Conversion of Alkyltantalum Chlorides to Fluorides Using Trimethyltin Fluoride as a Fluorinating Agent. Crystal Structures of (*p*-MeC$_6$H$_4$CH$_2$)$_3$TaF$_2$, (Me$_3$SnCl·Me$_3$SnF·TaF$_5$)$_n$, (Me$_3$Si)$_2$CHTaCl$_4$, {(Me$_3$Si)$_2$CHTaCl$_4$·[(Me$_3$Si)$_2$CH]$_2$Ta$_2$Cl$_6$(μ_2-O)}, and (Me$_3$Si)$_2$CHTaF$_4$[†]

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The reactions of alkyltantalum chlorides with trimethyltin fluoride were found to be highly dependent on the number of organic ligands on tantalum as well as on the electronic and the steric nature of the substituents. The synthesis of trialkyltantalum difluorides of general formula (RCH$_2$)$_3$TaF$_2$ (R = Ph, **1**; R = *p*-Tol, **2**; R = Me$_3$Si, **3**) and the first example of the alkyltantalum tetrafluoride (Me$_3$Si)$_2$CHTaF$_4$ (**8**) are reported. The compounds (*p*-MeC$_6$H$_4$-CH$_2$)$_3$TaF$_2$, (Me$_3$SnCl·Me$_3$SnF·TaF$_5$)$_n$, (Me$_3$Si)$_2$CHTaCl$_4$, {(Me$_3$Si)$_2$CHTaCl$_4$·[(Me$_3$Si)$_2$CH]$_2$Ta$_2$Cl$_6$(μ_2-O)}, and (Me$_3$Si)$_2$CHTaF$_4$ respectively have been characterized by single-crystal X-ray structural analysis.

Introduction

The chemistry of alkyltantalum chlorides has been the subject of numerous investigations due to their ability to act as precursors for the preparation of alkylidene and alkylidyne compounds in reactions using alkylmagnesium or alkyllithium reagents.[1] In contrast, the number of corresponding alkyltantalum fluorides is limited. However, (Me$_3$CCH$_2$)$_3$TaF$_2$ was obtained by Schrock et al. in low yield in an attempt to prepare [(Me$_3$CCH$_2$)$_4$Ta]$^+$BF$_4^-$ by the reaction of (Me$_3$CCH$_2$)$_3$-Ta(=CHCMe$_3$) with HBF$_4$.[1]

In our previous work we developed general methods for the preparation of fluorine-containing compounds of main group elements and early transition metals using organotin fluorides as fluorinating reagents.[2] Due to our interest in the preparation and chemistry of organometallic fluorides, we decided to explore convenient synthetic routes to the different types of alkyltantalum fluorides by halogen exchange reactions using trimethyltin fluoride as a fluorine source.
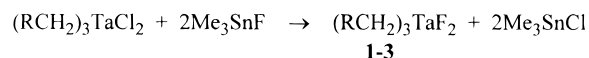
Results and Discussion

Reaction of Trimethyltin Fluoride with Trialkyltantalum Dichlorides. Reaction of Me$_3$SnF with

Scheme 1

$$(RCH_2)_3TaCl_2 + 2Me_3SnF \rightarrow (RCH_2)_3TaF_2 + 2Me_3SnCl$$
$$\textbf{1-3}$$

1 R = Ph

2 R = *p*-Tol

3 R = Me$_3$Si

(RCH$_2$)$_3$TaCl$_2$ (R = Ph, *p*-Tol, Me$_3$Si) in dichloromethane or THF as a solvent was found to be a convenient route to high-yield synthesis of the corresponding difluorides, after sublimation, distillation, or recrystallization from pentane (Scheme 1). Using Me$_3$TaCl$_2$ as a starting material leads to the formation of a mixture of non-characterizable and poorly soluble products. This may be due to the low shielding of the tantalum atom in Me$_3$-TaCl$_2$ that leads to side reactions, such as the substitution of the methyl groups by fluorine. A similar methyl group substitution reaction has already been observed and used as a synthetic method for the preparation of the aminoaluminum difluorides from the corresponding dimethylaminoallanes and Me$_3$SnF.[3]

Compounds **1**−**3** are colorless or yellow crystalline solids, extremely sensitive to moisture and air, and very soluble in aromatic or hydrocarbon solvents. In contrast to the thermally unstable starting materials, the difluorides **1**−**3** show remarkable thermal stability and

[†] Dedicated to Professor U. Wannagat on the occasion of his 75th birthday.

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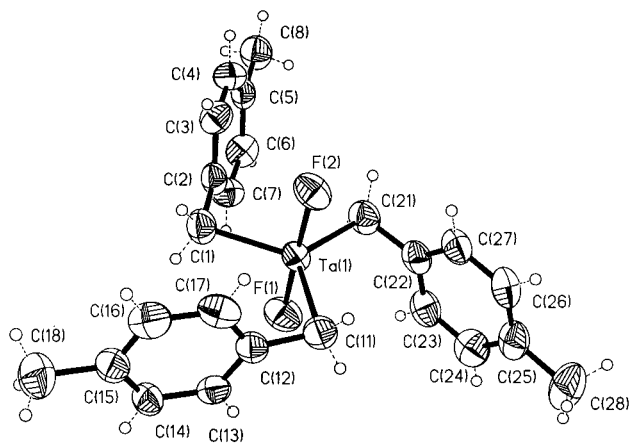
Figure 1. Molecular structure of (p-MeC$_6$H$_4$CH$_2$)$_3$TaF$_2$ in the solid state.

can be stored for months at room temperature in an inert atmosphere. No decomposition is observed upon heating **1**−**3** for hours in toluene.

