

Synthesis and characterisation of trifluoro(η^5 -*n*-propyltetramethylcyclopentadienyl) metal(IV) -compounds of the elements of Group IV

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Abstract

A series of trifluoro metal complexes of titanium, zirconium and hafnium containing the *n*-propyltetramethylcyclopentadienyl ligand (C_5Me_4nPr) have been synthesised by metathesis reactions of the trichloro analogue using three equivalents of Me_3SnF . X-ray analysis of $(C_5Me_4nPr)TiF_3$ **1** confirms the presence of two $(C_5Me_4nPr)TiF_3$ moieties with two fluorine atoms bridging the metal atoms resulting in a centre of symmetry. The starting materials $(C_5Me_4nPr)MCl_3$ ($M = Zr, Hf$) were prepared by reaction of $(C_5Me_4nPr)Li$ with MCl_4 ($M = Zr, Hf$). © 1997 Published by Elsevier Science S.A.

Keywords: Tin; Group 4; Cyclopentadienyl; Early transition metals; Fluorine; Halide; Catalysis

1. Introduction

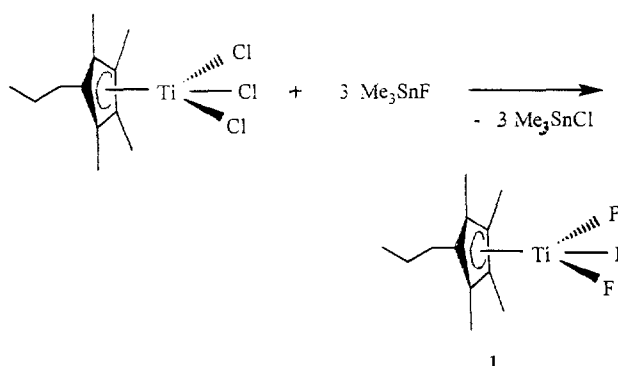
New and efficient synthetic routes for the preparation of organometallic fluorides of Group IV elements have been developed by us recently [1,2]. In these complexes, the distinct tendency of fluoride ligands of the early transition metals to form bridges [3] leads to compounds with several degrees of oligomerisation. Continuing our studies in this area, herein we report on the synthesis and structure of new Group IV organometallic fluorides.

2. Results and discussion

Compound **1**, $(C_5Me_4nPr)TiF_3$, was obtained in 84% yield from the metathesis reaction of $(C_5Me_4nPr)TiCl_3$ with three equivalents of Me_3SnF shown in Scheme 1. In the ^{19}F NMR spectrum, a broad singlet observed at δ 117.7 ppm shows the rapid exchange of the fluorine atoms in the terminal and bridging positions at room temperature. In the 1H NMR spectrum, the protons of the two different kinds of methyl group on the C_5Me_4nPr moiety result in two singlets at δ 2.05 and

1.95 ppm. The protons of the *n*-propyl unit give rise to three signals (at δ 2.63 (triplet), 1.16 (sextet (sx)) and 0.67 ppm (triplet)) with a coupling constant of 7 Hz. The mass spectrum shows the molecular ion at m/z 268.

The molecular structure of **1** is shown in Fig. 1. Crystal data are listed in Table 1. Fractional atomic coordinates are given in Table 2, and a list of selected bond distances and angles is given in Table 3. The core of the structure consists of two Ti atoms bridged by two fluorine atoms. Each metal atom is also bound to two terminally coordinated fluorine atoms and to a propyltetramethylcyclopentadienyl ligand. A centre of inversion



Scheme 1.

