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The tetracyclopentadienyls of titanium, zirconium and hafnium: new synthetic procedures and reactivity

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Abstract

In toluene as medium, the tetra(cyclopentadienyl) derivatives of Group 4 elements, MCp_4 (M = Ti, Zr, Hf), have been prepared in high yields from MCp_2Cl_2 and NaCp. The reactivity of $ZrCp_4$ with species containing active protons such as Ph_3SiOH or strong acids has been studied. Substituted bis(cyclopentadienyl) derivatives were produced except in the case of the reaction between $ZrCp_4$ and CF_3SO_3H. In this case, the tris(cyclopentadienyl) derivative $ZrCp_3(CF_3SO_3)$ was obtained as a pale yellow crystalline material, reactive with water to give the μ-oxo derivative of zirconium(IV), $[ZrCp_2(CF_3SO_3)]_2O$, which has been characterized by standard methods and by X-ray diffraction. Crystal data: $C_{22}H_{20}F_6O_7S_2Zr_2$, M = 756.96 g mol^{-1}, monoclinic, space group $C2/c$ (no. 15), $a = 19.525(4)$, $b = 9.028(2)$, $c = 16.152(5)$ Å, $\beta = 107.31(2)°$, $V = 2718.2(1)$ Å^3, $Z = 4$, $d_{calc} = 1.850$ g cm^{-3}, $\lambda(\text{Cu–K}_\alpha) = 1.54184$ Å, $T = 291$ K, $\mu = 85.66$ cm^{-1}, $F(000) = 1496$, $R = 0.054$, $Rw = 0.049$.

Keywords: Zirconium; X-ray diffraction; Derivative

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1. Introduction

Hydrocarbyl derivatives of bis(cyclopentadienyl) compounds of Group 4 elements (titanium, zirconium, hafnium) are of great interest for their implications in the activation of small molecules such as olefins, CO, CO_2, N_2, H_2, etc, [1]. A renewed interest for the fundamental properties of this class of compounds originated from the discovery that cationic metallocene alkyls of general formula $[MCp_2R]^+$ are catalytically active species in the homogeneus polymerization of olefins [2].

At variance with the large number of studies on MCp_2R_2 (R = organyl fragment) derivatives, the tetra(cyclopentadienyl) derivatives, MCp_4, M = Ti, Zr, Hf, represent a largely neglected class of related compounds. These compounds, as well as several of their cyclopentadienyl-substituted congeners were prepared in the seventies by a number of generally low-to-medium-yielding reactions [3], particularly for the zirconium and hafnium derivatives. Their reactivity has been studied, most of the work being confined to the reaction of MCp_4, M = Zr, Hf, with active protons in aqueous medium (water, hydrofluoric acid, nitric acid [4]): only one report exists on the reaction of $ZrCp_4$ with alcohols, thiols and chlorinated carboxylic acids [5]. It has also been reported that the thermal decomposition of $TiCp_4$ or the reduction of $ZrCp_4$ with KC_8 afford $TiCp_3$ ([3]b) or $ZrCp_3$ [6], respectively.

In the solid state $TiCp_4$ and $HfCp_4$ have a formal valence electron counting of 16 (two η^5- and two η^1-cyclopentadienyls); $ZrCp_4$ contains three η^5- and one η^1-cyclopentadienyl groups [7], corresponding to an electron counting of 20. The three compounds are fluxional in solution: $TiCp_4$ shows two broad singlets at room temperature (r.t.) which become sharp at low temperature (ca. −27°C) [3], while $ZrCp_4$ and $HfCp_4$ show one single resonance even at −150°C [8].

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Both in the solid state and in solution, the tetra(cyclopentadienyl) derivatives can be regarded to be similar to the bis(cyclopentadienyl)dialkyls of general formula MCp_2R_2. In the framework of our recent studies on organometallics of early transition elements [9], we therefore decided to reinvestigate these systems. In this paper we report on high-yield syntheses of MCp_4 (yields ranging from 60%, M = Ti, to 90%, M = Zr, Hf) and on their reactions with substances containing active protons in non aqueous media.

2. Results and discussion

2.1. Synthesis

The study of the MCp_4 derivatives, M = Ti, Zr, Hf, began with a re-examination of their synthetic procedures. A literature survey pointed out several facts: (a) the preparation of $TiCp_4$ had to be reconsidered in view of the fact that this substance has been reported as 'greenish–black' ([3]a) or 'violet-black' ([3]b), probably as a function of the nature of the solvent and temperature; (b) no direct 'cyclopentadienylation' reaction of $TiCl_4$ appeared to have been reported as yet; (c) details on the large scale preparation of MCp_4 are not readily available (especially in the case of $HfCp_4$); (d) the yields of the 'cyclopentadienylation reaction' starting from MCp_2Cl_2 are low especially in the case of the zirconium compound.

