Organometallic Fluorides of Zirconium and Hafnium in the Synthesis of Carboxylate Complexes: Molecular Structures of [{(η^5-C_5Me_5)ZrF($OCOCF_3$)$_2$}$_2$] and [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$]

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The reaction of [(η^5-C_5Me_5)ZrF_3] and [(η^5-C_5Me_5)HfF_3] with $Me_3SiOCOCF_3$ yields the dinuclear complexes [{(η^5-C_5Me_5)ZrF($OCOCF_3$)$_2$}$_2$] (**1**) and [{(η^5-C_5Me_5)HfF($OCOCF_3$)$_2$}$_2$] (**2**), regardless of the molar ratio employed. [(η^5-C_5Me_5)$_2$$ZrF_2$] reacts with 1 and 2 equiv of $Me_3SiOCOCF_3$ to form the mononuclear compounds [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] (**3**) and [(η^5-C_5Me_5)$_2$ZrF($OCOCF_3$)] (**4**), respectively. The molecular structures of **1** and **3** have been determined by single-crystal X-ray analysis: **1**, triclinic, $P\bar{1}$, $a = 9.508(3)$ Å, $b = 11.002(4)$ Å, $c = 17.528(3)$ Å, $\alpha = 78.55(4)$, $\beta = 76.80(2)$, $\gamma = 87.51(2)°$, $V = 1750(1)$ Å^3, $Z = 2$, $R = 0.0378$; **3**, monoclinic, $C2/c$, $a = 18.553(4)$ Å, $b = 9.110(2)$ Å, $c = 16.323(3)$ Å, $\beta = 114.88(3)°$, $V = 2503(1)$ Å^3, $Z = 4$, $R = 0.0457$. Compound **1** shows bridging bidentate and chelating carboxylate ligands as well as bridging fluorine atoms. The zirconium atoms are seven coordinated and have an 18-electron configuration. X-ray studies of **3** reveal two structural components where the carboxylate ligands coordinate in a monodentate (major component) and a chelating manner (minor component).

Introduction

Although carboxylate chemistry of group 4 metals has generated much interest, the vast majority of the work has been done using titanium.[1] Many titanium carboxylates containing the (η^5-C_5H_5) or (η^5-C_5Me_5) ligand are known, most of them based on [(η^5-C_5H_5)$_2$$TiCl_2$][2] or [($\eta^5$-$C_5Me_5$)$TiMe_3$].[3] Recently, we have reported on the synthesis of the first carboxylates of organotitanium fluorides from the reaction of [(η^5-C_5Me_5)TiF_3] and $Me_3SiOCOR$ (R = CF_3, C_6F_5).[4] The products, [{(η^5-C_5Me_5)TiF_2(OCOR)}$_2$], have been structurally characterized and have F atoms and carboxylate groups as bridging units.

In contrast, the chemistry of zirconium and hafnium carboxylates is less developed. Chlorozirconocene carboxylates of the general formula [(η^5-C_5H_5)$_2$ZrCl(OCOR)] (R = alkyl, aryl) result from the reaction of [((η^5-C_5H_5)$_2$ZrCl)$_2$O] with the corresponding carboxylic acids[5] or from reacting [(η^5-C_5H_5)$_2$$ZrCl_2$] with the sodium salts of carboxylic acids.[6] The molecular structures of these mononuclear complexes show chelating carboxylate ligands. Dinuclear complexes are also documented,[7] of which [{(η^5-C_5H_5)$_2$Zr($OCOCF_3$)(μ-OH)}$_2$] is structurally characterized and has carboxylate ligands coordinating in a monodentate fashion.[7a] Furthermore, dicarboxylates are known to act as (2 + 1)-dentate ligands, in which one chelating and one monodentate ligand coordinate to the metal centers. For instance, zirconocene complexes of isophthalic acid, terephthalic acid, and acetylenedicarboxylic acid have been structurally characterized.[8] However, all of these compounds are associated with the (η^5-C_5H_5)$_2$Zr fragment; the chemistry of the (η^5-C_5H_5)Zr or (η^5-C_5Me_5)Zr fragment has yet to be studied.