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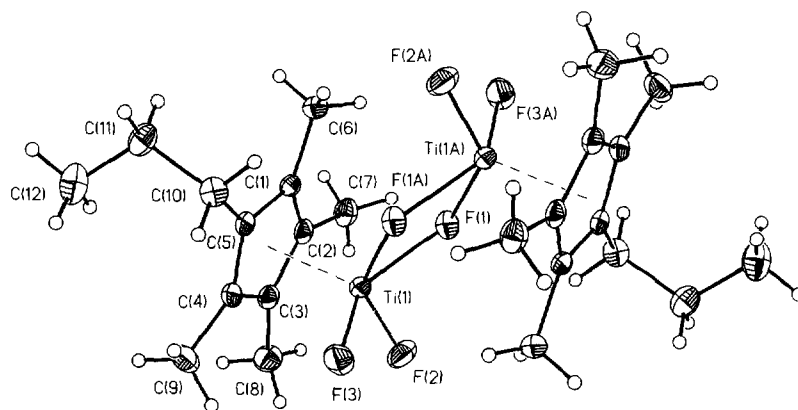


Fig. 1. Molecular structure of $[(C_5Me_4nPr)TiF_3]_2$ (**1**), showing 50% probability thermal ellipsoids for all the non-hydrogen atoms.

relates the two halves of the molecule. As a result, the two cyclopentadienyl ligands, as well as the two pairs of terminally bound fluorine atoms, lie on opposite sides of the four-membered ring formed by the metal atoms and the two bridging fluorine atoms. The average Ti–F(terminal) distance is 1.818(2) Å, while the two Ti–F(bridging) distances are 2.015(1) and 2.028(1) Å. The distance between the Ti atom and the centroid of the ring is 2.358(2) Å. As commonly observed for aliphatic side chains in five- and six-membered aromatic rings, the propyl ligand projects out of the plane of the ring in order to minimise the steric repulsions with the adjacent methyl groups. The angle between the plane of the ring and the plane defined by the two

Table 1
Crystal data for **1**

Formula	$C_{24}H_{38}F_6Ti_2$
Fw	536.34
Space group	$P\bar{1}$
Crystal size (mm ³)	0.40 × 0.30 × 0.30
<i>a</i> (Å)	8.612(2)
<i>b</i> (Å)	8.783(2)
<i>c</i> (Å)	9.010(2)
α (deg)	87.18(3)
β (deg)	65.75(3)
γ (deg)	80.69(3)
<i>V</i> (Å ³)	613(1)
<i>Z</i>	1
Temperature (K)	193(2)
ρ_c (g cm ⁻³)	1.453
μ (mm ⁻¹)	0.706
<i>F</i> (000)	280
2 θ range (deg)	8–48
No. of reflections measured	2302
No. of unique reflections	1889
No. of restraints	0
Refined parameters	150
Goodness-of-fit on <i>F</i> ²	1.086
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) (1700 reflections)	0.0336
<i>wR</i> 2 (all data)	0.0883
Highest diff. peak (e ⁺ Å ⁻³)	0.76

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Ti(1)	5049(1)	6319(1)	8606(1)	18(1)
F(1)	5025(2)	4050(2)	9142(2)	23(1)
F(2)	3748(2)	5956(2)	7538(2)	32(1)
F(3)	3687(2)	8131(2)	9489(2)	34(1)
C(1)	8075(3)	5667(3)	7666(3)	17(1)
C(2)	7629(3)	5426(3)	6350(3)	19(1)
C(3)	6923(3)	6882(3)	5954(3)	20(1)
C(4)	6920(3)	8019(3)	7030(3)	20(1)
C(5)	7635(3)	7263(3)	8095(3)	18(1)
C(6)	8922(3)	4450(3)	8439(3)	25(1)
C(7)	7860(3)	3894(3)	5559(3)	26(1)
C(8)	6280(4)	7199(3)	4630(3)	31(1)
C(9)	6277(3)	9710(3)	7025(3)	30(1)
C(10)	7926(3)	8001(3)	9409(3)	24(1)
C(11)	9810(3)	8259(3)	8835(3)	29(1)
C(12)	10329(4)	9432(4)	7493(4)	40(1)

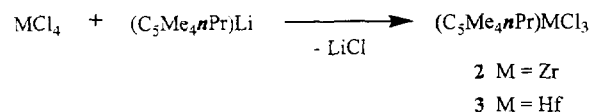
*U*_{eq} is defined as one-third of the trace of the orthogonalised *U*_{*ij*} tensor.