The spectral and analytical data for the difluorides **1**−**3** are summarized in the Experimental Section. Compounds **1**−**3** have ^{19}F NMR spectral signals in the low-field region (106−115 ppm) with characteristic ^3J(HF) coupling, indicating a high covalent contribution to the Ta−F bonds. The ^{1}H NMR spectra show signals for the CH$_2$ groups in the range 1.1−2.3 ppm, with characteristic ^3J(FH) coupling.

Compound **2** was characterized by a single-crystal structure analysis (Figure 1). Suitable single crystals of **2** were obtained from a pentane solution at −20 °C. To the best of our knowlegde, **2** is the first example of a structurally characterized trialkyltantalum difluoride.

The crystal data of **2** are given in Table 1, and selected bond lengths and angles in Table 2. The central TaF$_2$C$_3$ core of **2** in the solid state exhibits a trigonal-bipyramidal arrangement with two F atoms in the axial and three p-Tol groups in equatorial positions. The Ta−F bond lengths (1.877(3) and 1.924(3) Å) are comparable to the distances between Ta and terminal fluorine atoms found for [(η^5-C$_5$Me$_5$)TaF$_4$]·2AsF$_3$.[4] The Ta−CH$_2$ distances (2.149(5)−2.172(5) Å) are in good agreement with those observed for Ta(OAr)$_2$(CH$_2$Ph)$_3$ and Ta(CH$_2$C$_6$H$_4$-Me-p)$_5$.[5] The Ta−CH$_2$−C angles in **2** (range 95.1−98.3°) are significantly smaller than the "normal" M−C−C bond angles (112°). Related to this, the distances between the carbon atoms of the aromatic rings bonded to the methylene carbon and the metal (2.713−2.811 Å) are smaller than expected. As a consequence, in the solid state **2** shows a "propeller-like"configuration (Figure 2). A comparable phenomenon was previously observed for Ta(OAr)$_2$(CH$_2$Ph)$_3$ and Ta(CH$_2$C$_6$H$_4$Me-p)$_5$, where, however, only one of the benzyl ligands shows a smaller angle (90.4−94.8 Å) at the α-carbon atom, whereas the others fall in the normal range (108.4−125.7°).[5]

All attempts to obtain dialkyltantalum trifluorides (RCH$_2$)$_2$TaF$_3$ (R = Ph, p-MeC$_6$H$_4$, Me$_3$Si) using the corresponding chlorides and Me$_3$SnF were unsuccessful.

^{1}H NMR and mass spectroscopic investigations of the resulting solids indicated a complex mixture of products. In contrast to the fluorination of trialkyltantalum dichlorides, the trichloride reaction resulted in partial cleavage of the Ta−C bonds. This phenomenon was also observed in the reaction of (Me$_3$SiCH$_2$)TaCl$_4$ with excess Me$_3$SnF, which reacts in dichloromethane in a molar ratio of 1:5 to afford colorless crystals of (Me$_3$SnCl·Me$_3$-SnF·TaF$_5$)$_n$ (**4**) in a 14% yield.

Compound **4** was characterized by an X-ray structural analysis. It crystallizes in the orthorombic space group (*Pnma*) with four molecules in the unit cell. The monomer (Figure 3) consists of one TaF$_6$ octahedron and two Me$_3$Sn groups connected by a chlorine atom. The geometry around the tin atoms is trigonal bipyramidal with three methyl groups occupying equatorial positions, with the two axial positions being occupied by bridging chlorine and fluorine atoms. The molecule of **4** resides on a crystallographic mirror plane. The Ta(1)−F(4)−Sn(2) angle of 179.9° shows that the TaF$_6$ octahedron is bonded to a tin pyramid in a linear fashion. The Sn^2−Cl−Sn^1 angle is bent (132.3°).

The solid-state structure of **4** shows the formation of layers with a Sn−F distance of 3.59(3) Å between the chains and 2.54(9) Å within the chains.

Synthesis of (Me$_3$Si)$_2$CHTaCl$_4$ (5). In previous investigations it was shown that compounds containing the (Me$_3$Si)$_2$CH ligand generally give well-defined and very soluble crystalline products.[6] Consequently we prepared the monosubstituted tantalum halides (Me$_3$-Si)$_2$CHTaX$_4$ (X = Cl, **5**; X = Br, **6**) by the reaction of TaCl$_5$ and TaBr$_5$, respectively, with [(Me$_3$Si)$_2$CH]$_2$Zn in n-hexane (Scheme 2). The yield of the tetrachloride **5** (65%) was higher than that of the corresponding tetrabromide **6** (30%). Analytical and spectroscopic data for compounds **5** and **6** are given in the Experimental Section.

