First Mixed Fluoro−Chloro Group 4 Organometallics: Synthesis and Spectroscopic and Structural Characterization of [{$(C_5Me_5)ZrF_2Cl$}$_4$], [{$(C_5Me_5)HfF_2Cl$}$_4$], [$(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$], [$(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$], [$(C_5Me_4Et)_2ZrClF$], and [$(C_5Me_5)_2HfClF$]

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Tetrameric [{$(C_5Me_5)MF_3$}$_4$] (M = Zr, Hf) react smoothly with Me_3SiCl in CH_2Cl_2 at room temperature to give [{$(C_5Me_5)ZrF_2Cl$}$_4$] (**1**) and [{$(C_5Me_5)HfF_2Cl$}$_4$] (**2**), respectively, in high yield. Treatment of [{$(C_5Me_5)MF_3$}$_4$] (M = Zr, Hf) with Me_2AlCl in toluene gives mixtures of **1** and [$(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$] (**3**), and **2** and [$(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$] (**4**), respectively, in an approximately 1:1 molar ratio. Metallocene type complexes [$(C_5Me_4Et)_2ZrCl_2$] and [$(C_5Me_5)_2HfCl_2$] react with 1 equiv of Me_3SnF to give [$(C_5Me_4Et)_2ZrClF$] (**5**) and [$(C_5Me_5)_2HfClF$] (**6**), respectively. The complexes **1**−**6** were characterized by spectroscopic methods (^1H and ^{19}F NMR and mass spectroscopy). The solid state structures of **1**, **3**, and **5** were determined by single-crystal X-ray diffraction analyses.

Introduction

The chemistry of mono- and dicyclopentadienyl substituted group 4 chlorides has been extensively investigated over the past 3 decades. In marked contrast the corresponding fluorides have received little attention. This may be attributed in part to the fact that fluorinating procedures in the literature[1−3] are often complicated by problems involving separation of the fluorinating reagent from the product or competing reactions. For example, use of AsF_3 in the preparation of organometallic fluorides[4−6] bearing pentamethylcyclopentadienyl (C_5Me_5) substituents is complicated by transfer of the C_5Me_5 group from the metal center to the arsenic atom.[4] The use of hydrogen fluoride on the other hand leads to cleavage of the carbon−metal bond in many cases.[3]

In a recent paper we reported the first use of trimethyltin fluoride as fluorinating reagent in the preparation of a wide range of cyclopentadienyl substituted group 4 fluorides (Scheme 1).[7] The ease with which cyclopentadienyl substituted group 4 fluorides may be prepared from the corresponding chlorides via this method is remarkable. The fact that the resulting trimethyltin chloride may be readily removed in vacuo and then recycled makes this an ideal fluorinating system.

Subsequently, we found that both [{$(C_5Me_5)ZrF_3$}$_4$] and [{$(C_5Me_5)TiF_3$}$_2$] in combination with methylalumoxane (MAO) form highly active catalytic systems suitable for the polymerization of ethylene.[8] Brintzinger, Sinn, and Kaminsky have shown in their fundamental work that alkyl derivatives of group 4 metallocenes are of crucial importance in such systems.[9] Indeed, in the reaction of trimethylaluminium (TMA) with [{$(C_5Me_5)ZrF_3$}$_4$], in a 4:1 molar ratio, selective exchange of fluorine atoms for methyl groups does occur. Furthermore, reaction of excess TMA with [{$(C_5Me_5)ZrF_3$}$_4$] results in the formation of a fluorine free $Zr_3Al_6C_7$ cluster compound.[10]

Scheme 1

$$CpMCl_3 + 3Me_3SnF \rightarrow CpMF_3 + 3Me_3SnCl$$

$$M = Zr, Hf; Cp = C_5Me_5$$

$$M = Ti; Cp = C_5Me_5, C_5Me_4Et, C_5H_5, C_5H_4Me$$

Following our work on the cyclopentadienyl substituted group 4 fluorides and the observation of their exceptionally high catalytic activity, we decided to explore the possibility of partial fluorination of the group 4 chlorides using Me_3SnF or to find alternative methods for the preparation of mixed fluoro−chloro compounds. Intramolecular fluorine−chlorine exchange reactions have been reported in conjunction with the preparation of silylhydrazine ring systems, using Me_3SiCl as the exchange reagent.[11−13] In order to explore the feasibility of Me_3SiCl for the preparation of mixed fluoro−chloro derivatives, we have

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Table 1. Numbering Scheme, Yields, Melting Points, and ^{19}F NMR Spectral Data for Complexes **1**−**6**

complex	yield (%)	mp (°C)	^{19}F NMR (δ)
$[(C_5Me_5)ZrF_2Cl\}_4]$ (**1**)	82	347^a	19.9 (m, 4F), −30.9 (m, 2F), −59.2 (m, 2F)^b
$[(C_5Me_5)HfF_2Cl\}_4]$ (**2**)	90	335	−46.5 (m, 4F), −58.5 (m, 2F), −84.3 (m, 2F)^b
mixture of **1** and $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**3**)		279^a	**1** and −28.1 (m, 1F), −49.6 (m, 1F), −105.2 (m, 4F)^b
mixture of **2** and $[(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**4**)		234^a	**2** and −49.0 (dq, 1F), −75.4 (dq, 1F), −111.9 (dd, 4F)^b
$[(C_5Me_4Et)_2ZrClF]$ (**5**)	83	140	−45.0 (s)^c
$[(C_5Me_5)_2HfClF]$ (**6**)	75	172	−17.9 (s)^c

^{a} Decomposition onset. ^{b} Solvent: $CDCl_3$. ^{c} Solvent: C_6D_6.

carried out reactions of $[\{(C_5Me_5)MF_3\}_4]$ (M = Zr, Hf) with Me_3SiCl. We have also performed similar studies using Me_2AlCl as exchange reagent. In the following account we present the details of these investigations which have led to the preparation and structural characterization of the first series of cyclopentadienyl substituted group 4 mixed fluoro−chloro complexes. The X-ray crystal structures of three new mixed fluoro−chloro compounds $[\{(C_5Me_5)_2ZrF_2Cl\}_4]$ (**1**), $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**3**), and $[(C_5Me_4Et)ZrClF]$ (**5**) along with ^{19}F NMR studies of these and the analogous hafnium derivatives are discussed.