Table 3

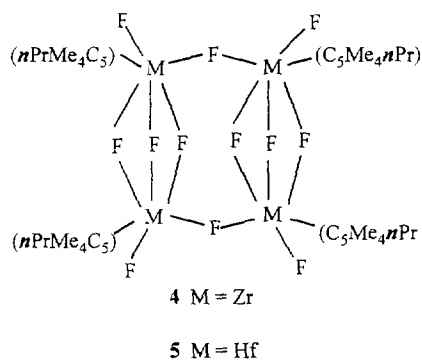
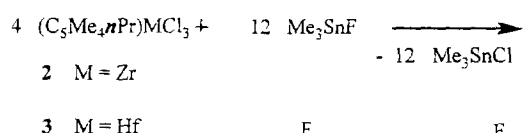
Selected bond lengths (Å) and angles (deg) for **1**

Ti(1)–F(1)	2.028(1)
Ti(1)–F(1) ^Y	2.015(1)
Ti(1)–F(2)	1.821(2)
Ti(1)–F(3)	1.815(2)
Ti(1)–X(1A)	2.358(2)
F(2)–Ti(1)–F(3)	93.08(8)
F(1) ^Y –Ti(1)–F(1)	69.80(7)
Ti(1) ^Y –F(1)–Ti(1)	110.20(7)

Symmetry transformation used to generate equivalent atoms (indicated by prime): $-x + 1, -y + 1, -z + 2$.



Scheme 2.



Scheme 3.

secondary carbons of the propyl ligand (C(10) and C(11)) and the atom the side chain is attached to C(5) is 80.3°.

The trichloro(η^5 -*n*-propyltetramethylcyclopentadienyl)metal(IV) complexes of zirconium (**2**) and hafnium (**3**) were prepared by reaction of (C₅Me₄*n*Pr)Li with the appropriate tetrachlorides of these metals (Scheme 2). Fluorination using Me₃SnF resulted in the formation of the trifluoro complexes **4** and **5** (Scheme 3). The ¹⁹F NMR spectra show four signals which can be assigned by comparison with the related (C₅Me₅)MF₃ (M = Zr, Hf) complexes which have a tetrameric structure in solution [2]. The terminal fluorine atoms give rise to signals at δ 97.84 (**4**) and 41.81 ppm (**5**). The assignment of the remaining three singlets to the bridging fluorine atoms follows that in Ref. [2]. The ¹H NMR spectra do not differ significantly from that of **1**. The tetrameric nature of these complexes is further demonstrated under mass spectrometric conditions by the fragment with *m/z* 1080 ((C₅Me₄*n*Pr)ZrF₃)₄ minus one C₅Me₄*n*Pr unit).

3. Crystal structure determination

The intensities were collected using ω -2 θ scans on a Siemens AED2 four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and applying the Lernd Profile method [4]. The structure was solved by direct methods (SHELXS-90) [5] and refined vs. F^2 by the least squares using all data (SHELXL-93) [6]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in idealized positions. Weighting schemes were of the form $w^{-1} = [\sigma^2(F_o)^2 + (g_1P)^2 + g_2P]$ with $P = (F_o^2 + 2F_c^2)/3$, where $g_1 = 0.0406$ and $g_2 = 0.5716$.

Supplementary material deposited at the Cambridge Crystallographic Data Centre comprises the full list of bond distances and angles, anisotropic displacement

parameters, hydrogen atom coordinates and isotropic displacement parameters.

4. Experimental section

All reactions were performed under dry nitrogen by Schlenk, vacuum-line and inert-atmosphere box techniques. Solvents were freshly distilled from sodium and degassed prior to use. Literature methods were used for the preparation of C₅Me₄*n*Pr (analogously to C₅Me₅) [7] and Me₃SnF [8]. (C₅Me₄*n*Pr)TiCl₃ was received from S. Lenk and W. Kaminsky, Hamburg. NMR spectra were recorded on a Bruker AM 250 instrument with SiMe₄ (¹H) and CCl₃F (¹⁹F) as internal standards. Electron impact (EI) mass spectra were measured on Finnigan MAT 8230 and Varian MAT CH5 instruments at 70 eV (ca. $1.12 \times 10^{-17} \text{ J}$). IR spectra were obtained on a Bio-Rad FTS 7 spectrophotometer as Nujol mulls between KBr or CsI plates. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry of the University of Göttingen.