In an attempt to crystallize (Me$_3$Si)$_2$CHTaCl$_4$ from n-hexane at −30 °C during a three month period, partial hydrolysis occurred to give {(Me$_3$Si)$_2$CHTaCl$_4$·[(Me$_3$-Si)$_2$CH]$_2$Ta$_2$Cl$_6$(μ_2-O)} (**7**), which was characterized by an X-ray structural investigation. The structure of **7** is shown in Figure 4, and selected bond lengths and angles are given in Table 4.

Complex **7** crystallizes in the triclinic *P$\bar{1}$* space group with (Me$_3$Si)$_2$CHTaCl$_4$ × 0.5[(Me$_3$Si)$_2$CH]$_2$Ta$_2$Cl$_6$(μ_2-O) per unit cell. The tantalum has a trigonal bipyramidal environment with the organic ligands in equatorial positions.

Crystals of pure **5** suitable for X-ray studies were grown from n-hexane at −30 °C. The molecular structure of **5** is shown in Figure 5, and selected bond distances and angles are given in Table 5. Compound **5** crystallizes in the *P$\bar{1}$* space group with four molecules per unit cell (two independent molecules in the asymmetric unit). The tantalum center has a trigonal-bipyramidal environment, with the organic ligands in equatorial positions and two different Ta−Cl bond distances (Ta−Cl$_{eq}$ 2.296(7) Å, Ta−Cl$_{ax}$ 2.313(7) Å).

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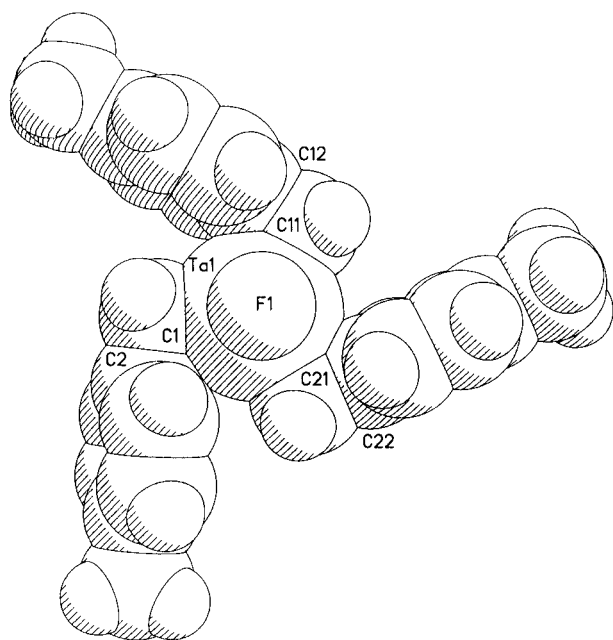
Table 1. Crystallographic Data for Compounds 2, 4, 5, 7, and 8

	2	**4**	**5**	**7**	**8**
empirical formula	$C_{24}H_{27}F_2Ta$	$C_6H_{18}ClF_6Sn_2Ta$	$C_7H_{19}Cl_4Si_2Ta$	$C_7H_{19}Cl_4Si_2Ta$ + $0.5C_{14}H_{38}Cl_6OSi_4Ta_2$	$C_{14}H_{38}F_8Si_4Ta_2$
fw	534.41	657.98	482.15	482.16 + 0.5 × 909.41	832.70
color of crystal	yellow	colorless	yellow	yellow	colorless
temp (K)	203(2)	200(2)	203(2)	133(2)	203(2)
cryst size (mm)	0.7 × 0.4 × 0.4	0.9 × 0.6 × 0.6	0.8 × 0.8 × 0.6	0.5 × 0.4 × 0.4	0.8 × 0.3 × 0.3
cryst syst	monoclinic	orthorombic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$Pnma$	$P\bar1$	$P\bar1$	$P2_1/c$
a (Å)	6.413(2)	22.136(4)	9.046(2)	8.990(3)	6.3858(13)
b (Å)	14.390(5)	10.036(2)	13.477(3)	13.370(3)	24.935(5)
c (Å)	23.593(9)	7.5621(15)	14.581(3)	13.668(3)	17.406(4)
α (deg)	90	90	66.54(2)	89.77(3)	90
β (deg)	96.05(2)	90	82.71(3)	76.56(3)	93.63(3)
γ (deg)	90	90	79.36(3)	79.18(3)	90
cell vol (Å)	2165.0(13)	1680.0(6)	1599.8(5)	1568.1(7)	2766.0(10)
Z	4	4	4	2	4
ρ_c (g mm^{-3})	1.640	2.601	2.002	1.984	2.000
μ (mm^{-1})	5.099	9.640	7.657	7.727	8.133
$F(000)$	1048	1192	920	894	1584
2θ range (deg)	3.52−25.11	3.68−22.52	3.55−22.47	2.14−25.00	3.57−22.46
no. of data measd, unique	5527, 3839	3605, 1167	5287, 4120	20 190, 5513	3587, 3544
	(R_{int} = 0.0191)	(R_{int} = 0.1009)	(R_{int} = 0.0725)	(R_{int} = 0.0362)	(R_{int} = 0.1115)
R,^{a} $wR2^b$ ($I > 2\sigma(I)$)	0.0315, 0.0776	0.0283, 0.0769	0.0435, 0.1116	0.0275, 0.0654	0.0526, 0.1485
R, $wR2$ (all data)	0.0378, 0.0868	0.0292, 0.0775	0.0445, 0.1168	0.0333, 0.0667	0.0561, 0.1534
goodness of fit, S^c	1.098	1.183	1.125	1.101	1.233
no. of refined params	247	93	266	263	266
largest diff peak/hole (e Å^{-3})	1.029/−1.118	1.648/−0.885	3.471/−2.535	1.675/−1.451	2.969/−1.342