Experimental Section

All experiments were performed under a dry N_2 atmosphere using conventional Schlenk techniques or a drybox. Reagent grade solvents were dried over sodium/benzophenone and distilled under N_2 prior to use. Deuterated solvents, $CDCl_3$ and C_6D_6, were trap-to-trap distilled from CaH_2. $[\{(C_5Me_5)ZrF_3\}_4]$,[7] $[\{(C_5Me_5)HfF_3\}_4]$,[7] $[(C_5Me_4Et)_2ZrCl_2]$,[14] and $[(C_5Me_5)_2HfCl_2]$ [15] were prepared according to literature methods. Trimethylsilyl chloride and dimethylaluminium chloride (DMAC) were purchased from Aldrich Chemical Co. and used without further purification.

Nuclear magnetic resonance spectra were recorded on a Bruker AM 250 spectrometer. The ^{1}H and ^{19}F NMR chemical shifts are quoted in parts per million (ppm) downfield from external standards, TMS and $CFCl_3$, respectively. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer as Nujol mulls between KBr plates. Mass spectra (*m/z*) were obtained on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Melting points were determined on a HWS SG 3000 melting point apparatus and are uncorrected. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

Synthesis of $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (1). Excess Me_3SiCl (1.99 g, 10.32 mmol) was added dropwise over a period of 0.5 h to a rapidly stirred opaque solution of $(C_5Me_5)ZrF_3$ (1.04 g, 3.67 mmol) in CH_2Cl_2 (50 mL) at 20 °C. The reaction solution was stirred for a further 72 h and then taken to dryness in vacuo. The white residue **1** was washed with CH_2Cl_2 (5 mL) and dried in vacuo; yield 0.90 g (82%), dec onset 347 °C.. Anal. Calcd for $C_{40}H_{60}Cl_4F_8Zr_4$ (1199.60): C, 40.05; H, 5.04; Cl, 11.82. Found: C, 39.6; H, 5.4; Cl, 11.7. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, Cp*). ^{19}F NMR ($CDCl_3$): δ −19.9 (m, 4F), −30.9 (m, 2F), −59.2 (m, 2F). MS (EI, 70 eV), *m/z* (%)): 1198 (<0.1) $[C_{40}H_{60}F_8Cl_4Zr_4]$, 879 (2.4) $[C_{30}H_{45}Cl_3F_5Zr_3]$, 579 (3.2) $[C_{20}H_{30}Cl_2F_3Zr_2]$, 298 (29.5) $[C_{10}H_{15}ClF_2Zr]$, 119 (100).

$[\{(C_5Me_5)HfF_2Cl\}_4]$ (2). The synthesis of **2** proceeded as described for complex **1**. Me_3SiCl (1.25 g, 11.51 mmol) was added dropwise to a stirred solution of $(C_5Me_5)HfF_3$ (0.85 g, 2.29 mmol) in CH_2Cl_2 (40 mL). The white product **2** was washed with CH_2Cl_2 (5 mL) and dried in vacuo; yield, 0.80 g (90%), mp 335 °C. Anal. Calcd for $C_{40}H_{60}Cl_4F_8Hf_4$ (1548.68): C, 31.02; H, 3.91; Cl, 9.16. Found: C, 30.8; H, 3.8; Cl, 9.2 ^{1}H NMR ($CDCl_3$): δ 2.09 (s, Cp*). ^{19}F NMR ($CDCl_3$): δ −46.5 (m, 4F), −58.5 (m, 2F), −84.3 (m, 2F). MS (EI, 70 eV), *m/z* (%): 1548 (<0.1) $[C_{40}H_{60}F_8Cl_4Hf_4]$, 1143 (1.6) $[C_{30}H_{45}Cl_3F_5Hf_3]$, 755 (4.0) $[C_{20}H_{30}Cl_2F_3Hf_2]$, 388 (50.4) $[C_{10}H_{15}ClF_2Hf]$, 135 (100).

Mixture of $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (1) and $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (3). An equimolar amount of DMAC (3.60 mmol in hexane) was added dropwise by syringe to a rapidly stirred opaque yellow solution of $(C_5Me_5)ZrF_3$ (1.00 g, 3.53 mmol) in toluene (50 mL) at 20 °C. On stirring for 0.5 h at room temperature the white product mixture began to precipitate from the yellow reaction solution. The reaction mixture was stirred for a further 24 h and then concentrated to *ca*. 5 mL in volume. The white solid mixture was separated from the yellow supernatant by filtration, washed with toluene (5 mL), and dried in vacuo; yield, 0.77 g, dec. onset 279 °C. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, Cp*), 2.08 (s, Cp*). ^{19}F NMR ($CDCl_3$): δ −20.0 (m, 4F), −28.1 (m, 1F), −30.8 (m, 2F), −49.6 (m, 1F), −59.2 (m, 2F), −105.2 (m, 4F). MS (EI, 70 eV), *m/z* (%): 1198 (<0.1) $[C_{40}H_{60}F_8Cl_4Zr_4]$.

Mixture of $[\{(C_5Me_5)HfF_2Cl\}_4]$ (2) and $[(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (4). A mixture of complexes **2** and **4** was obtained in a fashion similar to that described for the mixture of **1** and **3**. An equimolar amount of DMAC (2.70 mmol in hexane) was added to a stirred solution of $(C_5Me_5)HfF_3$ (1.00 g, 2.70 mmol) in toluene (30 mL). The product mixture was filtered off, washed with toluene (5 mL), and dried in vacuo; yield, 0.54 g, dec. onset 234 °C. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, Cp*), 1.90 (s, Cp*). ^{19}F NMR ($CDCl_3$): δ −46.3 (m, 4F), −49.0 (dq, 1F), −58.3 (m, 2F), −75.4 (dq, 1F), −84.4 (m, 2F), −111.9 (dd, 4F). MS (EI, 70 eV), *m/z* (%) 1548 (<0.1) $[C_{40}H_{60}F_8Cl_4Hf_4]$.