4.1. Preparation of (C₅Me₄*n*Pr)TiF₃ **1**

A mixture of 0.88 g (2.77 mmol) (C₅Me₄*n*Pr)TiCl₃ and 1.52 g (8.31 mmol) Me₃SnF in 30 ml toluene was stirred at room temperature until it turned to a clear solution. After heating to 50 °C for 0.5 h all volatiles were removed in vacuo at 40 °C. The yellow-orange precipitate was sublimed at 90 °C ($1.3 \times 10^{-7} \text{ bar}$) to yield 0.64 g (84%) of **1**. Melting point (m.p.) 102 °C; ¹H NMR (C₆D₆) δ 2.63 (2H, t, $J = 7 \text{ Hz}$, CH₃CH₂CH₂), 2.05 (6H, s, C₅Me₄), 1.95 (6H, s, C₅Me₄), 1.16 (2H, sx, $J = 7 \text{ Hz}$, CH₃CH₂CH₂), 0.67 (3H, t, $J = 7 \text{ Hz}$, CH₃CH₂CH₂) ppm. ¹⁹F NMR (C₆D₆) δ 117.77 (broad s) ppm. IR (CsI) ν 1496 m, 1263 m, 1114 m, 1027 m, 822 s, 640 vs, 613 vs, 481 s, 450 s, 425 m cm⁻¹. Mass spectrum (*m/z*, %) 268 (M⁺, 18), 163 (C₅Me₄*n*Pr, 48), 135 (C₅Me₅, 100). Anal. Found: C, 53.3; H, 7.2; F, 20.7. C₁₂H₁₉F₃Ti. Calc.: C, 53.70; H, 7.09; F, 21.30%.

4.2. Preparation of (C₅Me₄*n*Pr)ZrCl₃ **2**

5.00 g (29.40 mmol) (C₅Me₄*n*Pr)Li and 6.85 g (29.40 mmol) ZrCl₄ (freshly sublimed) were mixed and heated under reflux for 2 days in 150 ml toluene. After hot filtration all volatiles were removed in vacuo. The pale yellow precipitate was sublimed at 120 °C ($1.3 \times 10^{-7} \text{ bar}$) to yield 8.37 g (79%) of **2**. M.p. 98 °C; ¹H NMR (C₆D₆) δ 2.65 (2H, t, $J = 7 \text{ Hz}$, CH₃CH₂CH₂), 2.08 (6H, s, C₅Me₄), 2.00 (6H, s, C₅Me₄), 1.15 (2H, sx, $J = 7 \text{ Hz}$, CH₃CH₂CH₂), 0.75 (3H, t, $J = 7 \text{ Hz}$, CH₃CH₂CH₂) ppm. IR (CsI) ν 1639 m, 1263 m, 1168 m, 1156 m, 1089 m, 1026 w, 892 m, 816 s, 737 vs, 727 vs, 464 s, 376 s, 328 s cm⁻¹. Mass spectrum (*m/z*, %)

360 (M^+ , 20), 333 (M^+ Cl, 100). Anal. Found: C, 41.6; H, 5.5; Cl, 29.5. $C_{12}H_{19}Cl_3Zr$. Calc.: C, 39.96; H, 5.27; Cl, 29.51%.

