Organometallics **1994,** *13,* 1251-1256

Trimethyltin Fluoride: A New Fluorinating Reagent for the Preparation of Organometallic Fluorides

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Received September 7, 1993®

Me_3SnF (1) reacts with $Cp'MCl_3$ to give $Cp'MF_3$ (**2**, Cp′ = C_5Me_5, M = Ti; **2a**, Cp′ = C_5Me_4Et, M = Ti; **2b**, Cp′ = C_5H_5, M = Ti; **2c**, Cp′ = C_5H_4Me, M = Ti; **3**, Cp′ = C_5Me_5, M = Zr; **4**, Cp′ = C_5Me_5, M = Hf) in high yields. The reaction of Cp_2TiCl_2, $[C_5H_3(Me)(SiMe_3)]_2ZrCl_2$, and $(C_5Me_5)_2HfCl_2$ with Me_3SnF yields Cp_2TiF_2 (**5**), $[C_5H_3(Me)(SiMe_3)]_2ZrF_2$ (**6**), and $(C_5Me_5)_2HfF_2$ (**7**), respectively. Treatment of $(Cp^*TiClO)_3$ (Cp^* = C_5Me_5) with Me_3SnF leads to the eight-membered ring $(Cp^*TiFO)_4$ (**8**). The reaction of the organotitanium(III) chlorides $(Cp_2TiCl)_2$ (Cp = C_5H_5), $[(C_5H_4Me)_2TiCl]_2$, and $Cp^*{}_2TiCl$ with Me_3SnF gives the corresponding fluorides $(Cp_2TiF)_2$ (**9**), $[(C_5H_4Me)_2TiF]_2$ (**10**), and $Cp_2{}^*TiF$ (**11**), respectively. An alternative method for the preparation of compounds **9** and **10** is the reduction of Cp_2TiF_2 and $(C_5H_4Me)_2TiF_2$, respectively, using sodium amalgam. The structures of **2c**, **3**, **4**, and **10** were determined by single-crystal X-ray diffraction. Compounds **3** and **4** are isostructural and form tetramers in the solid as well as in solution. **10** is a fluorine-bridged dimer in the crystalline state.

Introduction

The first organometallic chloride, Zeise's salt, was prepared in 1827. Although organometallic chlorides are readily available and extensively used, the corresponding fluorides are scarcely known. The reason for this different development is the lack of procedures for the preparation of organometallic fluorides. Furthermore, their low solubilities in most of the common solvents have rendered them of very limited practical use. Since the solubility of an organometallic fluoride increases with increasing size of the organic group, the solubility limitations should be overcome by the use of bulky organic substituents.

Numerous reports on fluorinating reagents can be found in the literature.[1-3] They are mainly based on two principles. The first one uses metathesis of the corresponding chlorides. The difficulty of this procedure in the case of organometallic compounds is the separation of the reagent from the product. Thus, the products obtained by this method have been reported to contain significant amounts of the fluorinating reagent. This was demonstrated in the reaction of Cp^*TiF_3 (Cp^* = C_5Me_5) with sodium fluoride, giving adducts of crown ether type compounds.[4] On the other hand, hydrogen fluoride, a common fluorinating reagent, easily cleaves many carbon–metal bonds. The second approach utilizes oxidative fluorinating reactions. These synthetic methods[1-3] have limited use in case of organometallic compounds due to the easy cleavage of the carbon–metal and carbon–hydrogen bonds. In recent years we have reported[5-7] the successful use of AsF_3 for the preparation of organometallic fluorides. However, we observed that the reaction of AsF_3 and Cp^*ZrCl_3 results in the formation of Cp^*AsCl_2. In addition to the fluorine–chlorine exchange, transfer of the Cp^* group from zirconium to arsenic occurred.[5]

Therefore, it was highly desirable to have a better fluorinating reagent for group 4 organometallic systems. Group 4 compounds of this type have been shown to be important catalysts in the polymerization of olefins.

Results and Discussion

Cp^*TiF_3 was previously prepared from the corresponding chloride species by reaction with AsF_3.[5] Some attempts to isolate the homologous zirconium and hafnium complexes were unsuccessful, since the cleavage of the zirconium–carbon bonds was observed. Instead, we found that a suitable fluorinating agent is Me_3SnF (**1**).[8] This reagent reacted in a molar ratio of 3:1 with $Cp'MCl_3$ (M = Ti,[9] Zr,[10] Hf[11]) in toluene to give compounds $Cp'MF_3$ (**2–4**) in high yields.

$$Cp'MCl_3 + \underset{\mathbf{1}}{3Me_3SnF} \rightarrow \underset{\mathbf{2\text{–}4}}{Cp'MF_3} + 3Me_3SnCl$$

2, M = Ti, Cp′ = C_5Me_5;[5] **2a**, M = Ti, Cp′ = C_5Me_4Et;[5] **2b**, M = Ti, Cp′ = C_5H_5;[12] **2c**, M = Ti, Cp′ = C_5H_4Me; **3**, M = Zr, Cp′ = C_5Me_5; **4**, M = Hf, Cp′ = C_5Me_5

To our knowledge, **1** has not been used previously as a fluorinating reagent in the preparation of transition-metal

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® Abstract published in *Advance ACS Abstracts,* March 1, 1994.

