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Synthesis and spectroscopic characterization of a series of substituted cyclopentadienyl Group 4 fluorides; crystal structure of the acetylacetonato complex [(acac)$_2$(η-C$_5$Me$_5$)Zr(μ-F)SnMe$_3$Cl] †

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A series of mono- and di-substituted cyclopentadienyl Group 4 fluorides $[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(R')}\text{-}1,3\}_n\mathrm{F}_m]$, ($n = m = 2$ and $n = 1, m = 3$; R = H or SiMe$_3$; R′ = H, Me or SiMe$_3$), [Ti(η-C$_5$Me$_5$)$_2$F$_2$] and [Zr(η-C$_5$H$_5$)$_2$F$_2$] have been prepared *via* the reaction of the corresponding chlorides with SnMe$_3$F. The compounds have been characterized by means of ^{1}H and ^{19}F NMR, IR and mass spectroscopy and chemical analyses. The solvent dependence of the reactions using SnMe$_3$F is discussed. To demonstrate the wide applicability of this fluorinating system the acetylacetonatofluoro complex [(acac)$_2$(η-C$_5$Me$_5$)Zr(μ-F)SnMe$_3$Cl] has been prepared and its crystal structure determined.

The chemistry of pentamethylcyclopentadienyl substituted Group 4 fluorides has proven to be a fertile area of research with far-reaching results. For instance we have shown that large clusters based on fluoride-bridged organometallic units provide the opportunity to isolate inorganic solids such as NaF and Li$_2$O which otherwise exist only as large three-dimensional aggregates.[1,2] More pertinent, however, to this study is the high catalytic activity displayed by [Ti(η-C$_5$H$_5$)F$_3$], [Ti(η-C$_5$H$_4$Me)F$_3$] and [Ti(η-C$_5$Me$_5$)F$_3$] in combination with methylaluminoxane, [(AlMeO)$_n$], in the polymerization of styrene.[3] In all cases the fluorides show higher activities than those of the corresponding well known Ziegler–Natta catalytic systems. It is known that alkyl derivatives of Group 4 metallocenes play a crucial role in such catalytic systems.[4] We have demonstrated that in the reaction of trimethylaluminium with [Zr(η-C$_5$Me$_5$)F$_3$] selective replacement of fluorine atoms for methyl groups does in fact occur with concurrent formation of a fluoride-bridged zirconium–aluminium complex.[5]

Access to a wide range of cyclopentadienyl-substituted Group 4 fluorides is possible *via* the reaction of trimethyltin fluoride with the corresponding chlorides in toluene.[6] Heretofore, fluorinating procedures described in the literature were frequently complicated by problems involving separation of the fluorinating reagent from the product or competing reactions.[7–9] As shown in Scheme 1, removal of the SnMe$_3$Cl by-product and solvent *in vacuo* allows the preparation of fluorides in almost quantitative yields. With the availability of the fluorides in large quantities it is now possible to study in detail the chemistry of these exciting new compounds.

$$[\mathrm{MLCl_3}] + 3\mathrm{SnMe_3F} \xrightarrow{\text{Toluene}} [\mathrm{MLF_3}] + 3\mathrm{SnMe_3Cl}$$

M = Zr or Hf; L = η-C$_5$Me$_5$; M = Ti, L = η-C$_5$Me$_5$, η-C$_5$Me$_4$Et, η-C$_5$H$_5$ or η-C$_5$H$_4$Me

Scheme 1

It is well known that modification of the catalyst ligand system can lead to specific changes in the properties of Group 4 metallocenes.[10] Even the introduction of one substituent on the cyclopentadienyl ring is sufficient to introduce novel features into the catalytic behaviour, reactivity and stability of these compounds.[11] Thus, in order to study further the potential effects of incorporating methyl or more bulky SiMe$_3$ groups into the cyclopentadienyl ligand of Group 4 fluorides we have undertaken the preparation of the series of compounds $[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(R')}\text{-}1,3\}_2\mathrm{F}_2]$ and $[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(R')}\text{-}1,3\}\mathrm{F}_3]$ (R = H or SiMe$_3$; R′ = H, Me or SiMe$_3$). The compounds have been characterized by means of ^{1}H and ^{19}F NMR, IR and mass spectroscopies and chemical analyses. In addition, to demonstrate the broad applicability of our fluorinating system we describe the preparation and structural details for the acetylacetonatofluoro complex [(acac)$_2$(η-C$_5$Me$_5$)Zr(μ-F)-SnMe$_3$Cl].