NMR monitoring of the reaction of $TiCl_4$ with NaCp in C_6D_6 showed that $TiCp_2Cl_2$ (5.97 ppm) [10] and $TiCp_3Cl$ (5.59 ppm) ([3]a) are intermediates to $TiCp_4$. Also, NMR experiments have shown that the reaction of MCp_2Cl_2 (M = Zr, Hf) with NaCp in C_6D_6 proceeds with the intermediate rapid formation of MCp_3Cl, which slowly reacts to give the final product. From a qualitative comparison, hafnium appears to react more slowly than zirconium: this is consistent with the general trend for substitution reactions in inorganic systems of cations in their usual oxidation state [11], i.e. rates decrease from 4d to 5d.

The formation of MCp_4 from MCp_2Cl_2 and NaCp can be summarized as described in (Eq. (1)), M = Ti, and (Eq. (2)), M = Zr, Hf.

$$TiCl_4 \overset{NaCp}{\rightarrow} TiCp_2Cl_2 \overset{NaCp}{\rightarrow} TiCp_3Cl \overset{NaCp}{\rightarrow} TiCp_4 \qquad (1)$$

$$MCp_2Cl_2 \overset{NaCp}{\rightarrow} MCp_3Cl \overset{NaCp}{\rightarrow} MCp_4 \qquad M = Zr, Hf \qquad (2)$$

By operating in toluene in a biphasic system, $TiCp_4$ has been obtained as a dark brown solid from either $TiCl_4$ or $TiCp_2Cl_2$ and NaCp. In both cases, the reaction is fast and no control of the temperature is required during the reaction and subsequent work-up as in the case of the preparations performed in THF ([3]a) or Et_2O ([3]b); no decomposition is noticed at r.t. and $TiCp_4$ was isolated in satisfactory yields. In our hands $TiCp_4$ is a dark brown solid extremely sensitive to moisture and gives dark coloured solutions (from green to blue) in toluene or in ethereal solvents.

As far as zirconium and hafnium are concerned, the lower solubility of MCp_4 (M = Zr, Hf) with respect to $TiCp_4$, requires an extraction (with toluene at ca. 50°C under reduced pressure) of the solid materials originated from Eq. (2): we have thus obtained good (80%) [12] to excellent (86%) yields of $ZrCp_4$ and $HfCp_4$, respectively.

MCp_3Cl is slowly converted to MCp_4 (M = Zr, Hf) in the presence of excess NaCp. We have not been able to isolate pure $ZrCp_3Cl$ or to reproduce the synthesis of $ZrCp_3Cl$ reported by Etievant and coworkers [13]. By the reaction of $ZrCp_2Cl_2$ with NaCp (1:1 molar ratio), $ZrCp_3Cl$ is effectively formed but in a mixture with $ZrCp_2Cl_2$: all attempts to separate the compounds were unsuccessful. Moreover, we have not been able to obtain $ZrCp_3Cl$ in a pure state by alternative routes such as the reactions of $ZrCp_4$ with stoichiometric amounts of $ZrCp_2Cl_2$. On the other hand, $HfCp_3Cl$ is the only cyclopentadienyl derivative in solution (5.71 ppm) when equimolar amounts of $HfCp_4$ and $HfCp_2Cl_2$ are mixed in C_6D_6.

Other potential cyclopentadienylating agents, beside NaCp, have been taken into consideration, in toluene as medium. No reaction takes place between $ZrCp_2Cl_2$ and TlCp. By taking into consideration the M–Cl bond energies of the dinuclear molecules in the gas phase as a homogeneus set of comparative data (Tl–Cl, 372.8; Zr–Cl, 489.5 kJ mol^{-1}) [14], the possibility existed that in the case of thallium the thermodynamically favoured reaction was the reverse, i.e. the formation of TlCp from $ZrCp_4$. In fact, $ZrCp_4$ reacts with TlCl in toluene to give a quantitative conversion to $ZrCp_2Cl_2$ and TlCp, see Eq. (3).

$$ZrCp_4 + 2TlCl \rightarrow ZrCp_2Cl_2 + 2TlCp \qquad (3)$$

Thus, tetra(cyclopentadienyl)zirconium(IV) behaves as a cyclopentadienylating agent of thallium(I).

The effect of the solvent was studied. In the $ZrCp_2Cl_2$/NaCp system, when THF was used as medium, an inseparable mixture of $ZrCp_4$ and decomposition products was obtained. $ZrCp_4$ is not stable in THF and slowly reacts to give a suspension containing an almost insoluble, yellow material. A GC/MS analysis of the solution showed the presence of dicyclopentadiene as major product.

2.2. Reactivity

The study of reactivity was mainly confined to $ZrCp_4$.

$ZrCp_4$ promptly reacts with Ph_3SiOH to give compound **4**, deriving from protonolysis of two cyclopentadienyl rings, see Eq. (4). Compound **4** is known to be obtained in high yields from $ZrCp_2Me_2$ and Ph_3SiOH [15].

$$ZrCp_4 + 2Ph_3SiOH \rightarrow ZrCp_2(Ph_3SiO)_2\mathbf{(4)} + 2CpH \quad (4)$$

Attempts to obtain the product of monosubstitution $ZrCp_3(Ph_3SiO)$ failed even when using a Zr/Si molar ratio of 1 (in this case half of the starting material was recovered unchanged).