Compared to organometallic chlorides, the corresponding fluorides have not been studied to any great extent, due to the problems of synthesis. Only recently have group 4 organometallic fluorides been used as starting materials, and they have been shown to exhibit completely different chemical and coordination behavior compared with chloro complexes.[9] For example, reaction of [(η^5-C_5Me_5)MF_3] (M = Zr, Hf) with Me_3Al in different stoichiometries leads to a variety of zirconium− and hafnium−aluminum complexes,[10] while reaction with Me_3SiX (X = Cl, Br) gives mixed fluoro−halo complexes.[11] No investigations have been carried out using [(η^5-C_5Me_5)$_2$$ZrF_2$] as a starting material. Herein we report on the preparation, characterization and single-crystal X-ray diffraction study of the novel dinuclear complexes [{(η^5-C_5Me_5)MF($OCOCF_3$)$_2$}$_2$]

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(M = Zr, Hf) and of the mononuclear complexes [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] and [(η^5-C_5Me_5)$_2$ZrF($OCOCF_3$)], from the reaction of [(η^5-C_5Me_5)MF_3] (M = Zr, Hf) and [(η^5-C_5Me_5)$_2ZrF_2$] with the trimethylsilyl ester of trifluoroacetic acid.

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. C_6D_6 was trap-to-trap distilled from calcium dihydride. [(η^5-C_5Me_5)ZrF_3], [(η^5-C_5Me_5)HfF_3], [(η^5-C_5Me_5)$_2ZrF_2$],[9] and $Me_3SiOCOCF_3$[12] were prepared according to published methods. NMR spectra were recorded on a Bruker AM 250 spectrometer. ^1H and ^{19}F NMR data are listed in ppm downfield from $SiMe_4$ and $CFCl_3$, respectively. IR spectra were recorded on a Perkin-Elmer Bio-Rad Digilab FTS-7 spectrophotometer (Kel-F mulls between NaCl plates in the range 4000−1350 cm^{-1}). Mass spectra were obtained on a Finnigan MAT System 8230 or a Varian MAT CH 5 mass spectrometer. Melting points (uncorrected) were measured using a Büchi 510 and a HWS-SG 3000 apparatus. Elemental analyses were performed by the Beller laboratory (Göttingen, Germany) or in our institute.

Preparation of [{(η^5-C_5Me_5)ZrF($OCOCF_3$)$_2$}$_2$] (1). To a solution of [(η^5-C_5Me_5)ZrF_3] (0.82 g, 2.89 mmol) in toluene (30 mL) was added $Me_3SiOCOCF_3$ (1.08 g, 5.79 mmol) in toluene (20 mL). The reaction mixture was stirred for 24 h, after which time the volume of the solution was slowly reduced under vacuum (15 mL), and the product began to crystallize. Precipitation of colorless crystals of **1** was completed by storing at −25 °C. The reaction yielded 1.01 g (74%) of pure product, mp 276 °C. ^1H NMR (C_6D_6): δ 1.70 (s, (η^5-C_5Me_5)). ^{19}F NMR (C_6D_6): δ −75.9 (s, 6F, CF_3), −76.9 (s, 6F, CF_3), −82.1 (s, 2F). MS (EI), *m/e* (%): 942 [M] (18), 827 [M − $OCOCF_3$] (45), 805 [M − (η^5-C_5Me_5)] (22), 263 [(η^5-C_5Me_5)ZrF_2] (100). IR: 2962 (m), 2928 (m), 1671 (s), 1614 (s), 1511 (m), 1488 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{30}F_{14}O_8Zr_2$ (942.97): C, 35.66; H, 3.21; F, 28.21. Found: C, 35.4; H, 3.3; F, 28.4.