$[(C_5Me_4Et)_2ZrClF]$ (5). A suspension of Me_3SnF (0.79 g, 4.32 mmol) in toluene (40 mL) was added to a stirred solution of $(C_5Me_4Et)_2ZrCl_2$ (2.00 g, 4.34 mmol) in toluene (80 mL). The resulting mixture was refluxed for 8 h and then taken to dryness under vacuum to yield the crude product **5**. Recrystallization of the pale yellow residue from hot petroleum ether (bp 90−100 °C) afforded colorless crystals of **5**; yield, 1.60 g (83%), mp 140 °C. Anal. Calcd for $C_{22}H_{34}ClFZr$ (444.19): C, 59.5; H, 7.7; F, 4.3. Found: C, 57.8; H, 7.7; F, 4.4. ^{19}F NMR (C_6D_6), δ −45 (s). IR (Nujol, cm^{-1}): 1261 (m), 1024 (m), 700 (m), 543 (m), 326. MS (EI, 70 eV), *m/z* (%): 442 (40) $[C_{22}H_{34}ClFZr]$.

$[(C_5Me_5)_2HfClF]$ (6). The preparation of complex **6** followed the procedure outlined for **5**. $(C_5Me_5)_2HfCl_2$ (2.50 g, 4.80 mmol) and Me_3SnF (0.88 g, 4.80 mmol) reacted in toluene (80 mL) to give $(C_5Me_5)_2HfClF$; yield, 1.82 g (75%), mp 172 °C. Anal. Calcd for $C_{20}H_{30}ClFHf$ (503.40): C, 47.7; H, 6.0; Cl, 7.0; F, 3.8. Found: C, 49.2; H, 6.6; Cl, 7.1; F, 3.7. ^{19}F NMR (C_6D_6): δ −17.92. IR (Nujol, cm^{-1}): 1262 (m), 1022 (m), 803 (s), 722 (m), 541 (m), 340 (m), 301 (st). MS (EI, 70 eV), *m/z* (%): 504 (22) $[C_{20}H_{30}ClFHf]$.

X-ray Measurements of 1, 3, and 5. The intensities for the structures were collected on a Stoe-Siemens AED four-circle diffractometer using graphite monochromated Mo Kα radiation (λ = 71.103 pm). The structures were solved by direct methods with SHELXS-90[16] and refined by full-matrix least-squares using SHELXL-93.[17] The hydrogen atoms were added in calculated positions and refined "riding" on their respective carbon atom. Absorption corrections were applied using a semiemperical method. Pale yellow crystals of **1** suitable for X-ray analyses were obtained from the DMAC toluene reaction solution. Fractional crystallization of the same reaction mixture at room temperature yielded crystals of **3**. Crystals of **1** and **3** were isomorphous with different Cl/F ratios. In both cases 1.5 toluene molecules were present per molecular unit. Colorless crystals of **5** suitable for X-ray diffraction studies were grown from a hot petroleum ether (bp 90−

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Table 2. Crystallographic Data for **1**, **3**, and **5**

	1	**3**	**5**
empirical formula	$C_{61}H_{84}Cl_{4.43}F_{7.57}Zr_4$	$C_{61}H_{84}Cl_{5.28}F_{6.72}Zr_4$	$C_{22}H_{34}ClFZr$
fw	1483.04	1496.98	444.16
data collecn at T (°C)	−120	−120	−120
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	Monoclinic	Monoclinic	Triclinic
space group	C2/c	C2/c	$P\bar{1}$
unit cell dimens			
a (Å)	25.209(5)	25.163(5)	8.576(1)
b (Å)	13.331(3)	13.457(3)	14.439(2)
c (Å)	21.820(4)	21.849(4)	17.841(4)
α (deg)	90	90	76.74(1)
β (deg)	118.15(3)	118.87(3)	83.52(1)
γ (deg)	90	90	89.00(1)
V (Å^3)	6465(2)	6479(2)	2136.5(6)
Z	4	4	4
ρ (g cm^{-3})	1.524	1.535	1.381
absorp coeff, μ (mm^{-1})	0.868	0.899	0.650
F(000)	3014	3041	928
cryst dimens (mm)	0.8 × 0.5 × 0.5	0.5 × 0.5 × 0.4	0.8 × 0.4 × 0.3
measd 2θ range (deg)	7.12−50.12	7.10−50.00	6.02−45.06
data measd, unique	6233, 5690	12 102, 5657	7254, 5579
R,[a] R_{w2}[b] ($I > 2\sigma(I)$)	$R_1 = 0.098$, 0.258	$R_1 = 0.036$, 0.092	$R_1 = 0.042$, 0.105
R, R_{w2} (all data)	$R_1 = 0.101$ $R_{w2} = 0.2693$	$R_1 = 0.048$ $R_{w2} = 0.0990$	$R_1 = 0.045$ $R_{w2} = 0.1120$
goodness of fit, S[c]	1.05	1.05	1.00
refined params	345	345	472
restraints	6	6	0
largest diff peak, hole (10^{-2} e nm^{-3})	4109, −3332	1456, −756	1129, −1010

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{w2} = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/\sum(n - p)]^{1/2}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

Table 3. Selected Bond Lengths and Angles for $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (**1**), $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**3**), and $[(C_5Me_4Et)_2ZrClF]$ (**5**)

complex	bond length (Å)		bond angle (deg)	
1	Zr(1)−Cl(1)	2.441(2)	(C_5Me_5)−Zr(1)−Cl(1)	106.2
	Zr(2)−Cl(2)	2.454(2)	(C_5Me_5)−Zr(2)−Cl(2)	106.6
3	Zr(1)−Cl(1)	2.438(1)	Cl(4)−Zr(2)−Zr(1)	50.86(7)
	Zr(2)−Cl(2)	2.448(1)	(C_5Me_5)−Zr(1)−Cl(1)	106.3
	Zr(1)−Cl(4)	2.617(4)	(C_5Me_5)−Zr(2)−Cl(4)	101.9
	Zr(2)−Cl(4)	2.617(4)	(C_5Me_5)−Zr(2)−Cl(2)	106.8
			(C_5Me_5)−Zr(2)−Cl(4)	102.6
5	Zr(1)−Cl(1)	2.440(2)	F(1)−Zr(1)−Cl(1)	98.10
	Zr(2)−Cl(2)	2.446(1)	F(2)−Zr(2)−Cl(2)	96.77
	Zr(1)−F(1)	2.012(3)	(C_5Me_5)−Zr(1)−Cl(1)	103.8
	Zr(2)−F(2)	1.991(3)	(C_5Me_5)−Zr(2)−Cl(2)	103.8

100 °C) solution of the complex. Crystals of **5** possess two molecules in the asymmetric unit. Relevant crystallographic data of **1**, **3**, and **5** are given in Table 2; fractional coordinates and equivalent isotropic displacement coefficients of **1**, **3**, and **5** are given in Tables 4−6, respectively.