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0276-7333/94/2313-1251$04.50/0

Table 1. Numbering Scheme, Yields, Melting Points, and Elemental Analysis Data for Complexes 2–11

reactant	product	compd no.	yields (%)	mp (°C)	anal. found (calcd) (%) C	H	F
$(C_5Me_5)TiCl_3$	$(C_5Me_5)TiF_3$	**2**	92	180	49.8 (50.02)	6.1 (6.29)	23.6 (23.74)
Cp^1TiCl_3[a]	Cp^1TiF_3	**2a**	92	139	51.8 (51.98)	6.7 (6.74)	22.0 (22.43)
$(C_5H_5)TiCl_3$	$(C_5H_5)TiF_3$	**2b**	87	151–170[d]	35.2 (35.33)	2.9 (2.97)	33.2 (33.53)
Cp^2TiCl_3[b]	Cp^2TiF_3	**2c**	90	134–151[d]	38.9 (39.27)	3.6 (3.83)	30.7 (30.98)
$(C_5Me_5)ZrCl_3$	$(C_5Me_5)ZrF_3$	**3**	94	>350	42.2 (42.38)	5.5 (5.33)	19.5 (20.11)
$(C_5Me_5)HfCl_3$	$(C_5Me_5)HfF_3$	**4**	93	>350	31.1 (32.40)	4.3 (4.08)	15.2 (15.37)
$(C_5H_5)_2TiCl_2$	$(C_5H_5)_2TiF_2$	**5**	98	245[d]	55.6 (55.59)	4.5 (4.66)	17.2 (17.59)
$Cp^3{}_2ZrCl_2$[c]	$Cp^3{}_2ZrF_2$	**6**	85	109	49.7 (50.07)	6.8 (7.00)	8.7 (8.80)
$(C_5Me_5)_2HfCl_2$	$(C_5Me_5)_2HfF_2$	**7**	92	207	49.4 (49.33)	6.4 (6.21)	8.0 (7.79)
$[(C_5Me_5)TiClO]_3$	$[(C_5Me_5)TiFO]_4$	**8**	87	325	55.1 (55.07)	6.9 (6.93)	9.2 (9.36)
$[(C_5H_5)_2TiCl]_2$	$[(C_5H_5)_2TiF]_2$	**9**	90	228	60.6 (60.95)	5.1 (5.11)	9.3 (9.64)
$(C_5H_5)_2TiF_2$	$[(C_5H_5)_2TiF]_2$	**9**	95	228	61.1 (60.95)	5.2 (5.11)	9.2 (9.64)
$[(Cp^2)_2TiCl]_2$[b]	$[(Cp^2)_2TiF]_2$	**10**	89	105[d]	63.6 (64.02)	6.0 (6.27)	8.0 (8.44)
$(Cp^2)_2TiF_2$[b]	$[(Cp^2)_2TiF]_2$	**10**	92	105[d]	63.7 (64.02)	6.0 (6.27)	8.1 (8.44)
$(C_5Me_5)_2TiCl$	$(C_5Me_5)_2TiF$	**11**	88	184	71.0 (71.21)	8.9 (8.96)	5.8 (5.62)

[a] $Cp^1 = C_5Me_4Et$. [b] $Cp^2 = C_5H_4Me$. [c] $Cp^3 = C_5H_3Me(SiMe_3)$. [d] Decomposition.

fluorides. However, Schmidbaur et al.[13] reported the preparation of dialkylgallium fluorides by reaction of 1 with R_3Ga. Although Me_3SnF in the solid state forms a chainlike structure of tin and fluorine atoms[14] and it is insoluble in organic solvents, it reacts with organotransition metal(IV) chlorides under mild conditions. The resulting Me_3SnCl in the reaction is easily removed in vacuo and converted with aqueous KF or sodium fluoride to the starting material. Furthermore, reactions of Me_3SnF with Cp_2TiCl_2,[15] $[C_5H_3(Me)(SiMe_3)]_2ZrCl_2$,[16] and $(C_5Me_5)_2HfCl_2$[11] gave in good yields Cp_2TiF_2[17] (**5**), $[C_5H_3(Me)(SiMe_3)]_2ZrF_2$ (**6**), and $(C_5Me_5)_2HfF_2$ (**7**), respectively ($Cp = C_5H_5$).

We observed that in the case of $(Cp^*TiClO)_3$[18] ring expansion occurred to give the eight-membered cyclic compound $(Cp^*TiFO)_4$[19] (**8**). The identification of the eight-membered ring was accomplished by mass spectroscopy (EI: *m/z* 872 (M^+)).

Finally, titanium(III) compounds reacted with Me_3SnF to give organometallic titanium(III) fluorides in high yields. The reaction of $(Cp_2TiCl)_2$,[20] $[(C_5H_4Me)_2TiCl]_2$,[21] and $Cp^*{}_2TiCl$[22] with 1 gave $(Cp_2TiF)_2$[20] (**9**), $[(C_5H_4Me)_2TiF]_2$ (**10**), and $Cp^*{}_2TiF$ (**11**), respectively. Compounds **9–11** are purified by sublimation in vacuo, and compounds **9** and **10** can be also purified by recrystallization using a THF/hexane mixture. Compounds **9–11** are green solids. They are soluble in polar solvents such as toluene or THF without decomposition. In hexane **9** and **10** are moderately soluble, while **11** is highly soluble in this solvent. An alternative method for the preparation of compounds **9** and **10** is the reduction of Cp_2TiF_2[17] and $(C_5H_4Me)_2TiF_2$,[23,24] respectively, using sodium amalgam in toluene as a reducing agent. However, this method has the disadvantage that the reducing agent can not be recycled as easily as Me_3SnCl. The numbering scheme, yields, melting points, and elemental analysis data for compounds **2–11** are collected in Table 1.

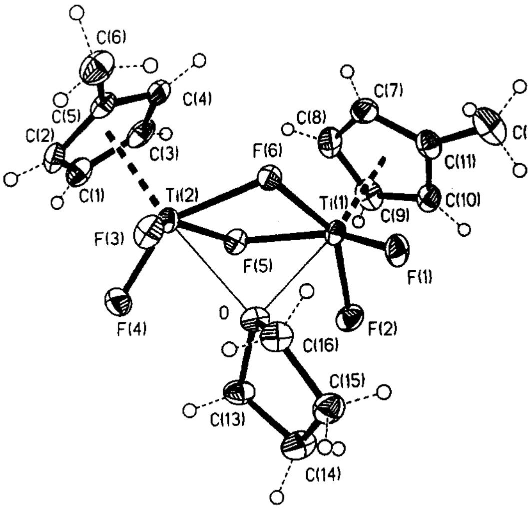

Figure 1. Molecular structure of $[(C_5H_4Me)TiF_3]_2 \cdot THF$ (**2c**).