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. ^{c} $S = [\sum w(F_o^2 - F_c^2)^2]/[\sum (n - p)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (p-MeC$_6$H$_4$CH$_2$)$_3$TaF$_2$ (2)

Ta(1)−F(1)	1.877(3)	F(1)−Ta(1)−C(11)	88.9(2)
Ta(1)−F(2)	1.924(3)	F(2)−Ta(1)−C(11)	91.9(2)
Ta(1)−C(1)	2.149(5)	C(1)−Ta(1)−C(11)	120.2(2)
Ta(1)−C(11)	2.151(5)	F(1)−Ta(1)−C(21)	88.3(2)
Ta(1)−C(21)	2.172(5)	F(2)−Ta(1)−C(21)	89.8(2)
Ta(1)−C(2)	2.784(5)	C(1)−Ta(1)−C(21)	119.4(2)
Ta(1)−C(12)	2.713(5)	C(11)−Ta(1)−C(21)	120.4(2)
Ta(1)−C(22)	2.811(5)	C(2)−C(1)−Ta(1)	98.3(3)
F(1)−Ta(1)−F(2)	178.08(14)	C(12)−C(11)−Ta(1)	95.1(3)
F(1)−Ta(1)−C(1)	90.1(2)	C(22)−C(21)−Ta(1)	98.3(4)
F(2)−Ta(1)-C(1)	90.9(2)		

Figure 3. Molecular structure of **4** in the solid state.

Scheme 2

$$[(Me_3Si)_2CH]_2Zn + 2TaX_5 \rightarrow 2(Me_3Si)_2CHTaX_4 + ZnX_2$$
$$\textbf{5-6}$$

5 X = Cl

6 X = Br

Figure 2. "Propeller-like" configuration of **2** in the solid state (space-filling model).

Conversion of 5 to (Me$_3$Si)$_2$CHTaF$_4$ Using Me$_3$SnF.
The reaction of **5** with trimethyltin fluoride (in a molar ratio 1:4) at room temperature in dichloromethane
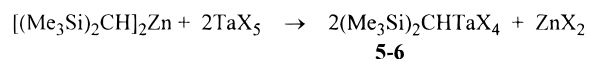
resulted in the formation of the corresponding tetrafluoride **8** as a colorless crystalline product in a 52% yield after sublimation (Scheme 3). To the best of our knowledge, **8** is the first example of an alkyltantalum tetrafluoride.

Spectroscopic and analytical data for **8** are given in the Experimental Section. The ^{19}F NMR of **8** in dichloromethane at room temperature shows a broad signal (81.5 ppm), indicative of dynamic processes. At −95 °C, three signals appeared (123, 103, and −29 ppm) with the correct integration of 1:2:1. Thus, in solution at −95 °C three types of fluorine atoms can be observed (two kinds of terminal, one bridging), in agreement with the solid-state structure (vide infra).

Compound **8** was characterized by single-crystal X-ray diffraction analysis. The molecular structure of **8** is shown in Figure 6, and selected bond lengths and angles are listed in Table 6. Compound **8** crystallizes in the monoclinic space group ($P2_1/c$) with two molecules in the unit cell. Each tantalum center has an octahedral environment. The molecules within the crystal are found
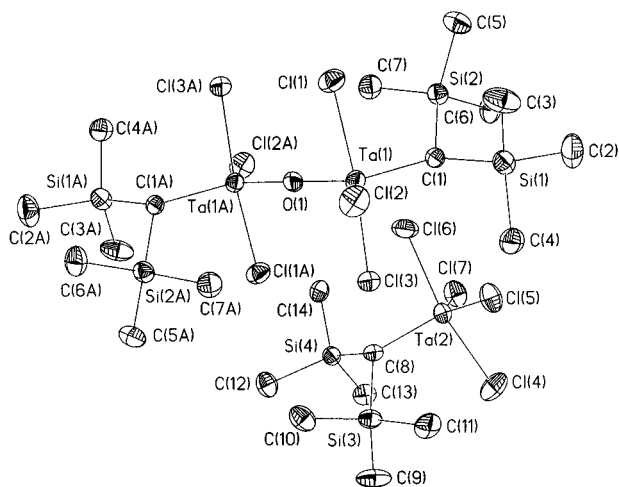
Figure 4. Crystal structure of **7** in the solid state. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

