Preparation and Crystal Structure of $[AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]$ †

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The reaction of WCl_3N with hexafluoroacetone in acetonitrile in the presence of a catalytic amount of triethylamine, followed by the addition of tetraphenylarsonium chloride, yields orange crystals of $[AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]$. The *X*-ray structure [space group $C2/c$, a = 2 511.3(12), b = 1 194.5(10), c = 1 950.6(9) pm, β = 102.31(5)°, Z = 4, and R = 0.064 for 1 933 unique observed reflections] shows that the anion lies on a crystallographic two-fold axis through the central carbon atom; there is a short W=N bond [174.3(15) pm] and the W=N–C unit is almost linear [176.9(14)°].

Transition-metal nitride complexes have been extensively studied,[1] but reactions with hexafluoroacetone appear not to have been reported. Hexafluoroacetone usually forms metallocycles[2,3] or undergoes (cyclo)addition with unsaturated ligands.[4] As shown here, its reaction with a W≡N bond takes a different course, with retention of a W=N bond and elimination of the oxygen atom. The fate of the oxygen is puzzling, but i.r. spectra indicated that other products containing W–O bonds were formed, although not isolated.

Experimental

The ^{19}F n.m.r. spectrum was recorded on a Bruker 60-E spectrometer at 75.39 MHz. Fluorine chemical shifts are relative to C_6F_6 as internal reference. The i.r. spectrum was recorded on a Perkin-Elmer BE 180 spectrophotometer using Nujol mull. The chemical analysis was performed by Mikroanalytisches Laboratorium Beller, Göttingen. Trichloronitridotungsten(VI), WCl_3N, was prepared by a published method.[5] Reactions were carried out using carefully dried solvents in a dry nitrogen atmosphere.

Preparation of $[AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]$ (**1**).—Hexafluoroacetone (13.5 g, 81 mmol) was condensed in a pressure flask containing WCl_3N (2.5 g, 8.2 mmol) dissolved in acetonitrile (40 cm^3). After addition of a few drops of NEt_3, the reaction mixture was stirred for 36 h at room temperature, and the volatile components removed under vacuum at 35 °C. The salt $AsPh_4Cl$ (3.4 g, 8.2 mmol) was added to the residual orange material, and the mixture stirred overnight in methylene chloride (30 cm^3). The resulting dark orange solution was filtered (and the small amount of insoluble yellow solid discarded). Hexane was added (20 cm^3) and the two layers were allowed to stand at +5 °C for 3 d. The solution deposited orange crystals, which were dried *in vacuo* after decanting off the mother-liquor (2.1 g, 31%), decomp. 208—210 °C (Found: C, 37.0; H, 2.5; N, 1.7. $C_{51}H_{40}As_2Cl_{10}F_6N_2W_2$ requires C, 36.7; H, 2.4; N, 1.7%). Infrared spectrum: 1 485m, 1 440s, 1 275s, 1 265s, 1 245s, 1 230 (sh), 1 225s, 1 185m, 1 160w, 1 100vw, 1 080s, 1 020w, 1 000s, 965s, 925m, 850w, 755s, 740s, 730s, 685s, 590w, 535w, 475s, 460s, and 325m cm^{-1}. ^{19}F N.m.r. spectrum (CH_2Cl_2–$CDCl_3$): δ 79.4 p.p.m. (s).

Crystallography.—Crystal data for complex (**1**). $C_{51}H_{40}As_2Cl_{10}F_6N_2W_2$, M = 1 666.95, monoclinic, space group $C2/c$, a = 2 511.3(12), b = 1 194.5(10), c = 1 950.6(9) pm, β = 102.31(5)°, U = 5.7168 nm^3, Z = 4, D_c = 1.937 Mg m^{-3}, $F(000)$ = 3 192, $\lambda(\text{Mo-}K_\alpha)$ = 71.069 pm, $\mu(\text{Mo-}K_\alpha)$ = 5.78 mm^{-1}, crystal dimensions 0.15 × 0.15 × 0.25 mm.

4 054 Reflections were measured by a profile-fitting procedure[6] on a Stoe-Siemens four-circle diffractometer for $2\theta < 45°$. After Lorentz, polarisation, and semiempirical absorption corrections, equivalent data were merged to yield 1 933 unique reflections with $F > 4\sigma(F)$ which were used for all calculations, performed with the SHELXTL system of programs (written by G. M. S.). The structure was solved by the heavy-atom method and refined with complex neutral-atom scattering factors, riding hydrogen atoms [C–H = 96 pm with H on the external C–C–C bisectors, $U(H) = 1.2\ U_{eq}(C)$], the remaining atoms anisotropic, and weights $w = [\sigma^2(F) + 0.005F^2]^{-1}$ to R' = 0.053 (R = 0.064). A final difference map showed no peaks $> 10^{-6}$ e pm^{-3}, and an analysis of variance showed no systematic trends with $|F|$ or sinθ. Final co-ordinates are given in Table 1, bond lengths and angles in Table 2. The anion of complex (**1**) is shown in the Figure.