Recently we investigated the structures of Cp^*TiF_3 and $(C_5Me_4Et)TiF_3$.[5] It is rather surprising that Cp^*TiF_3 forms a fluorine-bridged dimer in the solid state while the latter is tetrameric. To provide further insight into this structure, we studied the single-crystal structure of $(C_5H_4Me)TiF_3$ (**2c**). In order to obtain single crystals of **2c**, recrystallization from THF was necessary. Figure 1 shows the molecular structure of **2c** with one molecule of THF. The structure consists of fluorine-bridged dimers of $(C_5H_4Me)TiF_3$ and one THF molecule coordinated through oxygen to both titanium atoms. The structural data show that the Ti–F–Ti bridges are approximately symmetrical (with average bond lengths of Ti–F = 2.030 Å) and the Ti–O–Ti bridge is unsymmetrical. All the other fluorine atoms are terminal with Ti–F bond lengths of 1.823 Å (mean). Their intramolecular geometrical parameters are collected in Table 4. These values are comparable to those

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Table 2. Crystallographic Data for the Complexes $[(C_5H_4Me)TiF_3]_2\cdot THF$ (2c), $(Cp^*ZrF_3)_4$ (3), $(Cp^*HfF_3)_4$ (4), and $[(C_5H_4Me)_2TiF]_2$ (10)

	2c	**3**	**4**	**10**
formula	$C_{16}H_{22}F_6OTi_2$	$C_{40}H_{60}F_{12}Zr_4$	$C_{40}H_{60}F_{12}Hf_4$	$C_{24}H_{28}F_2Ti_2$
fw	440.14	1133.76	1482.84	450.24
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	6.5960(10)	17.607(2)	17.700(2)	11.189(2)
b, Å	15.329(3)	13.277(2)	13.366(2)	80.580(10)
c, Å	17.262(3)	19.774(3)	19.907(2)	11.851(2)
β, deg	90	102.28(1)	101.81(2)	105.64(1)
V, nm^3	1.7454(5)	4.5168(11)	4.6099(10)	1.0289(3)
Z	4	4	4	2
μ(Mo Kα), mm^{-1}	0.976	0.974	9.051	0.80
D_{calcd}, g cm^{-3}	1.67	1.67	2.14	1.45
color	yellow	colorless	colorless	green
cryst dimens, mm^3	0.8 × 0.6 × 0.3	0.7 × 0.5 × 0.2	0.7 × 0.5 × 0.4	0.6 × 0.6 × 0.1
T, K	153(2)	153(2)	153(2)	153(2)
θ scan limits, deg	3.56–22.52	3.52–22.55	4.01–22.53	3.57–22.50
no. of rflns collcd	2707	6356	6997	2723
no. of indpt rflns	2270	5921	6017	1342
goodness of fit	1.115	1.051	1.096	1.046
R (all data)	0.022	0.081	0.047	0.041
R_w2 (all data)	0.060	0.194	0.094	0.111
no. of variables	229	505	525	127
residual density, e nm^3	−199 to +160	−1182 to +2071	−1674 to +1130	−438 to +473

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[(C_5H_4Me)TiF_3]_2\cdot THF$ (2c)

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	1641(1)	4546(1)	8318(1)	18(1)
Ti(2)	1391(1)	4676(1)	6460(1)	18(1)
F(1)	4278(2)	4519(1)	8646(1)	26(1)
F(2)	1109(2)	5603(1)	8752(1)	28(1)
F(3)	3919(2)	4695(1)	6030(1)	27(1)
F(4)	693(3)	5766(1)	6140(1)	30(1)
F(5)	−201(2)	4914(1)	7440(1)	20(1)
F(6)	2646(2)	3959(1)	7336(1)	20(1)
O	3309(3)	5587(1)	7372(1)	21(1)
C(1)	293(4)	4177(2)	5239(2)	24(1)
C(2)	−1449(5)	4378(2)	5662(2)	26(1)
C(3)	−1574(5)	3804(2)	6284(2)	27(1)
C(4)	97(5)	3236(2)	6246(2)	25(1)
C(5)	1264(5)	3458(2)	5584(2)	23(1)
C(6)	3146(5)	3020(2)	5309(2)	32(1)
C(7)	689(5)	3055(2)	8529(2)	31(1)
C(8)	−1081(5)	3543(2)	8447(2)	32(1)
C(9)	−1177(5)	4136(2)	9060(2)	30(1)
C(10)	558(5)	4005(2)	9522(2)	26(1)
C(11)	1709(5)	3320(2)	9206(2)	26(1)
C(12)	3635(5)	2955(2)	9528(2)	41(1)
C(13)	2794(4)	6511(2)	7411(2)	27(1)
C(14)	4375(5)	6906(2)	7948(2)	33(1)
C(15)	6146(5)	6264(2)	7932(2)	29(1)
C(16)	5523(4)	5577(2)	7344(2)	24(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Distances and Angles for $[(C_5H_4Me)TiF_3]_2\cdot THF$ (2c)[a]

(a) Bond Distances (Å)

Ti(1)–F(1)	1.829(2)	Ti(1)–F(2)	1.820(2)
Ti(1)–F(5)	2.022(2)	Ti(1)–F(6)	2.030(2)
Ti(1)–O	2.535(2)	Ti(2)–O	2.455(2)
Ti(1)–Cp(1)	2.057(3)		

(b) Bonds Angles (deg)

Ti(1)–F(5)–Ti(2)	105.31(7)	Ti(1)–F(6)–Ti(2)	104.28(7)
Ti(1)–O–Ti(2)	80.26(5)	F(5)–Ti(1)–F(6)	72.21(6)
F(1)–Ti(1)–Cp(1)	106.1(1)	F(5)–Ti(1)–Cp(1)	107.7(1)

[a] Here and elsewhere Cp in the tables refers to the centroid of the corresponding substituted cyclopentadienyl ring.