Results and Discussion

The syntheses of the fluoride compounds **1**–**9** are summarised in Scheme 2. Reaction of [Ti(η-C$_5$H$_4$Me)$_2$Cl$_2$] with SnMe$_3$F proceeds smoothly at room temperature in toluene to give [Ti(η-C$_5$H$_4$Me)$_2$F$_2$] **1** in almost quantitative yield. In contrast, the reactions of $[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(SiMe_3)}\text{-}1,3\}_2\mathrm{Cl}_2]$ (R = H, Me or SiMe$_3$) with SnMe$_3$F do not proceed in toluene, even on

$$[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_4\mathrm{Me})_2\mathrm{Cl}_2] + 2\mathrm{SnMe_3F} \xrightarrow{\text{Toluene}} \underset{\mathbf{1}}{[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_4\mathrm{Me})_2\mathrm{F}_2]} + 2\mathrm{SnMe_3Cl}$$

$$[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(SiMe_3)}\text{-}1,3\}_2\mathrm{Cl}_2] + 2\mathrm{SnMe_3F} \xrightarrow{\text{Acetonitrile}} [\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(SiMe_3)}\text{-}1,3\}_2\mathrm{F}_2] + 2\mathrm{SnMe_3Cl}$$

R = H **2**, Me **3** or SiMe$_3$ **4**

$$[\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(SiMe_3)}\text{-}1,3\}\mathrm{Cl}_3] + 3\mathrm{SnMe_3F} \xrightarrow{\text{Toluene}} [\mathrm{Ti}\{\eta\text{-C}_5\mathrm{H}_3\mathrm{R(SiMe_3)}\text{-}1,3\}\mathrm{F}_3] + 3\mathrm{SnMe_3Cl}$$

R = H **6**, Me **7** or SiMe$_3$ **8**

$$[\mathrm{Zr}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{Cl}_2] + 2\mathrm{SnMe_3F} \xrightarrow{\text{Dichloromethane}} \underset{\mathbf{9}}{[\mathrm{Zr}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{F}_2]} + 2\mathrm{SnMe_3Cl}$$

Scheme 2

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† *Non-SI unit employed:* bar = 10^5 Pa.

Table 1 Melting points and microanalyses for compounds **1**–**10**

	Compound	M.p./°C	Analysis (%)[a] C	H	F
1	$[Ti(\eta-C_5H_4Me)_2F_2]$	185–186	58.8 (59.0)	5.6 (5.7)	15.1 (15.6)
2	$[Ti\{\eta-C_5H_4(SiMe_3)\}_2F_2]$	125–127	53.2 (53.3)	7.1 (7.3)	10.7 (10.6)
3	$[Ti\{\eta-C_5H_3Me(SiMe_3)-1,3\}_2F_2]$	196–198	55.1 (55.6)	7.3 (7.8)	9.2 (9.8)
4	$[Ti\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2F_2]$	160–162	52.7 (52.3)	8.3 (8.4)	7.8 (7.5)
5	$[Ti(\eta-C_5Me_5)_2F_2]$	194–196	67.2 (67.4)	8.5 (8.5)	11.0 (10.7)
6	$[Ti\{\eta-C_5H_4(SiMe_3)\}F_3]$	83–85	39.6 (39.7)	6.0 (5.4)	22.9 (23.6)
7	$[Ti\{\eta-C_5H_3Me(SiMe_3)-1,3\}F_3]$	41–43	42.0 (42.2)	5.7 (5.9)	22.7 (22.3)
8	$[Ti\{\eta-C_5H_3(SiMe_3)_2-1,3\}F_3]$	94–95	41.7 (42.0)	6.8 (6.7)	18.2 (18.2)
9	$[Zr(\eta-C_5H_5)_2F_2]$	decomp.	46.2 (46.3)	4.1 (3.9)	14.1 (14.7)
10	$[(acac)_2(\eta-C_5Me_5)Zr(\mu-F)-SnMe_3Cl]$	130–131	43.1 (43.0)	6.1 (6.0)	2.7 (3.0)[b]