Preparation of [{(η^5-C_5Me_5)HfF($OCOCF_3$)$_2$}$_2$] (2). The synthesis of **2** proceeded as described for complex **1**. $Me_3SiOCOCF_3$ (1.51 g, 8.11 mmol) in toluene (20 mL) was added dropwise to a stirred solution of [(η^5-C_5Me_5)HfF_3] (1.50 g, 4.05 mmol) in toluene (30 mL). Filtration gave **2** as colorless crystals (1.86 g, 82%), mp 202 °C. ^1H NMR (C_6D_6): δ 1.78 (s, (η^5-C_5Me_5)). ^{19}F NMR (C_6D_6): δ −75.9 (s, 6F, CF_3), −76.5 (s, 6F, CF_3), −103.8 (s, 2F). MS (EI), *m/e* (%): 1118 [M] (45), 1005 [M − $OCOCF_3$] (35), 983 [M − (η^5-C_5Me_5)] (75), 353 [(η^5-C_5Me_5)HfF_2] (100). IR: 2960 (m), 2926 (m), 1682 (s), 1617 (s), 1516 (m), 1492 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{30}F_{14}Hf_2O_8$ (1117.50): C, 30.09; H, 2.71; F, 23.80. Found: C, 30.2; H, 2.7; F, 23.7.

Preparation of [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] (3). To a solution of [(η^5-C_5Me_5)$_2ZrF_2$] (1.35 g, 3.38 mmol) in toluene (30 mL) was slowly added a solution of $Me_3SiOCOCF_3$ (1.26 g, 6.67 mmol) in toluene (15 mL). The mixture was stirred for 24 h, and the solution was reduced slowly under vacuum (15 mL). Yellow crystals of **3** were obtained; yield 1.72 g (87%), mp 226 °C. ^1H NMR (C_6D_6): δ 1.65 (s, (η^5-C_5Me_5)). ^{19}F NMR (C_6D_6): δ −74.4 (s, CF_3). MS (EI), *m/e* (%): 586 [M] (5), 473 [M − $OCOCF_3$] (20), 451 [M − (η^5-C_5Me_5)] (30), 263 [(η^5-C_5Me_5)ZrF_2] (100). IR: 2961 (m), 2923 (m), 1730 (s), 1718 (s), 1624 (m), 1559 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{30}F_6O_4Zr$ (587.71): C, 49.05; H, 5.14; F, 19.40. Found: C, 48.9; H, 5.1; F, 19.2.

Preparation of [(η^5-C_5Me_5)$_2$ZrF($OCOCF_3$)] (4). To a solution of [(η^5-C_5Me_5)$_2ZrF_2$] (1.27 g, 3.18 mmol) in *n*-hexane (40 mL) was slowly added a solution of $Me_3SiOCOCF_3$ (0.56 g, 3.01 mmol) in *n*-hexane (10 mL). The mixture was stirred for 24 h, and the solution was reduced slowly under vacuum (15 mL). Colorless crystals of **4** were obtained: yield 0.92 g (62%); mp 119 °C. ^1H NMR (C_6D_6): δ 1.72 (d, (η^5-C_5Me_5)). ^{19}F NMR (C_6D_6): δ 51.5 (s, 1F), −74.7 (s, 3F, CF_3). MS (EI), *m/e* (%) 492 [M] (15), 379 [M − $OCOCF_3$] (10), 357 [M − (η^5-C_5Me_5)] (25), 263 [(η^5-C_5Me_5)ZrF_2] (100). IR: 2957 (m), 2915 (m), 1721 (s), 1627 (s), 1403 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{30}F_4O_2Zr$ (493.69): C, 53.52; H, 6.12; F, 15.39. Found: C, 53.4; H, 6.1; F, 15.2.

