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Reactions of Bis(cyclopentadienyl)dimethylzirconium with Fluorocarbon Acids. Structure, Dynamic Properties, and ^{91}Zr NMR Spectra of $(C_5H_5)_2Zr[HC(SO_2CF_3)_2\text{-}O,O'][HC(SO_2CF_3)_2\text{-}O]$

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Reaction of $Cp_2Zr(CH_3)_2$ with 1 and 2 equiv of fluorocarbon acids such as $H_2C(SO_2CF_3)_2$ yields $Cp_2Zr(CH_3)[HC(SO_2CF_3)_2]$ and $Cp_2Zr[HC(SO_2CF_3)_2]_2$, respectively. The structure of the latter compound (crystal data: $P\bar{1}$, $a = 8.834$ (2) Å, $b = 15.480$ (5) Å, $c = 20.887$ (6) Å, $\alpha = 109.71$ (2)°, $\beta = 90.64$ (2)°, $\gamma = 95.20$ (2)° at −100 °C, $Z = 4$, $R = 0.033$, $R_w = 0.045$) demonstrates two $HC(SO_2CF_3)_2$ ligands. One is bidentate and the other one monodentate, both being bonded to Zr through the sulfone oxygen atoms. The two types of ligands interconvert rapidly on the NMR time scale. ^{91}Zr chemical shifts are reported.

Introduction

We have previously pointed out the advantages of use of the fluorocarbon acids $H_2C(SO_2CF_3)_2$ (1), $PhCH(SO_2CF_3)_2$ (2), and $HN(SO_2CF_3)_2$ (3) for synthesis of cationic organometallic compounds. These include solubility in noncoordinating, apolar solvents and the nonhygroscopic nature of 1 and 2.[1] With few exceptions, $HC(SO_2CF_3)_2^-$ and its congeners do not coordinate to complex cations formed from middle- and late-transition-metal elements. In $(Ph_3P)_2Pt(H)[HC(SO_2CF_3)_2\text{-}C]$, the fluorocarbon acid moiety is covalently bonded to platinum through the methine carbon atom,[2,3] and in $Ti_2(\mu\text{-}i\text{-}PrO)_2(i\text{-}PrO)_4[HC(SO_2CF_3)_2\text{-}O,O']_2$, the $HC(SO_2CF_3)_2$ ligand is bonded to titanium through the sulfone oxygen atoms.[4] Reactions of 1 with bis(cyclopentadienyl) alkyl derivatives of the electropositive element zirconium have been studied in the expectation of obtaining actual or incipient cationic complexes. Such materials, e.g. $[Cp_2Zr(CH_3)(THF)][BPh_4]$, have attracted attention as ethylene polymerization catalysts,[5] as have alkylchromium cations.[6] X-ray photoelectron spectroscopy data indicate that $Cp_2Zr(CH_3)^+$ is the active species in the $Cp_2Zr(CH_3)_2$–$(CH_3AlO)_x$ olefin polymerization catalyst system.[7] Surface-supported cationic thorium complexes are also active as olefin polymerization catalysts.[8] Protonation of $Cp^*{}_2Zr(CH_3)_2$ ($Cp^* = (CH_3)_5C_5$) with CF_3SO_3H to form $Cp^*{}_2Zr(CF_3SO_3)_2$, which can be methylated by $(CH_3)_3Al$ to produce $Cp^*{}_2Zr(CH_3)(CF_3SO_3)$, has been reported.[9] Described here are the reactions of $Cp_2Zr(CH_3)_2$ (4) with the fluorocarbon acids 1–3 and the characterization of $HC(SO_2CF_3)_2^-$ complexes of $Cp_2Zr(CH_3)^+$ and of Cp_2Zr^{2+}. We believe that ^{91}Zr NMR spectroscopy is potentially a very useful characterization technique for organozirconium compounds and discuss the ^{91}Zr NMR spectra of these materials.

Results and Discussion

Although 1 appears unreactive toward the metal–carbon σ bonds in, for example, $CH_3Mn(CO)_5$ and $Ph_3SnC_3H_5$, reaction of 4 with 1 equiv of 1 in toluene is rapid and quantitative at room temperature. The product, $Cp_2Zr(CH_3)[HC(SO_2CF_3)_2]$ (5), is isolated in 68% yield after evaporation of the solvent and recrystallization from hexane. The compound $Cp_2Zr(CH_3)[PhC(SO_2CF_3)_2]$ (6) is similarly prepared. Spectroscopic and analytical data are given in Tables I and II, respectively. Although the remaining Zr–CH_3 group in 5 and 6 can be removed by reaction with an additional 1 equiv of fluorocarbon acid (eq 1), the rate of this reaction is slower than that leading

$$Cp_2Zr(CH_3)_2 \xrightarrow{H_2C(SO_2CF_3)_2} Cp_2Zr(CH_3)[HC(SO_2CF_3)_2] + CH_4 \xrightarrow{H_2C(SO_2CF_3)_2} Cp_2[HC(SO_2CF_3)_2]_2 + CH_4 \quad (1)$$

to loss of the first methyl group as methane and, therefore, the reaction can be controlled by adjusting the fluorocarbon acid:4 ratio. The nitrogen-centered acid 3 is more reactive, and so $Cp_2Zr(CH_3)[N(SO_2CF_3)_2]$ (7) was not obtained in pure form owing to contamination with $Cp_2Zr[N(SO_2CF_3)_2]_2$. The hafnium analogue of 5, $Cp_2Hf(CH_3)[HC(SO_2CF_3)_2]$ (8), was prepared from $Cp_2Hf(CH_3)_2$ and 1, but the reaction is slower than with 4, probably because of the greater strength of the Hf–C bond that is anticipated from the short metal–carbon bond distance.[10] Reaction of 4 in toluene with CF_3SO_3H produces $Cp_2Zr(CH_3)(CF_3SO_3)$ (9). It is difficult to obtain 9 in pure form when the reaction is run on a large scale because, unlike 1, CF_3SO_3H is not very soluble in toluene and so it is hard to avoid localized high concentrations of this acid. All of these $Cp_2Zr(CH_3)^+$ derivatives are oxygen-sensitive; the solids turn yellow or orange after brief exposure to air.

