

Synthesis and structural characterization of sulfonates, phosphinates and carboxylates of organometallic Group 4 metal fluorides¹

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Abstract

Reaction of $[\text{Cp}^* \text{TiF}_3]$ ($\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$) with $\text{Me}_3\text{SiOSO}_2\text{-}p\text{-C}_6\text{H}_4\text{CH}_3$, $\text{Me}_3\text{SiOPh}_2$ and $1,2\text{-(Me}_3\text{SiOCO)}_2\text{C}_6\text{H}_4$ yields the dinuclear complexes $[\{\text{Cp}^* \text{TiF}(\mu\text{-F})(\mu\text{-OSO}_2\text{-}p\text{-C}_6\text{H}_4\text{CH}_3)\}_2]$ (**1**), $[\{\text{Cp}^* \text{TiF}(\mu\text{-F})(\mu\text{-OPh}_2)\}_2]$ (**2**) and $[\{\text{Cp}^* \text{TiF}(\mu\text{-F})(\mu\text{-OCO-}o\text{-C}_6\text{H}_4\text{CO}_2\text{SiMe}_3)\}_2]$ (**3**). The molecular structures of **1** and **2** have been determined by single-crystal X-ray analysis. In complexes **1–3**, the two titanium atoms are connected by bridging fluorine atoms as well as bridging sulfonate, phosphinate and carboxylate groups respectively. Each titanium atom is also bonded to a terminal fluorine atom. Reaction of $[\text{Cp}_2^* \text{ZrF}_2]$ with $1,2\text{-(Me}_3\text{SiOCO)}_2\text{C}_6\text{H}_4$ leads to the mononuclear pentacoordinate 18-electron species $[\text{Cp}_2^* \text{ZrF}(\mu\text{-OCO-}o\text{-C}_6\text{H}_4\text{CO}_2\text{SiMe}_3)]$ (**4**) and its structure was determined by X-ray crystallographic methods. © 1998 Elsevier Science S.A.

Keywords: Group 4; Halides; Transition metals; Titanium; Zirconium

1. Introduction

Contrary to the large amount of information regarding organometallic Group 4 chlorides, relatively little is known about the corresponding fluorides. The main reasons for this have been the comparative difficulty in preparing the fluoride compounds or separating them from the fluorinating reagent [1–3]. We have recently reported on the use of trimethyltin fluoride as a fluorinating agent in the preparation of a wide range of cyclopentadienyl-substituted Group 4 fluorides from the corresponding chloro complexes [4], and thus, detailed investigations into the chemistry of organometallic Group 4 fluorides have now been undertaken [5–10]. The unique reactivity and coordination behaviour of these fluorides allow many interesting and previously unobtainable compounds to be isolated. In many of these cases, the driving force in the reactions is the

formation of trimethylsilyl fluoride as by-product [7,8,10]. By using trimethylsilyl esters of sulfonic and phosphinic acids in combination with an organometallic Group 4 metal fluoride, such as $[\text{Cp}^* \text{TiF}_3]$ ($\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$), it may be possible to generate discrete ionic species of the form $[\text{Cp}^* \text{TiF}_2]^+ [\text{RSO}_3]^-$ or $[\text{Cp}^* \text{TiF}_2]^+ [\text{R}_2\text{PO}_2]^-$, with the elimination of Me_3SiF . A similar Group 4 ionic species with a sulfonate counterion was found when using the trifluoromethanesulfonate ligand, i.e. $[\text{Cp}_2\text{Zr}(\text{H}_2\text{O})_3]^{2+} [\text{CF}_3\text{SO}_3]_2^-$ ($\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$) [11]. Cationic organometallic species have been intensively researched, especially with regard to Ziegler–Natta polymerization catalysis [12]. It has been established that the active species found in the $[\text{Cp}_2\text{ZrX}_2]/\text{MAO}$ ($\text{X} = \text{Cl}$ or Me ; $\text{MAO} =$ methylalumoxane) catalytic system is the cation $[\text{Cp}_2\text{ZrMe}]^+$ [13,14].

Here we describe the reactions of organometallic Group 4 fluorides with trimethylsilyl esters of sulfonic, phosphinic and carboxylic acids, and report on molecular structures which gives an insight on the coordination behaviour of the fluoride as well as the ancillary ligands.