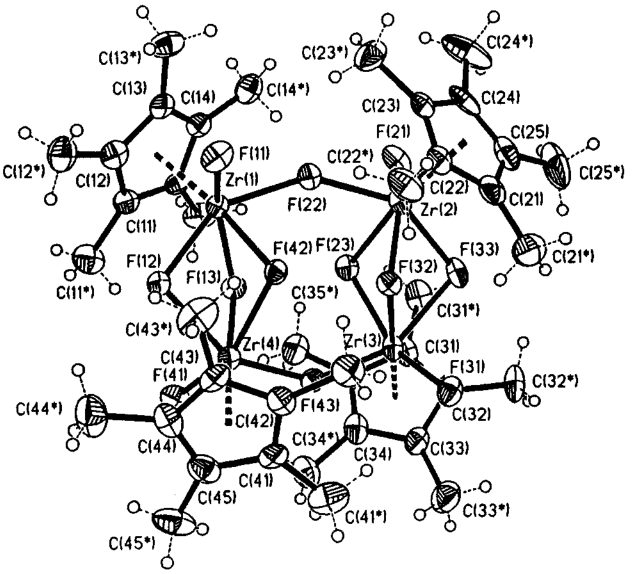

Figure 2. Molecular structure of $[(C_5Me_5)ZrF_3]_4$ (3).

determined for Cp^*TiF_3.[5] However, in 2c the coordination geometry is distorted octahedral rather than distorted trigonal pyramidal as found in Cp^*TiF_3. A single-crystal X-ray diffraction study of compounds 3 and 4 was also undertaken. Single crystals of 3 and 4 were obtained by recrystallization from hexane and toluene, respectively. A diagram and labeling scheme of compound 3 are presented in Figure 2; selected bond lengths and angles are given in Table 6. The structure consists of a symmetric arrangement of four Cp^*ZrF_3 molecules. The zirconium atoms are coordinated in a highly distorted octahedral geometry. The fluorine atoms connect the zirconium atoms through alternating single and triple bridging configuration. In addition, one fluorine atom is terminally bonded to each zirconium atom. The terminal (mean 1.955 Å) and bridging Zr–F bond lengths (mean 2.136 Å) show the expected differences. The bond lengths of the bridging fluorine atoms indicate (Zr(1)–F(42) and Zr(4)–F(42)) that they are not always symmetrically arranged between the zirconium atoms. Compound 4 is isostructural with 3. The molecular structure of 4 is shown in Figure 3, and selected bond lengths and angles of 4 are given in Table 8. The ^{19}F NMR spectra of 3 and 4 show the expected

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $[(C_5Me_5)ZrF_3]_4$ (3)

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	7969(1)	607(1)	2354(1)	23(1)
F(11)	9079(2)	913(4)	2564(2)	35(1)
F(12)	7705(2)	1854(3)	2968(2)	28(1)
F(13)	6919(2)	305(3)	2682(2)	25(1)
Zr(2)	7989(1)	−2402(1)	2729(1)	25(1)
F(21)	7465(3)	−3002(4)	1833(3)	43(1)
F(22)	8140(2)	−958(3)	2318(2)	27(1)
F(23)	6862(2)	−1742(3)	2672(2)	28(1)
Zr(3)	6771(1)	−2036(1)	3706(1)	25(1)
F(31)	7269(3)	−2365(4)	4654(3)	36(1)
F(32)	7945(2)	−1661(3)	3666(2)	27(1)
F(33)	7331(2)	−3287(3)	3313(3)	32(1)
Zr(4)	7244(1)	952(1)	3696(1)	23(1)
F(41)	6227(2)	1566(4)	3411(2)	35(1)
F(42)	8222(2)	234(3)	3439(2)	26(1)
F(43)	6796(2)	−474(3)	3894(2)	26(1)
C(11)	7078(5)	1609(7)	1462(4)	31(2)
C(12)	7851(4)	1888(7)	1419(4)	30(2)
C(13)	8195(5)	1021(7)	1169(4)	28(2)
C(14)	7634(4)	235(6)	1065(4)	28(2)
C(15)	6945(4)	600(6)	1248(4)	27(2)
C(11*)	6492(5)	2294(8)	1691(5)	44(2)
C(12*)	8257(5)	2867(7)	1607(5)	43(2)
C(13*)	8986(5)	978(8)	1022(5)	42(2)
C(14*)	7743(5)	−777(7)	779(5)	39(2)
C(15*)	6202(4)	36(8)	1197(5)	39(2)
C(21)	9088(5)	−3207(7)	3550(5)	38(2)
C(22)	9400(4)	−2339(6)	3302(4)	29(2)
C(23)	9379(4)	−2470(6)	2596(5)	30(2)
C(24)	9068(4)	−3434(7)	2400(5)	38(2)
C(25)	8875(5)	−3891(7)	2999(6)	42(2)
C(21*)	9017(5)	−3411(9)	4284(5)	57(3)
C(22*)	9711(5)	−1423(8)	3729(5)	45(2)
C(23*)	9685(5)	−1762(8)	2116(6)	52(3)
C(24*)	8976(6)	−3932(10)	1711(6)	71(4)
C(25*)	8536(6)	−4902(8)	3028(8)	73(4)
C(31)	5600(4)	−2973(6)	3091(5)	34(2)
C(32)	5764(4)	−3308(7)	3793(5)	35(2)
C(33)	5624(5)	−2500(7)	4232(5)	35(2)
C(34)	5385(4)	−1666(7)	3784(5)	35(2)
C(35)	5364(4)	−1959(6)	3094(5)	32(2)
C(31*)	5647(5)	−3585(7)	2462(5)	43(2)
C(32*)	6025(5)	−4364(7)	4037(6)	43(3)
C(33*)	5713(6)	−2555(8)	5000(6)	53(3)
C(34*)	5129(5)	−661(7)	4011(5)	41(2)
C(35*)	5108(5)	−1307(7)	2466(5)	42(2)
C(41)	7408(5)	919(6)	4987(4)	29(2)
C(42)	5637(6)	−2383(10)	2423(6)	49(3)
C(43)	5619(6)	−2272(8)	1713(5)	39(2)
C(44)	5919(7)	−3126(11)	1469(6)	61(4)
C(45)	6132(7)	−3782(9)	2021(8)	62(4)
C(46)	6012(10)	−3792(17)	3315(9)	144(10)
C(47)	5328(8)	−1673(14)	2878(7)	91(5)
C(48)	5292(7)	−1377(12)	1291(7)	77(5)
C(49)	5975(8)	−3336(15)	732(7)	100(6)
C(50)	6492(11)	−4817(12)	2009(14)	158(11)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

four-line pattern, due to the different trans arrangements of the fluorine atoms. This demonstrates the existence of the tetrameric unit also in solution.