On the other hand, $[N^nBu_3H][CF_3SO_3]$ reacts promptly with tetra(cyclopentadienyl)zirconium(IV) to give $ZrCp_3(CF_3SO_3)$, Eq. (5), and only the use of a $[N^nBu_3H][CF_3SO_3]$/Zr molar ration of 2 allows the preparation of the bis(cyclopentadienyl) derivative $ZrCp_2(CF_3SO_3)_2$, vide infra.

$$ZrCp_4 + [N^nBu_3H][CF_3SO_3]$$

$$\rightarrow ZrCp_3(CF_3SO_3) + N^nBu_3 + CpH \quad (5)$$

The experimentally verified reactions between $ZrCp_4$ and Ph_3SiOH or $[N^nBu_3H][CF_3SO_3]$ suggest that the driving force of the proton transfer reactions to Cp is the formation of the zirconium–oxygen bond.

The availability of $ZrCp_4$ and the fact that the reactions reported in Eqs. (4) and (5) are reminescent of the protonolysis of $ZrCp_2Me_2$ by alcohols or carboxylic acids [15–18], prompted us to investigate the reactions of $ZrCp_4$ with fluorinated, strong acids such as CF_3COOH and CF_3SO_3H.

The choice of the fluorinated acids stems from the fact that the conjugate base of these acids should be a relatively weak ligand and, in principle, species such as $ZrCp_3L$ should become stable enough, with respect to the product of disubstitution $ZrCp_2L_2$, to be isolatable (see Eq. (6)).

$$ZrCp_4 \overset{HX}{\rightarrow} ZrCp_3X \overset{HX}{\rightarrow} ZrCp_2X_2$$

$$X = CF_3COO, CF_3SO_3 \quad (6)$$

In this connection, it is worth mentioning that compounds of general formula MCp_3X are known in the literature and examples are: $ZrCp_3Cl$ [13], $ZrCp_3H$ [19], $ZrCp_3\cdots H\cdots AlEt_3$ [20], or $M[E(\eta^5\text{-}C_5H_4)_2]CpCl$, M = Zr, Hf, E = CMe_2 [21], M = Zr E = $SiMe_2$, CMe_2CMe_2 [22], $Cp_3Zr(P_4H)$ [23]. Polystyrene-linked zirconium and hafnium tris(cyclopentadienyl) derivatives of general formula (polystyrene-Cp)MCp_2Cl have been prepared [24]. Noteworthy is a recent paper by Erker and coworkers with a crystallographic and synthetic study on donor-ligand-stabilized tris(cyclopentadienyl) cations of zirconium(IV) of general formula $[ZrCp_3L]^+$ [25].

The reaction of $ZrCp_4$ with CF_3COOH in toluene is fast and produces the known $ZrCp_2(CF_3COO)_2$ [16] independent of the acid/Zr molar ratio (see Eq. (7)).

$$ZrCp_4 + 2CF_3COOH \rightarrow ZrCp_2(CF_3COO)_2 + 2CpH \quad (7)$$

On the other hand, the reaction of one equivalent of CF_3SO_3H with $ZrCp_4$, (Eq. (8)), produces the tris(cyclopentadienyl) derivative **5**, which easily forms the bis(cyclopentadienyl) **6** upon treatment with one equivalent of the acid.

$$ZrCp_4 \underset{-CpH}{\overset{CF_3SO_3H}{\rightarrow}} ZrCp_3(CF_3SO_3)\mathbf{(5)} \underset{-CpH}{\overset{CF_3SO_3H}{\rightarrow}} ZrCp_2(CF_3SO_3)_2\mathbf{(6)} \quad (8)$$

Compound **5** is so prone to give **6** that the preparation of **5** must be performed under high dilution of the reactants and by slow addition of a heptane solution of the acid (see Section 3) to a toluene suspension of $ZrCp_4$. By operating in this way, **5** has been isolated in good yields as a pale yellow crystalline material extremely sensitive to moisture. As a matter of fact, while recording the ^{1}H-NMR spectrum of **5** we observed the quick reduction of the intensity of the resonance of the Cp protons at 6.03 ppm (only one peak is observed due to the rapid exchange of the Cp ligands), probably due to adventitious water; at the same time, the resonances typical of CpH grow together with a signal at 5.82 ppm. In the ^{19}F-NMR spectrum, the intensity of the -77.8 ppm resonance decreases while the resonance at -78.3 ppm, due to $[ZrCp_2(CF_3SO_3)]_2O$, vide infra, increases.

This observation prompted us to investigate the reaction of **6** with moisture (NMR) and with water on a preparative scale. The NMR experiment confirmed the observations reported above and we isolated the μ-oxo derivative of zirconocene **7** containing triflate as additional ligand (Eq. (9))

$$2ZrCp_3(CF_3SO_3) + H_2O$$

$$\rightarrow [ZrCp_2(CF_3SO_3)]_2O + 2CpH\mathbf{(7)} \quad (9)$$

Compound **7** has been characterized by conventional analytical and spectroscopic methods; moreover, a X-ray crystallographic study has shown the compound to be a centrosymmetric μ-oxo derivative of zirconium(IV), see Fig. 1.