Ta(1)−F(3)	1.840(8)	F(1)−Ta(1)−F(4)	88.8(2)
Ta(1)−F(5)	1.845(8)	F(3)−Ta(1)−F(2)	89.0(4)
Ta(1)−F(1A)	1.861(5)	F(5)−Ta(1)−F(2)	178.9(4)
Ta(1)−F(1)	1.861(5)	F(1A)−Ta(1)−F(2)	88.6(2)
Ta(1)−F(4)	1.894(7)	F(1)−Ta(1)−F(2)	88.6(2)
Ta(1)−F(2)	1.916(6)	F(4)−Ta(1)−F(2)	89.7(3)
Sn(2)−F(4)	2.514(7)	C(3)−Sn(2)−F(4)	87.2(4)
Sn(2)−Cl(1)	2.555(3)	C(1)−Sn(2)−F(4)	82.3(3)
Sn(1)−Cl(1)	2.562(2)	C(1A)−Sn(2)−F(4)	82.3(3)
F(3)−Ta(1)−F(5)	92.2(4)	C(3)−Sn(2)−Cl(1)	100.0(3)
F(3)−Ta(1)−F(1A)	91.2(2)	C(1)−Sn(2)−Cl(1)	94.2(3)
F(5)−Ta(1)−F(1A)	91.4(2)	C(1A)−Sn(2)−Cl(1)	94.2(3)
F(3)−Ta(1)−F(1)	91.2(2)	F(4)−Sn(2)−Cl(1)	172.8(2)
F(5)−Ta(1)−F(1)	91.4(2)	C(4)−Sn(1)−Cl(1)	97.7(3)
F(1A)−Ta(1)−F(1)	176.3(4)	C(2)−Sn(1)−Cl(1)	93.8(2)
F(3)−Ta(1)−F(4)	178.6(4)	C(2A)−Sn(1)−Cl(1)	93.8(2)
F(5)−Ta(1)−F(4)	89.2(4)	Sn(2)−Cl(1)−Sn(1)	132.26(12)
F(1A)−Ta(1)-F(4)	88.8(2)	Ta(1)−F(4)−Sn(2)	180.0(3)
C(4)−Sn(1)−C(2)	120.2(3)	C(4)−Sn(1)−C(2A)	120.2(3)
C(2)−Sn(1)−C(2A)	117.3(6)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7

Ta(1)−O(1)	1.8813(6)	Ta(2)−C(8)	2.021(5)
Ta(1)−C(1)	2.059(5)	Ta(2)−Cl(4)	2.3060(17)
Ta(1)−Cl(1)	2.3353(16)	Ta(2)−Cl(5)	2.2938(15)
Ta(1)−Cl(2)	2.3100(15)	Ta(2)−Cl(6)	2.3390(17)
Ta(1)−Cl(3)	2.3362(16)	Ta(2)−Cl(7)	2.3048(15)
O(1)−Ta(1)−C(1)	115.55(13)	O(1)−Ta(1)−Cl(3)	89.24(4)
O(1)−Ta(1)−Cl(2)	128.17(4)	Cl(2)−Ta(1)−Cl(1)	86.77(6)
C(1)−Ta(1)−Cl(2)	116.26(14)	Cl(1)−Ta(1)−Cl(3)	172.97(5)
Cl(2)−Ta(1)−Cl(3)	88.80(6)	C(8)−Ta(2)−Cl(5)	112.01(14)
Cl(7)−Ta(2)−Cl(6)	87.42(6)	Si(3)−C(8)−Ta(2)	120.5(2)
Cl(4)−Ta(2)−Cl(6)	168.44(6)	Cl(7)−Ta(2)−Cl(4)	86.39(6)
Cl(5)−Ta(2)−Cl(7)	134.94(5)		

to be connected by bridging fluorine atoms. In agreement with the ^{19}F NMR spectrum in solution at low temperatures, three types of fluorine atoms were found in the solid state. The tantalum bridging fluorine bond distances (2.42 Å) are significantly longer than the corresponding distances of the nonbridging fluorines. However they are longer (by about 0.2 Å) than those in $[(\eta^5\text{-}C_5Me_5)TaF_4]\cdot 2AsF_3$.[4] All terminal Ta−F bond lengths are in the range 1.860(11)−1.867(11) Å. The C(1)−Ta(1)−F(5) angle (171°) indicates a slight distortion of the octahedral environment. The angle between two of the octahedrons, Ta(1)−F(5)−Ta(2), is about 141°, which leads to the formation of zigzag chains in the crystal of **8**. The inorganic centers are surrounded by hydrophobic
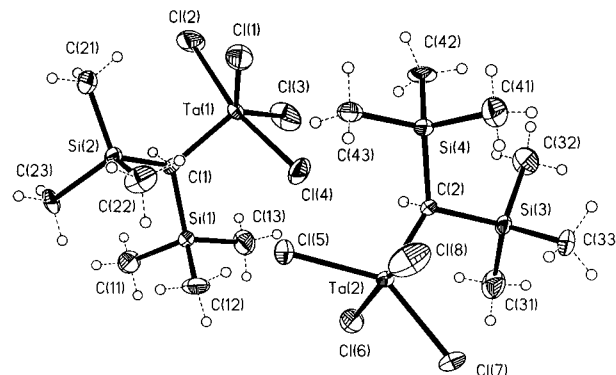
Figure 5. Two molecules of $(Me_3Si)_2CHTaCl_4$ (**5**) in the asymmetric unit.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5 (average)