In dichloromethane, 5 and 6 are nonelectrolytes. Therefore, 5 for example is formulated in accordance with the 18-electron rule as $Cp_2Zr(CH_3)[HC(SO_2CF_3)_2\text{-}O,O']$, in

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Table I. NMR Data[a,b]

$Cp_2ZrMe[HC(SO_2CF_3)_2]$ (**5**)	^1H, 6.26 (Cp), 4.18 ($HC(SO_2CF_3)_2$), 0.46 (CH_3); ^{13}C, 120.7 (CF_3, J_{CF} = 324), 113.8 (Cp), 50.8 ($HC(SO_2CF_3)_2$), 38.7 (CH_3, J_{CH} = 122); ^{19}F, −80.3
$Cp_2ZrMe[PhC(SO_2CF_3)_2]$ (**6**)	^1H, 6.25, 0.45; ^{13}C, 121.4 (J_{CF} = 322), 113.5, 38.1 (CH_3, J_{CH} = 122); ^{19}F, −76.9
$Cp_2ZrMe[N(SO_2CF_3)_2]$ (**7**)	^1H, 6.41, 0.68; ^{13}C, 119.7 (J_{CF} = 320), 114.8, 40.8 (J_{CH} = 121); ^{19}F, −78.2
$Cp_2HfMe[HC(SO_2CF_3)_2]$ (**8**)	^1H, 6.35, 4.1, 0.43; ^{13}C, 112.9, 50.6, 37.7
$Cp_2ZrMe(CF_3SO_3)$ (**9**)	^{13}C, 113.3, 36.3; ^{19}F, −77.2[c]
$Cp_2ZrMe[HC(SO_2)_2(CF_2)_3]$ (**11**)	^1H, 6.42, 4.37, 0.66; ^{13}C, 114.4, 53.5, 40.2 (Me); ^{19}F, −117.7, −122.0 (SO_2CF), −113.6, −113.5 (CCF)
$Cp_2Zr(CH_3CO)[HC(SO_2CF_3)_2]$ (**12**)	^1H, 6.03, 4.17, 3.05 (CH_3); ^{13}C, 317.0 (CH_3CO, d, $^2J_{CH}$ = 7; T_1 = 2.5 s), 120.7 (CF_3), 110.6 (Cp), 53.6 (CSO_2), 33.7 (CH_3, dd, J_{CH} = 130, J_{CC} = 21)[d]
$K[Cp_2ZrMe[C(SO_2CF_3)_2]]$ (**13**)	^1H, 5.85, 0.0 (CH_3); ^{13}C, 112.6 (J_{CF} = 331), 110.9, 57.3 (C_{ipso}, s), 31.1 (CH_3, q, J_{CH} = 121); ^{19}F, −78.6[e]
$Cp_2Zr[HC(SO_2CF_3)_2]_2$ (**14**)	^1H, 6.65, 4.32; ^{13}C, 120.7 (J_{CF} = 324), 118.4; ^{19}F, −79.8
$Cp_2Zr[PhC(SO_2CF_3)_2]_2$ (**15**)	^1H, 7.5 (m), 6.52; ^{13}C, 137.2 (C_{ortho}), 132.6 (C_{ipso}), 128.7 (C_{meta}), 128.5 (C_{para}), 122.9 (J_{CF} = 323), 116.6 (Cp); ^{19}F, −77.7[f]
$Cp_2Zr[N(SO_2CF_3)_2]_2$ (**16**)	^1H, 6.52; ^{13}C, 120.9 (J_{CF} = 321), 116.6 (Cp); ^{19}F, −78.7[f]
$Cp_2Zr[HC(SO_2)_2(CF_2)_3]_2$ (**17**)	^1H, 6.70 (Cp), 4.58; ^{13}C, 118.4; ^{19}F, −117.5, −121.7 (SO_2CF), −112.6, −132.5 (CCF)
$Cp_2Zr(CF_3SO_3)_2$ (**18**)	^1H, 6.76; ^{13}C, 118.7; ^{19}F, −77.5
$Cp_2ZrMe(OSiMe_2\text{-}t\text{-}Bu)$	^{13}C, 110.0 (Cp), 26.2 (t-Bu CH_3), 20.8 ($ZrCH_3$), 19.0 (t-Bu), −2.8 ($SiCH_3$); ^{29}Si, 11.7
$Cp_2Zr[C_3H_5C(SO_2CF_3)_2]_2$ (**19**)	^1H, 6.61 (Cp), 5.92 (=CH, m), 5.18 (d, =CH_2, $J_{CH(trans)}$ = 17), 5.08 (d, =CH_2, $J_{CH(cis)}$ = 10), 3.20 (d, CH_2, 7); ^{13}C, 136.7 (=CH, J_{CH} = 155), 121.2 (J_{CF} = 327), 118.4 (Cp), 116.9 (=CH_2, J_{CH} = 153), 60.8 ($C(SO_2)_2$)

[a] Chemical shifts in ppm; coupling constants in Hz. [b] CD_2Cl_2 solvent unless otherwise noted. [c] Toluene solvent. [d] C–C couplings observed in the $CH_3{}^{13}CO$ analogue. [e] THF-d_8 solvent. [f] CD_3CN solvent.

Table II. Analytical and Yield Data

compd (yield, %)	anal. calcd (found), %
5 (68)	C, 32.6 (31.9); H, 2.7 (2.6); S, 12.4 (12.3); Zr, 17.7 (18.0); mol wt, 515 (503, osmometric in C_6H_6)
6 (51)	C, 40.6 (40.2); H, 3.0 (3.0)
11 (71)	C, 34.1 (34.2); H, 2.8 (2.8)
12 (95)	C, 33.1 (32.7); H, 2.6 (2.5); mol wt, 543 (550, in $CHCl_3$).
14 (64)	C, 24.7 (24.6); H, 1.5 (1.5); S, 16.4 (16.1); Zr, 11.7 (11.9); mol wt, 779 (775, in $CHCl_3$)
15 (32)	C, 36.1 (36.4); H, 2.1 (2.4)
16 (82)	C, 21.5 (21.6); H, 1.3 (1.0); N, 3.6 (3.6)
17 (56)	C, 26.9 (26.7); H, 1.5 (1.6)
18 (52)	C, 28.4 (27.6); H, 2.0 (2.0)
19 (70)	C, 30.7 (30.4); H, 2.3 (2.6)

Table III. Conductance Data

compd	concn, 10^{-3} M (CH_2Cl_2)	Λ, Ω^{-1} cm^2 mol^{-1}	concn, 10^{-3} M (CH_3CN)	Λ, Ω^{-1} cm^2 mol^{-1}
5	1.9	1.0	2.8	72
6	1.8	1.7	1.9	69
11	2.5	1.5	2.0	89
14	1.6	2.3	1.9	110
15			1.8	175
17	1.8	1.7	1.1	171
18	1.7	<0.1	1.7	129
19	2.1	1.8	1.2	201
$[Pr_4N][HC(SO_2CF_3)_2]$	1.3	32	1.5	153
$[Pr_4N][N(SO_2CF_3)_2]$	1.3	30	1.3	146
$[PPN][HC(SO_2CF_3)_2]$[a]	1.0	64	0.9	133

[a] PPN is $(Ph_3P)_2N^+$.