[a] Calculated values in parentheses. [b] Cl, 5.5 (5.6)%.

Table 2 Proton, ^{19}F NMR and IR spectroscopic data for compounds **1**–**9**

Compound	^1H NMR, δ SiMe$_3$	Me	Ring protons	^{19}F, δ	IR/cm^{-1}
1	—	2.12	6.32, 5.95	60.8 (s)	567, 547
2	0.21	—	6.53, 6.47	72.1 (s)	567, 524
3	0.17	2.06	6.64, 6.04, 5.96	79.0 (s)	569, 553
4	0.25	—	6.66, 6.52, 5.96	80.3 (s)	574, 553
5	—	1.91	—	50.3 (s)	571, 557
6*	0.17	—	6.33, 6.23	164.5 (s)	—
7*	0.23	2.01	6.44, 6.17, 6.05	162.0 (s)	—
8*	0.25	—	7.07, 6.66	171.9 (s)	—
9	—	—	6.42	16.8 (s)	—

Spectra were recorded on a Bruker AM250 spectrometer in $CDCl_3$ unless otherwise stated. * In C_6D_6.

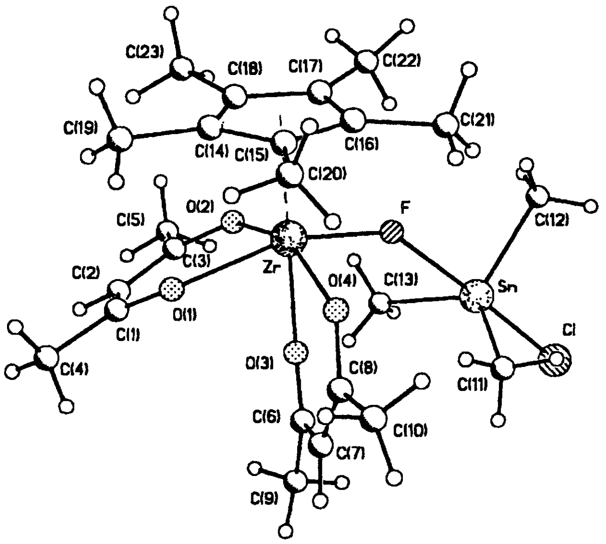

Fig. 1 Crystal structure of $[(acac)_2(\eta-C_5Me_5)Zr(\mu-F)SnMe_3Cl]$ **10** giving the numbering scheme used

refluxing for extended periods. However, when acetonitrile is used as reaction solvent the fluorinations proceed smoothly to give compounds **2**–**4**. The piano-stool compounds $[Ti\{\eta-C_5H_3R(SiMe_3)-1,3\}F_3]$ (R = H **6**, Me **7** or SiMe$_3$ **8**) are prepared by the reaction of the corresponding chlorides with $SnMe_3F$ in toluene. The solvent dependence of the fluorinating system is further accentuated in the reaction of $[Zr(\eta-C_5H_5)_2Cl_2]$ with $SnMe_3F$ which only proceeds in dichloromethane. The dependence is not fully understood, however the presence of bulky substituents on the cyclopentadienyl ring does not appear to have any influence within a series of compounds. This new synthetic route to compounds **2**–**4** and **9** complements the related methods reported in the literature independently by Köpf, Klouras, Winter and Wilkinson, respectively.[12–15] In the case of compounds **3** and **4** our method provides an improved synthesis over the literature procedures. The mixed acetylacetonato–fluoro complex $[(acac)_2(\eta-C_5Me_5)Zr(\mu-F)SnMe_3Cl]$ **10** is conveniently prepared from the corresponding chloride† by reaction with $SnMe_3F$ in toluene (Scheme 3). Interestingly, in the case of **10** the $SnMe_3Cl$ reaction by-product remains co-ordinated *via* a fluoride bridge to the zirconium centre. However, on standing *in vacuo* over a long period of time we found that **10** decomposes to give $[Zr(\eta-C_5Me_5)(acac)_2F]$ **11** and $SnMe_3Cl$.