Table 1. Crystal Data for **1** and **3**

	1	**3**
formula	$C_{28}H_{30}F_{14}O_8Zr_2$	$C_{24}H_{30}F_6O_4Zr$
fw	942.96	587.70
cryst size (mm)	0.50 × 0.40 × 0.20	0.50 × 0.35 × 0.30
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	9.508(3)	18.553(4)
b (Å)	11.002(4)	9.110(2)
c (Å)	17.528(3)	16.323(3)
α (deg)	78.55(4)	90
β (deg)	76.80(2)	114.88(3)
γ (deg)	87.51(2)	90
V (Å^3)	1750(1)	2503(1)
Z	2	4
T (K)	210(2)	193(2)
ρ_c (g·mm^{-3})	1.790	1.560
μ (cm^{-1})	7.16	5.12
F(000)	936	1200
2θ range (deg)	5−45	5−45
no. of reflns measd	8579	7351
no. of unique reflns	4570	2232
no. of restraints	0	389
no. of refined param	451	239
R1 [$I > 2\sigma(I)$]	0.0378	0.0457
wR2[a] (all data)	0.0599	0.1008

[a] $wR2 = \{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Zr(1)−F(1)	2.147(4)	F(1)−Zr(2)	2.145(4)
Zr(1)−F(2)	2.142(4)	F(2)−Zr(2)	2.137(4)
Zr(1)−O(1)	2.208(5)	Zr(2)−O(2)	2.212(5)
Zr(1)−O(3)	2.234(4)	Zr(2)−O(4)	2.224(5)
Zr(1)−O(11)	2.320(5)	Zr(2)−O(21)	2.282(5)
Zr(1)−O(12)	2.286(5)	Zr(2)−O(22)	2.318(5)
F(2)−Zr(1)−F(1)	71.49(13)	Zr(2)−F(2)−Zr(1)	108.7(2)
O(1)−Zr(1)−O(3)	146.9(2)	F(2)−Zr(2)−F(1)	71.64(13)
O(12)−Zr(1)−O(11)	56.8(2)	O(2)−Zr(2)−O(4)	147.0(2)
Zr(2)−F(1)−Zr(1)	108.2(2)	O(21)−Zr(2)−O(22)	56.9(2)

Crystal Structure Solution and Refinement. Diffraction data of compound **1** were collected on a Siemens-Stoe AED four-circle diffractometer at 210 K with Mo Kα radiation (λ = 0.710 73 Å). Diffraction data of compound **3** were collected at 193 K using a Siemens-Stoe Huber four-circle diffractometer equipped with a SMART CCD area detector, with Mo Kα radiation (λ = 0.710 73 Å). The sample to detector distance was set to be 6 cm. Reflections were collected by means of a φ-scan rotation (step-width 0.3°), with an exposure time of 15 s/frame.

Both structures were solved by direct method using SHELXS-90[13] and refined versus F^2 by the least-squares method with all data (SHELXL-93).[14] In compounds **1** and **3** all non-hydrogen atoms were refined anisotropically. In both structures the hydrogens are inserted in calculated positions.

Crystallographic data are listed in Table 1 and selected bond lengths (Å) and angles (deg) are given in Tables 2 and 3.

Results and Discussion

Reaction of [(η^5-C_5Me_5)MF_3] (M = Zr, Hf) with the trimethylsilyl ester of trifluoroacetic acid in toluene results in the formation of the dimers [{(η^5-C_5Me_5)ZrF($OCOCF_3$)$_2$}$_2$] (**1**) and [{(η^5-C_5Me_5)HfF($OCOCF_3$)$_2$}$_2$] (**2**), via elimination of trimethysilyl fluoride. It was found that products **1** and **2** were formed regardless of the molar ratio of the starting materials employed, but the highest yields were obtained when a ratio of