Results and Discussion

Synthesis and Characterization of $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (1), $[\{(C_5Me_5)HfF_2Cl\}_4]$ (2), $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (3), and $[(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (4). The dimeric solid state structure of $[\{(C_5Me_5)ZrCl_3\}_2]$ shows two bridging and four terminal chlorine atoms.[18] Reaction of $[\{(C_5Me_5)ZrCl_3\}_2]$ with 4 equiv of Me_3SnF might then be expected to give $[\{(C_5Me_5)ZrF_2Cl\}_2]$, with substitution of the four terminal chlorine atoms taking place. Attempts at partial fluorination of $[\{(C_5Me_5)ZrCl_3\}_2]$ with Me_3SnF did not succeed, and only the completely substituted product $[\{(C_5Me_5)ZrF_3\}_4]$ was detected along with unreacted starting material. We therefore choose an alternative strategy to prepare these mixed fluoro−chloro derivatives starting from the trifluorides, $[\{(C_5Me_5)ZrF_3\}_4]$ and $[\{(C_5Me_5)HfF_3\}_4]$, the syntheses of which we have reported recently.[7]

The reaction of $[\{(C_5Me_5)ZrF_3\}_4]$ with excess Me_3SiCl in CH_2Cl_2 proceeds smoothly at room temperature to give the white air sensitive complex **1** in high yield (Scheme 2). In this reaction selective replacement of the four terminal fluorines of $[\{(C_5Me_5)ZrF_3\}_4]$ with chlorines is achieved. Complex **2** is isolated in a similar way from the reaction of $[\{(C_5Me_5)HfF_3\}_4]$ with Me_3SiCl. Since the solvent, excess Me_3SiCl and Me_3SiF formed during the reaction may be readily removed in vacuo, this method provides a convenient route to monochloro−difluoro complexes in high yields. The driving force for this reaction is attributed to the formation of Me_3SiF, a compound with a very stable Si−F bond.[19] When toluene is used as reaction solvent, instead of CH_2Cl_2, only two of the terminal fluorine atoms are substituted by chlorines. Complexes **1** and **2** were characterized by elemental analyses and ^1H and ^{19}F NMR spectroscopy. Complex **2** melts at 335 °C, while **1** decomposes at 347 °C. The mass spectrum of **1** shows a very weak molecular ion peak at m/z 1198. No peaks corresponding to the fragments $M^{*}-F$ or $M^{+}-Cl$ are observed. Subsequent ionization products formed in the spectrum are $[\{(C_5Me_5)Zr\}_3Cl_3F_5]^+$, $[\{(C_5Me_5)Zr\}_3Cl_2F_6]^+$, $[\{(C_5Me_5)Zr\}_3ClF_7]^+$, and $[\{(C_5Me_5)Zr\}_3F_8]^+$. A similar behavior is observed for the mass spectrum of the hafnium complex **2**.

Scheme 2

$$[(Cp^*MF_3)_4] + 4Me_3SiCl \rightarrow [(Cp^*MF_2Cl)_4] + 4Me_3SiF$$

$$M = Zr\ (\mathbf{1}),\ Hf\ (\mathbf{2});\ Cp^* = C_5Me_5$$

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(18) Martin, A.; Mena, M.; Palacios, F. *J. Organomet. Chem.* **1994,** *480,* C10.

(19) Bulkowski, J. E.; Stacy, R.; van Dyke, C. H. *J. Organomet. Chem.* **1975,** *87,* 137.

Table 4. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (**1**)

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	4281(1)	8054(1)	1520(1)	33(1)
Cl(1)	3519(1)	7205(1)	1722(1)	50(1)
F(1)	5000	7629(3)	2500	36(1)
Zr(2)	4156(1)	10458(1)	1672(1)	31(1)
Cl(2)	4305(1)	11325(1)	773(1)	44(1)
F(2)	5000	10868(3)	2500	32(1)
F(3)	4756(2)	9374(2)	1567(2)	35(1)
F(4)[b]	3672(6)	9258(4)	961(7)	37(1)[b]
Cl(4)[c]	3414(9)	9260(7)	677(10)	37(4)[c]
F(5)	4212(2)	9132(2)	2224(2)	37(1)
C(1)	4398(4)	7893(5)	457(3)	47(2)
C(2)	3884(3)	7345(7)	316(4)	56(2)
C(3)	4064(4)	6507(6)	761(4)	58(2)
C(4)	4704(4)	6559(5)	1194(3)	48(2)
C(5)	4901(3)	7434(5)	993(3)	44(2)
C(1*)	4424(5)	8802(7)	63(5)	76(3)
C(2*)	3251(5)	7568(12)	−237(5)	100(4)
C(3*)	3682(6)	5622(8)	764(7)	100(4)
C(4*)	5105(6)	5789(7)	1703(5)	83(3)
C(5*)	5540(4)	7767(7)	1273(5)	65(2)
C(6)	3142(3)	11248(5)	1238(3)	44(1)
C(7)	3224(3)	10606(5)	1782(4)	45(2)
C(8)	3707(3)	10992(6)	2418(3)	48(2)
C(9)	3890(3)	11876(5)	2243(4)	50(2)
C(10)	3557(3)	12060(5)	1527(4)	43(2)
C(6*)	2671(4)	11180(8)	486(4)	69(2)
C(7*)	2852(4)	9690(7)	1712(6)	73(3)
C(8*)	3910(5)	10554(8)	3123(4)	78(3)
C(9*)	4359(4)	12602(7)	2769(5)	78(3)
C(10*)	3586(4)	12991(5)	1162(5)	61(2)
C(21)	2628(5)	11910(7)	−1893(7)	79(3)
C(22)	3015(4)	11544(6)	−1222(5)	63(2)
C(23)	2924(4)	10624(7)	−1023(5)	65(2)
C(24)	2458(4)	10030(7)	−1450(5)	68(2)
C(25)	2062(5)	10353(8)	−2099(6)	80(3)
C(26)	2140(5)	11288(11)	−2328(5)	87(4)
C(27)	2710(7)	12868(10)	−2158(10)	136(7)
C(1#)	4655(7)	4916(14)	−193(10)	129(4)
C(2#)	5077(9)	5641(14)	−123(12)	129(4)
C(3#)	5685(8)	5470(16)	313(13)	129(4)
C(4#)	5872(7)	4574(18)	680(11)	129(4)
C(5#)	5451(9)	3849(14)	610(11)	129(4)
C(6#)	4842(8)	4020(13)	173(11)	129(4)
C(7#)	4021(7)	5094(21)	−649(12)	129(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] o = 0.79(2); o = occupancy. [c] o = 0.21(2).