which the $HC(SO_2CF_3)_2^-$ anion acts as a bidentate ligand and bonds to zirconium by means of its nongeminal oxygen atoms. This mode of bonding has been crystallographically established in $Ti_2(\mu\text{-}i\text{-PrO})_2(i\text{-PrO})_4[HC(SO_2CF_3)_2\text{-}O,O']_2$ and is probably a general feature of $HC(SO_2CF_3)_2^-$ derivatives of electropositive metals. Consistent with this is the high solubility of **5** in hexane, which is indicative of its covalent nature. The ^{19}F NMR spectra of **5**, **6**, and **7** in CD_2Cl_2 are invariant between +27 and −100 °C and comprise singlets in the −77 to −80 ppm range. The two CF_3 groups in the $HC(SO_2CF_3)_2\text{-}O,O'$ ligand are geometrically nonequivalent and should give rise to two ^{19}F resonances. That such are not observed indicates that the ligands in **5**, **6**, and **7** are fluxional, undergoing in solution an effective C_2 rotation that permutes the two fluorine environments. The effect of O,O′-coordination on the electron density distribution in the $PhC(SO_2CF_3)_2$ ligand is manifested in the ^{13}C chemical shifts of the phenyl ipso carbon, 125.96 ppm (CH_2Cl_2 solution). $\delta(^{13}C)$ values for the ipso carbons in **2** and $[(n\text{-Bu})_4N][PhC(SO_2CF_3)_2]$ are 119.4 and 132.0 ppm, respectively.[11] It is known that introduction of unit negative charge leads to a ca. 160 ppm deshielding of the phenyl ipso carbon nucleus.[11] In the context of this crude approximation, about half the negative charge introduced by deprotonation of $PhCH(SO_2CF_3)_2$ is transferred to the $Cp_2Zr(CH_3)$ moiety upon coordination via the sulfone oxygen atoms. Both this bonding mode and the stereochemical nonrigidity proposed are unequivocally demonstrated below for $Cp_2Zr[HC(SO_2CF_3)_2]_2$.

Attempts were made to force a different type of bonding by use of the cyclic fluorocarbon acid $H_2C(SO_2)_2(CF_2)_3$ (**10**), in which it was hoped that incorporation of the SO_2 groups into a six-membered ring would disfavor chelation.[12] However, the ^{19}F NMR spectrum of $Cp_2Zr(CH_3)[HC(SO_2)_2(CF_2)_3]$ (**11**) at 27 °C shows two doublets (due to F–F coupling) centered at −119.6 (4 F, SO_2CF_2) and −123.6 (2 F, CCF_2) ppm. The SO_2CF fluorine nuclei in the stereochemically nonrigid c-$HC(SO_2)_2(CF_2)_3$ ring are equivalent, so **11** also is fluxional. The ^{91}Zr NMR chemical shifts of **5** and **11** are very similar, +20 and +80 ppm, respectively (vide infra), indicating that they have similar structures.

In acetonitrile, **5**, **6**, **7**, and **11** behave as 1:1 electrolytes with molar conductances ranging from 72 to 89 Ω^{-1} cm^2 mol^{-1} (cf. Table III). We believe that this reflects solvolysis to produce the $Cp_2Zr(CH_3)(CH_3CN)_2^+$ cation, whose BPh_4^- salt has been reported earlier.[13] Tetrahydrofuran is slowly polymerized by **6**, so measurements were not made in this solvent.

In dichloromethane solution, **5** consumes 1 equiv of carbon monoxide to produce $Cp_2Zr(CH_3CO)[HC(SO_2CF_3)_2]$ (**12**). The conductance of a 1.6 × 10^{-3} M so-

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(12) The fluorocarbon acid $H_2C(SO_2)_2(CF_2)_3$ was prepared from $FO_2S(CF_2)_3SO_2F$ by the method of Koshar and Mitsch.[15] Full details of the synthesis and crystal structure will be published separately.

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lution in dichloromethane is 2.8 Ω^{-1} cm^2 mol^{-1}, and ν_{CO} is 1562 cm^{-1} (Nujol). The ^{19}F NMR spectrum comprises a singlet down to −100 °C. These data indicate that **12** contains a η^2-acetyl group and a fluxional, monodentate, oxygen-bonded $HC(SO_2CF_3)_2$ ligand so that zirconium achieves an 18-electron configuration. That only one molecule of CO has been incorporated follows from the ^{13}C NMR spectrum of the $CH_3{}^{13}CO$ analogue (ν_{CO} = 1522 cm^{-1}), in which the acetyl methyl carbon atom appears as a 22-Hz doublet at 33.6 ppm; the CH_3CO carbon atom gives rise to a singlet at 317.0 ppm. The $Cp_2Zr(CH_3CO)$ fragment in **12** is probably similar to that in crystallographically characterized $Cp_2Zr(\eta^2\text{-}CH_3CO)(CH_3)$ (ν_{CO} = 1545 cm^{-1}).[14] In solution, the latter compound dissociates with loss of CO, whereas **12** (and also $[Cp_2Zr(COCH_3)(CH_3CN)][BPh_4]$[5d]) is stable.

A reaction between **5** and excess potassium hydride in THF-d_8 was carried out in an attempt to deprotonate the $Zr{-}CH_3$ group and thus form a $Zr{=}CH_2$ derivative. Instead, however, it appears that the proton on the $HC(SO_2CF_3)_2$ ligand is removed to form $K[Cp_2Zr(CH_3)[C(SO_2CF_3)_2\text{-}O,O']]$ (**13**). In its gated ^{1}H-decoupled ^{13}C NMR spectrum, the $Zr{-}CH_3$ group appears as a 121-Hz quartet (δ 31.1) and the $C(SO_2CF_3)_2$ carbon as a singlet at 57.3 ppm. The ^{19}F NMR spectrum consists of a singlet at δ −78.6. Compound **13** is the first complex containing the $C(SO_2CF_3)_2{}^{2-}$ dianion as a ligand. However, it is known that **1** reacts with 2 equiv of CH_3MgCl to form the putative $(ClMg)_2C(SO_2CF_3)_2$ and 2 equiv of methane.[15] No reaction between **5**, **6**, or **7** and ethylene was observed. Evidently, molecules with oxygen or other donor functions are required in order to displace the coordinated fluorocarbon acid ligands.