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¹ Dedicated to Professor Ken Wade on the occasion of his 65th birthday and in recognition of his outstanding contributions to inorganic and organometallic chemistry.

2. Results and discussion

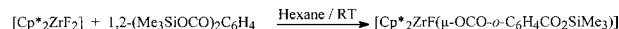
2.1. Synthesis and characterization of complexes 1–4

Recent studies from our laboratory have shown that $[\text{Cp}^* \text{TiF}_3]$ ($\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$) reacts with trimethylsilyl esters of carboxylic acids to form dinuclear complexes of the type $[\{\text{Cp}^* \text{TiF}_2(\text{OCOR})\}_2]$ [15]. Complexes **1–3** are prepared in essentially the same way, i.e. via reaction of $[\text{Cp}^* \text{TiF}_3]$ and a trimethylsilyl ester of the relevant acid (Scheme 1).

Since there is no reaction when $[\text{Cp}^* \text{TiF}_3]$ is replaced by $[\text{Cp}^* \text{TiCl}_3]$ it may be surmised that the formation of Me_3SiF acts as a driving force in these reactions.

All compounds were obtained as crystalline materials and were fully characterized by their spectral data and by elemental analyses. Both ^1H and ^{19}F NMR spectra of complexes **1–3** (in CDCl_3) show the presence of isomers in solution. For example, two sets of Cp^* resonances (2.22 and 2.25 ppm for **1**, 2.14 and 2.15 ppm for **2** and 2.16 and 2.17 ppm for **3**), and of *p*-methyl groups in the case of **1** (2.23 and 2.28 ppm), in 3:1 relative intensity are evident in the respective ^1H NMR spectra. The complex ^{19}F NMR spectra of **1–3** show bridging and terminal fluorine atoms. The multiplets of the terminal fluorine atoms appear at 212.5 ppm for **1**, 170.3 ppm for **2** and 174.1 ppm for **3**. For the bridging fluorine atoms, multiplets are observed at -15.9 and -18.5 ppm (compound **1**), -29.5 and -35.1 ppm (compound **2**) and -4.8 and -10.5 ppm (compound **3**), indicating that they are magnetically non-equivalent. Further signals in the ^{19}F NMR spectra, probably due to isomerization processes, could not be assigned clearly. A ^{31}P NMR spectrum of **2** was also obtained, showing a doublet at 35.1 ppm and a multiplet at 31.9 ppm.

Complex **4** was characterized by infrared and ^1H and ^{19}F NMR spectroscopy as well as mass spectrometry (EI). There is a singlet at 34.3 ppm in the ^{19}F NMR spectrum of **4**, while the ^1H NMR spectrum indicated



4

Scheme 2.

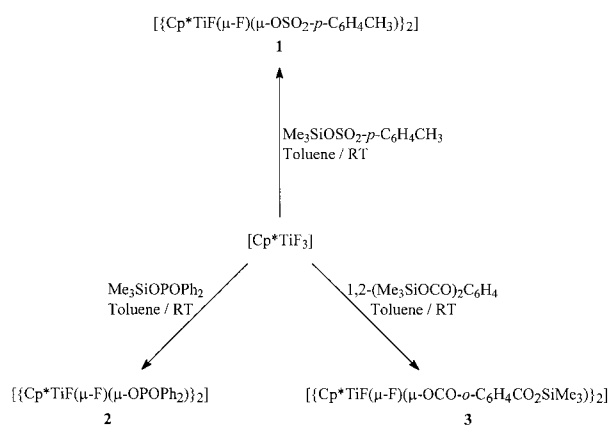
the retention of one trimethylsilyl ester group in the complex, with a singlet for SiMe_3 appearing at 0.53 ppm.

Reaction of $[\text{Cp}^*_2\text{ZrF}_2]$ with $1,2\text{-(Me}_3\text{SiOCO)}_2\text{C}_6\text{H}_4$ could, in theory, yield a polynuclear dicarboxylate complex, where the carboxylate groups would act as (2 + 1)-dentate ligands, such that each zirconium atom has three ligating oxygen atoms [16,17]. However, this is not the case. Instead, only one carboxylate group chelates to the zirconium centre leaving a terminal fluorine atom still bonded to zirconium (Scheme 2). The probable reason for this is the steric crowding around the central zirconium atom. Since the carboxylate groups are in mutual *ortho* positions, it would be necessary for two bulky Cp^*_2Zr units to be very close to one another to facilitate (2 + 1)-dentate dicarboxylate ligation. Therefore, only one trimethylsilyl ester group may react with the fluorine attached to zirconium to form the chelating carboxylate, while the second fluorine remains unreacted.