A second and more exceptional chlorinating reagent was found in Me_2AlCl (DMAC). Reaction of $[\{(C_5Me_5)ZrF_3\}_4]$ with an equimolar (Al:Zr) solution of DMAC in toluene at room temperature gives a mixture of **1** and $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**3**) in an approximately 1:1 molar ratio (Scheme 3). Similarly, reaction of $[\{(C_5Me_5)HfF_3\}_4]$ with DMAC in toluene gives a mixture of **2** and $[(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**4**).

Scheme 3

$$[(Cp^*MF_3)_4] + 4Me_2AlCl \rightarrow [(Cp^*MF_2Cl)_4] + [Cp^*_4M_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4] + Me_2AlF$$

M = Zr (**1** and **3**), Hf (**2** and **4**); Cp* = C_5Me_5

In addition to the substitution of the four terminal fluorines in $[\{(C_5Me_5)MF_3\}_4]$ (M = Zr, Hf), two of the outer bridging fluorines, one from each of the triple fluorine bridges, are also replaced by chlorines in **3** and **4**. Interestingly, even this further fluorine−chlorine substitution does not lead to disruption of the tetrameric structure typical of $[\{(C_5Me_5)MF_3\}_4]$ (M = Zr, Hf). While **1** and **2** could be isolated in their pure form, compounds **3** and **4** could not be isolated but were characterized by ^1H and ^{19}F NMR (vide infra). The mixture of **1** and **3** decomposes at 279 °C, and the mass spectrum (EI) is similar to that described for **1**. No parent molecular ion is observed for **3**. The numbering scheme, yields, melting points, and ^{19}F NMR spectral data for all complexes **1**−**6** are collected in Table 1.

Table 5. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (**3**)

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	4271(1)	8028(1)	1503(1)	21(1)
Cl(1)	3513(1)	7177(1)	1701(1)	36(1)
F(1)	5000	7645(2)	2500	23(1)
Zr(2)	4139(1)	10443(1)	1667(1)	20(1)
Cl(2)	4282(1)	11309(1)	772(1)	31(1)
F(2)	5000	10815(2)	2500	23(1)
F(3)	4727(1)	9357(2)	1546(1)	25(1)
F(4)	3675(7)	9238(6)	982(8)	26(2)[b]
Cl(4)	3408(2)	9239(1)	676(2)	27(1)[c]
F(5)	4186(1)	9112(2)	2194(1)	24(1)
C(1)	4397(2)	7852(3)	446(2)	33(1)
C(2)	3887(2)	7266(4)	313(2)	43(1)
C(3)	4088(2)	6457(3)	780(3)	42(1)
C(4)	4722(2)	6549(3)	1212(2)	34(1)
C(5)	4913(2)	7425(3)	1006(2)	29(1)
C(1*)	4405(3)	8756(4)	40(3)	64(2)
C(2*)	3244(3)	7404(7)	−277(3)	93(3)
C(3*)	3714(3)	5573(4)	776(4)	82(2)
C(4*)	5131(3)	5804(4)	1739(3)	61(2)
C(5*)	5555(2)	7777(4)	1305(3)	52(1)
C(6)	3133(2)	11270(3)	1253(2)	29(1)
C(7)	3218(2)	10603(3)	1799(2)	33(1)
C(8)	3709(2)	10965(3)	2431(2)	35(1)
C(9)	3914(2)	11857(3)	2275(2)	34(1)
C(10)	3562(2)	12051(3)	1552(2)	30(1)
C(6*)	2637(2)	11231(4)	512(3)	51(1)
C(7*)	2833(2)	9716(4)	1731(3)	55(1)
C(8*)	3931(3)	10515(4)	3143(3)	58(2)
C(9*)	4384(2)	12546(4)	2795(3)	61(2)
C(10*)	3589(2)	12977(3)	1190(3)	45(1)
C(21)	2571(3)	11857(4)	−1967(4)	67(2)
C(22)	2980(2)	11554(4)	−1291(3)	55(1)
C(23)	2922(2)	10660(4)	−1036(3)	51(1)
C(24)	2461(3)	10052(4)	−1427(3)	55(1)
C(25)	2043(3)	10306(5)	−2078(3)	63(2)
C(26)	2085(3)	11196(6)	−2360(3)	75(2)
C(27)	2633(5)	12812(6)	−2268(6)	155(6)
C(1#)	4594(3)	4753(7)	−204(5)	110(2)
C(2#)	4889(4)	5607(7)	−246(6)	110(2)
C(3#)	5510(4)	5675(8)	151(7)	110(2)
C(4#)	5837(3)	4889(10)	589(6)	110(2)
C(5#)	5543(5)	4035(8)	631(5)	110(2)
C(6#)	4921(5)	3967(6)	234(6)	110(2)
C(7#)	3946(3)	4683(11)	−618(7)	110(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] o = 0.36(1); o = occupancy. [c] o = 0.64(1).