Both methyl groups in **4** may be removed by reaction with 2 equiv of fluorocarbon acids in toluene at room temperature, and in this way, $Cp_2Zr[HC(SO_2CF_3)_2]_2$ (**14**), $Cp_2Zr[PhC(SO_2CF_3)_2]_2$ (**15**), $Cp_2Zr[N(SO_2CF_3)_2]_2$ (**16**), $Cp_2Zr[HC(SO_2)_2(CF_2)_3]_2$ (**17**), and $Cp_2Zr(CF_3SO_3)_2$ (**18**) were obtained. Compound **14** is formulated on the basis of the crystal structure described below as $Cp_2Zr[HC(SO_2CF_3)_2\text{-}O,O'][HC(SO_2CF_3)_2\text{-}O]$; that is, it contains one oxygen-bonded bidentate ligand and one monodentate oxygen-bonded $HC(SO_2CF_3)_2$ group (cf. Figure 2). Compounds **14**–**18** are nonelectrolytes in dichloromethane. They behave as 2:1 electrolytes in acetonitrile (cf. Table III) because of solvolysis to produce $Cp_2Zr(CH_3CN)_3{}^{2+}$, the $BPh_4{}^-$ salt of which has recently been reported.[13] This point has been confirmed by ^{91}Zr NMR spectroscopy (vide infra). Solutions of **14** in THF are unstable because of rapid polymerization of the solvent; **14** also causes very fast cationic polymerization of methyl vinyl ether. No reaction was observed between CH_2Cl_2 solutions of **14**–**17** and ethylene, doubtless because Zr–O bonds are stronger than any Zr–C bonds that could be formed. A phenomenological measure of this preference for bonding to oxygen is seen in $Cp_2Zr[CH_2{=}CHCH_2C(SO_2CF_3)_2\text{-}O,O']_2$ (**19**). This compound contains an allyl group attached to the methine carbon atom of the fluorocarbon acid ligand. Both ^{1}H and ^{13}C NMR data show that the allyl groups are merely pendant and are not bonded to zirconium.

Dynamic Properties. The mono- and bidentate fluorocarbon acid ligands in **14**–**16** interconvert rapidly on the NMR time scale, as their ^{19}F NMR spectra show only singlets at −77 to −80 ppm even at low temperature; the spectra of **11** and **17** comprise AA′MM′XY patterns.[12]

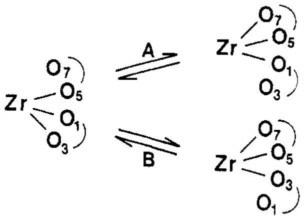

Figure 1. Proposed low- (A) and high-temperature (B) exchange processes in $Cp_2Zr[HC(SO_2CF_3)_2]_2$. For clarity, only zirconium and nearby sulfone oxygen atoms are shown.

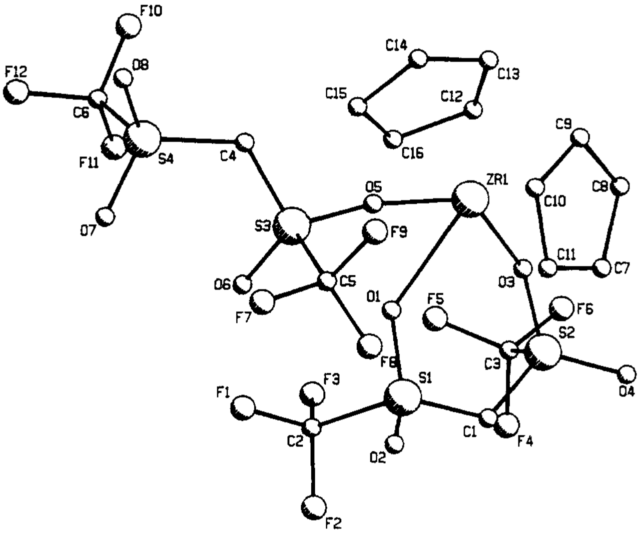

Figure 2. PLUTO drawing of the structure of $Cp_2Zr[HC(SO_2CF_3)_2]_2$.

Limiting low-temperature ^{19}F spectra have been obtained only for **14**. At −94 °C, the 376-MHz ^{19}F NMR spectrum in CD_2Cl_2 exhibits four singlets of equal area at −82.07, −81.31, −79.99, and −79.23 ppm. As the temperature is increased to ca. −70 °C, coalescence occurs, and at −57 °C, the −82.07, −79.99 and −81.31, −79.23 ppm resonances merge in a *pairwise* fashion to give *two* singlets at −80.8 and −80.0 ppm. These in turn coalesce on warming to −47 °C, and thus, at room temperature only a singlet at −79.9 ppm is observed. Occurrence of *two* two-site exchange processes is explicable in terms of interconversion of the mono- and bidentate ligands shown in Figure 1. At low temperature, the "dangling" oxygen, O7 or O8 in Figure 2, can displace the "lateral" oxygen, O3. This permutes O7 (or O8) and O3 and also O5 and O1. Concomitantly, the nearby, chemically inequivalent CF_3 groups also interchange in a pairwise fashion, as is observed. We suggest that, at slightly higher temperature, permutation of the "lateral" (O7 or O8) and "central" (O1) oxygen atoms occurs. If this happens two or more times, O7 (or O8), O1, O3, and O5 can all rapidly interconvert and this would give rise to a single ^{19}F resonance. Analysis of the variable-temperature ^{19}F spectra of **14** has been carried out in this context, and we find that the free energies of activation of these low- and high-temperature processes are 8.5 ± 0.2 and 10.0 ± 0.2 kcal mol^{-1} at −94 and −44 °C, respectively.

Zirconium-91 NMR Spectra. Few studies of ^{91}Zr NMR spectra have been published.[16] We find this to be a helpful technique, and in the compounds reported here, the chemical shift range is quite large. ^{91}Zr (11% natural abundance) is readily observed at 9.4 T without resort to

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Table IV. ^{91}Zr Chemical Shifts

compd (solvent)	$\delta(^{91}\mathrm{Zr})$ $(w/2)$[a]
$Cp_2Zr(Me)[HC(SO_2CF_3)_2]$ (CH_2Cl_2)	20 (7000)
$Cp_2Zr(Me)[PhC(SO_2CF_3)_2]$ (CH_2Cl_2)	139 (6000)
$Cp_2Zr(Me)[N(SO_2CF_3)_2]$ (CH_2Cl_2)	94 (4000)
$Cp_2Zr(Me)(CF_3SO_3)$ (toluene)	56 (3500)
$Cp_2Zr(Me)[HC(SO_2)_2(CF_2)_3]$ (CH_2Cl_2)	80 (5000)
$Cp_2Zr(CH_3CO)[HC(SO_2CF_3)_2]$ (CH_2Cl_2)	−400 (7000)
$Cp_2Zr[HC(SO_2CF_3)_2]_2$ (CH_2Cl_2)	−331 (180)
$Cp_2Zr[N(SO_2CF_3)_2]$ (glyme)[b]	−270 (1500)
$Cp_2Zr[N(SO_2CF_3)_2]$ (CH_3CN)	−455 (2000)
$Cp_2Zr(CF_3SO_3)_2$ (CH_2Cl_2)	−302 (400)
Cp_2ZrMe_2 (C_6D_6)	385 (2300)
$Cp_2Zr(CH_2Ph)_2$ (toluene)	380 (2800)
$Cp_2Zr(Me)Cl$ (CH_2Cl_2)	126 (1400)
Cp_2ZrCl_2 (CH_2Cl_2)	−113 (250)[c]
$Cp_2Zr(Me)(OSiMe_2\text{-}t\text{-}Bu)$ (toluene)	−110 (3700) [80 °C]
$(Me_5Cp)ZrMe_3$ (toluene)	455 (700)
$(Me_5Cp)ZrClMe_2$ (toluene)	263 (600)
$(Me_2Cp)_2ZrMe_2$ (toluene)	455 (1700)
n-BuB(pyrazolyl)$_3$ZrCl$_3$ ($CDCl_3$)	563 (200) [55 °C]
$CpCo[(EtO)_2PO]_3ZrCl_3$ ($CDCl_3$)	355 (3000) [55 °C]
$CpZrCl_3 \cdot MeOC_2H_4OMe$ ($CDCl_3$)	125 (3600) [50 °C]
$CpZrCl_3 \cdot Me_2NC_2H_4NMe_2$ ($CDCl_3$)	195 (2600) [50 °C]