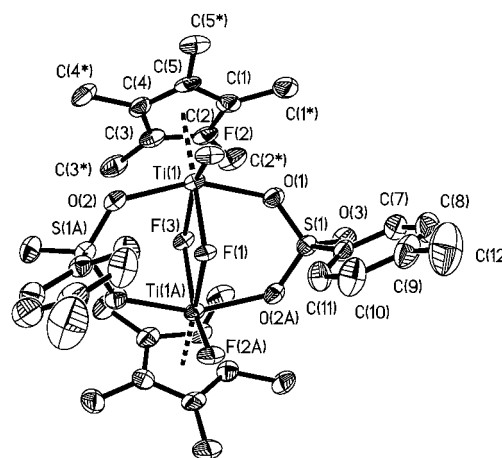
In terms of reactivity, complex **4** proved to be relatively inert and stable towards air and water. Similar poor reactivity was observed for other Group 4 dicarboxylates with a formal 18-electron configuration [17,18], due to the increased difficulty in nucleophilic substitutions at the metal centre.

2.2. Molecular structures of 1, 2 and 4

The molecular structures of **1** and **2** were determined by X-ray crystallography and are depicted in Figs. 1 and 2, together with the atom-labelling scheme. Selected bond distances and angles are listed in Table 1. Compounds **1** and **2** have no ionic character, but both are



Scheme 1.

Fig. 1. Molecular structure of compound **1**. Hydrogen atoms are omitted for clarity.

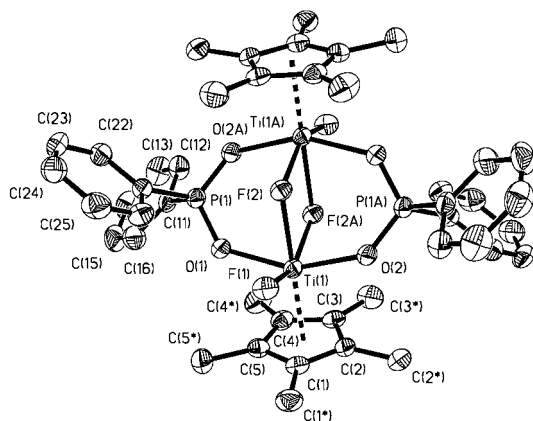


Fig. 2. Molecular structure of compound **2**. Hydrogen atoms are omitted for clarity.

covalent dinuclear complexes with the titanium atoms bridged by fluorine atoms as well as sulfonate (in the case of **1**) and phosphinate groups (in **2**). However, both compounds differ in their exact geometry. While the Cp* ligands in **1** adopt a mutual *cis* arrangement, the opposite is found in **2**. This *trans* arrangement in **2** is similar to that found in previously studied organotitanium fluoro-carboxylates [15]. Curiously, **1** is more symmetrical than **2**. For instance, within the central Ti₂F₂ rhomboid of **1** all Ti–F distances are almost identical (Ti(1)–F(1) 2.022(3) Å and Ti(1)–F(3) 2.042(3) Å) as are the angles at the fluorine atoms (Ti(1)–F(1)–Ti(1a) 109.6(2)° and Ti(1)–F(2)–Ti(1a) 108.0(2)°). In **2**, however, there is a lesser degree of symmetry indicated by the differences in bond lengths within the Ti₂F₂ rhomboid (Ti(1)–F(2a) 1.961(2) Å and Ti(1)–F(2) 2.227(2) Å). The large difference between