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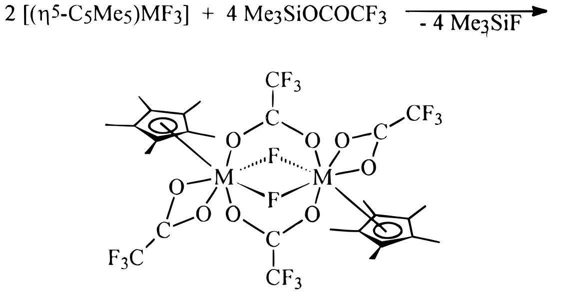
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

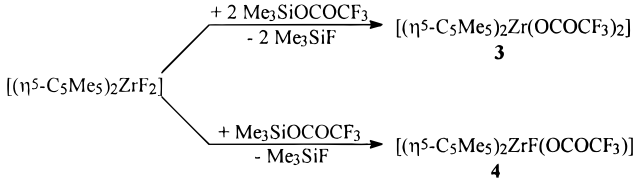
Major Component (Figure 2)			
Zr(1)−O(1)	2.087(3)	Zr(1)−O(1a)	2.087(3)
Minor Component (Figure 3)			
Zr(1)−O(1′)	2.35(2)	Zr(1)−O(2′)	2.43(3)
Zr(1)−O(1′a)	2.35(2)	Zr(1)−O(2′a)	2.43(3)
Major Component (Figure 2)			
O(1)−Zr(1)−O(1a)	98.6(2)		
Minor Component (Figure 3)			
O(1′)−Zr(1)−O(2′)	53.8(6)	O(1′a)−Zr(1)−O(2′a)	53.8(6)

Scheme 1



1 M = Zr
2 M = Hf

Scheme 2



2:1 in favor of the ester was used (Scheme 1). Significantly, no reaction was observed when the analogous [(η^5-C_5Me_5)MCl_3] was used, indicating that the formation of Me_3SiF acts as a driving force in the reactions.

Complexes **1** and **2** were characterized by elemental analyses, and infrared, ^1H and ^{19}F NMR spectroscopy. The ^{19}F NMR spectra of **1** and **2** show one singlet for the metal-bonded F atoms (−82.1 and −103.8 ppm, respectively, which are in the range typical for F atoms bridging two metal centers[11]), and two singlets for the CF_3 groups. This suggests two different types of coordination modes of the carboxylate ligand in solution. Similarly, this arrangement occurs in the solid state, as shown by the X-ray structure of **1**. In the IR spectra of **1** and **2** there are two sets of asymmetric carboxylate vibrations (1671 and 1614 cm^{-1} for **1**; 1682 and 1617 cm^{-1} for **2**) as well as two sets of symmetric vibrations (1511 and 1488 cm^{-1} for **1**; 1516 and 1492 cm^{-1} for **2**). These correspond to the two different modes of bonding of the trifluoroacetate ligand, *i.e.* bridging bidentate and chelating.

Treatment of [(η^5-C_5Me_5)$_2ZrF_2$] with 2 equiv of trimethylsilyl trifluoroacetate gives the mononuclear species [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] (**3**). Unlike tetrameric [(η^5-C_5Me_5)ZrF_3], [(η^5-C_5Me_5)$_2ZrF_2$] is a monomer; probably due to the steric bulk of the two (η^5-C_5Me_5) ligands.[9] Therefore, the single-crystal X-ray structure of **3** revealed the expected monomeric species. The reactivity of [(η^5-C_5Me_5)$_2ZrF_2$] also differed from that of [(η^5-C_5Me_5)ZrF_3] in that the monosubstituted species, [(η^5-C_5Me_5)$_2$ZrF($OCOCF_3$)] (**4**), could be formed when one molar equivalent of $Me_3SiOCOCF_3$ was used (Scheme 2).