[a] Shifts in ppm relative to external 1 M Cp_2ZrBr_2 in THF; line widths at half-maximum in Hz. [b] Glyme is 1,2-dimethoxyethane. [c] From ref 16a.

heroic measures. By the method of McGlinchey et al.,[16a] 1 M Cp_2ZrBr_2 in THF has been employed as the external reference. ^{91}Zr has $I = {}^5/_2$ and, therefore, because of fast quadrupolar relaxation, often gives rise to broad lines. Often too these are found atop a base line that undulates because of pulse breakthrough and acoustic ringing, problems frequently encountered with low-γ nuclei such as ^{17}O. Base line roll can be reduced by removing early parts of the FID (but with serious degradation of the signal to noise ratio) or by plotting narrow portions of the spectrum. ^{91}Zr NMR spectroscopy must be employed with caution when mixtures or otherwise uncharacterized materials are studied. Species having narrow line widths become deceptively prominent in the spectra, and compounds in which the zirconium coordination is highly unsymmetrical and in which the electric field gradients are large may not be observable at all. A conspicuous example is Cp_4Zr.[16]

The chemical shift range is so large that solvent effects are negligible, providing that the solvent is nonreactive. Temperature effects on chemical shifts are usually insignificant in the face of large (kilohertz) line widths. An exception is $(PhCMe_2CH_2)_4Zr$, which has a high-symmetry coordination geometry. Its narrow ^{91}Zr resonance occurs at unusually low field and moves from 2680 ppm ($w/2$ = 940 Hz) at 23 °C to 2650 ppm ($w/2$ = 440 Hz) at 80 °C in toluene. In common with other quadrupolar nuclei, the line width decreases with increasing temperature. For example, the ^{91}Zr spectrum at 25 °C of $Cp_2Zr(CH_3)[HC(SO_2CF_3)_2]$ in toluene consists of a broad singlet centered at −20 ppm with a half-width of 7000 Hz; at 80 °C, the line width decreases to 2800 Hz and the chemical shift is unchanged within experimental error.

Most of the compounds studied in this work are generally of the type Cp_2ZrXYZ, where X, Y, and Z represent coordinated atoms in the additional ligands. Their 37-MHz ^{91}Zr chemical shifts, collected in Table IV, are seen to span about 900 ppm. They exhibit an inverse halogen effect usually encountered with high-Z nuclei in which paramagnetic terms dominate the chemical shift tensor. Thus, for Cp_2ZrCl_2 and $Cp_2Zr(CH_3)_2$, $\delta(^{91}\mathrm{Zr})$ values are −113 and 385, respectively. The methyl chloro compound $Cp_2ZrCl(CH_3)$ has a $\delta(^{91}\mathrm{Zr})$ value of 126; replacement of Cl by CH_3 in the Cp_2ZrXYZ system leads to a 250 ppm downfield shift. Such additivity relationships, though useful, are restricted to similar types of compounds. For example, $\delta(^{91}\mathrm{Zr})$ values for $Cp^*Zr(CH_3)_3$ and $Cp^*ZrCl(CH_3)_2$ are 455 and 263, respectively, so here, replacement of Cl by CH_3 leads to a smaller downfield shift, 192 ppm.

The ^{91}Zr chemical shifts for compounds containing the $Cp_2Zr(CH_3)$ moiety range from 126 ($Cp_2ZrCl(CH_3)$) to 20 ppm (**5**). In these compounds, zirconium is bonded to electronegative atoms (Cl) or to oxygen in the strongly electron-withdrawing $HC(SO_2CF_3)_2$ or $N(SO_2CF_3)_2$ groups. In $Cp_2Zr(CH_3)(OSiMe_2\text{-}t\text{-}Bu)$, in which the trialkylsiloxy group is arguably relatively electron releasing, $\delta(^{91}\mathrm{Zr})$ is −110 ppm. Fluorocarbon acid ligands attached to zirconium are quite susceptible to solvolysis (vide supra), and so, in this case, solvent effects on ^{91}Zr shielding are significant. Given that the Cp_2Zr^{2+} moiety has a pronounced tendency to coordinate to three additional, equatorial groups,[13,17] these data indicate that replacing one nitrogen (in CH_3CN) by oxygen (in dimethoxyethane) in the Zr first coordination core leads to a downfield shift of ca. 50 ppm. Approximately the same effect is seen in $Cp_2Zr[N(SO_2CF_3)_2]$, whose ^{91}Zr chemical shifts in CH_3CN and 1,2-dimethoxyethane are −455 and −270 ppm, respectively. That solvolysis of **14** by CH_3CN produces $Cp_2Zr(CH_3CN)_3^{2+}$ is confirmed by ^{91}Zr NMR spectroscopy for in this solvent, it exhibits the same chemical shift as authentic $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$. Zirconium in fluorocarbon acid derivatives of Cp_2Zr^{2+} is strongly shielded, with the ^{91}Zr shifts in CH_2Cl_2 typically being −300 ppm; these materials (cf. **14**, **16**, **17**) have relatively narrow line widths (ca. 500 Hz). The ^{91}Zr spin–lattice relaxation time, T_1, in **14** is 1.5 ms.

Similar trends are seen in the compounds [n-Bu(pyrazolyl)$_3$]ZrCl$_3$[18] ($\delta(^{91}\mathrm{Zr})$ 563) and $CpCo[(EtO)_2PO]_3ZrCl_3$[19] (355 ppm) and also in $CpZrCl_3 \cdot MeOC_2H_4OMe$ (125 ppm) and $CpZrCl_3 \cdot Me_2NC_2H_4NMe_2$[20] (195 ppm).