Table 1
Bond distances (Å) and angles (deg) for **1** and **2**

1		2	
Ti(1)–F(1)	2.022(3)	Ti(1)–F(1)	1.848(2)
Ti(1)–F(2)	1.827(4)	Ti(1)–F(2)	2.227(2)
Ti(1)–F(3)	2.042(3)	Ti(1)–F(2a)	1.961(2)
Ti(1)–O(1)	2.070(5)	Ti(1)–O(1)	2.040(2)
Ti(1)–O(2)	2.094(5)	Ti(1)–O(2)	2.036(2)
S(1)–O(1)	1.484(5)	P(1)–C(11)	1.801(4)
S(1)–O(2a)	1.478(5)	P(1)–O(1)	1.509(3)
S(1)–O(3)	1.429(5)	P(1)–O(2a)	1.516(3)
S(1)–C(6)	1.762(7)		
Ti(1)–F(1)–Ti(1a)	109.6(2)	Ti(1)–F(2)–Ti(1a)	108.97(8)
Ti(1)–F(3)–Ti(1a)	108.2(2)	Ti(1)–F(2a)–Ti(1a)	109.41(8)
F(3)–Ti(1)–F(1)	71.2(2)	F(2)–Ti(1)–F(2a)	71.03(8)
F(2)–Ti(1)–O(1)	92.9(2)	F(2)–Ti(1a)–F(2a)	70.59(8)
F(2)–Ti(1)–O(2)	89.7(2)	F(1)–Ti(1)–O(1)	90.46(10)
O(1)–Ti(1)–O(2)	154.8(2)	F(1)–Ti(1)–O(2)	92.13(10)
O(3)–S(1)–O(1)	112.0(3)	O(1)–Ti(1)–O(2)	155.13(10)
O(3)–S(1)–C(6)	108.5(3)	O(1)–P(1)–O(2a)	116.07(13)
O(1)–S(1)–O(2a)	111.5(3)	C(11)–P(1)–C(21)	105.2(2)
		O(1)–P(1)–C(11)	111.0(2)

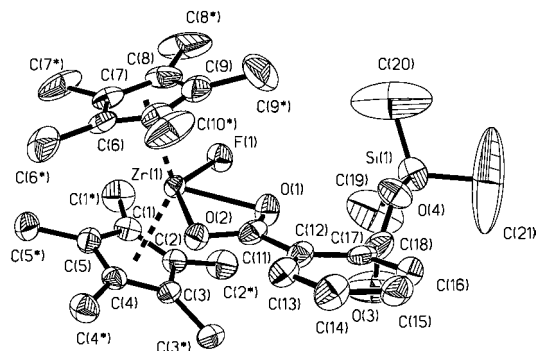


Fig. 3. Molecular structure of compound **4**. Hydrogen atoms are omitted for clarity.

the bridging Ti–F distances in **2** is surprising but a similar arrangement exists in $[(Cp^*TiF_2(detphmal))_2]$ (detphmal = diethylphenylmalonate) where the bridging Ti–F distances are 1.940(2) and 2.170(3) Å [2]. The Ti–F distances for the terminal fluorine atoms in **1** and **2** are similar (1.827(4) Å in **1** and 1.848(2) Å in **2**) and these are in the usual range found for Cp*Ti-fluoride complexes [2,15,19].

Relatively little structural information is known regarding early transition metal sulfonates or phosphinates and, to the best of our knowledge, compounds **1** and **2** represent the first structurally characterized organotitanium sulfonate (other than trifluoromethanesulfonate organotitanium trifluoromethanesulfonates see Ref. [20]) and phosphinate respectively. The sulfonate groups in **1** are tetrahedral with typical S–O and S–C bond distances [21]. As expected, the S–O(bonded) distances are longer than the S–O(free) ones. Similarly, the phosphinato groups in **2** are also tetrahedral and the P–O and P–C bond distances are in close agreement with those of other diphenylphosphinate complexes [22].

The molecular structure of **4** is shown in Fig. 3 and selected bond distances and angles are collated in Table 2. The central zirconium atom is pentacoordinate, being

Table 2
Bond distances (Å) and angles (deg) for **4**

Zr(1)–F(1)	1.976(4)
Zr(1)–O(1)	2.278(5)
Zr(1)–O(2)	2.316(4)
O(1)–C(11)	1.260(9)
O(2)–C(11)	1.281(8)
Si(1)–O(4)	1.700(6)
O(4)–C(18)	1.325(10)
F(1)–Zr(1)–O(1)	77.4(2)
F(1)–Zr(1)–O(2)	134.4(2)
O(1)–Zr(1)–O(2)	57.0(2)
O(1)–C(11)–O(2)	119.2(6)
C(11)–O(1)–Zr(1)	92.9(4)
C(11)–O(2)–Zr(1)	90.6(4)

surrounded by two pentamethylcyclopentadienyl ligands, a fluorine atom and two oxygen atoms of the aromatic carboxylate ligand (OCO-*o*-C₆H₄CO₂SiMe₃). The carboxylate group bonds to the zirconium atom in a chelating fashion. The Zr–O distances in **4** are not equal (Zr(1)–O(1) 2.278(5) Å and Zr(1)–O(2) 2.316(4) Å) and this is consistent with many other organozirconium carboxylate complexes [16,17,23–25]. Similarly, the internal angles within the four-membered ring formed by the chelation of the carboxylate ligand to zirconium are also in agreement with related complexes [16,17,23–25].