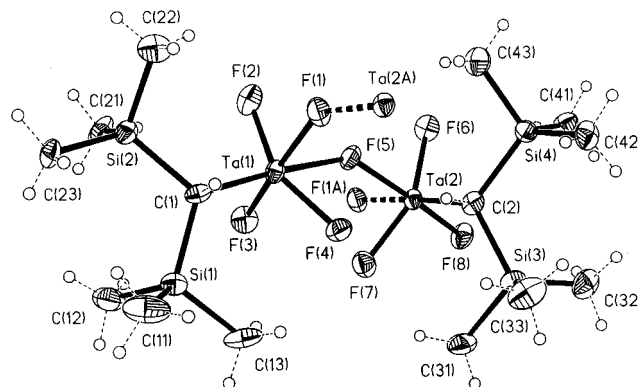|	
Ta(1)−C(1), Ta(2)−C(2)	2.046(2)
Ta(1)−Cl(1), Ta(2)−Cl(7)	2.299(7)
Ta(1)−Cl(2), Ta(2)−Cl(6)	2.316(2)
Ta(1)−Cl(3), Ta(2)−Cl(5)	2.293(7)
Ta(1)−Cl(4), Ta(2)−Cl(8)	2.311(2)
Cl(2)−Ta(1)−Cl(4), Cl(6)−Ta(2)−Cl(8)	165.01(5)
Cl(1)−Ta(1)−Cl(3), Cl(5)−Ta(2)−Cl(7)	138.20(4)
C(1)−Ta(1)−Cl(1), C(2)−Ta(2)−Cl(7)	111.6(7)
C(1)−Ta(1)−Cl(2), C(2)−Ta(2)−Cl(6)	97.9(7)
C(1)−Ta(1)−Cl(3), C(2)−Ta(2)−Cl(5)	110.1(7)
C(1)−Ta(1)−Cl(4), C(2)−Ta(2)−Cl(8)	97.0(2)

Figure 6. Two molecules of **8**, with bridging fluorine atoms. Further interactions are omitted for clarity.
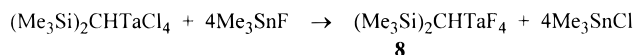
Scheme 3

$(Me_3Si)_2CHTaCl_4 + 4Me_3SnF \rightarrow (Me_3Si)_2CHTaF_4 + 4Me_3SnCl$
8

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 8

Ta(1)−F(1)	1.971(11)	Ta(2)−F(5)−Ta(1)	141.0(5)
Ta(1)−F(2)	1.860(11)	F(2)−Ta(1)−F(3)	91.1(5)
Ta(1)−F(3)	1.864(11)	F(2)−Ta(1)−F(4)	151.1(5)
Ta(1)−F(4)	1.867(11)	F(6)−Ta(2)−F(5)	85.6(5)
Ta(1)−F(5)	2.418(11)	C(1)−Ta(1)−F(5)	171.4(6)
Ta(1)−C(1)	2.05(2)	F(8)−Ta(2)−F(5)	171.5(5)
F(3)−Ta(1)−F(1)	172.2(5)	F(6)−Ta(2)−F(7)	148.6(5)

ligands, thus accounting for the solubility of **8** in nonpolar hydrocarbon solvents.

Experimental Section

General Methods and Materials. All the reactions were performed in deoxygenated argon or dinitrogen atmosphere using glovebox and high-vacuum techniques. The starting materials were prepared according to literature methods[7] and were freshly sublimed or recrystallized prior to use. Aromatic,

hydrocarbon, and etherated solvents were dried over Na/K alloy and vacuum transferred to the reaction flasks prior to use. Dichloromethane was dried over CaH_2 and vacuum transferred prior to use. NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments. Chemical shifts are reported in δ scale with reference to external $SiMe_4$ for ^1H and ^{13}C and CCl_3F for ^{19}F nuclei. Mass spectra were obtained on Finnigan MAT system 8230 and a Varian MAT CH5 mass spectrometer. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between CsI plates. Melting points were obtained on a HWS-SG 3000 apparatus. Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.[8]

Preparation of $(PhCH_2)_3TaF_2$ (1). To a mixture of $(C_6H_5-CH_2)_3TaCl_2$ (6.71 g, 13 mmol) and Me_3SnF (4.68 g, 26 mmol) was condensed CH_2Cl_2 (100 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for an additional 8 h. All volatiles were removed in vacuo and the residue sublimed at 80 °C (0.05 Torr) to afford yellow crystals. Yield: 5.23 g (83%). Mp: 92 °C. ^1H NMR (C_6D_6): 2.57 (t, 6H, J(FH) = 7.1 Hz, CH_2); 6.95−7.1 (mult, 15H, arom H). ^{13}C NMR (C_6D_6): 74.52 (tripl, J(FC) = 7.1 Hz, CH_2$). ^{19}F NMR (C_6D_6): 110.22 (hept, J(HF) = 7.1 Hz). IR: v 1950 w, 1875 w, 1804 w, 1740 w, 1596 m, 1573 m, 1488 s, 1450 s, 1408 m, 1264 w, 1201 m, 1181 w, 1156 w, 1088 m, 1181 w, 1156 w, 1087 m, 1030 m, 972 m, 906 m, 811 w, 796 m, 753 s, 727 m, 695 s, 622 m, 596 s, 463 s, 343 s. EI MS (70 eV): m/e (%) $[M^+ - PhCH_2]$, 401 (100). Anal. Calcd for $C_{21}H_{21}F_2Ta$: C, 51.25; H, 4.27; F, 7.72. Found: C, 50.9; H, 3.9; F, 7.4.