$$[Zr(\eta-C_5Me_5)(acac)_2Cl] + SnMe_3F \longrightarrow [(acac)_2(\eta-C_5Me_5)Zr(\mu-F)SnMe_3Cl]\ \mathbf{10}$$

$$\mathbf{10} \xrightarrow{in\ vacuo} [Zr(\eta-C_5Me_5)(acac)_2F]\ \mathbf{11} + SnMe_3Cl$$

Scheme 3

The appearance, yields, melting points and elemental analyses for compounds **1**–**10** are summarized in Table 1. Compounds **1**–**5** are air stable as is the case for the corresponding chlorides. While **9** was found to be stable in air over short periods of time, **6**–**8** and **10** were unstable. As expected the fluorides display thermal stabilities similar to those of the chlorides. Proton, ^{19}F NMR and IR data for compounds **1**–**9** are presented in Table 2. The ^1H NMR spectra of **1**–**9** are straightforward. The ^{19}F NMR spectra display single resonances indicating that, at least in solution, the fluorine atoms are equivalent and that the compounds are most likely monomeric. In the IR spectra of metallocene fluorides the metal–fluorine stretching vibrations occur at *ca.* 550 cm^{-1} while the corresponding absorptions for the other halides are below 400 cm^{-1}.[16] On the basis of comparison with the IR spectra of the corresponding chlorides and existing data[16] we have assigned the Ti–F stretching vibrations for compounds **1**–**5** as shown in Table 2. Clearly substitution of the ring protons by methyl and trimethylsilyl groups has only minor effects on the positions of the Ti–F absorptions.

The molecular structure of $[(acac)_2(\eta-C_5Me_5)Zr(\mu-F)-SnMe_3Cl]$ **10** is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The slightly distorted octahedral co-ordination of the Zr atom resembles that observed for the two titanium atoms in the dimeric complex

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† The compound $[Zr(\eta-C_5Me_5)(acac)_2Cl]$ was prepared by the reaction of $[Zr(\eta-C_5Me_5)Cl_3]$ with 2 equivalents of lithium acetylacetonate.

Table 3 Selected bond lengths (Å) and angles (°) for [(acac)$_2$(η-C$_5$Me$_5$)-Zr(μ-F)SnMe$_3$Cl] **10**