Some selected distances and angles are reported in Table 1. The Zr–C mean distances and the Zr–O(1) separation of 2.509 and 1.946(1) Å, respectively, are similar to those observed in the other structurally characterized μ-oxo zirconocene derivatives: $[ZrCp_2Cl]_2O$ [2.50 and 1.94 Å (mean value)] [27], $[ZrCp_2Me]_2O$ [2.474 (mean value) and 1.948(1) Å] [28], $[ZrCp_2(SPh)]_2O$ [2.547 (mean value) and 1.968(3) Å] [29], $[ZrCp_2(NCO)]_2O$ [Zr–O = 1.946(3) Å] [30]. The Cp ligands are substantially planar with a maximum deviation from planarity of 0.007 Å. The Zr-ring centroid distances are 2.211(2) and 2.218(3) Å.

The Zr–O–Zr fragment is almost linear [175.6(5)°] as observed in $[ZrCp_2Cl]_2O$ [168.9(8)°] [27], $[ZrCp_2Me]_2O$

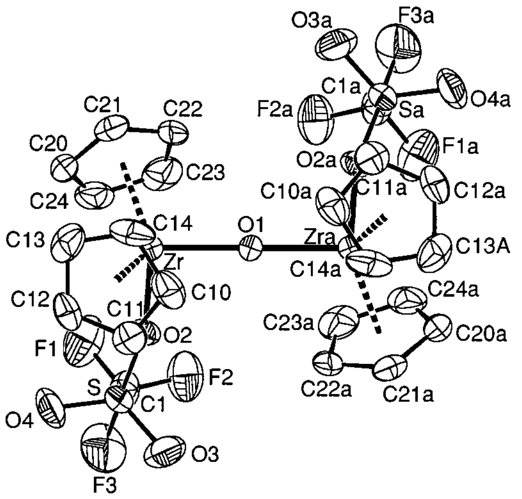

Fig. 1. PLATON [26] plot of the molecular structure of $[ZrCp_2(CF_3SO_3)]_2O$. Displacement ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond distance (Å) and angles (°) of $[ZrCp_2(CF_3SO_3)]_2O$

	Zr	O1	1.946(1)		S	O4	1.403(6)
	Zr	O2	2.129(6)		S	O2	1.472(5)
	S	C1	1.80(1)		S	O3	1.414(7)
O1	Zr	O2	94.9(2)	O2	S	O3	111.5(4)
Zr	O1	Zr	175.6(5)	O2	S	O4	112.7(4)
Zr	O2	S	153.2(4)				

Estimated standard deviations in parentheses refer to the least significant digit.

[174.1(3)°] [28], $[ZrCp_2(SPh)]_2O$ [165.8(2)°] [29] and $[ZrCp_2(NCO)]_2O$ [165.7(2)°] [30]. The linearity of the M–O–M bridge, as observed in other structurally characterized μ-oxo derivatives of Group 4 [31], suggests that maximum overlap of the empty orbitals of the MCp_2X fragments with lone pairs on oxygen [32] is operative in compound **7**. The resulting increase of bond order results in the Zr–O(1) distance [1.946(1)] which is shorter than the Zr–O(2) separation [2.129(6) Å]; the latter is comparable to those observed in $ZrCp_2(CF_3SO_3)_2\cdot THF$ [2.219(6) Å] [33], $[ZrCp_2(bipy)(CF_3SO_3)]CF_3SO_3$ [2.228(7) Å] [34] and $\{[ZrCp_2(CF_3SO_3)]_2(\mu\text{-}H)_2\cdot 0.5THF$ [2.205(2) Å] [35].

3. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were recorded on a FT-1725X instrument on solutions or nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air.

^1H-(200 MHz, TMS as reference) and ^{19}F-NMR (188 MHz, $CFCl_3$ as reference) spectra were measured on a Varian Gemini 200BB instrument.

$TiCp_2Cl_2$ (Fluka) and $ZrCp_2Cl_2$ (Fluka) were commercial products used without purification. Ph_3SiOH and $AgCF_3SO_3$ were commercial products (Aldrich) dried on P_4O_{10} in vacuo for 24 h prior to use.

$HfCp_2Cl_2$ [10] and the cyclopentadienyl derivatives of sodium and thallium were prepared according to literature [36]. $NaCp\cdot x THF$ was prepared from finely divided sodium and freshly prepared cyclopentadiene in THF. The colorless solution was evaporated to dryness and the resulting solid was transferred into vials sealed under an argon atmosphere. The compound contains variable amounts of THF depending on the drying conditions. TlCp was obtained from a vigorously stirred aqueous solution of TlOH (from Tl_2SO_4 and NaOH) and cyclopentadiene. The pale yellow solid was dried on P_4O_{10} in vacuo for 24 h, transferred into vials and sealed under an argon atmosphere.