Single crystals of compound **10** were obtained by slowly concentrating a solution of **10** dissolved in hexane. The structure of **10** involves a dimer of a four-membered Ti_2F_2 ring (Figure 4). The titanium atoms have a distorted-tetrahedral coordination sphere with F–Ti–F angles of 70.43(8)°. The fluorine atoms are symmetrically arranged. In Table 10 the selected bond lengths and angles of **10** are given. A comparison with $[Cp_2TiF_2]_3Ti$[25] shows the same coordination geometry at the tetrahedral coordinated titanium atoms (F–Ti–F = 71.15(6)°).

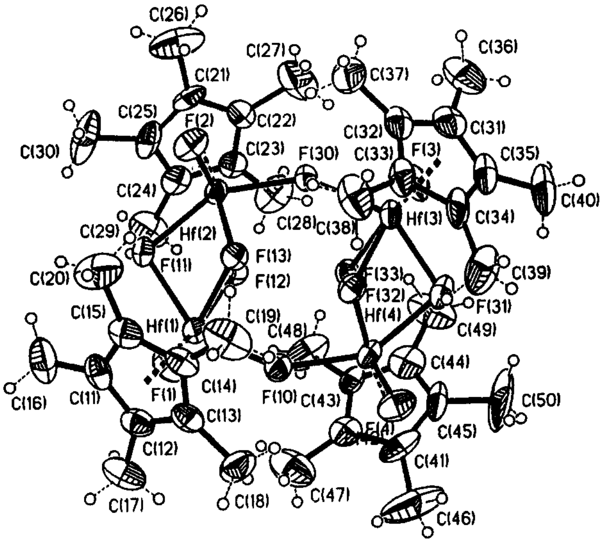

Figure 3. Molecular structure of $[(C_5Me_5)HfF_3]_4$ (**4**).

Table 6. Selected Bond Lengths and Bond Angles for $[(C_5Me_5)ZrF_3]_4$ (3)

	Bond Lengths (Å)		
Zr(1)–F(11)	1.953(4)	Zr(1)–F(22)	2.104(4)
Zr(1)–F(42)	2.156(4)	Zr(2)–F(22)	2.121(4)
Zr(4)–F(42)	2.121(4)	Zr(1)–Zr(4)	3.2124(13)
Zr(1)–F(12)	2.161(4)	Zr(1)–Cp(1)	2.198(8)
Zr(4)–F(12)	2.160(4)		
	Bond Angles (deg)		
Zr(1)–F(22)–Zr(2)	148.2(2)	F(22)–Zr(1)–F(42)	78.8(2)
F(22)–Zr(1)–F(11)	93.2(2)	Zr(1)–Cp(1)–F(11)	105.6(2)
Zr(1)–F(42)–Zr(4)	97.4(2)	Zr(1)–Cp(1)–F(12)	105.2(2)
F(11)–Zr(1)–F(12)	92.6(2)	Zr(1)–Cp(1)–F(22)	105.4(2)
F(13)–Zr(1)–F(42)	70.2(2)		

Conclusions

This paper describes the synthesis and characterization of organometallic fluorides of group 4 using Me_3SnF for the first time as a fluorinating reagent. Preliminary experiments demonstrate that Me_3SnF can also be used for the preparation of other organotransition-metal and main-group fluorides, such as Cp^*TaF_4, PF_3, and SOF_2, in quantitative yield. Furthermore, the resulting Me_3SnCl can easily be recycled, yielding the starting material Me_3SnF. This is a striking improvement over other fluorinating reagents. A further improvement may be realized by using other organic substituents bonded to tin rather than methyl groups.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or a drybox. Reagent grade toluene, hexane, and THF were distilled prior to use from benzophenone ketyl under nitrogen. Reagent grade acetonitrile was distilled from calcium hydride. Deuterated solvents, $CDCl_3$ and C_6D_6, were trap-to-trap distilled from CaH_2. Me_3SnF was synthesized by published methods[8] and sublimed at 100 °C/10^{-4} mbar prior to use.

^1H and ^{19}F NMR data are listed in ppm downfield from TMS and $CFCl_3$, respectively. NMR spectra were recorded on a Bruker AM 250 spectrometer. IR spectra were recorded on a Perkin-Elmer Bio-Rad Digilab FTS-7, and mass spectra were recorded on a Finnigan MAT System 8230 and Varian MAT CH5 (EI).

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[25] Liu, F.-Q.; Gornitzka, H.; Stalke, D.; Roesky, H. W. *Angew. Chem.* **1993**, *105*, 447; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 442.