Structure of $Cp_2Zr[HC(SO_2CF_3)_2\text{-}O,O'][HC(SO_2CF_3)_2\text{-}O]$. The structure of **14** has been determined by X-ray diffraction methods. The unit cell contains two crystallographically independent molecules, one of which is shown in Figure 1 along with the numbering scheme. There is some scatter in the metrical data. For example, the ranges of S–O, S–O(Zr), S–C(CF_3), and S–C(methine) distances over both molecules are 1.409 (3)–1.425 (3) 1.454 (2)–1.462 (2), 1.828 (4)–1.845 (4), and 1.637 (4)–1.666 (3) Å, respectively. The ranges [averages] of Zr–η^5-C distances in molecules 1 and 2 are 2.464 (4)–2.541 (4) [2.500] and 2.461 (5)–2.503 (4) Å [2.483 Å], respectively. We consider that interpretation of these variations in terms of understandable structural features is not warranted. Therefore, selected bond distances and angles are given in Table V only for molecule 1. A complete listing of all distances and angles is available as supplementary material.

Compound **14** exhibits the familiar "bent back" $Cp_2M(XYZ)$ structure, with the angle between zirconium and the two staggered C_5H_5 centroids being 130.1°. This angle is somewhat small, but it is known to be so in Zr(IV) compounds more than in those containing Zr(II).[10]

There are two $HC(SO_2CF_3)_2$ ligands. One has the cisoid conformation occurring in the free anion.[3] It is bonded to zirconium through two nongeminal sulfone oxygen at-

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Table V. Selected Bond Distances and Angles in $Cp_2Zr[HC(SO_2CF_3)_2]_2$

Distances (Å)			
Zr1–O1	2.243 (2)	S3–C5	1.845 (4)
Zr1–O3	2.259 (2)	Zr–C7	2.241 (4)
Zr1–O5	2.237 (2)	Zr–C8	2.475 (4)
S3–O5	1.462 (2)	Zr–C9	2.493 (4)
S3–O6	1.420 (2)	Zr–C10	2.504 (4)
S4–O7	1.425 (3)	Zr–C11	2.527 (4)
S4–O8	1.415 (3)	Zr–C12	2.501 (4)
S1–O1	1.454 (2)	Zr–C13	2.489 (4)
S1–O2	1.424 (3)	Zr–C14	2.464 (4)
S2–O3	1.409 (3)	Zr–C15	2.498 (4)
S1–C2	1.828 (4)	Zr–C16	2.511 (4)
S1–C1	1.643 (4)	S3–C4	1.637 (4)
S2–C3	1.835 (6)	S4–C4	1.666 (3)
S2–C1	1.640 (4)	S4–C6	1.831 (4)
Angles (deg)			
O_1–Zr1–O5	72.45 (8)	O7–S4–O8	119.5 (2)
O1–Zr1–O3	70.79 (9)	S1–C1–S2	124.9 (2)
S1–C1–S2	124.9 (2)	S3–C4–S4	122.5 (2)
S3–C4–S4	122.5 (2)	Zr1–O1–S1	137.6 (2)
O1–S1–O2	118.6 (2)	Zr1–O3–S2	139.6 (2)
O3–S2–O4	118.3 (2)	Zr1–O5–S3	154.6 (2)
O5–S3–O6	118.3 (2)		

oms, O1 and O3. The other is is attached to the metal only through O5. Both O7 and O8 are too far removed, as a result of twisting of the ligand about the C4–S4 bond that generates a transoid conformation, to interact significantly with the metal. Thus, the Zr–O7 and Zr–O8 separations are 7.056 and 6.595 Å, respectively. The distances from Zr to O1, O3, and O5, which may be viewed as being in equatorial positions, are 2.243 (2), 2.259 (2), and 2.237 (2) Å, respectively; the maximum displacement from the Zr1,O1,O3,O5 least-squares plane, 0.04 Å, occurs at Zr1. There appears not to be a striking difference among the lengths of the bonds between zirconium and the center or side oxygen atoms. Indeed, the monodentate $HC(SO_2CF_3)_2$ ligand forms the shortest Zr–O bond, but at least some of the difference may be attributable to the chelate effect in the CS_2O_2 ring. In contrast, in $[Cp_2Zr(H_2O)_3][CF_3SO_3]_2$, the center Zr–O bond (2.195 (7) Å) is shorter than the two side Zr–O bonds (2.261 (7) and 2.239 (7) Å).[17b] Collectively, the Zr–O bonds in **14** are quite long, which is reflected in its facile solvolysis. They may be compared with 1.91 (1) (Zr–O–Si) and 2.33 (2) Å (Zr–O–C) in (dimethoxyethane)$ZrCl_2(OSiPh_3)_2$,[21] 1.948 (1) Å in $[Cp_2Zr(CH_3)]_2O$,[22] 2.096 (Zr–O–C) and 2.295 Å (Zr–O–N) in $Zr(CH_3COCHCOCH_3)_2(NO_3)_2$,[23] and 2.219 (6) (Zr–O–S) and 2.278 (9) Å (Zr–O–C) in $Cp_2Zr(CF_3SO_3)_2$·THF.[17a]

The bidentate $HC(SO_2CF_3)_2$ ligand is rather symmetrical, and the most significant deviation, which occurs for nonobvious reasons, is S2–O4 = 1.409 (3) Å. Bond lengths in the monodentate $HC(SO_2CF_3)_2$ are more irregular. Coordination of zirconium to O5 significantly lengthens the S–O bond to 1.462 (2) Å and is associated with a lengthening of the distal C–S bond. Thus, C4–S4 is 1.666 (3) Å, whereas the C4–S3, C1–S1, and C1–S2 distances are 1.637 (4), 1.643 (4), and 1.640 (4) Å, respectively.

Experimental Section

Reactions were carried out under a nitrogen atmosphere. Toluene and hexane were deoxygenated and stored over NaK alloy. 1,2-Dimethoxyethane was distilled from $Na-Ph_2CO$. CD_2Cl_2 used to prepare NMR samples was stored over CaH_2 on a vacuum line. Fluorocarbon acids, prepared by the method of Koshar and Mitsch,[15] were gifts of R. J. Koshar. Cp_2ZrMe_2 was made by the method of Samuel and Rausch.[24] NMR spectra were obtained on a Varian XL-400 instrument, whose ^1H operating frequency is 400 MHz. Positive chemical shifts are downfield of internal $(CH_3)_4Si$ (^1H, ^{13}C, ^{29}Si) or $CFCl_3$ (^{19}F) references.