Results and Discussion

Trichloronitridotungsten(VI) reacts with excess of hexafluoroacetone in acetonitrile in the presence of a catalytic amount of

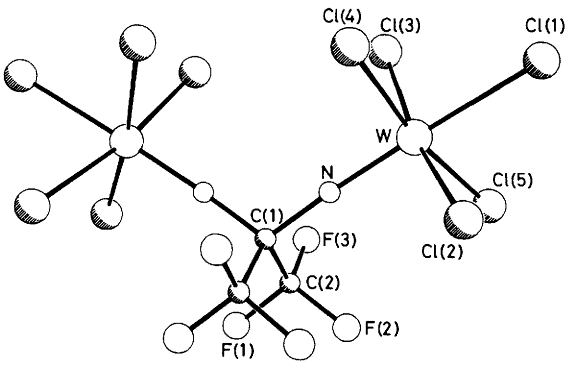

Figure. The $[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]^{2-}$ anion in complex (**1**), with unique non-hydrogen atoms labelled

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† Bis(tetraphenylarsonium) μ-[bis(trifluoromethyl)methylenedi-imino-*NN′*]-bis(pentachlorotungstate).

Supplementary data available: Further details of the crystal structure determination have been deposited with the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, whence they may be obtained by quoting the deposition number CSD-51277, the names of the authors, and the journal reference.

Table 1. Atom co-ordinates (× 10^4) for $[AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]$ (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	3 928(1)	7 431(1)	7 122(1)	C(21)	4 523(6)	3 147(16)	5 631(10)
Cl(1)	3 077(2)	6 392(5)	6 783(3)	C(22)	4 803(10)	3 377(20)	5 111(12)
Cl(2)	3 425(2)	8 560(5)	7 723(4)	C(23)	5 347(10)	3 572(21)	5 297(12)
Cl(3)	4 319(3)	6 085(6)	6 542(4)	C(24)	5 607(9)	3 586(20)	5 963(12)
Cl(4)	4 124(3)	6 280(6)	8 100(4)	C(25)	5 342(7)	3 366(20)	6 492(11)
Cl(5)	3 602(3)	8 405(7)	6 092(3)	C(26)	4 802(7)	3 182(18)	6 310(11)
F(1)	5 463(6)	10 277(12)	6 977(9)	C(31)	3 385(7)	3 931(14)	4 813(11)
F(2)	4 604(5)	10 251(11)	6 667(9)	C(32)	3 325(8)	4 953(19)	5 072(11)
F(3)	5 065(5)	8 963(12)	6 328(7)	C(33)	3 048(9)	5 796(22)	4 682(11)
N	4 529(6)	8 204(12)	7 336(7)	C(34)	2 822(8)	5 612(21)	3 973(14)
C(1)	5 000	8 885(23)	7 500	C(35)	2 874(10)	4 572(25)	3 701(13)
C(2)	5 018(9)	9 593(17)	6 883(14)	C(36)	3 140(9)	3 749(24)	4 108(12)
As	3 759(1)	2 809(2)	5 411(1)	C(41)	3 514(6)	2 642(19)	6 263(10)
C(11)	3 676(8)	1 384(17)	4 967(9)	C(42)	3 515(10)	1 610(20)	6 561(12)
C(12)	3 142(8)	946(22)	4 692(13)	C(43)	3 359(9)	1 559(18)	7 156(13)
C(13)	3 127(12)	−113(25)	4 376(15)	C(44)	3 158(7)	2 385(21)	7 489(10)
C(14)	3 533(15)	−671(22)	4 301(14)	C(45)	3 160(11)	3 430(19)	7 190(11)
C(15)	4 037(13)	−267(24)	4 563(15)	C(46)	3 321(11)	3 538(20)	6 560(13)
C(16)	4 103(10)	739(18)	4 867(11)				

Table 2. Bond lengths (pm) and angles (°) for $[AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}]$ (**1**) with estimated standard deviations in parentheses; a prime denotes atoms generated by the two-fold axis $1 - x, y, \frac{3}{2} - z$