In pentacoordinate chloro-carboxylate complexes of zirconium, the steric crowding of the coordination environment around the central zirconium atom leads to subsequent elongation of the Zr–Cl bond lengths [24,25]. However, in the case of **4**, the Zr–F distance (1.976(4) Å) is in close agreement with those found in tetracoordinate complexes such as [Cp₂ZrF₂] (1.98(1) Å) [26] or [(C₅Me₄Et)₂ZrClF] (2.002(3) Å) [7]. The rest of the molecule shows no significant variation from expected parameters.

3. Experimental details

3.1. General comments

All reactions were performed under an atmosphere of dry nitrogen by employing either Schlenk line techniques or an inert atmosphere glove-box. Solvents were freshly distilled from sodium and degassed prior to use. CDCl₃ and C₆D₆ were trap-to-trap distilled from calcium dihydride. [Cp*TiF₃] [4], [Cp₂ZrF₂] [4], Me₃SiOPOPh₂ [27], Me₃SiOSO₂C₆H₄CH₃ [28] and 1,2-(Me₃SiOCO)₂C₆H₄ [28] were prepared according to published methods. NMR spectra were recorded on a Bruker AM 250 spectrometer. ¹H, ¹⁹F and ³¹P NMR data are listed in parts per million downfield from SiMe₄, CFC₃ and 85% H₃PO₄ respectively. IR spectra were recorded on a Perkin–Elmer Bio-Rad Digilab FTS-7 spectrophotometer (Kel-F mulls between NaCl plates in the range of 4000 to 1350 cm⁻¹ or Nujol mulls between KBr plates). Mass spectra were obtained on Finnigan MAT System 8230 or Varian MAT CH 5 mass spectrometers. Melting points (uncorrected) were measured using Büchi 510 and HWS-SG 3000 apparatus. Elemental analyses were performed by the Beller laboratory (Göttingen, Germany) or in our institute.

3.2. Synthesis

3.2.1. Preparation of [(Cp*TiF(μ-F)(μ-OSO₂-*p*-C₆H₄CH₃))₂] (**1**)

To a stirred solution of [Cp*TiF₃] (0.60 g, 2.50 mmol) in toluene (50 ml) was added a solution of Me₃SiOSO₂C₆H₄CH₃ (0.61 g, 2.50 mmol) in toluene

(20 ml). The mixture was stirred for 24 h, after which time all the volatiles were removed in vacuo and the residue extracted with dichloromethane (30 ml). After concentrating to ca. 15 ml and cooling to –25 °C, red crystals of **1** were obtained (0.81 g, 83%); m.p. 214 °C. Anal. Found: C, 51.5; H, 5.5; F, 10.2. Calc.: C, 52.0; H, 5.7; F, 9.7. IR (KBr, Nujol): 1499 (m), 1266 (s), 1143 (m), 1125 (s), 1106 (vs), 1005 (s), 813 (m), 807 (m), 684 (m), 617 (m), 448 (m) cm⁻¹. MS: *m/z* 525 (M – Cp* – F – CH₃ – C₆H₄CH₃, 2), 372 (M/2 – F, 1), 256 (M/2 – Cp*, 1), 221 (Cp*TiF₂, 10), 135 (Cp*, 100%). ¹H NMR (200 MHz, CDCl₃): δ 2.22, 2.25 (s, Cp*), 2.23, 2.28 (s, CH₃), 7.02 (d, ³J_{HH} = 8 Hz, *m*-C₆H₄), 7.09 (d, ³J_{HH} = 8 Hz, *m*-C₆H₄), 7.56 (d, ³J_{HH} = 8 Hz, *o*-C₆H₄), 7.61 (d, ³J_{HH} = 8 Hz, *o*-C₆H₄) ppm. ¹⁹F NMR (188 MHz, CDCl₃): δ –41.7 (t, ²J_{FF} = 24 Hz, bridging F), –40.8 (t, ²J_{FF} = 24 Hz, bridging F), –27.9 (m, bridging F), –18.5 (dt, ²J_{FF} = 98 Hz, ²J_{FF} = 35 Hz, bridging F), –15.9 (dt, ²J_{FF} = 98 Hz, ²J_{FF} = 35 Hz, bridging F), 212.5 (dd, ²J_{FF} = 98 Hz, ²J_{FF} = 35 Hz, term. F), 214.3 (dd, ²J_{FF} = 98 Hz, ²J_{FF} = 35 Hz, term. F), 215.8 (d, ²J_{FF} = 24 Hz, term. F), 217.2 (d, ²J_{FF} = 24 Hz, term. F) ppm.