Table 7. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $[(C_5Me_5)HfF_3]_4$ (4)

	x	*y*	*z*	*U*(eq)[a]
Hf(1)	7056(1)	632(1)	2656(1)	31(1)
F(1)	5946(3)	933(5)	2436(3)	54(2)
F(10)	6876(3)	−916(4)	2679(3)	41(1)
F(11)	7320(3)	1851(4)	2040(2)	36(1)
F(12)	6807(3)	262(4)	1583(2)	34(1)
F(13)	8077(3)	318(4)	2316(2)	37(1)
C(11)	7172(6)	1914(9)	3566(5)	47(3)
C(12)	6820(6)	1072(10)	3811(5)	47(3)
C(13)	7364(6)	291(9)	3927(5)	43(3)
C(14)	8057(6)	614(9)	3746(5)	44(3)
C(15)	7935(6)	1627(10)	3524(5)	45(3)
C(16)	6801(9)	2891(10)	3382(6)	76(4)
C(17)	6020(7)	1076(12)	3962(6)	68(4)
C(18)	7212(8)	−714(9)	4219(6)	63(4)
C(19)	8770(7)	13(13)	3817(6)	76(4)
C(20)	8540(8)	2287(12)	3311(6)	77(5)
Hf(2)	7758(1)	964(1)	1315(1)	31(1)
F(2)	8777(3)	1539(5)	1596(3)	52(2)
C(21)	7904(7)	1918(9)	263(5)	51(3)
C(22)	7615(7)	987(9)	40(5)	45(3)
C(23)	6864(6)	900(9)	178(5)	43(3)
C(24)	6703(6)	1788(9)	498(5)	46(3)
C(25)	7348(8)	2419(9)	560(6)	56(3)
C(26)	8688(9)	2346(15)	209(8)	103(6)
C(27)	8006(10)	206(13)	−347(6)	92(6)
C(28)	6328(8)	33(11)	−3(6)	73(4)
C(29)	5956(8)	2041(12)	724(6)	77(4)
C(30)	7442(12)	3455(11)	849(8)	109(7)
Hf(3)	8223(1)	−1990(1)	1309(1)	35(1)
F(3)	7724(3)	−2308(5)	375(3)	57(2)
F(30)	8187(3)	−445(4)	1122(3)	35(1)
F(31)	7667(3)	−3210(4)	1702(3)	46(2)
F(32)	8127(3)	−1684(4)	2327(3)	39(1)
Hf(4)	7007(1)	−2337(1)	2275(1)	37(1)
F(4)	7575(4)	−2933(6)	3202(4)	66(2)
F(33)	7063(3)	−1602(4)	1352(3)	36(1)
C(31)	9345(6)	−2458(10)	790(6)	54(3)
C(32)	9586(6)	−1626(9)	1203(6)	49(3)
C(33)	9600(6)	−1911(9)	1895(6)	49(3)
C(34)	9387(6)	−2929(9)	1905(6)	51(3)
C(35)	9206(6)	−3257(9)	1213(6)	52(3)
C(36)	9277(8)	−2516(13)	24(7)	84(5)
C(37)	9854(7)	−621(10)	989(7)	68(4)
C(38)	9868(7)	−1269(11)	2522(6)	66(4)
C(39)	9340(7)	−3535(11)	2546(7)	75(4)
C(40)	8942(8)	−4307(10)	981(9)	83(5)
C(41)	5948(7)	−3343(11)	2610(7)	69(4)
C(42)	8165(5)	874(7)	4848(4)	32(2)
C(43)	8321(5)	1801(6)	4535(4)	29(2)
C(44)	7633(5)	2403(7)	4474(5)	36(2)
C(45)	7094(5)	1888(7)	4774(5)	40(2)
C(41*)	7049(6)	130(8)	5375(5)	51(3)
C(42*)	8721(5)	3(8)	5005(5)	40(2)
C(43*)	9044(5)	2083(8)	4296(5)	48(3)
C(44*)	7528(7)	3459(8)	4177(5)	60(3)
C(45*)	6313(6)	2280(10)	4834(5)	57(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Microanalyses were performed by Beller Laboratory (Göttingen, Germany) or in our institute.

$(C_5Me_5)TiF_3$[5] (2). To a suspension of Me_3SnF (5.49 g, 30.0 mmol) in toluene (30 mL) was added a solution of $(C_5Me_5)TiCl_3$[9] (2.89 g, 10.0 mmol) in toluene (50 mL). The resulting mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum and the orange residue sublimed at 110 °C/10^{-2} mbar to yield 2.2 g (92%) of orange **2**. ^1H NMR (C_6D_6): δ 1.93 (s). ^{19}F NMR (C_6D_6): δ 124.0 (s).

$(C_5Me_4Et)TiF_3$[5] (2a). The same procedure was applied using $(C_5Me_4Et)TiCl_3$[26] (3.03 g, 10.0 mmol) and Me_3SnF (5.49 g, 30.0 mmol) to give orange **2a** (2.3 g, 92%). ^1H NMR (C_6D_6): δ 2.63 (q, J_{HH} = 7.7 Hz, 2H), 2.01 (s, 6H), 1.95 (s, 6H), 0.71 (t, J_{HH} = 7.7 Hz, 3H). ^{19}F NMR: δ 121.3 (s).

$(C_5H_5)TiF_3$[12] (2b). A suspension of Me_3SnF (5.49 g, 30.0 mmol) and $(C_5H_5)TiCl_3$[27] (2.20 g, 10.0 mmol) was stirred for 10 h in toluene (100 mL) at room temperature. The solvent was removed under vacuum and the residue sublimed at 110 °C/10^{-2} mbar to afford 1.53 g (87%) of orange-yellow **2b** after recrystallization from THF/hexane. Mass spectrum: *m/z* 170 (M^+). IR (Nujol,

Table 8. Selected Bond Lengths and Bond Angles for $[(C_5Me_5)HfF_3]_4$ (4)

Bond Lengths (Å)			
Hf(1)–F(1)	1.965(6)	Hf(1)–F(10)	2.095(6)
Hf(1)–F(13)	2.099(5)	F(10)–Hf(4)	2.094(6)
Hf(2)–F(13)	2.140(5)	Hf(1)–Hf(2)	3.1997(7)
Hf(1)–F(11)	2.148(5)	Hf(1)–Cp(1)	2.178(10)
Hf(2)–F(11)	2.133(5)		
Bond Angles (deg)			
Hf(4)–F(10)–Hf(1)	145.3(2)	F(10)–Hf(1)–F(12)	78.1(2)
F(1)–Hf(1)–F(10)	93.3(3)	Hf(1)–Cp(1)–F(1)	106.3(3)
Hf(2)–F(12)–Hf(1)	98.0(2)	Hf(1)–Cp(1)–F(10)	106.7(3)
F(1)–Hf(1)–F(11)	92.4(3)	Hf(1)–Cp(1)–F(11)	105.3(3)
F(13)–Hf(1)–F(12)	69.4(2)		