4.3. Preparation of $(C_5Me_4nPr)HfCl_3$ **3**

3 was prepared analogously to **2** using 1.50 g (8.82 mmol) $(C_5Me_4nPr)Li$ and 2.38 g (8.82 mmol) $HfCl_4$ to give 3.44 g (87%) **3**. The product was recrystallised from 60 ml hot *n*-hexane. M.p. 87°C, 1H NMR (C_6D_6) δ 2.40 (2H, t, $J = 7$ Hz, $CH_3CH_2CH_2$), 1.95 (6H, s, C_5Me_4), 1.85 (6H, s, C_5Me_4), 1.18 (2H, sx, $J = 7$ Hz, $CH_3CH_2CH_2$), 0.70 (3H, t, $J = 7$ Hz, $CH_3CH_2CH_2$) ppm. IR (CsI) ν 1261 s, 1170 m, 1090 s, 1026 s, 883 s, 803 s, 740 m, 723 m, 469 s, 379 vs, 340 vs, 315 vs, 262 s cm^{-1} . Mass spectrum (m/z , %) 448 (M^+ , 19), 419 ($M^+ - CH_3CH_2$, 100). Anal. Found: C, 32.3; H, 4.5; Cl, 23.6. $C_{12}H_{19}Cl_3Hf$. Calc.: C, 32.14; H, 4.24; Cl, 23.74%.

4.4. Preparation of $(C_5Me_4nPr)ZrF_3$ **4**

0.90 g (2.50 mmol) $(C_5Me_4nPr)ZrCl_3$ were added to 1.38 g (7.50 mmol) Me_3SnF and heated under reflux for 6 h in 50 ml toluene. All volatiles were removed in vacuo, and the colourless solid was recrystallised from 40 ml hot *n*-hexane to get 0.57 g (74%) **4**. M.p. 330°C (decomposition), 1H NMR (C_6D_6) δ 2.60 (2H, t, $J = 7$ Hz, $CH_3CH_2CH_2$), 2.15 (6H, s, C_5Me_4), 2.05 (6H, s, C_5Me_4), 1.45 (2H, sx, $J = 7$ Hz, $CH_3CH_2CH_2$), 0.95 (3H, t, $J = 7$ Hz, $CH_3CH_2CH_2$) ppm. ^{19}F NMR (C_6D_6) δ 97.84 (s), -25.75 (s), -50.44 (s), -72.64 (s) ppm. IR (KBr) ν 1306 m, 1262 s, 1154 m, 1093 s, 1030 s, 819 s, 804 s, 723 s, 586 s, 549 vs, 531 s, 438 m cm^{-1} . Mass spectrum (m/z , %) 1080 ($M_4^+ - C_5Me_4nPr$, 7), 915 ($M_4^+ - 2C_5Me_4nPr$, 100). Anal. Found: C, 45.47; H, 5.74; F, 17.9. $C_{12}H_{19}F_3Zr$. Calc.: C, 46.30; H, 6.11; F, 18.33%.

4.5. Preparation of $(C_5Me_4nPr)HfF_3$ **5**

The analogous reaction of 2.50 g (5.58 mmol) $(C_5Me_4nPr)HfCl_3$ with 3.06 g (16.64 mmol) Me_3SnF yielded in 1.87 g (84%) **5**. M.p. 325°C (decomposition), 1H NMR (C_6D_6) δ 2.62 (2H, t, $J = 7$ Hz, $CH_3CH_2CH_2$), 2.20 (6H, s, C_5Me_4), 2.05 (6H, s, C_5Me_4), 1.45 (2H, sx, $J = 7$ Hz, $CH_3CH_2CH_2$), 0.90 (3H, t, $J = 7$ Hz, $CH_3CH_2CH_2$) ppm. ^{19}F NMR (C_6D_6) δ 41.81 (2F, s), -53.43 (2F, s), -77.27 (1F, s), -97.66 (1F, s) ppm. IR (sI) ν 1305 m, 1262 s, 1169 m, 1154 m, 1091 s, 1032 s, 819 m, 801 s, 724 s, 550 vs, 526 vs, 516 s, 433 s, 418 m, 380 s, 332 m, 301 m, 279 m cm^{-1} . Mass spectrum (m/z , %) 400 (M^+ , 18), 371 ($M^+ - CH_3CH_2$, 100). Anal. Found: C, 36.6; H, 5.0; F, 14.7. $C_{12}H_{19}F_3Hf$. Calc.: C, 36.13; H, 4.77; F, 14.30%.

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