Synthesis of Tetrafluoro(η^5-pentamethylcyclopentadienyl)tantalum(V) and *X*-Ray Crystal Structure of its AsF_3 Solvate, $[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]\cdot 2AsF_3$ *

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The compound $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) reacts with excess of AsF_3 to form the crystalline complex $[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]\cdot 2AsF_3$ (**2**) which has been investigated by single-crystal *X*-ray diffraction analysis. The AsF_3 can be removed *in vacuo* to give $[Ta(\eta^5\text{-}C_5Me_5)F_4]$ (**3**). Compound (**3**) is soluble in common organic solvents, *e.g.* diethyl ether, toluene, or acetonitrile.

A current topic in organometallic chemistry is the ability of metal centres in high oxidation states, in particular Re^{VII}, to stabilize alkyl and aryl bonds to the metal.[1] Generally high oxidation states of transition metals are achieved with oxygen or fluorine. However, transition-metal fluorides are either too reactive or insoluble in most organic solvents to be used as starting materials, *e.g.* TaF_5 forms a tetramer in the solid state.[2] A facile access to fluorinated transition-metal derivatives is the chlorine–fluorine exchange in liquid AsF_3. We report the preparation of $[Ta(\eta^5\text{-}C_5Me_5)F_4]$, which shows good solubility in common organic solvents.

Experimental

Arsenic trifluoride was prepared by reaction of HF with As_2O_3,[3] $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ according to the literature.[4] All experiments were carried out under dry nitrogen. Solvents were carefully dried. The standard for ^1H n.m.r. spectroscopy was $SiMe_4$ and for ^{19}F n.m.r. was $CFCl_3$.

Preparation of $[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]\cdot 2AsF_3$ (**2**).—In a typical experiment, solid $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ (10.5 g, 23 mmol) was treated with AsF_3 (8 cm^3, 21.6 g, 164 mmol). The reaction mixture turned dark red with evolution of heat. The solution was kept under reflux for 1 h, then cooled to 0 °C. After 15 h reddish crystals of compound (**2**) were collected. Typical yields are about 45%. The product was recrystallized from AsF_3 as colourless needles. N.m.r.: ^1H (26 °C, CD_3CN), δ 2.14 (qnt, $^4J_{FH}$ = 1 Hz); ^{19}F (CD_3CN), δ 21.0 (sixteen-line pattern), and −47.0 p.p.m. (s, AsF_3).

Preparation of $[Ta(\eta^5\text{-}C_5Me_5)F_4]$ (**3**).—A sample of compound (**2**) was heated to 150 °C under vacuum (10^{-2} mbar, 1 Pa) for 2 h. A $CDCl_3$ solution of the resulting white powder does not show a signal at δ −47.0 p.p.m. in the ^{19}F n.m.r. spectrum (Found: C, 29.6; H, 3.9; F, 18.8. $C_{10}H_{15}F_4Ta$ requires C, 30.6; H, 3.8; F, 19.4%).

Single-crystal X-*Ray Diffraction Study of Compound* (**2**).—Crystals suitable for *X*-ray crystallographic studies were obtained by slowly cooling a hot solution of compound (**2**) in AsF_3 to room temperature.

Crystal data. $C_{20}H_{30}As_2F_{14}Ta_2$, M = 1 048.2, triclinic, a = 11.229(6), b = 11.314(6), c = 13.800(7) Å, α = 80.42(1), β = 70.15(1), γ = 62.24(1)°, U = 1 459.1 Å^3, T = 298 K, D_c = 2.386 g cm^{-3}, Z = 2, $F(000)$ = 976, space group $P\bar{1}$, colourless needles 0.2 × 0.2 × 0.6 mm, $\mu(Mo\text{-}K_\alpha)$ = 9.75 mm^{-1}.

Data collection and processing. STOE four-circle diffractometer, T = 298 K, graphite-monochromated Mo-K_α radiation, 7 612 reflections measured ($2\theta_{max.}$ = 45 °C), 3 806 unique ($R_{int.}$ = 0.017), giving 3 614 with $|F_o| > 3\sigma(|F_o|)$ for use in all calculations; empirical absorption correction applied.

Structure analysis and refinement. The structure was solved by heavy-atom methods (SHELXS)[5] and refined to R = 0.043, R' = 0.055 with the weighting scheme $w^{-1} = [\sigma^2(|F_o|) + 0.0004|F_o|^2]$. Fractional co-ordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The metathetical halogen exchange between $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) and AsF_3 leads to complex (**2**) in an exothermal reaction. Crystalline (**2**) can be obtained free of AsF_3 by prolonged heating in vacuum to yield (**3**) as a white powder [equations (1) and (2)].

$$\underset{(1)}{6[Ta(\eta^5\text{-}C_5Me_5)Cl_4]} + 14AsF_3 \longrightarrow \underset{(2)}{3[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]\cdot 2AsF_3} + 8AsCl_3 \quad (1)$$

$$\underset{(2)}{[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]\cdot 2AsF_3} \xrightarrow[10^{-2}\,mbar]{150\,°C,\,2\,h} \underset{(3)}{2[Ta(\eta^5\text{-}C_5Me_5)F_4]} + 2AsF_3 \quad (2)$$

Compound (**3**) is soluble in ether, acetonitrile, chloroform, and toluene. More than 2 g of it may be dissolved by 10 cm^3 of acetonitrile. This fact makes (**3**) an interesting substitute for $[(TaF_5)_4]$, which is insoluble in organic solvents. Compared to $[(TaF_5)_4]$, (**3**) should react in a much more selective way. In solution (**3**) is monomeric. The signals of the methyl protons appear as a quintet ($^4J_{FH}$ = 1 Hz) due to coupling with four equivalent fluorine atoms. The ^{19}F n.m.r. spectrum is also consistent with a monomeric species showing a sixteen-line pattern at δ 21.0 p.p.m. This monomeric behaviour makes (**3**) a