Zr–F	2.030(2)	O(1)–C(1)	1.282(5)
Zr–O(2)	2.137(3)	O(2)–C(3)	1.278(5)
Zr–O(1)	2.144(3)	O(3)–C(6)	1.256(5)
Zr–O(3)	2.205(3)	O(4)–C(8)	1.301(5)
Zr–O(4)	2.115(3)	C(1)–C(2)	1.395(6)
Zr–C(14)	2.576(4)	C(2)–C(3)	1.397(6)
Zr–C(15)	2.554(4)	C(6)–C(7)	1.408(6)
Zr–C(16)	2.515(4)	C(6)–C(9)	1.505(6)
Zr–C(17)	2.529(4)	C(7)–C(8)	1.363(6)
Zr–C(18)	2.566(4)	C(8)–C(10)	1.503(6)
F–Sn	2.462(2)	C(14)–C(18)	1.403(7)
Sn–C(11)	2.127(5)	C(14)–C(15)	1.414(7)
Sn–C(12)	2.123(5)	C(15)–C(16)	1.420(7)
Sn–C(13)	2.127(4)	C(16)–C(17)	1.400(6)
Sn–Cl	2.485(1)	C(17)–C(18)	1.408(7)
F–Zr–O(4)	95.1(1)	C(11)–Sn–F	83.2(2)
F–Zr–O(2)	87.6(1)	C(13)–Sn–F	83.6(1)
O(4)–Zr–O(1)	87.4(1)	C(12)–Sn–Cl	96.2(2)
O(2)–Zr–O(1)	79.3(1)	C(11)–Sn–Cl	95.0(2)
F–Zr–O(3)	78.2(1)	C(13)–Sn–Cl	96.3(1)
F–Sn–Cl	177.8(1)	C(1)–O(1)–Zr	133.0(2)
O(4)–Zr–O(3)	77.5(1)	C(3)–O(2)–Zr	133.6(3)
O(2)–Zr–O(3)	78.1(1)	C(6)–O(3)–Zr	132.7(2)
O(1)–Zr–O(3)	76.7(1)	C(8)–O(4)–Zr	134.8(3)
Zr–F–Sn	146.0(1)	C(1)–C(2)–C(3)	124.3(4)
C(12)–Sn–C(11)	115.7(3)	O(2)–C(3)–C(2)	123.6(3)
C(12)–Sn–C(13)	117.4(2)	O(3)–C(6)–C(7)	124.6(4)
C(11)–Sn–C(13)	123.8(2)	C(8)–C(7)–C(6)	123.0(4)
C(12)–Sn–F	85.9(2)		

[{Ti(η-C$_5$Me$_5$)F$_2$[O=C(OEt)C(Ph)=C(OEt)–O]}$_2$] **12**.[17] In **12** the two bridging fluorines of the symmetry-related titanium atoms replace one of the bidentate acetylacetonate ligands present in **10**.

The Zr–O(3) bond length in compound **10** is longer than the average of the remaining Zr–O distances [2.205(3) *vs.* 2.132(3) Å, respectively]. The O(3)–C(6) distance is, in turn, significantly shorter than the corresponding bond length involving the second co-ordinating oxygen within the same acetylacetonate ligand [O(3)–C(6) 1.256(5) and O(4)–C(8) 1.301(5) Å]. The two remaining distances within the six-membered ring formed by co-ordination of this acetylacetonate with the Zr atom are also unequal [C(6)–C(7) 1.408(6) and C(7)–C(8) 1.363(6) Å]. The same tendency toward an asymmetric electron density distribution was observed for the two acetylacetonato groups in the structure of [Zr(η-C$_5$H$_5$)(acac)$_2$Cl][18] where a chlorine atom and a C$_5$H$_5$ group are *trans* to the longest Zr–O distances in both acetylacetonate ligands. However in **10** no similar long–short alternation is observed in the acac ligand co-ordinating the Zr atom in the equatorial plane. The differences between corresponding bond lengths in this second acetylacetonate ligand are within the experimental error.

The Zr–F–Sn bond angle is 146.0(1)°. The Zr–F distance [2.030(2) Å] in compound **10** appears to be longer than the terminal Ti–F distance in **12** [1.833(3) Å] and it is nearly identical to the average Ti–F distance of the bridging fluorines [2.055(3) Å]. The five co-ordination of Sn in **10** represents the intermediate step in the substitution process of the chlorine by fluorine on Zr. The average C[Me]–Sn–Cl angle in **10** is 95.8(2)°, while the corresponding value in the distorted trigonal-bipyramidal geometry in the chain-like structure of SnMe$_3$Cl is 99.9(2)°.[19] The Sn–F bond length [2.462(2) Å] is of the same order as that found for the longest of the Sn–F distances in the polymeric structure of SnMe$_3$F,[20] where the metal atom shows an analogous five-co-ordination. The long Sn–F distance in **10**, relative to the wide range of reported Sn^{IV}–F distances involving terminal fluorine atoms, is also in agreement with the description of this structure as a fairly unstable intermediate in the fluorination process of the corresponding chloride compound.