Preparation of $(p\text{-}MeC_6H_4CH_2)_3TaF_2$ (2). The method of preparation is analogous to that of **1**, using $(p\text{-}MeC_6H_4CH_2)_3$-$TaCl_2$ (1.12 g, 1.97 mmol) and Me_3SnF (0.8 g, 4.34 mmol). The resulting crude product **2** was recrystallized from pentane (10 mL) at -26 °C. Yield: 0.76 g (72%), yellow crystals. Mp: 124 °C. ^1H NMR (C_6D_6): 2.11 (s, 9H, CH_3); 2.68 (t, 6H, J(FH) = 7.1 Hz, CH_2); 6.94−7.15 (mult, 12H, arom H). ^{13}C NMR (C_6D_6): 20.83 (s, CH_3$); 68.92 (tripl, J(FC) = 6.8 Hz, CH_2$). ^{19}F NMR (C_6D_6): 107.19 (hept, J(HF) = 7.1 Hz). IR: v 1897 w, 1645 w, 1612 w, 1504 s, 1465 s, 1307 w, 1216 m, 1199 m, 1128 s, 1113 s, 1022 m, 1007 m, 891 w, 812 s, 736 s, 712 m, 668 w, 642 w, 593 s, 574 s, 487 s, 466 s, 308 s. EI MS (70 eV): m/e (%) $[M^+ - p\text{-}Tol]$, 429 (30), $[M^+ - p\text{-}Tol - 1,4\text{-}(CH_3)_2C_6H_4]$, 323 (20), $[p\text{-}Tol^+]$, 105 (100). Anal. Calcd for $C_{24}H_{27}F_2Ta$: C, 53.96; H, 5.05; F, 7.11. Found: C, 53.6; H, 5.2; F, 6.8.

Preparation of $(Me_3SiCH_2)_3TaF_2$ (3). The method of preparation is analogous to that of **1**, using $(Me_3SiCH_2)_3TaCl_2$ (5.6 g, 11 mmol) and Me_3SnF (5.0 g, 27 mmol). Yield: 2.6 g (49%) after distillation, pale yellow oil. Bp: 68−70 °C (0.02 Torr). ^1H NMR ($CDCl_3$): 0.12 (s, 27H, CH_3); 1.18 (t, 6H, J(FH) = 7.5 Hz, CH_2). ^{13}C NMR ($CDCl_3$): 1.66 (s, CH_3$); 76.02 (t, J(FC) = 7.6 Hz, CH_2$). ^{19}F NMR ($CDCl_3$): 115.70 (hept, J(HF) = 7.5 Hz). IR: v 2955 m, 2898 w, 1442 w, 1406 w, 1316 w, 1260 m, 1249 s, 1118 w, 1009 w, 953 m, 913 m, 848 s, 834 s, 749 m, 697 m, 689 m, 601 m, 510 w. EI MS (70 eV): m/e (%) $[M^+ - CH_3]$, 465 (10), $[M^+ - CH_2SiMe_3]$, 393 (100). Anal. Calcd for $C_{12}H_{33}F_2Si_3Ta$: C, 30.0; H, 6.9; F, 7.9. Found: C, 29.4; H, 5.9; F, 7.5.

Preparation of $(Me_3SnCl\cdot Me_3SnF\cdot TaF_5)_n$ (4). To a mixture of $(Me_3SiCH_2)TaCl_4$ (5.0 g, 12.2 mmol) and Me_3SnF (12.0 g, 65.6 mmol) was condensed CH_2Cl_2 (50 mL). After 12 h of stirring at room temperature all volatiles were removed in

vacuo, and the oily residue crystallized to a colorless solid. Yield: 1.1 g (14%). Mp: 65 °C. ^1H NMR ($CDCl_3$): 0.80 (s, 18H, CH_3). ^{19}F NMR ($CDCl_3$): 44.72 (s). ^{119}Sn NMR ($CDCl_3$): 238.6 (s). IR: v 1715 w, 1621 w, 1261 w, 1250 w, 1201 w, 1097 w, 1017 w, 887 w, 851 w, 833 w, 795 m, 721 w, 701 w, 607 s, 584 s, 557 s, 543 s, 425 m. EI MS (70 eV): m/e (%) $[TaF_4]$, 257 (5), $[Me_3SnCl]$, 200 (4), $[Me_3SnCl - Me]$, 185 (100), $[Me_3Sn]$, 165 (38). Anal. Calcd for $C_6H_{18}ClF_6Sn_2Ta$: C, 10.95; H, 2.76; Cl, 5.39; F, 17.33; Sn, 36.08. Found: C, 10.6; H, 2.9; Cl, 5.7; F, 17.5; Sn, 35.7.