W–Cl(1)	243.7(7)	W–Cl(2)	232.6(8)	C(15)–C(16)	133.4(36)	C(21)–C(22)	137.9(33)
W–Cl(3)	230.4(9)	W–Cl(4)	231.8(8)	C(21)–C(26)	136.0(26)	C(22)–C(23)	135.8(35)
W–Cl(5)	231.4(8)	W–N	174.3(15)	C(23)–C(24)	132.3(31)	C(24)–C(25)	136.7(34)
F(1)–C(2)	136.6(26)	F(2)–C(2)	129.8(25)	C(25)–C(26)	134.6(24)	C(31)–C(32)	134.3(29)
F(3)–C(2)	134.3(29)	N–C(1)	141.5(22)	C(31)–C(36)	139.8(30)	C(32)–C(33)	136.0(32)
C(1)–C(2)	147.9(30)	As–C(11)	190.1(20)	C(33)–C(34)	139.6(32)	C(34)–C(35)	136.8(39)
As–C(21)	191.9(16)	As–C(31)	188.9(18)	C(35)–C(36)	134.6(37)	C(41)–C(42)	136.3(33)
As–C(41)	190.3(20)	C(11)–C(12)	143.1(28)	C(41)–C(46)	135.5(34)	C(42)–C(43)	130.4(37)
C(11)–C(16)	136.8(32)	C(12)–C(13)	140.4(40)	C(43)–C(44)	133.7(34)	C(44)–C(45)	137.8(34)
C(13)–C(14)	125.3(47)	C(14)–C(15)	135.0(46)	C(45)–C(46)	137.8(37)		
Cl(1)–W–Cl(2)	83.9(2)	Cl(2)–W–Cl(3)	87.3(3)	As–C(11)–C(16)	123.8(15)	As–C(11)–C(12)	120.1(16)
Cl(2)–W–Cl(3)	170.4(3)	Cl(1)–W–Cl(4)	86.6(2)	C(11)–C(12)–C(13)	115.4(22)	C(12)–C(11)–C(16)	116.1(20)
Cl(2)–W–Cl(4)	88.4(3)	Cl(3)–W–Cl(4)	87.2(3)	C(13)–C(14)–C(15)	119.1(28)	C(12)–C(13)–C(14)	125.8(28)
Cl(1)–W–Cl(5)	83.9(3)	Cl(2)–W–Cl(5)	91.0(3)	C(11)–C(16)–C(15)	123.0(24)	C(14)–C(15)–C(16)	120.5(29)
Cl(3)–W–Cl(5)	91.9(3)	Cl(4)–W–Cl(5)	170.5(3)	As–C(21)–C(26)	120.4(15)	As–C(21)–C(22)	121.3(14)
Cl(1)–W–N	177.9(5)	Cl(2)–W–N	96.2(5)	C(21)–C(22)–C(23)	118.6(20)	C(22)–C(21)–C(26)	118.3(16)
Cl(3)–W–N	92.8(6)	Cl(4)–W–N	95.5(5)	C(23)–C(24)–C(25)	121.4(21)	C(22)–C(23)–C(24)	121.5(25)
Cl(5)–W–N	94.0(5)	W–N–C(1)	176.9(14)	C(21)–C(26)–C(25)	122.8(20)	C(24)–C(25)–C(26)	117.3(19)
N–C(1)–C(2)	108.2(10)	N–C(1)–N′	109.8(22)	As–C(31)–C(36)	123.6(16)	As–C(31)–C(32)	119.6(15)
C(2)–C(1)–C(2′)	110.3(25)	N–C(1)–C(2′)	110.1(11)	C(31)–C(32)–C(33)	123.3(20)	C(32)–C(31)–C(36)	116.7(19)
F(1)–C(2)–F(3)	103.4(20)	F(1)–C(2)–F(2)	104.9(16)	C(33)–C(34)–C(35)	118.4(22)	C(32)–C(33)–C(34)	119.2(23)
F(1)–C(2)–C(1)	113.5(17)	F(2)–C(2)–F(3)	106.2(19)	C(31)–C(36)–C(35)	121.7(24)	C(34)–C(35)–C(36)	120.7(23)
F(3)–C(2)–C(1)	111.0(17)	F(2)–C(2)–C(1)	116.7(21)	As–C(41)–C(46)	120.2(18)	As–C(41)–C(42)	119.7(17)
C(11)–As–C(31)	111.2(8)	C(11)–As–C(21)	107.4(8)	C(41)–C(42)–C(43)	116.7(22)	C(42)–C(41)–C(46)	120.0(21)
C(11)–As–C(41)	106.2(9)	C(21)–As–C(31)	109.3(8)	C(43)–C(44)–C(45)	115.3(21)	C(42)–C(43)–C(44)	127.8(23)
C(31)–As–C(41)	113.7(9)	C(21)–As–C(41)	108.7(7)	C(41)–C(46)–C(45)	120.5(22)	C(44)–C(45)–C(46)	119.3(22)

base (triethylamine) to give an intermediate product, which was converted into complex (**1**) by addition of tetraphenylarsonium chloride [equation (1)]. Suitable single crystals of (**1**) for *X*-ray

$$N{\equiv}WCl_3 + (CF_3)_2CO \xrightarrow[\text{(ii) } Ph_4As^+Cl^-]{\text{(i) } NEt_3,\ CH_3CN} [AsPh_4]_2[(WCl_5)_2\{\mu\text{-}NC(CF_3)_2N\}] \quad (1)$$

analysis were formed when a layer of hexane was added above a solution in CH_2Cl_2.

The anion in complex (**1**) lies on a crystallographic two-fold axis which passes through the central carbon atom, which is tetrahedrally co-ordinated. The W=N bond of 174.3(15) pm is a little longer than that in $[WCl_5(NC_2Cl_5)]^-$, which the authors considered [7] to be a triple bond. Since the geometry at nitrogen is almost linear [176.9(14)°], a triply bonded resonance extreme with a positive formal charge on N may make a significant contribution. The W–Cl bond *trans* to N [243.7(7) pm] is longer than the mean of the other four [231.6(8) pm], and the equatorial chlorines are bent away from the nitrogen [mean N–W–Cl 94.6(5)°] as observed in other pentachloroimidotungstates.[7]

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