Trifluoromethanesulfonic acid, CF_3SO_3H, was used in a mixture with the corresponding anhydride as a solution in heptane (0.026 M). The total amount of trifluorosulfonate groups was determined by acid/base titration in aqueous solution, while the $CF_3SO_3H/(CF_3SO_3)_2$ molar ratio was obtained from the ^{19}F-NMR spectrum.

$[N^nBu_3H][CF_3SO_3]$ was prepared by slow addition of N^nBu_3 to a heptane solution of $CF_3SO_3H/(CF_3SO_3)_2O$, vide supra. The colorless solid was filtered and dried in vacuo (92% yield). ^1H-NMR ($CDCl_3$, 25°C): $\delta = 8.8$ (br, 1 H), 3.06 (m, 6 H), 1.71 (m, 6 H), 1.46 (m, 6 H), 0.98 (t, 9 H). ^{19}F-NMR ($CDCl_3$, 25°C): $\delta = -78.46$ (s).

3.1. Preparation of MCp_4, $M = Ti, Zr, Hf$

3.1.1. NMR study of the reaction of MCp_2Cl_2 ($M = Zr, Hf$) with NaCp

M = Zr. A NMR tube was charged with $ZrCp_2Cl_2$ (0.014 g, 0.048 mmol), C_6D_6 (1 ml) and $NaCp\cdot 0.5THF$ (0.033 g, 0.27 mmol) for a NaCp/Zr molar ratio of 5.6. A spectrum recorded after 5 min showed the presence of $ZrCp_3Cl$ ($\delta = 5.69$ ppm) [13] as the only product in solution. After ca. 15 h shaking at r.t., the spectrum showed one signal only at 5.57 ppm typical of $ZrCp_4$ ([3]h)([8]b).

By using NaCp/Zr molar ratios < 4, a mixture of $ZrCp_2Cl_2$, $ZrCp_3Cl$ and $ZrCp_4$ was found after comparable reaction times.

M = Hf. A NMR tube was charged with $HfCp_2Cl_2$ (0.016 g, 0.042 mmol), C_6D_6 (1 ml) and $NaCp\cdot 0.5THF$ (0.032 g, 0.26 mmol), for a NaCp/Hf molar ratio of 6.5. A spectrum recorded after 5 min showed a signal due to unreacted starting material ($\delta = 5.82$ ppm) [10] and a new resonance at $\delta = 5.71$ ppm ($HfCp_3Cl$). After 30 min shaking at r.t., the spectrum showed signals at 5.71

and 5.63 ppm, the latter typical of $HfCp_4$ [8]. After ca. 40 h shaking at r.t., $HfCp_4$ was the only cyclopentadienyl compound present in solution.

By using NaCp/Hf molar ratios <4, a mixture of $HfCp_2Cl_2$, $HfCp_3Cl$ and $HfCp_4$ was found after a reaction time of ca. 50 h.

3.1.2. Preparation

M = Ti, **1**. (a) from $TiCl_4$. A solution of $TiCl_4$ (0.125 g, 1.32 mmol) in toluene (50 ml) was treated at r.t. with solid NaCp·0.08THF (0.74 g, 7.9 mol). The colour of the suspension quickly changed from yellow to red to brown and, after ca. 10 min, to blue–green. After 4 h stirring at r.t., the suspension was filtered, the solid was washed with toluene (10 ml) and the solution was dried in vacuo at r.t. The brown residue was suspended in heptane (10 ml) and filtered. The solid was dried in vacuo at r.t. (0.13 g, 33% yield) and identified as $TiCp_4$ ([3]a) by ^{1}H-NMR (200 MHz, C_6D_6, 25°C): $\delta = 5.30$ (s), 6.00 (s) ppm.

(b) from $TiCp_2Cl_2$. A suspension of $TiCp_2Cl_2$ (1.35 g, 5.4 mmol) in toluene (150 ml) was treated with NaCp·0.2THF (2.74 g, 26.7 mmol) obtaining a brown suspension, that quickly turned blue–green. After 2 h stirring at r.t., the suspension was filtered. The filtrate was evaporated to dryness under reduced pressure at r.t. and heptane (25 ml) was added; the resulting suspension was filtered, the brown solid was dried in vacuo and identified as $TiCp_4$ ([3]a) (1.00 g, 60% yield) by ^{1}H-NMR (200 MHz, C_6D_6, 25°C): $\delta = 5.30$ (s), 6.00 (s) ppm. The solid material is stable at r.t. and can be stored in sealed vials under an argon atmosphere at -30°C for several months.

