[8] with bidentate carboxylate groups (209.5−220.6 pm) and much larger than for the titanium carboxylates with monodentate carboxylate groups $Cp_2TiMe(OCOC_6H_5)Cr(CO)_3$[9] (194.0 pm)

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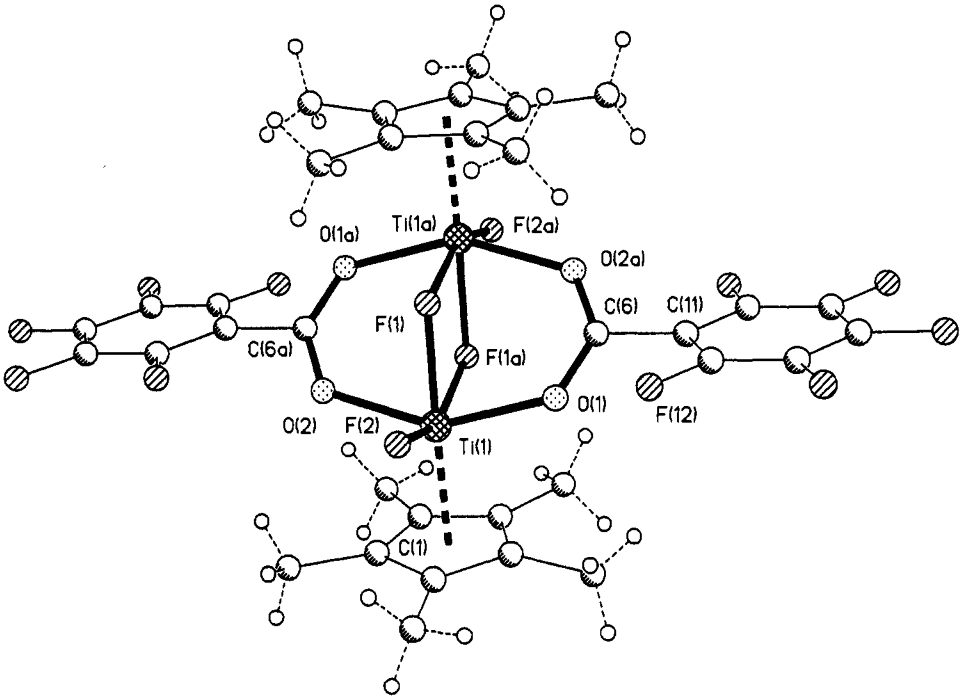

Figure 2. Molecular structure of $(\mathrm{Cp^*TiF_2OCOC_6F_5})_2$ (**2**).

or $\mathrm{Cp_2Ti(OCOC_6H_5)_2}$[16] (194.6 pm). The Ti−F distances for the two bridging F atoms are different (about 10 pm). For the dimeric $(\mathrm{Cp^*TiF_3})_2\cdot 2\mathrm{AsF_3}$[4] these Ti−F distances are nearly equal (200.2 and 202.1 pm), for $(\mathrm{Cp^*TiF_2(O{=}C(OEt)C(C_6H_5){=}C(OEt){-}O)})_2$[4] a much greater difference (23 pm) is found. The Ti−F distances for the terminal F atoms are in the usual range found for other Cp*−titanium fluorides.[4,17]

Conclusions. The reactions of either titanium fluorides or titanium alkyls with carboxylates differ. With the fluorides the facile elimination of $\mathrm{Me_3SiF}$ leads to dimeric structures with carboxylate groups and F atoms as bridging units.

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Supporting Information Available: Listings of crystal data, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles and ORTEP drawings showing an alternate view of **1** and the complete molecule of **2** with the solvent molecules (14 pages). Ordering information is given on any current masthead page.

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