Experimental

All experiments were performed under a dry nitrogen atmosphere using conventional Schlenk techniques or a dry-box. Acetonitrile, dichloromethane and toluene were dried according to literature methods and distilled under N$_2$ prior to use. Deuteriated solvents, CDCl$_3$ and C$_6$D$_6$, were trap-to-trap distilled from CaH$_2$. Literature methods for the preparation of starting materials are cited at relevant points.

Nuclear magnetic resonance spectra were recorded on a Bruker AM 250 spectrometer. The ^{1}H, ^{13}C and ^{19}F chemical shifts are quoted in parts per million (ppm) downfield from external standards, SiMe$_4$ and CFCl$_3$, respectively. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer as KBr pellets, mass spectra (*m*/*z*) on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Melting points were determined on a HWS SG 3000 apparatus and are uncorrected. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

Syntheses

[Ti(η-C$_5$H$_4$Me)$_2$F$_2$] 1. A suspension of [Ti(η-C$_5$H$_4$Me)$_2$Cl$_2$][21] (2.77 g, 10.00 mmol) and SnMe$_3$F[6] (3.66 g, 20.00 mmol) in toluene (80 cm^3) was stirred for 12 h at 90 °C. On removal of the SnMe$_3$Cl by-product formed during the reaction and solvent *in vacuo* the residue was sublimed at 120 °C (10^{-2} mbar) to give the yellow solid compound **1** (2.20 g, 90%); δ_H(CDCl$_3$) 6.32 (m, 2 H), 5.95 (m, 2 H) and 2.12 (m, 3 H); δ_F(CDCl$_3$) 60.8 (s); *m*/*z* 244 (M^+); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1503s, 1452m, 1368m, 1354m, 1249m, 1053m, 1037s, 867s, 840s, 822s, 619m, 567s, 547s, 418s and 360m.

[Ti{η-C$_5$H$_4$(SiMe$_3$)}$_2$F$_2$] 2.[12] A typical procedure for the preparation of compounds **2**–**5** is as follows. A suspension of SnMe$_3$F (0.38 g, 2.10 mmol) and [Ti{η-C$_5$H$_4$(SiMe$_3$)}$_2$Cl$_2$][21] (0.39 g, 1.00 mmol) was stirred in refluxing acetonitrile (30 cm^3) for 10 h. The SnMe$_3$Cl formed during the reaction and solvent were then removed *in vacuo* and the residue sublimed at 120 °C (10^{-2} mbar) affording the bright yellow product **2** (0.28 g, 80%); δ_H(CDCl$_3$) 6.53 (m, 2 H), 6.47 (m, 2 H) and 0.21 (s, 9 H); δ_F(CDCl$_3$) 72.1 (s); *m*/*z* 360 (M^+); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1404m, 1373m, 1246s, 1177m, 1056s, 1043m, 906s, 837s, 823s, 757m, 623m, 567s, 524s and 412s.

[Ti{η-C$_5$H$_3$Me(SiMe$_3$)-1,3}$_2$F$_2$] 3.[13] Reaction of [Ti{η-C$_5$H$_3$Me(SiMe$_3$)-1,3}$_2$Cl$_2$][21] (0.42 g, 1.00 mmol) with SnMe$_3$F (0.38 g, 2.10 mmol) in refluxing acetonitrile yielded the yellow product **3** (0.37 g, 95%); δ_H(CDCl$_3$) 6.64 (m, 1 H), 6.04 (m, 1 H), 5.96 (m, 1 H), 2.06 (s, 3 H) and 0.17 (s, 9 H); δ_F(CDCl$_3$) 79.0 (s); *m*/*z* 388 (M^+); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1500m, 1415m, 1244s, 1108s, 961m, 919s, 837s, 758s, 696m, 654m, 629m, 569s, 553s, 423s and 380m.