As might be expected treatment of $[\{(C_5Me_5)ZrF_3\}_4]$ with excess DMAC in toluene leads to $[\{(C_5Me_5)ZrCl_3\}_2]$. Porri reported that in the reaction of $V(acac)_3$ with DMAC a similar ligand exchange of the acac groups for Cl atoms also occurred.[20]

In all the above reactions of DMAC with $[\{(C_5Me_5)MF_3\}_4]$ the aluminium by product is likely to be Me_2AlF. While in these reactions we were not able to isolate Me_2AlF, evidence for its formation was found earlier in the reactions of $[\{(C_5Me_5)ZrF_3\}_4]$ with $AlMe_3$, where the Me_2AlF that is formed also functions as a ligand in the product.[10]

Crystal Structures of $[\{(C_5Me_5)ZrF_2Cl\}_4]$ (1) and $[(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4]$ (3). The molecular struc-

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(20) Giarrusso, A.; Amari, G.; Verona, S.; Porri, L. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 315.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (A^2 × 10^3) for [($C_5Me_4Et)_2ZrClF$] (**5**)

	x	y	z	U(eq)^a
Zr(1)	−1116(1)	808(1)	−2405(1)	22(1)
Cl(1)	−3755(2)	1378(1)	−2102(1)	57(1)
F(1)	65(4)	2027(2)	−2491(1)	43(1)
C(1)	111(5)	212(3)	−3582(2)	25(1)
C(1*)	1546(5)	−383(3)	−3660(2)	33(1)
C(1")	1961(7)	−457(4)	−4500(3)	50(1)
C(2)	−1484(5)	−113(3)	−3449(2)	28(1)
C(2*)	−2041(7)	−1118(4)	−3344(3)	48(1)
C(3)	−2450(5)	697(3)	−3594(2)	33(1)
C(3*)	−4204(6)	656(5)	−3597(3)	60(2)
C(4)	−1484(5)	1530(3)	−3807(2)	30(1)
C(4*)	−2010(7)	2535(4)	−4007(3)	50(1)
C(5)	97(5)	1220(3)	−3811(2)	26(1)
C(5*)	1519(6)	1866(4)	−4048(3)	46(1)
C(6)	−439(5)	−788(3)	−1564(2)	24(1)
C(6*)	−210(6)	−1763(3)	−1720(2)	32(1)
C(6")	169(6)	−2477(3)	−987(3)	40(1)
C(7)	−1825(5)	−472(3)	−1190(2)	27(1)
C(7*)	−3401(5)	−964(4)	−1029(3)	45(1)
C(8)	−1447(5)	344(3)	−925(2)	28(1)
C(8*)	−2515(7)	850(4)	−424(3)	48(1)
C(9)	171(5)	544(3)	−1146(2)	26(1)
C(9*)	1096(6)	1311(3)	−955(3)	43(1)
C(10)	796(5)	−138(3)	−1555(2)	24(1)
C(10*)	2510(5)	−233(4)	−1827(3)	40(1)
Zr(2)	6346(1)	5655(1)	−2359(1)	22(1)
Cl(2)	−6063(2)	7373(1)	−2514(1)	56(1)
F(2)	−8613(3)	5566(2)	−1956(1)	42(1)
C(21)	−4958(5)	5373(3)	−3640(2)	27(1)
C(21*)	−3247(5)	5227(4)	−3853(2)	35(1)
C(21")	−2848(6)	5244(4)	−4716(3)	48(1)
C(22)	−6121(5)	4624(3)	−3359(2)	27(1)
C(22*)	−5830(6)	3576(3)	−3229(3)	37(1)
C(23)	−7616(5)	5055(3)	−3383(2)	27(1)
C(23*)	−9163(5)	4546(4)	−3183(3)	38(1)
C(24)	−7411(5)	6055(3)	−3660(2)	27(1)
C(24*)	−8714(6)	6766(4)	−3758(3)	41(1)
C(25)	−5767(5)	6239(3)	−3837(2)	29(1)
C(25*)	−5008(6)	7187(4)	−4233(3)	45(1)
C(26)	−4281(5)	4577(3)	−1689(2)	23(1)
C(26*)	−3027(5)	3952(3)	−1966(2)	30(1)
C(26")	−1960(6)	3565(3)	−1338(3)	41(1)
C(27)	−5775(5)	4258(3)	−1281(2)	24(1)
C(27*)	−6512(6)	3291(3)	−1181(3)	37(1)
C(28)	−6380(5)	4968(3)	−901(2)	25(1)
C(28*)	−7879(5)	4886(3)	−364(3)	38(1)
C(29)	−5306(5)	5737(3)	−1090(2)	25(1)
C(29*)	−5411(6)	6603(3)	−754(3)	40(1)
C(30)	−4023(5)	5503(3)	−1590(2)	26(1)
C(30*)	−2570(5)	6111(3)	−1908(3)	40(1)

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

tures of **1** and **3** with labeling schemes are shown in Figures 1 and 2, respectively. Complexes **1** and **3** are isostructural and crystallize in the monoclinic system with space group *C*2/*c*. In both cases the crystals contain 1.5 toluene molecules per structural unit which are omitted from Figures 1 and 2. Selected bond lengths and angles for **1** and **3** are presented in Table 3. The structures of **1** and **3** consist of symmetric arrangements of four (C_5Me_5)Zr units similar to that observed for [{(C_5Me_5)ZrF_3}$_4$]. In **1** the Zr atoms are connected by alternating single and triple fluorine bridges with one terminal chlorine atom attached to each Zr. In **3** the arrangement is similar with the outer fluorine atom of the two triple bridges also substituted by chlorine. For **1** and **3** the mean terminal Zr−Cl distances are 2.448 and 2.443 Å, respectively, and the bridging Zr−Cl bond lengths for **3** (mean 2.627 Å) are similar to those observed for [{(C_5Me_5)$ZrCl_3$}$_2$].[18] The bridging Zr−F bond lengths for both complexes are comparable to those found for [{(C_5Me_5)ZrF_3}$_4$].[7]

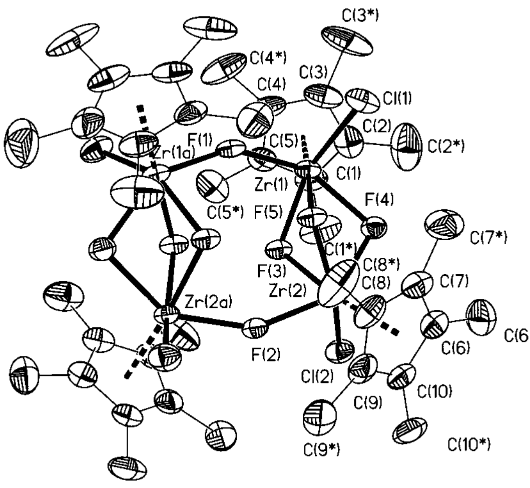

Figure 1. Crystal structure of [{($C_5Me_5)ZrF_2Cl$}$_4$] (**1**) giving the numbering scheme used in Table 3.