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* Di-μ-fluoro-bis[trifluoro(η-pentamethylcyclopentadienyl)tantalum(V)]–trifluoroarsenic (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Atomic co-ordinates (× 10^4) for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ta	1 161(1)	4 530(1)	735(1)	F(4′)	4 541(5)	3 338(5)	6 065(4)
F(1)	316(6)	4 392(8)	2 171(4)	C(1′)	7 036(12)	1 143(9)	5 503(7)
F(2)	194(6)	6 413(6)	906(5)	C(11′)	6 119(13)	502(11)	6 183(9)
F(3)	977(5)	4 949(5)	−721(4)	C(2′)	8 012(10)	1 368(9)	5 751(7)
F(4)	1 219(7)	2 858(6)	575(6)	C(12′)	8 352(15)	1 001(12)	6 739(9)
C(1)	3 055(10)	4 010(11)	1 497(7)	C(3′)	8 691(9)	1 930(9)	4 868(8)
C(11)	2 841(13)	3 931(14)	2 633(8)	C(13′)	9 850(11)	2 219(12)	4 806(12)
C(2)	2 947(9)	5 154(9)	859(7)	C(4′)	8 116(9)	2 053(8)	4 067(7)
C(12)	2 525(13)	6 500(12)	1 232(10)	C(14′)	8 493(13)	2 580(12)	3 010(8)
C(3)	3 296(10)	4 788(10)	−165(7)	C(5′)	7 049(9)	1 579(8)	4 463(7)
C(13)	3 369(11)	5 704(12)	−1 095(7)	C(15′)	6 258(12)	1 484(12)	3 854(10)
C(4)	3 639(10)	3 427(10)	−183(7)	As(2)	8 579(2)	9 248(2)	532(2)
C(14)	4 149(11)	2 609(12)	−1 124(8)	F(21)	8 541(28)	10 507(20)	1 026(16)
C(5)	3 471(10)	2 934(10)	848(8)	F(22)	7 879(25)	10 233(16)	−407(19)
C(15)	3 775(14)	1 526(11)	1 171(10)	F(23)	7 225(18)	9 220(23)	1 363(21)
Ta′	6 232(1)	3 562(1)	5 435(1)	As(1)	−1 812(1)	6 572(1)	3 647(1)
F(1′)	6 269(7)	3 690(5)	6 763(4)	F(11)	−2 487(24)	7 918(24)	2 865(18)
F(2′)	7 241(5)	4 618(5)	4 946(5)	F(12)	−493(16)	5 584(18)	4 248(15)
F(3′)	5 416(5)	4 399(4)	4 250(3)	F(13)	−661(14)	7 173(17)	3 226(9)
				F(14)	−2 780(8)	7 540(10)	4 693(7)

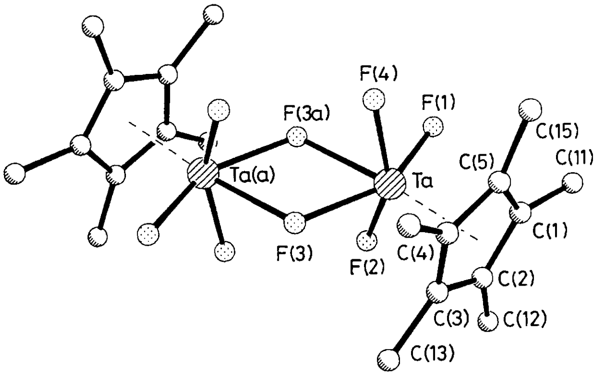

Figure. Molecular structure and labelling scheme for compound (**2**)

Table 2. Selected bond lengths (Å) and angles (°)

Ta–F(1)	1.900(5)	Ta′–F(1′)	1.877(7)
Ta–F(2)	1.901(6)	Ta′–F(2′)	1.908(7)
Ta–F(3)	2.044(5)	Ta′–F(3′)	2.038(5)
Ta–F(4)	1.909(8)	Ta′–F(4′)	1.918(6)
Ta–F(3a)	2.195(6)	Ta′–F(3a)	2.180(4)
Ta–(C_5Me_5)	2.122	Ta′–(C_5Me_5)′	2.117
Ta–C(av.)	2.440	Ta′–C′(av.)	2.438
Ta–F(3)–Ta(a)	111.8(2)	Ta′–F(3′)–Ta′(a)	112.1(2)
F(3)–Ta–F(3a)	68.2(2)	F(3′)–Ta′–F(3′a)	67.9(2)
F(3a)–Ta–F(1)	81.1(2)	F(3′a)–Ta′–F(1′)	82.0(2)
F(3a)–Ta–F(2)	76.0(3)	F(3′a)–Ta′–F(2′)	76.5(2)
F(3a)–Ta–F(4)	75.8(3)	F(3′a)–Ta′–F(4′)	76.5(2)

useful precursor for substitution reactions with various ligands to form compounds with unusual properties, such as tantalum–main group element multiple bonds.

The Figure shows one of the two crystallographically independent molecules of compound (**2**). Each molecule is placed on an inversion centre. There are no interactions between AsF_3 and $[\{Ta(\eta^5\text{-}C_5Me_5)F_4\}_2]$. One molecule of AsF_3 is disordered. As a consequence of the dimerization, tantalum has a distorted octahedral environment if one considers the cyclopentadienyl as a point ligand. The exocyclic tantalum–fluorine bonds (Table 2) are significantly longer than in $[(TaF_5)_4]$.[2]

Acknowledgements

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