M = Zr, **2**, Hf, **3**. The compounds were prepared by a modification of the published procedure consisting of extracting the crude reaction mixture with toluene under reduced pressure. Only the preparation of the compound with M = Zr is described in detail, the other being performed in a similar way, the only difference being the reaction time: 12 h for zirconium, 48 h for hafnium. A suspension of $ZrCp_2Cl_2$ (2.13 g, 7.3 mmol) in toluene (250 ml) was treated with NaCp·0.2THF (3.45 g, 33.7 mmol). After 12 h stirring at r.t., the resulting yellow suspension was filtered and the solid was extracted for about 6 h with refluxing toluene under reduced pressure (bath temperature, ca. 50°C). The extract was evaporated to dryness under reduced pressure at r.t. and heptane (25 ml) was added; the resulting suspension was filtered, and the yellow solid was dried in vacuo and identified as $ZrCp_4$ ([3]h)([8]b) (2.21 g, 80% yield) by ^{1}H-NMR (200 MHz, C_6D_6, 25°C): $\delta = 5.57$ (s).

Solid **2** (0.04 g, 0.11 mmol) was dissolved in THF (5 ml) giving a yellow solution. After 48 h stirring at r.t., a suspension of a yellow–orange solid in a light-yellow solution was obtained. The volatiles were removed from the solution by distillation under reduced pressure. A GC/MS analysis of the solution showed the presence of dicyclopentadiene [(*m*/*z*; assignment, relative abundance, %): 132, M^+, 35; 117, $M^+ - CH_3$, 5; 91, $C_7H_7^+$, 5; 66, $C_5H_6^+$, 100; 51,$C_5H_6 - CH_3^+$, 5; 39, $C_3H_3^+$, 8.

$HfCp_4$ ([8]b), yellow, 86% yield. ^{1}H-NMR (200 MHz, C_6D_6, 25°C): $\delta = 5.63$ (s). The spectrum remains unchanged at -90°C.

3.2. Reaction of 2 with TlCl

Solid TlCl (0.155 g, 0.65 mmol) and $ZrCp_4$ (0.111 g, 0.32 mmol) were stirred in toluene for ca. 72 h at r.t. During this period, the starting yellow suspension became almost colorless. After filtration, the solution was dried in vacuo at r.t. and the residue was dissolved in C_6D_6 and identified by ^{1}H-NMR as a ca. 2:1 mixture of TlCp (6.05 ppm) and $ZrCp_2Cl_2$ (5.91 ppm).

3.3. Reaction of 2 with compounds containing active protons

3.3.1. Ph_3SiOH

Ph_3SiOH (0.58 g, 2.1 mmol) was added to a yellow suspension of **2** (0.37 g, 1.05 mmol) in toluene (100 ml). After 5 h stirring at r.t., a colourless solution was obtained. After ca. 15 h, the solution was evaporated to dryness under reduced pressure at r.t. and heptane was added (10 ml). The suspension was filtered, the colorless solid was washed with heptane (3 × 5 ml) and dried in vacuo afforing $ZrCp_2(Ph_3SiO)_2$, **4** [15], (0.706 g, 98%), identified from analytical and spectral (IR, NMR) data. The same compound (IR, NMR) was obtained in a lower yield (41%) by using a Ph_3SiOH/Zr molar ratio of 1.

3.3.2. CF_3COOH

A suspension of **2** (0.18 g, 0.52 mmol) in toluene (15 ml) was cooled at ca. -40°C and treated with 0.09 ml of a $CF_3COOH/(CF_3CO)_2O$ mixture (5% w/w, 1.04 mmol of CF_3COOH). A colourless solution was obtained. The solvent was partially removed in vacuo at r.t., heptane (10 ml) was added and the resulting solid was filtered and dried in vacuo at r.t. The colorless solid (0.16 g, 82% yield) was identified as $ZrCp_2(CF_3COO)_2$ [16]. Anal. Found: C, 37.4; H, 1.8. $C_{14}H_{10}F_6O_4Zr$ Calc.: C, 37.6; H, 2.2. IR (nujol and PCTFE): $\tilde{\nu} = 3092$(mw), 1718(vs), 1405(ms), 1185(s), 1140(s), 1016(m), 808(s), 743(s), 718(m), 605(mw) cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6, 25°C): $\delta = 5.69$. ^{19}F-NMR (C_6D_6, 25°C): $\delta = -75.9$.

The same compound (IR, NMR) was obtained in a lower yield (36%) by using a CF_3COOH/Zr molar ratio of 1.

3.3.3. CF_3SO_3H (CF_3SO_3H/Zr molar ratio = 1)

A 0.026 M solution of CF_3SO_3H (75 ml, 1.95 mmol) in heptane-containing $(CF_3SO_3)_2O$ was added dropwise (2 h) to a suspension of **2** (0.73 g, 2.08 mmol) in toluene (100 ml). After 24 h stirring at r.t., the resulting pale-yellow suspension was filtered and the pale-yellow solid was dried in vacuo and identified as $ZrCp_3(CF_3SO_3)$, **5**, (0.54 g, 60% yield). Anal. Found: C, 44.2; H, 3.3. $C_{16}H_{15}F_3SO_3Zr$ Calc.: C, 44.1; H, 3.5. IR (nujol and PCTFE): $\tilde{v} = 3112$(w), 3047(w), 1444(m), 1339(ms), 1327(m), 1262(m), 1238(m), 1212(s), 1183(m), 1097(m), 1021(s), 815(s), 742(m), 687(m), 633(ms), 605(w), 592(w), 506(w) cm^{-1}. ^1H-NMR [37] (C_6D_6, 25°C): $\delta = 6.03$ (s). ^{19}F-NMR (C_6D_6, 25°C): $\delta = -77.8$ (s).