3.2.2. Preparation of [(Cp*TiF(μ-F)(μ-OPOPh₂))₂] (**2**)

2 was prepared in an analogous manner to that described for **1** using [Cp*TiF₃] (0.70 g, 2.90 mmol) and Me₃SiOPOPh₂ (0.86 g, 2.90 mmol). The crude product was recrystallized from dichloromethane to yield 1.02 g (80%) of red crystals of **2**; m.p. 236 °C. Anal. Found: C, 60.0; H, 5.5; F, 9.1. Calc.: C, 60.3; H, 5.8; F, 8.7. IR (KBr, Nujol): 1437 (s), 1262 (m), 1168 (m), 1146 (vs), 1128 (vs), 1069 (m), 1041 (vs), 1020 (vs), 996 (s), 804 (m), 749 (m), 733 (s), 695 (m), 629 (m), 602 (s), 489 (m), 448 (m) cm⁻¹. MS: *m/z* 857 (M – F, 22), 741 (M – Cp*, 15), 659 (M – OPOPh₂, 9), 419 (M/2 – F, 100), 135 (Cp*, 38%). ¹H NMR (200 MHz, CDCl₃): δ 2.14, 2.15 (s, Cp*), 7.43 (m, Ph) ppm. ¹⁹F NMR (188 MHz, CDCl₃): δ –35.1 (m, bridging F), –29.5 (dt, ²J_{FF} = 114 Hz, *J* = 35 Hz, bridging F), 6.3 (m, bridging F), 148.4 (m, term. F), 170.3 (dd, ²J_{FF} = 89 Hz, ²J_{FF} = 35 Hz, term. F) ppm. ³¹P NMR (100 MHz, DME/CDCl₃): δ 35.1 (d, *J*_{PF} = 33 Hz), 32.9 (m) ppm.

3.2.3. Preparation of [(Cp*TiF(μ-F)(μ-OCO-*o*-C₆H₄CO₂SiMe₃))₂] (**3**)

3 was prepared in an analogous manner to that described for **1** using [Cp*TiF₃] (1.00 g, 4.16 mmol) and 1,2-(Me₃SiOCO)₂C₆H₄ (1.29 g, 4.15 mmol). The crude product was recrystallized from dichloromethane to yield 2.78 g (73%) of red crystals of **3**; m.p. 182 °C. Anal. Found: C, 54.9; H, 6.1; F, 8.1. Calc.: C, 55.0; H, 6.2; F, 8.3. IR (NaCl, Kel-F): 1733 (m), 1688 (s), 1598 (m), 1582 (s), 1551 (s), 1486 (m), 1401 (s), 1377 (m) cm⁻¹. MS: *m/z* 872 (M – CO₂, 2), 761 (M –