Complexes **3** and **4** were characterized by elemental analyses, and infrared, ^1H and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of **3** shows a singlet for the CF_3 group of the trifluoroacetate ligand (−74.4 ppm), while the spectrum of **4** gives one singlet for the F atom bonded to the zirconium center (51.5 ppm) and one singlet for the CF_3 group of the acetate ligand (−74.7 ppm). The IR spectrum of **3** gives the asymmetric carboxylate vibrations at 1730 and 1718 cm^{-1} and the symmetric vibrations at 1624 and 1559 cm^{-1}. Similarly, the asymmetric absorption band for **4** can be found at 1721 cm^{-1}, while the symmetric band is at 1627 cm^{-1}.

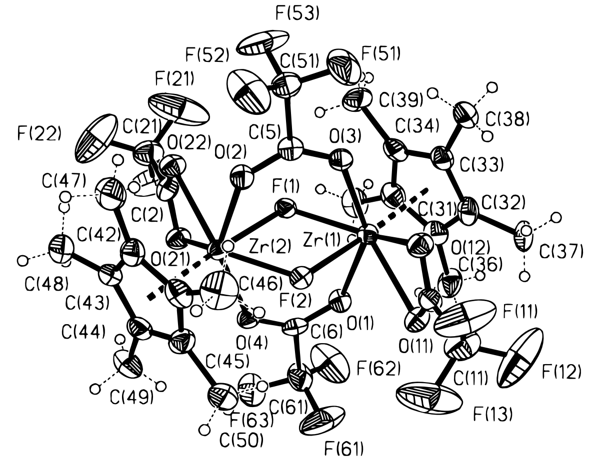


Figure 1. ORTEP plot of [(η^5-C_5Me_5)ZrF($OCOCF_3$)$_2$]$_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

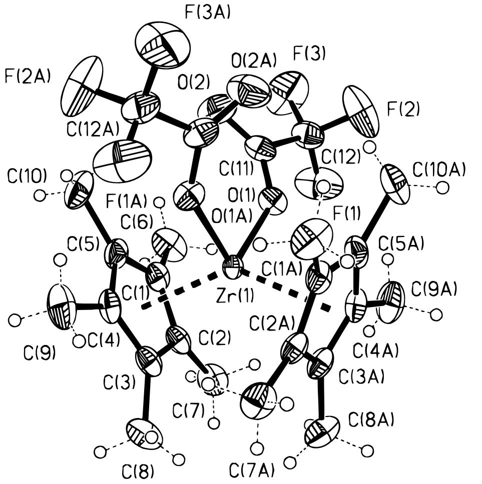


Figure 2. ORTEP plot of [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] (**3**) showing the major structural component (monodentate carboxylate ligand). Thermal ellipsoids are drawn at the 50% probability level.

Crystal Structures of 1 and 3. The crystal structures of compounds **1** and **3** (two structural components) are shown in Figures 1−3, respectively. Relevant bond distances and angles are reported in Tables 2 and 3.

The core of the dimeric structure of **1** consists of two Zr atoms bridged by two fluorine atoms and, on opposite sides of the four-membered ring thus formed, two carboxylate groups (Figure 1). Contrary to what was previously observed in the solid state structure of related carboxylates of organotitanium fluorides,[4] the F atoms in **1** are symmetrically bridging the two Zr atoms. The differences in the bond lengths are within experimental error (minimum 2.138(4) Å; maximum 2.147(4) Å). There is also another trifluoroacetate group coordinating each Zr atom in a chelating fashion. The Zr−O bond lengths (2.287(5) and 2.320(5) Å) are in agreement with known zirconocene carboxylates, where the carboxylate ligand is chelating. For instance, [(η^5-$CH_3C_5H_4$)$_2$ZrCl($OCOC_{10}H_7$-α)][6a] has Zr−O distances of 2.260(2) and 2.317(2) Å, while [(η^5-