[Ti{η-C$_5$H$_3$(SiMe$_3$)$_2$-1,3}$_2$F$_2$] 4.[14] The compound [Ti{η-C$_5$H$_3$(SiMe$_3$)$_2$-1,3}$_2$Cl$_2$][14] (0.54 g, 1.00 mmol) and SnMe$_3$F (0.38 g, 2.10 mmol) reacted to give the yellow product **4** (0.43 g, 81%); δ_H(CDCl$_3$) 6.66 (m, 1 H), 6.52 (d, 2 H) and 0.25 (s, 18 H); δ_F(CDCl$_3$) 80.3; (s); *m*/*z* 504 (M^+); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1404m, 1268m, 1245s, 1204m, 1091s, 916s, 835s, 751s, 695m, 574s, 553s, 470m, 404m and 360m.

[Ti(η-C$_5$Me$_5$)$_2$F$_2$] 5. The compound [Ti(η-C$_5$Me$_5$)$_2$Cl$_2$][22] (0.39 g, 1.00 mmol) and SnMe$_3$F (0.38 g, 2.10 mmol) reacted to give the orange-yellow product **5** (0.25 g, 70%); δ_H(CDCl$_3$) 1.91 (s); δ_F(CDCl$_3$) 50.3 (s); *m*/*z* 356 (M^+); $\tilde{\nu}_{max}$/cm^{-1}(KBr) 1502m, 1437s, 1375s, 1064m, 1022s, 808m, 634m, 612m, 571s, 557s, 537s, 436s and 386s.

[Ti{η-$C_5H_4(SiMe_3)$}F_3] 6. Complexes **6**–**8** were prepared according to the same procedure. A mixture of [Ti{η-$C_5H_4(SiMe_3)$}Cl_3][23] (2.91 g, 10.00 mmol) and $SnMe_3F$ (5.49 g, 30.00 mmol) was stirred in toluene (50 cm^3) at room temperature for 10 h. The toluene and $SnMe_3Cl$ were then removed *in vacuo* and sublimation of the residue at 80 °C (10^{-2} mbar) yielded the orange product **6** (1.95 g, 81%); $\delta_H(C_6D_6)$ 6.33 (m, 2 H), 6.23 (m, 2 H) and 0.17 (s, 9 H); $\delta_F(C_6D_6)$ 164.5 (s); *m*/*z* 241 (M^+ − Me); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1409m, 1373m, 1321m, 1186s, 1060s, 902s, 840s, 756s, 646s, 633s, 611s, 587s, 508s, 473s, 408s and 383m.

[Ti{η-$C_5H_3Me(SiMe_3)$-1,3}F_3] 7. The compound [Ti{η-$C_5H_3Me(SiMe_3)$-1,3}Cl_3][13] (1.53 g, 5.00 mmol) and $SnMe_3F$ (2.75 g, 15.00 mmol) reacted to give the orange product **7** (1.03 g, 80%); $\delta_H(C_6D_6)$ 6.44 (m, 1 H), 6.17 (m, 1 H), 6.05 (m, 1 H), 2.01 (s, 3 H) and 0.23 (s, 9 H); $\delta_F(C_6D_6)$ 162.0 (s); *m*/*z* 256 (M^+); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1416m, 1312m, 1249s, 1108s, 1059m, 958m, 920m, 870m, 843s, 757m, 692m, 672m, 645s, 606s, 508s and 469m.

[Ti{η-$C_5H_3(SiMe_3)_2$-1,3}F_3] 8. Reaction of [Ti{η-$C_5H_3(SiMe_3)_2$-1,3}Cl_3][24] (3.63 g, 10.00 mmol) and $SnMe_3F$ (5.49 g, 30.00 mmol) gave the bright yellow product **8** (2.83 g, 90%); $\delta_H(C_6D_6)$ 7.07 (m, 1 H), 6.66 (m, 2 H) and 0.25 (s, 18 H); $\delta_F(C_6D_6)$ 171.9 (s); *m*/*z* 299 [M^+(314) − Me(15)]; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1253s, 1212m, 1086s, 1061m, 912m, 843s, 760s, 672s, 652s, 632s, 466m and 416m.