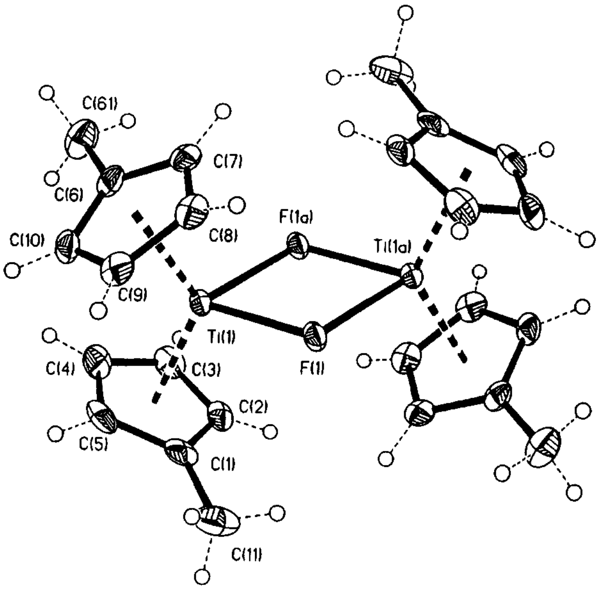

Figure 4. Molecular structure of $[(C_5H_4Me)_2TiF]_2$ (**10**) in the crystal.

Table 9. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $[(C_5H_4Me)_2TiF]_2$ (10)

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	8613(1)	358(1)	5302(1)	16(1)
F(1)	10529(2)	759(2)	5868(2)	20(1)
C(1)	8864(3)	−887(4)	7216(3)	26(1)
C(11)	9873(4)	−307(5)	8257(3)	41(1)
C(2)	8955(3)	−2164(4)	6422(3)	24(1)
C(3)	7810(3)	−2328(4)	5575(3)	26(1)
C(4)	6998(3)	−1160(5)	5838(3)	31(1)
C(5)	7653(3)	−270(4)	6842(3)	28(1)
C(6)	6954(3)	1715(4)	3860(3)	23(1)
C(61)	5979(3)	824(5)	2951(3)	35(1)
C(7)	8090(3)	2319(4)	3714(3)	23(1)
C(8)	8718(3)	3183(4)	4730(3)	23(1)
C(9)	7984(3)	3127(4)	5525(3)	25(1)
C(10)	6894(3)	2253(4)	4978(3)	24(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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(26) Alcock, N. W.; Toogood, G. E.; Wallbridge, G. H. *Acta Crystallogr., Sect. C* **1984**, *40*, 598.

(27) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

Table 10. Selected Bond Distances and Angles for $[(C_5H_4Me)_2TiF]_2$ (10)

(a) Bond Distances (Å)

Ti(1)–F(1)	2.092(2)	Ti(1)–F(1a)	2.091(2)
Ti(1)–Cp(1)	2.090(3)	Ti(1)–Cp(2)	2.077(3)

(b) Bond Angles (deg)

Ti(1)–F(1)–Ti	109.57(8)	F(1)–Ti(1)–F(1a)	70.43(8)
Cp(1)–Ti(1)–Cp(2)	128.9(1)	F(1)–Ti(1)–Cp(1)	110.8(1)
F(1)–Ti(1)–Cp(2)	109.7(1)		

cm^{-1}): 1304 m, 1037 m, 1098 s, 868 m, 831 s, 721 m, 641 s, 583 s, 511 s, 461 s, 402 s.

$(C_5H_4Me)TiF_3$ (2c). The same method as that described for **2b** was used. $C_5H_4MeTiCl_3$ (2.33 g, 10.0 mmol) and Me_3SnF (5.49 g, 30.0 mmol) were used to give 1.65 g (90%) of orange-yellow **2c**. ^1H NMR ($CDCl_3$): δ 6.72 (s), 6.50 (s), 2.45 (s). ^{19}F NMR ($CDCl_3$): δ 131.0. Mass spectrum: *m/z* 184 (M$^+$). IR (Nujol, cm^{-1}): 1065 m, 1033 s, 827 s, 642 s, 619 s, 603 s, 503 s, 404 s.

$(C_5Me_5)ZrF_3$ (3). A suspension of $(C_5Me_5)ZrCl_3$ (5.00 g, 15.0 mmol) and Me_3SnF (8.23 g, 45.0 mmol) in toluene (80 mL) was heated for 0.5 h under reflux. After the mixture was cooled to room temperature, a small quantity of solid was retained by filtration. The filtrate was evaporated to dryness in vacuo and the solid residue washed with hexane to yield 4.0 g (94%) of a white solid of **3**. ^1H NMR (C_6D_6): δ 2.02 (s). ^{19}F NMR (C_6D_6): δ 97.5 (m, 4F), −26.3 (m, 4F), −50.7 (m, 2F), −72.7 (m, 2F). Mass spectrum: *m/z* 831 (M$^+$). IR (Nujol, cm^{-1}): 574 s, 456 s, 425 s, 384 s.

$(C_5Me_5)HfF_3$ (4). A mixture of Cp^*HfCl_3 (4.60 g, 11.0 mmol) and Me_3SnF (6.03 g, 33.0 mmol) was reacted in toluene (80 mL) as described for **3** to yield 3.7 g (93%) of a white solid of **4**. ^1H NMR (C_6D_6): δ 2.07 (s). ^{19}F NMR (C_6D_6): δ 41.8 (m, 4F), −54.0 (m, 4F), −77.3 (m, 2F), −97.8 (m, 2F). Mass spectrum: *m/z* 1093 (M$^+$). IR (Nujol, cm^{-1}): 572 s, 563 s, 454 s, 367 s.