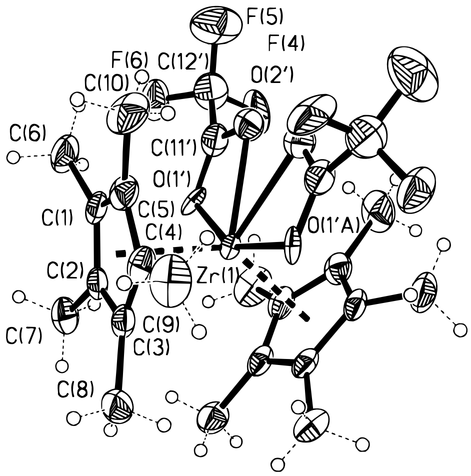


Figure 3. ORTEP plot of [(η^5-C_5Me_5)$_2$Zr($OCOCF_3$)$_2$] (**3**) showing the minor structural component (chelating carboxylate ligand). Thermal ellipsoids are drawn at the 50% probability level.

$CH_3C_5H_4$)$_2$Zr(IPHTH)]$_2$[8a] (IPHTH = dicarboxylate of isophthalic acid) has Zr−O distances of 2.262(5) and 2.306(5) Å. The Zr−O distances of the two bridging bidentate trifluoroacetate groups in **1** do not show any significant variation, as they range between 2.209(5) and 2.235(5) Å. In both types of ligand, chelating and bridging bidentate, the CF_3 groups are disordered.

Since each metal atom in compound **1** also binds to a pentamethylcyclopentadienyl moiety, this results in a coordination number of seven for the two Zr atoms, generating a formal 18-electron configuration for each metal. In the case of the titanium analog, it was found, on the basis of spectral analysis, that the second carboxylate group coordinates in a monodentate manner.[4] This difference in coordination number can be explained by the difference in the ionic radii of the two metals.

Compound **3** crystallizes with half the molecule in the asymmetric unit, the second half being related to the first one by a 2-fold axis. Although the trifluoroacetate ligands bind the metal atom in a monodentate fashion (Figure 2), a full occupancy refinement of the two oxygen atoms and C11 left three relatively high peaks in the electron density map (ca. 1.2 e/Å^3). A close inspection of the distribution of these peaks revealed that they might correspond to one carbon atom and the two oxygens of the carboxylate group binding the Zr atom in a chelating manner. The assignment of the peaks to the two oxygens and the carboxylic carbon of the disordered component of the trifluoroacetate ligand cleared the electron density map and resulted in a 9:1 relative occupation distribution of the two components, the major one corresponding to the monodentate ligand. No peaks assignable to the missing trifluoromethyl group of the second component appeared in the map, as they would be too close to the corresponding atoms of the monodentate ligand. We therefore completed the model of the chelating ligand by adding in the expected positions, and with an idealized geometry, the missing part of the ligand (Figure 3). The whole model could be refined anisotropically. The Zr−O distances in the two binding modes of the trifluoroacetate ligand vary from 2.087(3) to 2.39(2)$_{av}$ Å in going from monodentate to the chelating mode. The CF_3 group of the major component also shows some degree of rotational disorder.

The partial appearance of the chelating component of the carboxylate group suggests that an interchange occurs between the two coordination modes of the ligand. This results in the two fixed forms in the solid state, although the monodentate mode appears to be energetically favored.

Conclusion

In this study we have prepared, for the first time, organometallic fluoro−carboxylates of zirconium and hafnium from facile group 4 metal fluorides and trimethylsilyl esters. This novel route proved to be an efficient method for the synthesis of organometallic complexes, via elimination of trimethylsilyl fluoride. Bearing in mind our earlier studies regarding reactions of group 4 metal fluorides with different trimethylsilyl compounds,[10] it may be possible to generate a range of novel complexes by this method and investigations in this respect are currently under way.

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Supporting Information Available: Listings of crystal data, atomic coordinates, complete bond distances and angles, anisotropic displacement parameters, and hydrogen positional and thermal parameters for **1** and **3** (15 pages). Ordering information is given on any current masthead page.

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