Substituted Tungsten Fluorides

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Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

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WF_6 reacts with $HOCH_2CF_3$ to form $F_5W–OCH_2CF_3$ and *cis*-$WF_4(OCH_2CF_3)_2$. CsF is added to $F_5WOCH_2CF_3$, yielding the heptacoordinated anion $[F_6WOCH_2CF_3]^-$, which has a capped octahedral structure with the oxygen ligand in an equatorial position. The first step of the reaction of WF_6 with $HN(CH_2CF_3)_2$ results in $F_5WN(CH_2CF_3)_2$. Excess $HN(CH_2CF_3)_2$ causes deprotonation, yielding the heptacoordinated $[F_5W(\eta^2CF_3–CHN–CH_2CF_3)]^-$ anion. This can be described as a tungstaazacyclopropane derivative or a π complex between F_5W^- and $CF_3–CHN–CH_2CF_3$. The only case in which MoF_6 reacts similarly is the formation of $F_5Mo–OCH_2CF_3$.

Of the 15 known hexafluorides (SF_6, SeF_6, TeF_6, MoF_6, WF_6, TcF_6, ReF_6, RuF_6, OsF_6, RhF_6, IrF_6, PtF_6, UF_6. NpF_6, PuF_6), only a few − TeF_6, WF_6, and to some extent also UF_6 − have been considered as starting material for other hexacoordinated molecular compounds prepared by means of nucleophilic substitution. There are many reasons for the failure of such simple reactions, in particular the inertness of SF_6 and SeF_6 towards nucleophilic attack, and the oxidation strengths of most other hexafluorides, which prevents a controlled nucleophilic substitution.

In the case of TeF_6, the step-by-step replacement by OR or NR_2 ligands is well known.[1−10] For UF_6 the only thoroughly investigated case[11] seems to be the replacement of the fluorine ligand by the $OTeF_5$ group. WF_6 can be transformed step by step into WF_5OR and finally to $W(OR)_6$, although the latter is usually made from WCl_6.[12−14] CF_3CH_2OH has been treated with WF_6 to give the whole series $Cl_xW(OCH_2CF_3)_{6-x}$.[15] F_5W-NR_2 has been prepared in a similar manner; this is the starting point of another series that ends with the known $W(NR_2)_6$.[16−18] The ligand $-N{=}C(CF_3)_2$ replaces five fluorine atoms of WF_6 in $FW[NC(CF_3)]_2$.[19]

In the present study, we have chosen systems with R = CH_2-CF_3, in order to obtain some stabilization by the CF_3 group, and to avoid the inertness of fully fluorinated groups such as -C_2F_5.

$F_5WO-CH_2CF_3$, *cis*-$F_4WOCH_2CF_3]_2$, and $[F_6WOCH_2CF_3]^-$

The reaction of WF_6 and CF_3CH_2OH proceeds smoothly in two steps to F_5W-OCH_2CF_3 and *cis*-$F_4W(OCH_2CF_3)_2$. The first compound is a liquid, and is structurally characterized by the ^1H-, ^{19}F-, and ^{13}C-NMR spectra. The ^{19}F-NMR AB_4-type spectra for the F_5W group is, of course, typical. The same method clearly indicates the *cis* position of the two alkoxy groups in $F_4W(OCH_2CF_3)_2$ by means of the ^{19}F-NMR A_2B_2-type spectra. The latter compound can also be obtained in crystalline form, and the single-crystal structure determination gives a full account of the molecular structure (see Figure 1 and Table 1).