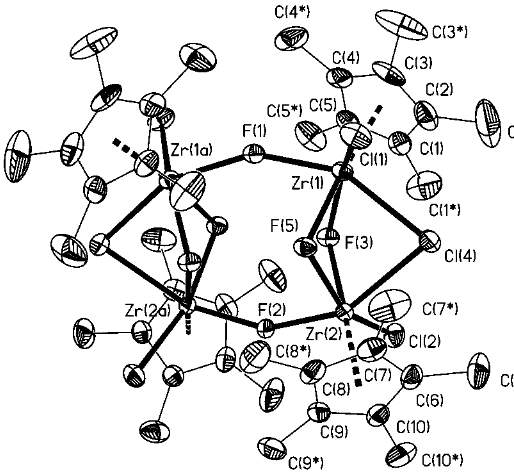

Figure 2. Crystal structure of [($C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$] (**3**) giving the numbering scheme used in Table 3.

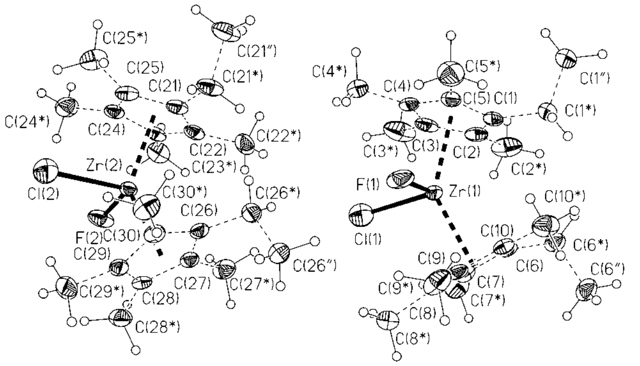

Figure 3. Asymmetric unit of [($C_5Me_4Et)_2ZrClF$] (**5**) giving the numbering scheme used in Table 3.

Synthesis and Characterization of [($C_5Me_4Et)_2ZrClF$] (5) and [($C_5Me_5)_2HfClF$] (6). In contrast to the failure to isolate mixed fluoro−chloro derivatives in the reactions of [{($C_5Me_5)ZrCl_3$}$_2$] with Me_3SnF, the analogous reactions of dicyclopentadienyl zirconium and hafnium dichlorides with Me_3SnF proceed cleanly by a methatical exchange of one chlorine atom for fluorine affording compounds [($C_5Me_4Et)_2ZrClF$] (**5**) and [($C_5Me_5)_2HfClF$] (**6**). As outlined in Scheme 4, reaction of Me_3SnF with [($C_5Me_4Et)_2ZrCl_2$] and [($C_5Me_5)_2HfCl_2$] in a 1:1 molar ratio leads to **5** and **6**, respectively. Complexes **5** and **6** were