Table VI. X-ray Crystallographic Experimental Details

A. Crystal Data

formula: $C_{16}H_{12}ZrF_{12}O_8S_4$
fw: 779.73
$F(000) = 1536$
cryst dimens: 0.15 × 0.20 × 0.25 mm
Mo Kα radiation ($\lambda = 0.71073$ Å)
temp: -100 ± 1 °C
triclinic space group: $P\bar{1}$
$\rho = 1.94$ g/cm^3
$\mu = 8.2$ cm^{-1}
$a = 8.834$ (2) Å
$b = 15.480$ (5) Å
$c = 20.887$ (6) Å
$\alpha = 109.71$ (2)°
$\beta = 90.64$ (2)°
$\gamma = 95.20$ (2)°
$V = 2675.2$ Å^3
$Z = 4$

B. Intensity Measurements

instrument: Enraf-Nonius CAD4 diffractometer
monochromator: graphite cryst, incident beam
attenuator: Zr foil, factor 18.6
takeoff angle: 2.8°
detector aperature: 2.0–2.4 mm horiz, 6.0 mm vert
cryst–detector dist: 21 cm
scan type: ω
scan rate: 1–10 deg/min (in ω)
scan width: $(1.0 + 0.350 \tan \theta)°$
max 2θ: 48.0°
no. of reflns measd: 8629 total, 8367 unique
cor: Lorentz–polarization, linear decay (from 1.000 to 1.030 on I), refln averaging (agreement on I = 1.5%), empirical abs (from 0.96 to 1.00 on I)

C. Structure Solution and Refinement

soln: Patterson method
H atoms: included as fixed contribn to the structure factor
refinement: full-matrix least squares
minimization function: $\sum w(|F_o| - |F_c|)^2$
least-squares wts: $4F_o^2/\sigma^2(F_o^2)$
anomalous dispersion: all non-H atoms
no. of rflns included: 6112 with $F_o^2 > 3.0\sigma(F_o^2)$
no. of params refined: 739
unweighted agreement factor: 0.033
weighted agreement factor: 0.045
esd of observn of unit wt: 1.71
convergence, largest shift: 0.09σ
high peak in final diff map: 0.62 (8) e/Å^3
computer hardware: PDP-11/44
computer software: SDP-PLUS[a]

[a] From Enraf-Nonius and B. A. Frenz and Associates, Inc.

^{91}Zr spectra were obtained at 37.18 MHz on the XL-400 instrument. Spectra of the reference, Cp_2ZrBr_2 in THF, were measured to determine the 90° pulse widths for the 10- and 5-mm broad-band probes: 33.5 and 15.5 μs, respectively. The ^{91}Zr T_1 value, measured by the inversion-recovery method, is 27 ms. Spectra were obtained by using a 10-ms acquisition time, a 15-ms recycle time, and 90° (13 μs) pulses.

The general synthetic procedure used was to slowly add 1 or 2 equiv of a toluene solution of the fluorocarbon acid to the Zr or Hf metallocene dissolved in the same solvent. Compounds containing only one $HC(SO_2CF_3)_2$ ligand are soluble in and can be recrystallized from hexane or hexane–toluene. The compounds containing two $HC(SO_2CF_3)_2$ ligands separate in analytically pure form from the reaction mixture. They can be recrystallized from dichloromethane. All reactions were carried out under nitrogen, and all of the Zr and Hf compounds reported here are air-sensitive.

$Cp_2Zr(CH_3)[HC(SO_2CF_3)_2]$ (5). A solution of 0.56 g (2 mmol) of $H_2C(SO_2CF_3)_2$ in 5 mL of toluene was added dropwise with stirring to 0.50 g (2 mmol) of Cp_2ZrMe_2 in 5 mL of the same solvent. Gas evolution occurred. After 18 h (the reaction is probably over before this), the solvent was removed under vacuum. The product was extracted with 35 mL of hexane, in which it is unusually soluble. The extract was concentrated to ca. 5 mL and