The same compound contaminated by small amounts of $ZrCp_2(CF_3SO_3)_2$, **6**, see below, was obtained by reaction of $ZrCp_4$ with $[NBu_3H][CF_3SO_3]$ in C_6D_6 in a 1:1 molar ratio.

3.3.4. CF_3SO_3H (CF_3SO_3H/Zr molar ratio = 2)

Triflic acid (containing ca. 15% of $(CF_3SO_2)_2O$; 0.1 ml, 1.0 mmol of CF_3SO_3H) was added at -60°C to a suspension of **2** (0.18 g, 0.51 mmol) in toluene (20 ml). A pale-brown solid immediately formed. After 0.5 h stirring at r.t., the suspension was cooled at -30°C overnight; after filtration, the resulting pale-brown solid was filtered and dried in vacuo (0.11 g) and identified as $ZrCp_2(CF_3SO_3)_2$, **6**, [17]. The solution was evaporated to dryness under reduced pressure at r.t. and heptane (10 ml) was added. The suspension was filtered and an additional crop (0.09 g) of $ZrCp_2(CF_3SO_3)_2$ was isolated (75% total yield). IR (nujol and PCTFE): $\tilde{v} = 3122$(w), 1439(w), 1337(s), 1321(s), 1292(m), 1267(s), 1238(vs), 1228(s), 1212(vs), 1176(s), 1129(w), 1098(m), 1071(m), 1028(vs), 859(m), 832(s), 767(w), 723(m), 669(w), 633(s), 620(m s), 589(m), 518(m), 508(w) cm^{-1}. ^1H-NMR ($CDCl_3$, 25°C): $\delta = 6.6$ (s). ^{19}F-NMR ($CDCl_3$, 25°C): $\delta = -77.5$ (s).

The same compound was obtained (60% yield) by reaction of $ZrCp_2Cl_2$ with two equivalents of $AgCF_3SO_3$ in toluene.

3.4. Reaction of $ZrCp_3(CF_3SO_3)$ with H_2O: synthesis of $[ZrCp_2(CF_3SO_3)]_2O$, 7

3.4.1. NMR monitoring

A NMR tube was charged with $ZrCp_3(CF_3SO_3)$ (0.016 g, 0.037 mmol) and C_6D_6 (1 ml) and the suspension was treated with H_2O (1 µl, 0.055 mmol). A ^1H-NMR spectrum recorded after 5 min showed a signal due to unreacted starting material ($\delta = 6.03$ ppm), and new resonances at $\delta = 5.82$ ppm, assigned to $[ZrCp_2(CF_3SO_3)]_2O$ (vide infra), and at 6.42, 6.50 and 2.93 ppm assigned to CpH [38]. The conversion of $ZrCp_3(CF_3SO_3)$ into $[ZrCp_2(CF_3SO_3)]_2O$ was almost complete in about 10 min.

3.4.2. Preparation

Water (2.6 µl, 0.14 mmol) was added to a suspension of $ZrCp_3(CF_3SO_3)$ (0.12 g, 0.27 mmol) in toluene (10 ml). After 4 h stirring at r.t., a colorless suspension was obtained which turned pale-yellow after 24 h stirring at r.t. The suspension was evaporated to dryness under reduced pressure at r.t. and the colourless solid dried in vacuo was identified as **7** (0.05 g, 49% yield). Anal. Found: C, 34.9; H, 2.6. $C_{22}H_{20}F_6O_7S_2Zr_2$ Calc.: C, 34.9; H, 2.7. IR (nujol and PCTFE): $\tilde{v} = 3112$(w), 1435(w), 1365(m), 1339(s), 1293(m), 1263(m), 1239(s), 1212(s), 1187(s), 1172(s), 1125(m), 1070(m), 1020(s), 917(w), 838(m), 815(s), 741(s), 633(s), 608(m), 593(m), 569(w), 525(w), 505(m) cm^{-1}. ^1H-NMR (C_6D_6, 25°C): $\delta = 5.82$ (s). ^{19}F-NMR (C_6D_6, 25°C): $\delta = -78.3$ (s).

3.5. Crystal structure solution and refinement of 7

A complete list of all atomic coordinates, anisotropic displacement parameters, and interatomic distances are available as Supplementary Material and have been deposited with the Fachinformationszentrum Karlsruhe, D-76344, Eggenstein-Leopoldshafen (FRG), depository number CSD-407980.

3.5.1. Crystal data

$C_{22}H_{20}F_6O_7S_2Zr_2$, M = 756.96 g mol^{-1}, monoclinic, space group C2/c (no. 15), $a = 19.525(4)$, $b = 9.028(2)$, $c = 16.152(5)$ Å, $\beta = 107.31(2)°$, $V = 2718.2(1)$ Å^3, $Z = 4$, $d_{calc} = 1.850$ g cm^{-3}, $\lambda(Cu{-}K_\alpha) = 1.54184$ Å, $T = 291$ K, $\mu = 85.66$ cm^{-1}, $F(000) = 1496$.