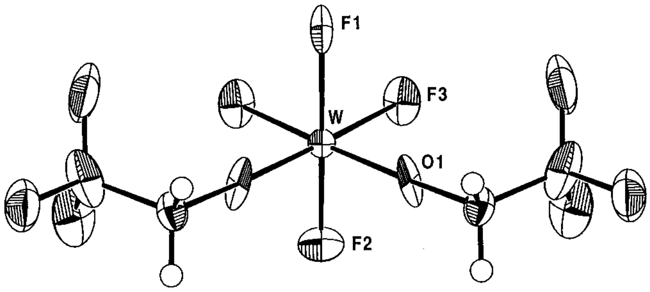

Figure 1. Structure of *cis*-$F_4W(OCH_2CF_3)_2$ in the crystal, ORTEP plot with 50% ellipsoids

Although the existence and structure of these two species is unsurprising, $F_5W-OCH_2CF_3$ is the starting material for a simple but theoretically interesting compound. It is easy to add CsF to obtain $Cs^+[WF_6OCH_2CF_3]^-$. This compound obviously has, according to a single-crystal structure determination, seven-coordinate tungsten atoms and one ligand that differs from the rest (see Figure 2 and Table 1).

WF_6 is known to add F^- to form WF_7^- and WF_8^{2-}; both anions are structurally fully characterized and turn out to be capped octahedral and square antiprismatic.[20−24] The latter structure seems to be the principle structure of the coordination number 8. For the coordination number 7 we know there are three different geometric orientations that have a very similar ligand repulsion, namely the capped octahedron, the capped trigonal prism, and the pentagonal bipyramid, listed in order of increasing ligand repulsion.[25] In the main-group series, the pentagonal bipyramid is always obtained, e.g. in IF_7 [26−29]; this is also the case for species with different ligands, such as IOF_6^-, $TeF_6OCH_3^-$

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Table 1. Selected bond lengths [pm] and angles [°]

cis-$F_4W(OCH_2CF_3)_2$	
W−F1	186(2)
W−F2	182(2)
W−F3	186(2)
W−O	181(1)
F1−W−F2	168.3(7)
F3−W−F3′	86.5(7)
etc.	
O−W−O′	93.2(9)
$Cs^+[WF_6OCH_2CF_3]^- \cdot CH_3CN$	
W−F1	189.9(7)
W−F2	192.0(6)
W−F3	190.0(7)
W−F4	191.4(7)
W−F5	186.7(8)
W−F6	188.4(7)
W−O	183.4(9)
F1−W−F2	135.4(3)
F1−W−F3	124.7(3)
F1−W−F4	136.1(3)
F1−W−F5	74.6(3)
F1−W−F6	73.0(3)
F1−W−O	79.1(4)
etc.	
FW−N(CH_2CF_3)$_2$ first modification, values for the second modification in brackets	
W−F1−5	181.9(4)−187.5(4) [182.9(7)−187.1(7)]
W−N	194.6(4) [197.1(8)]
W−N−C2	123.4(3) [122.8(5)]
W−N−C3	125.0(3) [123.7(6)]
C2−N−C3	111.6(4) [113.4(7)]
$[(CF_3CH_2)_2NH_2]^+[F_5W(\eta^2CF_3{-}CHN{-}CH_2CF_3)]^-$, first modification, values for the second modification in brackets	
W−F1−5	185.0(4)−197.9(4) [184.1(5)−196.2(5)]
W−N1	188.0(5) [187.0(8)]
W−C3	215.0(9) [212.8(9)]
N1−C3	142.6(10) [134.9(12)]
F−W−F	81.3(2)−95.2(2), 159.4(2), 166.4(2) [79.4(2)−93.3(2), 157.6(2), 169.8(3)]
N1−W−F5	161.8(2) [121.2(3)]
C3−W−F5	156.2(3) [160.4(3)]
N1−W−C3	40.8(3) [38.8(4)]
C3−N1-W	79.8(5) [81.0(5)]
N1−C3−W	59.4(4) [60.2(5)]

and $TeF_5(OCH_3)_2^-$.[30−33] The oxygen ligands always occupy axial positions in the pentagonal bipyramid. The pentagonal structures of XeF_5^- and $XeOF_5^-$ can be similarly explained.[34−36] Thus, in main-group compounds the overall structure (pentagonal bipyramid) is not the one with minimum interligand repulsion. However, the finer details such as the occupation of different sites by different ligands follow this ligand repulsion model. This finding calls for a theoretical explanation that is beyond the scope of this article.