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Table VII. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Zr1	0.00654 (4)	0.27157 (2)	0.07014 (2)	1.736 (7)	O8	−0.5154 (4)	0.0909 (2)	−0.2122 (2)	3.52 (8)
Zr2	0.51915 (5)	0.75404 (3)	0.35856 (2)	1.995 (8)	O9	0.7270 (4)	0.7070 (2)	0.3932 (2)	3.11 (7)
S1	−0.2617 (1)	0.36603 (7)	0.18578 (5)	2.76 (2)	O10	0.8848 (5)	0.5805 (2)	0.3808 (2)	4.9 (1)
S2	0.0326 (2)	0.36211 (8)	0.24823 (6)	3.38 (3)	O11	0.4596 (4)	0.7008 (2)	0.4453 (2)	3.40 (7)
S3	−0.3413 (1)	0.25354 (7)	−0.02804 (5)	2.11 (2)	O12	0.3794 (5)	0.5576 (2)	0.4685 (2)	5.6 (1)
S4	−0.5191 (1)	0.11773 (7)	−0.14043 (5)	2.42 (2)	O13	0.7061 (3)	0.7714 (2)	0.2924 (1)	2.55 (6)
S5	0.7916 (1)	0.64519 (7)	0.42203 (5)	2.78 (2)	O14	0.9809 (3)	0.7943 (2)	0.3257 (1)	2.66 (6)
S6	0.4913 (2)	0.63249 (8)	0.47645 (6)	3.79 (3)	O15	1.0136 (4)	0.9899 (2)	0.2010 (2)	4.46 (8)
S7	0.8638 (1)	0.79303 (7)	0.27829 (5)	2.13 (2)	O16	1.1619 (4)	0.8932 (2)	0.2463 (2)	3.69 (8)
S8	1.0332 (1)	0.94314 (8)	0.24845 (5)	2.81 (2)	C1	−0.1281 (6)	0.4069 (3)	0.2467 (2)	3.4 (1)
F1	−0.5197 (4)	0.2629 (3)	0.1648 (2)	5.99 (9)	C2	−0.4150 (6)	0.3008 (4)	0.2133 (3)	4.0 (1)
F2	−0.4768 (4)	0.3582 (3)	0.2662 (2)	7.6 (1)	C3	0.0116 (8)	0.2814 (4)	0.2955 (3)	6.0 (2)
F3	−0.3640 (4)	0.2361 (2)	0.2320 (2)	5.74 (8)	C4	−0.3541 (5)	0.1749 (3)	−0.1040 (2)	2.42 (9)
F4	−0.0481 (7)	0.3229 (4)	0.3542 (2)	10.7 (2)	C5	−0.3598 (5)	0.3672 (3)	−0.0363 (2)	3.1 (1)
F5	−0.0773 (5)	0.2078 (2)	0.2621 (2)	7.15 (9)	C6	−0.5270 (6)	0.0080 (4)	−0.1248 (3)	4.3 (1)
F6	0.1448 (5)	0.2589 (3)	0.3064 (2)	10.2 (1)	C7	0.1445 (6)	0.4329 (3)	0.1171 (2)	3.8 (1)
F7	−0.5240 (5)	0.0218 (2)	−0.0593 (2)	6.8 (1)	C8	0.2480 (5)	0.3717 (3)	0.0836 (3)	3.9 (1)
F8	−0.3420 (4)	0.4332 (2)	0.0231 (2)	4.80 (8)	C9	0.2083 (6)	0.3401 (3)	0.0141 (3)	3.6 (1)
F9	−0.2547 (3)	0.3840 (2)	−0.0767 (1)	4.01 (6)	C10	0.0782 (5)	0.3785 (3)	0.0059 (2)	3.3 (1)
F10	−0.4117 (4)	−0.0375 (2)	−0.1516 (2)	6.3 (1)	C11	0.0377 (5)	0.4348 (3)	0.0688 (3)	3.3 (1)
F11	−0.4946 (3)	0.3680 (2)	−0.0641 (1)	3.88 (6)	C12	0.1251 (6)	0.1374 (3)	0.0832 (2)	3.1 (1)
F12	−0.6537 (4)	−0.0436 (2)	−0.1535 (2)	6.8 (1)	C13	0.1720 (5)	0.1451 (3)	0.0227 (3)	3.3 (1)
F13	1.041 (4)	0.7576 (3)	0.4575 (2)	5.61 (9)	C14	0.0454 (6)	0.1266 (3)	−0.0214 (3)	3.7 (1)
F14	0.8606 (4)	0.7942 (3)	0.5248 (2)	8.3 (1)	C15	−0.0799 (6)	0.1046 (3)	0.0124 (3)	4.3 (1)
F15	0.5820 (5)	0.7762 (3)	0.5820 (2)	6.8 (1)	C16	−0.0301 (6)	0.1129 (3)	0.0783 (3)	3.4 (1)
F16	0.9847 (5)	0.6833 (3)	0.5232 (2)	9.1 (1)	C17	0.6611 (6)	0.5976 (3)	0.4586 (2)	3.8 (1)
F17	0.3514 (5)	0.7268 (4)	0.5812 (2)	9.5 (2)	C18	0.9276 (6)	0.7247 (4)	0.4861 (2)	4.2 (1)
F18	0.5265 (7)	0.6528 (3)	0.6036 (2)	10.4 (1)	C19	0.4909 (8)	0.7019 (5)	0.5672 (3)	6.0 (2)
F19	0.7729 (3)	0.6727 (2)	0.1592 (1)	4.58 (8)	C20	0.8698 (5)	0.8824 (3)	0.2535 (2)	2.75 (9)
F20	0.8860 (4)	0.6163 (2)	0.2248 (2)	5.10 (8)	C21	0.8848 (5)	0.6886 (3)	0.2051 (2)	3.2 (1)
F21	1.0149 (3)	0.6972 (2)	0.1756 (2)	4.38 (7)	C22	1.0619 (6)	1.0361 (3)	0.3313 (3)	3.6 (1)
F22	1.0720 (4)	1.0031 (2)	0.3814 (1)	4.85 (8)	C23	0.472 (1)	0.9106 (3)	0.3657 (3)	7.2 (2)
F23	0.9474 (4)	1.0877 (2)	0.3430 (2)	5.31 (8)	C24	0.3630 (8)	0.8840 (4)	0.4005 (4)	6.0 (2)
F24	1.1867 (4)	1.0898 (2)	0.3323 (2)	6.4 (1)	C25	0.4135 (8)	0.8770 (4)	0.4530 (3)	5.5 (2)
O1	−0.2066 (3)	0.2946 (2)	0.1283 (1)	2.52 (6)	C26	0.5621 (7)	0.8965 (4)	0.4615 (3)	4.7 (1)
O2	−0.3374 (5)	0.4364 (2)	0.1730 (2)	4.51 (9)	C27	0.6110 (6)	0.9210 (4)	0.4067 (4)	7.9 (2)
O3	0.0645 (4)	0.2987 (2)	0.1813 (1)	2.90 (7)	C28	0.4773 (6)	0.6139 (3)	0.2538 (3)	3.6 (1)
O4	0.1495 (5)	0.4296 (3)	0.2846 (2)	5.4 (1)	C29	0.3882 (7)	0.5949 (3)	0.3012 (3)	4.5 (1)
O5	−0.1826 (3)	0.2682 (2)	−0.0030 (1)	2.40 (6)	C30	0.2761 (6)	0.6582 (4)	0.3168 (3)	4.5 (1)
O6	−0.4575 (3)	0.2445 (2)	0.0163 (1)	2.69 (7)	C31	0.3003 (6)	0.7110 (4)	0.2747 (3)	4.4 (1)
O7	−0.6478 (3)	0.1588 (2)	−0.1070 (2)	3.19 (7)	C32	0.4245 (6)	0.6847 (4)	0.2382 (2)	3.8 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

then cooled to −78 °C. The white crystalline product was isolated by Schlenk filtration and dried under vacuum; yield 0.70 g (68%). IR (Nujol): strong bands at 3085, 3065, 1375, 1200, 1110, 1015, 815, 645, and 575 cm^{-1}.

The hafnium analogue 8 was similarly prepared, but with a 24-h reaction time. It was recrystallized from cold toluene–hexane. Compound 6 was recrystallized from dichloromethane–hexane.

$Cp_2Zr(CH_3CO)[HC(SO_2CF_3)_2]$ (12). A solution of 0.15 g of 5 in 5 mL of toluene, contained in a Schlenk flask, was freeze–pump–thaw-degassed and then pressured to 35 psi with carbon monoxide. After 15 min, a pale yellow oil separated. It crystallized on standing overnight and was isolated by filtration; yield 0.14 g.

$Cp_2Zr[N(SO_2CF_3)_2]_2$ (16). A solution of 1.0 g of Cp_2ZrMe_2 (2 mmol) in 10 mL of toluene was added with stirring to 1.12 g (4 mmol) of $HN(SO_2CF_3)_2$ in 8 mL of toluene. An exothermic reaction and vigorous gas evolution occurred. The product separated as white crystals that were collected on a filter, washed with fresh solvent, and then vacuum-dried. The yield was 1.28 g (82%). IR (Nujol): 3100, 1360, 1300, 1220, 1190, 1125, 1085, 1050, 1030, 1015, 1000, 825, 590 cm^{-1}. Recrystallization can be accomplished by rotary evaporation of a solution in dichloromethane–hexane.

The compound $Cp_2Zr(CH_3)(OSiMe_2$-*t*-Bu) was prepared from 1 equiv each of 4 and *tert*-butyldimethylsilanol by the method of Atwood et al.[21] $Cp^*Zr(CH_3)_3$, $Cp^*Zr(CH_3)_2Cl$,[25] and $(PhCMe_2CH_2)_4Zr$[26] were made by literature methods. Purity and composition were verified by mass spectrometry and NMR spectra.

Crystals of $Cp_2Zr[HC(SO_2CF_3)_2]_2$ were grown in a drybox by slow diffusion of toluene into a solution of 14 in dichloromethane. Experimental details of the structure determination are given in Table VI. Positional parameters and their estimated standard deviations are in Table VII. The program MISSYM[27] was used to see if there were any additional symmetry elements relating the two very similar molecules in the asymmetric unit. None were found.

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Supplementary Material Available: A description of the crystal structure data collection, structure solution, and refinement and listings of hydrogen atom positional parameters, all bond lengths and angles, and thermal parameters for non-hydrogen atoms (18 pages); a listing of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

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