Table 3
Crystal data for **1**, **2** and **4**

Compound	1 · 2 dioxane	2 · 2CH ₂ Cl ₂	4
Formula	C ₄₂ H ₆₂ F ₄ O ₁₀ S ₂ Ti ₂	C ₄₆ H ₅₄ Cl ₄ F ₄ O ₄ P ₂ Ti ₂	C ₃₁ H ₄₃ FO ₄ SiZr
Molecular weight	962.84	1046.43	617.96
Crystal size (mm ³)	0.40 × 0.40 × 0.20	0.70 × 0.50 × 0.30	0.50 × 0.50 × 0.30
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2/ <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	11.552(1)	17.100(2)	9.789(2)
<i>b</i> (Å)	15.321(2)	17.229(2)	9.947(2)
<i>c</i> (Å)	12.777(1)	16.441(3)	31.262(5)
α (deg)	90	90	90
β (deg)	97.030(10)	96.063(10)	90
γ (deg)	90	90	90
<i>V</i> (Å ³)	2244(4)	4817(1)	3044(1)
<i>Z</i>	2	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.425	1.443	1.348
μ (mm ⁻¹)	0.520	0.677	0.440
<i>F</i> (000)	1012	2160	1296
θ range (deg)	3.5–25	3.5–25	3.5–25
Reflections collected	3217	6183	5337
Independent reflections	2954	6173	5241
Data/restraints/parameters	2951/0/265	6173/0/569	5228/0/356
Goodness-of-fit on <i>F</i> ²	1.108	1.016	1.063
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0843	0.0445	0.0558
<i>R</i> 1 (all data)	0.0931	0.0556	0.0656
<i>wR</i> 2 (all data)	0.2285	0.1167	0.1646
Largest difference peak and hole (e ⁻ Å ⁻³)	1.646 and -0.875	0.827 and -0.569	0.476 and -0.528

COOSiMe₃, 5), 737 (M – Cp* – CO₂, 9), 645 (M – Cp* – COOSiMe₃ – F, 100), 497 (M – 2Cp* – SiMe₃ – 4F, 95) 135 (Cp*, 5%). ¹H NMR (200 MHz, CDCl₃): δ 0.20, 0.24 (s, SiMe₃), 2.16, 2.17 (s, Cp*), 7.18 (m, *m*-C₆H₄), 7.48 (m, *o*-C₆H₄) ppm. ¹⁹F NMR (188 MHz, CDCl₃): δ -10.5 (m, bridging F), -4.8 (m, bridging F), 174.1 (m, term. F), 176.8 (m, term. F) ppm.

3.2.4. Preparation of [Cp₂*ZrF(μ -OCO-*o*-C₆H₄CO₂SiMe₃)₂] (**4**)

To a solution of [Cp₂*ZrF₂] (0.75 g, 1.88 mmol) in hexane (30 ml) was added a solution of 1,2-(Me₃SiOCO)₂C₆H₄ (0.58 g, 1.87 mmol) in hexane (20 ml). After stirring for 24 h, the solution was concentrated to half its original volume whereby colourless crystals of **4** formed (0.78 g, 79%); m.p. 221 °C. Anal. Found: C, 60.1; H, 6.8; F, 2.9. Calc.: C, 60.3; H, 7.0; F, 3.1. IR (NaCl, Kel-F): 1719 (s), 1496 (s), 1430 (s), 1379 (s) cm⁻¹. MS: *m/z* 602 (M – Me, 4), 481 (M – Cp*, 7), 378 (Cp₂*ZrF, 12), 263 (Cp*ZrF₂, 100), 135 (Cp*, 20%). ¹H NMR (200 MHz, C₆D₆): δ 0.53 (s, 9H, SiMe₃), 1.85 (s, 30H, Cp*), 7.02 (m, 2H, *m*-C₆H₄), 7.17 (m, 2H, *o*-C₆H₄) ppm. ¹⁹F NMR (188 MHz, C₆D₆): δ 34.3 (s) ppm.

3.3. X-ray crystallography

Suitable crystals of **1** were grown from a dichloromethane and dioxane mixture and two dioxane

lattice molecules were found per molecular unit of **1**. Crystals of **2** were grown from dichloromethane and two molecules of CH₂Cl₂ were found per molecular unit of **2**. Crystals of **4** were grown from hexane. Relevant crystallographic data of **1**, **2** and **4** are given in Table 3. The intensities for the structures were collected on a Stoe–Siemens AED four-circle diffractometer using graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 153 K for **1** and at 213 K for **2** and **4**. All structures were solved by direct methods with SHELXS-90 [29] and refined by full-matrix least squares on *F*² using SHELXL-93 [30]. The hydrogen atoms were located geometrically and refined using a riding model. Absorption corrections, by azimuthal scans, were applied using a semiempirical method (SHELXTL [31]). Tables of fractional coordinates and equivalent isotropic displacement parameters, hydrogen atom coordinates, anisotropic displacement parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the BMBF for generous support of this work. S.A.A.S. is grateful to the Alexander von Humboldt Foundation for a postdoctoral fellowship.

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