[Zr(η-C_5H_5)$_2$$F_2$] 9.[15] A suspension of $SnMe_3F$ (0.38 g, 2.10 mmol) and [Zr(η-C_5H_5)$_2$$Cl_2$] (0.29 g, 1.00 mmol) in dichloromethane (30 cm^3) was stirred at room temperature until dissolution was complete. The solvent and $SnMe_3Cl$ formed during the reaction were then removed *in vacuo* and the white residue sublimed at 110 °C (10^{-2} mbar) to yield the white product **9** (0.19 g, 73%); $\delta_H(CDCl_3)$ 6.42 (s); $\delta_F(CDCl_3)$ 16.8 (s); *m*/*z* 258 (M^+); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1430m, 1013s, 855m, 816s, 546s, 526s and 359s.

[(acac)$_2$(η-C_5Me_5)Zr(μ-F)$SnMe_3Cl$] 10. A suspension of [Zr(η-C_5Me_5)(acac)$_2$Cl] (1.00 g, 2.17 mmol) and $SnMe_3F$ (0.39 g, 2.17 mmol) was stirred in toluene (25 cm^3) at 80 °C for 24 h. The reaction mixture was allowed to cool to room temperature and then filtered. Concentration of the yellow filtrate to half the original volume yielded orange crystals of compound **10** (1.38 g, 99%); $\delta_H(CDCl_3)$ 5.14 (s, 1 H), 5.07 (s, 1 H), 2.01 (s, 15 H), 1.72 (s, 3 H), 1.65 (s, 3 H), 1.53 (s, 6 H) and 0.49 (s, 9 H); $\delta_C(CDCl_3)$ 192.13, 190.26, 189.91, 185.19 (C=O), 122.42 (C_5Me_5), 102.98, 101.83 (CH), 26.99, 26.78, 26.33 (CH_3), 11.02 (C_5*Me*$_5$) and 1.33 ($SnMe_3$); $\delta_F(CDCl_3)$ 61.7 (s); *m*/*z* 442 [Zr(C_5Me_5)(acac)$_2$]; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1613s, 1596s, 1574s and 1526s.

Crystallography

Crystal data fan 10. $C_{23}H_{38}ClFO_4SnZr$ **10**, $M = 642.89$, monoclinic, $a = 13.984(3)$, $b = 9.712(2)$, $c = 21.308(4)$ Å, $\beta = 101.24(3)°$, $U = 2838(1)$ Å^3 (by least-squares refinements on diffractometer angles for 15 automatically centred reflections), space group $P2_1/c$, $Z = 4$, $D_c = 1.504$ g cm^{-3}, $F(000) = 1296$. Orange crystals, dimensions 0.20 × 0.17 × 0.10 mm, μ(Mo-Kα) = 1.371 mm^{-1}.

Data collection and processing. Intensity data were collected by the ω–2θ scan method at 220 K on a Siemens AED2 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) and according to the learnt-profile method.[25] Of the 6501 reflections measured ($3.5 \leqslant \theta \leqslant 22.5°$), 3665 were unique (merging $R = 0.033$) and all used in the refinement. Three standard reflections showed no significant variations in intensity during data collection.

Structure analysis and refinement. The structure was solved by direct methods (SHELXS 90).[26] Refinement was effected *versus* F^2 through the full-matrix least-squares technique (SHELXL 93).[27] The weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0557P)^2 + 2.5874P$ with $P = (F_o^2 + 2F_c^2)/3$ was applied in the final cycles of refinement. The converged residuals were $R1 = 0.036$ and $wR2 = 0.094$. A final Fourier-difference map showed no electron density > 0.72 or < -1.40 e Å^{-3}. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. All the hydrogen atoms were located in positions riding on the corresponding C atoms (C–H 0.96 and 0.93 Å for the sp^3 and the sp^2 carbons, respectively).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/5.

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