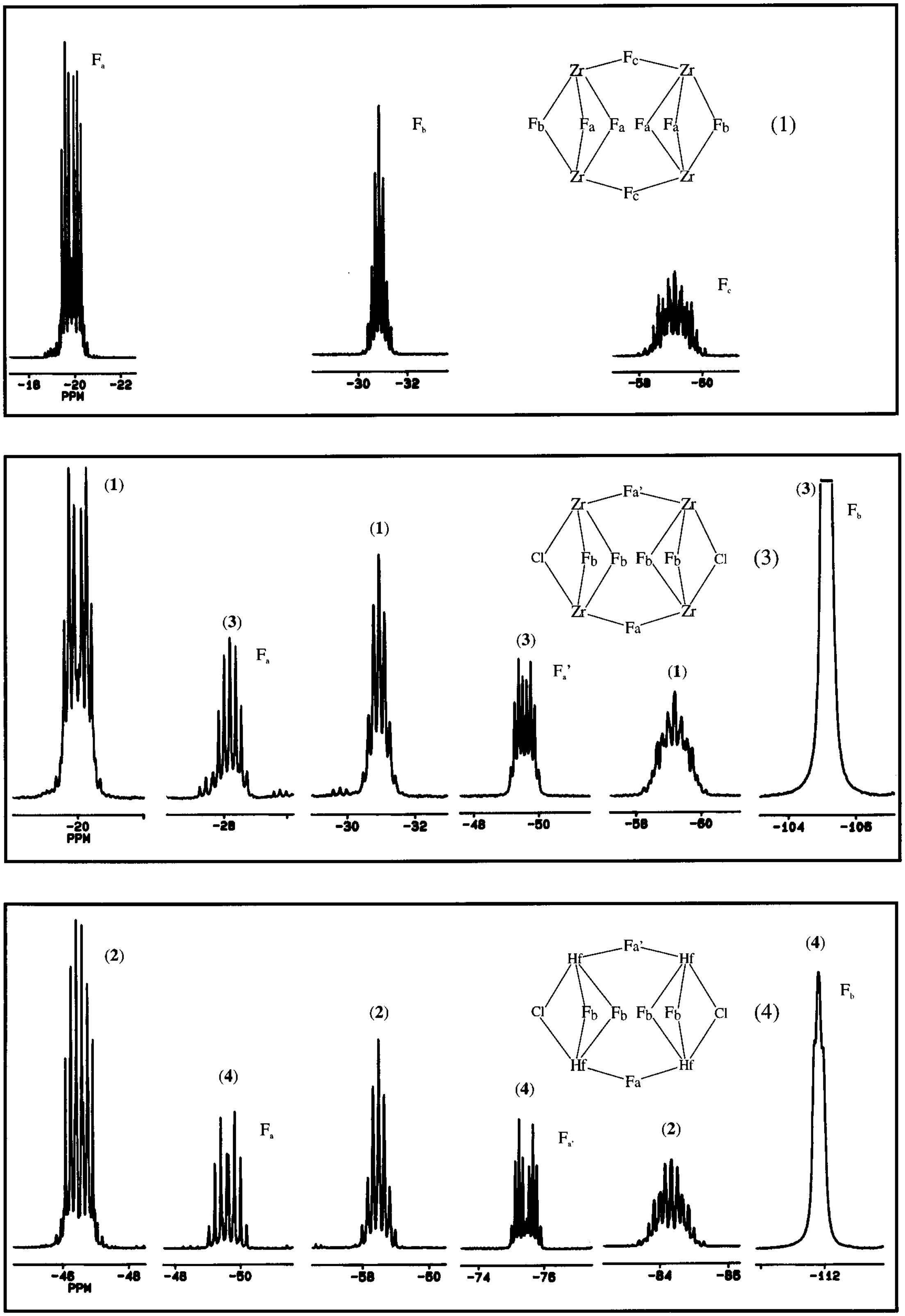

Figure 4. (a, top) ^{19}F NMR spectrum of [{(C_5Me_5)ZrF_2Cl}$_4$] (**1**) (75 MHz, $CDCl_3$, $CFCl_3$). (b, middle) ^{19}F NMR spectrum of **1** and [$(C_5Me_5)_4Zr_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$] (**3**) (75 MHz, $CDCl_3$, $CFCl_3$). (c, bottom) ^{19}F NMR spectrum of [{(C_5Me_5)HfF_2Cl}$_4$] (**2**) and [$(C_5Me_5)_4Hf_4(\mu\text{-}F)_2(\mu\text{-}F_2)_2(\mu\text{-}Cl)_2Cl_4$] (**4**) (75 MHz, $CDCl_3$, $CFCl_3$).

characterized by elemental analyses and ^{19}F NMR spectroscopy. For **5** and **6** the measured mass spectra are identical to the theoretically calculated isotope patterns.

Minacheva reported the preparation of [$(C_5Me_5)_2ZrClF$] from the corresponding dichloride using hydrogen fluoride. However, the structure was based solely on elemental analyses, and no structural characterization was carried out.[21] In order to confirm the structures of these compounds, we undertook an X-ray crystal structure investigation of **5**.

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(21) Minacheva, M. K.; Brainina, E. M.; Mikhailova, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985,** 2594; *Acad. Sci. USSR Bull. Chem. Sci.* **1985,** *34,* 2404; *Chem. Abstr.* **1985,** *105,* 209088r.

Scheme 4

$$[\mathrm{Cp_2MCl_2}] + \mathrm{Me_3SnF} \rightarrow [\mathrm{Cp_2MFCl}] + \mathrm{Me_3SnCl}$$

$$\mathrm{M} = \mathrm{Zr},\ \mathrm{Cp} = \mathrm{C_5Me_4Et}\ (\mathbf{5});\ \mathrm{M} = \mathrm{Hf},\ \mathrm{Cp} = \mathrm{C_5Me_5}\ (\mathbf{6})$$

Structure of [$(C_5Me_4Et)_2ZrClF$] (5). Complex **5** crystallizes in the triclinic system with the space group $P\bar{1}$. The structure consists of two molecules in the asymmetric unit with a distorted sandwich arrangement. Selected bond lengths and angles for **5** are presented in Table 3. While the organic substituents are disposed on the same sides of the molecules, the corresponding halogen atoms alternate in their positions. A comparison of the cyclopentadienyl rings in the two molecules shows their slightly twisted arrangement. The average Zr−Cl bond length is 2.433(8) Å, while the average Zr−F bond length is 2.002(3) Å and the average F−Zr−Cl bond angle is 97.44(9)°. These values are comparable to those determined for the corresponding dichlorides and difluorides, respectively.[7,14]

^{19}F NMR Spectroscopy of 1−6. The ^{19}F NMR spectrum of the tetrameric [$\{(C_5Me_5)ZrF_3\}_4$] shows four types of fluorine resonances which have been assigned to the terminal fluorines and three types of bridging fluorines.[7] Upon selective replacement of the terminal fluorines by chlorines, the resonance at +81 ppm observed in the spectrum of [$\{(C_5Me_5)ZrF_3\}_4$] is totally lost. The bridging fluorines in **1** are shown up as a complex second order spectrum with three distinct fluorine environments (Figure 4a). A similar behaviour is seen for the analogous hafnium derivative [$\{(C_5Me_5)HfF_2Cl\}_4$] (**2**) (Figure 4c).

Use of DMAC as the reagent for chlorination results in the formation of **1** and **3**, and **2** and **4** in the case of hafnium. The signals due to complexes **3** and **4** are easily picked out in the respective NMR spectra of the mixtures (Figure 4b,c). The NMR spectrum of **4** can be analyzed on a first order basis. Two fluorines F_a and $F_{a'}$ are shown up as doublets of quintets, while F_b is seen as a merged doublet of doublets (Figure 4c). It is of interest to note that fluorines F_b move considerably upfield to −112.0 ppm due to chlorination of the bridge position.

The ^{19}F NMR spectrum of complex **5** shows a singlet at 45.2 ppm which lies within the range found for corresponding difluorides, for example [$\{C_5H_3(Me)(SiMe_3)\}_2ZrF_2$] with a singlet at 38.25 ppm. In the case of **6** the singlet occurs at −17.92 ppm, which is in the same region as that observed for the corresponding difluoride, namely, −18.16 ppm.[7]

Conclusion

We have demonstrated the first syntheses of mixed fluoro−chloro group 4 cyclopentadienyl substituted compounds using two different synthetic strategies. In view of the documented catalytic activity of $(C_5Me_5)MCl_3$/MAO and $(C_5Me_5)MF_3$/MAO systems for the polymerization of olefins these mixed fluoro−chloro compounds are of interest from the point of their own catalytic potential. Also, we previously showed that the reactions of [$\{(C_5Me_5)ZrF_3\}_4$] with $AlMe_3$ proceed to give Zr/Al clusters. Thus, it is likely that the mixed fluoro−chloro derivatives can behave as new synthons for the preparation of novel M/Al clusters (M = Zr, Hf).

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and fully labeled figures of 50% anistropic displacement parameters for **1**, **3**, and **5** (27 pages). Ordering information is given on any current masthead page.

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