Single crystals of $[ZrCp_2(CF_3SO_3)]_2O$ were obtained by slow cooling of a toluene solution at -30°C. Diffraction data were collected at 291 K on a colorless rod of approximate dimensions 0.7 × 0.3 × 0.25 mm with an ENRAF NONIUS CAD4 diffractometer using graphite-monochromated $Cu{-}K_\alpha$ radiation ($\lambda = 1.54184$ Å). A total of 5031 reflections were recorded with the $\omega - 2\theta$ scan mode in the range $4.0 < \Theta < 68.0°$. An empirical absorption correction based on azimuthal ψ scans [39] was applied before averaging over symmetry equivalent data. 2637 independent intensities were used to solve the structure by direct methods [40]. A full-matrix least-squares refinement [41] based on 1484 unique observations with $I > 1.0\ \sigma(I)$ was carried out with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located in idealized positions with isotropic thermal parameters $U(H) = 1.3\ U(C)$ and allowed to ride on their C-atoms. Refinement converged with 178 parameters using a statistical weighting scheme $w = 1/[\Sigma^2(F_o)]$ at values of $R = 0.054$ and $R_w = 0.049$, GOF = 1.206. Atomic coordinates are given in Table 2. Calculations were performed using the SDP system of programs [41].

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $[ZrCp_2(CF_3SO_3)]_2O$

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
Zr	0.10254(4)	0.0394(1)	0.30898(4)	3.54(1)
S	0.1068(1)	0.2321(3)	0.4990(1)	4.82(6)
F1	0.1552(3)	0.4762(7)	0.4547(5)	10.1(2)
F2	0.0423(3)	0.4739(8)	0.4339(4)	9.3(2)
F3	0.1134(4)	0.4943(8)	0.5630(5)	11.3(2)
O1	0.000	0.0311(9)	0.250	3.6(2)
O2	0.0931(3)	0.1868(7)	0.4079(3)	4.7(2)
O3	0.0487(4)	0.1954(9)	0.5304(4)	8.5(2)
O4	0.1768(4)	0.1991(9)	0.5502(4)	7.7(2)
C1	0.1028(5)	0.430(1)	0.4861(7)	6.9(3)
C10	0.0770(6)	-0.219(1)	0.3461(6)	6.6(3)
C11	0.1076(5)	-0.151(1)	0.4237(6)	6.0(3)
C12	0.1782(5)	-0.118(1)	0.4316(6)	6.2(3)
C13	0.1913(5)	-0.169(1)	0.3541(6)	7.0(3)
C14	0.1257(6)	-0.229(1)	0.3036(6)	7.6(3)
C20	0.2097(5)	0.140(1)	0.2720(6)	6.7(3)
C21	0.1678(5)	0.064(1)	0.1981(5)	6.6(3)
C22	0.1034(5)	0.148(1)	0.1666(5)	6.7(3)
C23	0.1065(5)	0.267(1)	0.2190(6)	7.6(3)
C24	0.1726(5)	0.263(1)	0.2847(6)	7.3(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a^2*beta(1,1) + b^2*beta(2,2) + c^2*beta(3,3) + ab(cosγ)beta(1,2) + ac(cosβ)beta(1,3) + bc(cosα)beta(2,3)]. Estimated standard deviations in parentheses refer to the least significant digit.

4. Conclusions

A close re-examination of the synthetic procedures to the tetra(cyclopentadienyl) derivatives of titanium(IV), zirconium(IV) and hafnium(IV) has shown that: (a) the compounds are not stable in ethereal solvents; (b) the best preparative results have been obtained in aromatic hydrocarbons (toluene); (c) the nature of the cyclopentadienylating agent is critical: as a matter of fact, TlCp does not react with $ZrCp_2Cl_2$ ($ZrCp_4$ is really a cyclopentadienylating agent for TlCl), although its reaction with NaCp (a biphasic solid–liquid system) is complete and fast.

The use of THF may be harmful in some cases. As a matter of fact, $ZrCp_4$ is not stable in THF; the high affinity for oxygen of Group 4 elements in high oxydation state may trigger the deoxygenation of the ether.

The reactivity, which has been studied for $ZrCp_4$, is similar to that of $ZrCp_2R_2$ (R = hydrocarbyl group) derivatives, i.e. two cyclopentadienyl ligands are lost as CpH by reaction of $ZrCp_4$ with weak protic substances such as diols or tertiary ammonium salts: as a general rule, the product is the dicyclopentadienyl derivative $ZrCp_2L_2$ (L_2 = two singly negatively charged oxygen ligand). On the other hand, once a very strong Brønsted acid is used, high yields of the monosubstituted derivative $ZrCp_3(CF_3SO_3)$ are obtained. It is worth noting that only with the strong acid CF_3SO_3H, the product of monosubstitution can be isolated, presumably due to the weak coordinating power of the conjugated base.

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