$(C_5H_5)_2TiF_2$[16] (5). A suspension of Me_3SnF (2.92 g, 16.0 mmol) and Cp_2TiCl_2 (1.99 g, 8.0 mmol) in toluene (80 mL) was stirred at 80 °C for 4 h. The color of the suspension changed from red to yellow. Finally, the solvent was removed and the yellow solid sublimed at 130 °C/10^{-2} mbar to yield 1.7 g (98%) of a yellow solid of **5**. ^1H NMR ($CDCl_3$): δ 6.42 (t). ^{19}F NMR ($CDCl_3$): δ 64.2.

$[C_5H_3(Me)(SiMe_3)]_2ZrF_2$ (6). Compound **6** was prepared according to the method described for **5**. $[C_5H_3(Me)(SiMe_3)]_2ZrCl_2$[16] (2.31 g, 5.0 mmol) and Me_3SnF (1.83 g, 10.0 mmol) yield 1.8 g (85%) of **6** after sublimation at 100 °C/10^{-2} mbar. ^1H NMR (C_6D_6): δ 5.74–6.16 (m), 2.07 (qt, J_{HH} = 1.4 Hz), 0.24 (s). ^{19}F NMR (C_6D_6): δ 38.25. Mass spectrum: *m/z* 430 (M$^+$). IR (Nujol, cm^{-1}): 1252 s, 922 m, 839 s, 760 m, 549 s, 538 m, 461 m, 387 m.

$(C_5Me_5)_2HfF_2$ (7). Compound **7** was prepared according to the method described for **5**. $(C_5Me_5)_2HfCl_2$[11] (2.03 g, 3.9 mmol) and Me_3SnF (1.43 g, 7.8 mmol) yield 1.75 g (92%) of **7** after recrystallization from hexane. ^1H NMR (C_6D_6): δ 1.86 (t, J_{FH} = 0.7 Hz). ^{19}F NMR (C_6D_6): δ −18.16 (m). Mass spectrum: *m/z* 488 (M$^+$). IR (Nujol, cm^{-1}): 1261 m, 1024 m, 804 m, 555 m, 533 m, 344 s.

$(C_5Me_5TiFO)_4$[19] (8). A suspension of Me_3SnF (0.37 g, 2.1 mmol) in toluene (20 mL) was added to a solution of $(Cp^*TiClO)_3$[18] (0.48 g, 0.7 mmol) in toluene (40 mL). The mixture was stirred for 2 h at room temperature and then for 0.5 h at 50 °C. The solution was filtered, and the solvent was removed in vacuo from the filtrate. The resulting light yellow solid was recrystallized from hexane (30 mL) to give 0.39 g (87%) of **8**. ^1H NMR (C_6D_6): δ 2.09 (s). ^{19}F NMR (C_6D_6): δ 83.17. Mass spectrum: *m/z* 872 (M$^+$).

$[(C_5H_5)_2TiF]_2$[20] (9). (a) A mixture of $(Cp_2TiCl)_2$[18] (0.64 g, 1.5 mmol) and Me_3SnF (0.55 g, 3.0 mmol) was stirred in toluene (50 mL) for 5 h. The solvent was removed in vacuo after Me_3SnF had disappeared from the solution. The solid was recrystallized from THF (15 mL) and hexane (35 mL) to yield 0.53 g (90%) of **9**. Mass spectrum: *m/z* 197 (M$^+$). IR (Nujol, cm^{-1}): 1093 m, 793 s, 471 s, 380 s.

(b) A suspension of Cp_2TiF_2[16] (0.65 g, 3.0 mmol) in toluene (60 mL) was slowly added to sodium (0.07 g, 3.0 mmol) in 11 g of Hg at 0 °C. The reaction mixture was allowed to stand overnight. The color of the solution became green. Finally, the solution was filtered and the solvent removed in vacuo. The green residue was sublimed in vacuo (75 °C/10^{-2} mbar) to yield a green solid of **9** (0.56 g, 95%). Mass spectrum: *m/z* 197 (M$^+$).

$[(C_5H_4Me)_2TiF]_2$ (10). (a) Compound **10** was prepared according to the method (a) described for **9**. $[(C_5H_4Me)_2TiCl]_2$[20] (0.96 g, 2.0 mmol) and Me_3SnF (0.73 g, 4.0 mmol) gave 0.80 g (89%) of **10**. Mass spectrum: *m/z* 225 (M$^+$). IR (Nujol, cm^{-1}): 1071 m, 1037 s, 904 m, 851 s, 786 s, 771 s, 614 m, 393 s.

(b) Compound **10** was prepared analogously to the method for **9b**. $(C_5H_4Me)_2TiF_2$[23] (0.73 g, 3.0 mmol) and sodium (0.07 g, 3.0 mmol) in Hg (11 g) gave 0.62 g (92%) of **10** after sublimation at 35 °C/5 × 10^{-5} mbar.

$(C_5Me_5)_2TiF$ (11). A solution of Cp^*_2TiCl[22] (1.06 g, 3.0 mmol; toluene 30 mL) was dropped into a suspension of Me_3SnF (0.55 g, 3.0 mmol; toluene 30 mL). The solid disappeared after stirring for 3 h at room temperature. The solvent was removed in vacuo and the residue sublimed at 94 °C/10^{-2} mbar; 0.88 g (88%) of **10** as a green solid was obtained. Mass spectrum: *m/z* 337 (M$^+$). IR (Nujol, cm^{-1}): 1261 m, 1022 s, 562 s, 445 s.

X-ray Structure Analyses for 2c, 3, 4, and 10. Diffraction data were collected on a STOE four-circle diffractometer using Mo Kα radiation. Refinement was made by full-matrix least squares on all F^2 values using SHELXL-93. Hydrogen atoms were positioned geometrically.

Final atomic coordinates and equivalent isotropic thermal parameters are given in Tables 3, 5, 7, and 9. Crystallographic data for compounds **2c**, **3**, **4**, and **10** are collected in Table 2.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagenwerk-Stiftung, BMFT, and Hoechst AG.

Supplementary Material Available: For compounds **2c**, **3**, **4**, and **10** tables of crystal data and structure refinement details, displacement parameters, hydrogen atom coordinates, and all bond distances and angles (28 pages). Ordering information is given on any current masthead page.

OM9306178