Preparation of $(Me_3Si)_2CHTaCl_4$ (5). To a suspension of $TaCl_5$ (7.0 g, 19.5 mmol) in n-hexane (100 mL) was added $[(Me_3Si)_2CH]_2Zn$ (3.0 g, 7.8 mmol) dropwise at room temperature. After complete addition, the reaction mixture was stirred for an additional 8 h. The precipitate of $ZnCl_2$ was filtered off and the residue crystallized at -70 °C, to yield yellow crystals of **5**. Mp: 68 °C. Yield: 4.9 g (65%). ^1H NMR ($CDCl_3$): 0.45 (s, 18H, CH_3); 4.65 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): 4.2 (s, CH_3$); 146.3 (s, CH). ^{29}Si NMR ($CDCl_3$): 5.98 (s, SiMe_3). IR: v 1407 m, 1254 s, 1157 w, 1052 w, 926 m, 899 s, 853 vs, 836 vs, 780 s, 751 m, 696 s, 652 s, 606 m, 579 w, 522 w, 456 m, 382 m, 349 s, 282 m. EI MS (70 eV): m/e (%) $[M^+ - Me]$, 467 (50), $[M^+ - TMS-Cl]$, 359 (100), $[M^+ - CH(SiMe_3)_2]$, 323 (25). Anal. Calcd for $C_7H_{19}Cl_4Si_2Ta$: C, 17.44; H, 3.97; Cl, 29.41. Found: C, 17.8; H, 4.1; Cl, 29.1.

Preparation of $(Me_3Si)_2CHTaBr_4$ (6). The method of preparation is analogous to that of **5**, using $TaBr_5$ (3.0 g, 5 mmol) and $[(Me_3Si)_2CH]_2Zn$ (0.8 g, 2.1 mmol), orange crystals. Mp: 79 °C. Yield: 0.81 g (30%). ^1H NMR ($CDCl_3$): 0.52 (s, 18H, CH_3), 4.45 (s, 1H, CH). ^{29}Si NMR ($CDCl_3$): 2.52 (s, SiMe_3). IR: v 1405 m, 1264 m, 1254 s, 1251 s, 1098 w, 1024 s, 927 m, 888 s, 852 vs, 832 vs, 778 s, 751 m, 692 m, 674 s, 646 s, 632 m, 603 m, 438 w, 332 w, 261 s, 236 s, 228 s. EI MS (70 eV): m/e (%) $[M^+ - Me]$, 645 (5), $[M^+ - Br]$, 579 (15), $[M^+ - Me-Br]$, 565 (5), $[M^+ - SiMe_3-Br]$ 491 (40), $[SiMe_3^+]$, 73 (100). Anal. Calcd for $C_7H_{19}Br_4Si_2Ta$: C, 12.87; H, 2.92. Found: C, 13.3; H, 3.1.

Preparation of $(Me_3Si)_2CHTaF_4$ (8). The method of preparation is analogous to that of **1**, using $(Me_3Si)_2CHTaCl_4$ (2.4 g, 5 mmol), Me_3SnF (3.6 g, 20 mmol), and CH_2Cl_2 (20 mL). The residue was sublimed at 90 °C (0.05 Torr), yielding colorless crystals of **8**. Mp: 96 °C. Yield: 2.1 g (52%). ^1H NMR ($CDCl_3$): 0.28 (s, 18H, CH_3); 3.09 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): 2.5 (s, CH_3$); 110.7 (s, CH). ^{19}F NMR ($CDCl_3$): 81.5 (br). ^{29}Si NMR ($CDCl_3$): 8.10 (s, SiMe_3). IR: v 1409 m, 1305 s, 1254 s, 955 m, 920 s, 864 s, 839 vs, 784 m, 757 s, 723 m, 704 m, 688 m, 643 vs, 625 s, 579 w, 516 s, 504 s, 394 w, 302 w, 270 w. EI MS (70 eV): m/e (%) $[M^+ - Me]$, 401 (45), $[M^+ - TMS-F]$, 309 (100), $[SiMe_3^+]$, 73 (35). Anal. Calcd for $C_7H_{19}F_4Si_2Ta$: C, 20.19; H, 4.60. Found: C, 19.9; H, 4.7.

Crystal Structure Solution and Refinement for 2, 4, 5, 7, and 8 (Table 1). Data for structures **2**, **4**, **5**, and **8** were collected on a STOE AED2 four-circle diffractometer with Mo Kα radiation. In the case of compound **7** data were collected on a Stoe-Siemens-Huber four-circle diffractometer with Siemens CCD area detector by use of φ and ω scans. A semiempirical absorption correction was applied. All structures were solved by direct methods (SHELXS-96)[9] and refined against F^2 using SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed.

Supporting Information Available: Tables of crystal data, non-hydrogen fractional coordinates and U values, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and U values of **2**, **4**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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