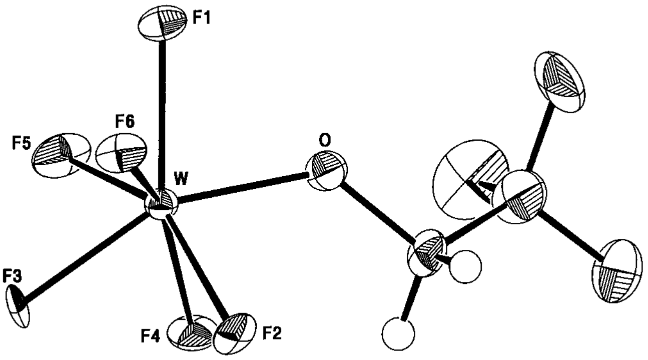

Figure 2. Structure of the $[F_6WOCH_2CF_3]^-$ anion in $Cs^+[F_6WOCH_2CF_3]^-$, ORTEP plot with 50% ellipsoid

The situation of the transition-metal compounds is also not straightforward. WF_7^- and MoF_7^- display the capped octahedral structure that the simple ligand-repulsion picture leads us to expect.[20] However, the structure of isoelectronic ReF_7 might best be described as pentagonal bipyramidal, although it is distorted into the direction of a capped octahedron.[37] ReF_7^-, with just one d electron more than WF_7^- and ReF_7, has a regular pentagonal bipyramidal structure,[38] as has $ReOF_6^-$[38], surprising results that also require a theoretical explanation beyond the interligand-repulsion model.

The reaction of $F_5W{-}OCH_2CF_3$ with CsF allows a test on a seven-coordinate structure, in which one ligand differs from the other six. It should be kept in mind that the analogous reaction between $F_5W{-}OCH_3$ and F^- yields only WF_5O^- and CH_3F[39] The structure of the anion $[F_6WOCH_2CF_3]^-$ is shown in Figure 2. If viewed from the direction of W−F1, the (pseudo) threefold symmetry of the anion becomes visible.

This symmetry clearly shows that the capped octahedral structure of WF_7^- is retained in $[WF_6OCH_2CF_3]^-$. A capped octahedron has three different positional sites: the capping position, three equatorial positions, and three basal positions. The $-OCH_2CF_3$ ligand occupies an equatorial position, which is obviously the site towards which the larger ligands are directed, since the W−F bond lengths of the equatorial bonds in WF_7^- are shorter than those of the basal and capping fluorine atoms.

The difference in W−F bond lengths are nearly the same as those in WF_7^-, allowing for certain small deviations induced by the one different ligand. This is also the case for the bond angles within the anion (see Table 1).

It should be kept in mind that these structures are fluxional in solution. As in WF_7^-, the different fluorine atoms in $[F_6WOCH_2CF_3]^-$ show only one signal without $^{183}W{-}^{19}F$ coupling, indicating rapid intermolecular fluorine exchange.

In order to check the above described structural model, we attempted to treat *cis*-$F_4W(OCH_2CF_3)_2$ with CsF. Unfortunately, however, the resulting product could not be obtained in single-crystal form.

$F_5W-N(CH_2CF_3)_2$ and $[F_5W(\eta^2CF_3-CHN-CH_2CF_3)]^-$

Like with $F_5W-N(CH_2CH_3)_2$[16], the compound $F_5W-N(CH_2CF_3)_2$ can readily be obtained from WF_6 and $HN(CH_2CF_3)_2$. It is a crystalline solid and stable at room temperature. Crystal structure investigations resulted in two different crystallizations from pentane or isopentane, a red needle-shaped modification at low temperature, and a brown one at room temperature. However, the two modifications of the $WF_5-N(CH_2CF_3)_2$ molecules are very similar (see Figure 3 and Table 1). In both cases, the nitrogen environment is completely planar, while $N(CH_2CF_3)_3$ has a pyramidally surrounded nitrogen atom. In contrast to the (alkoxy)tungsten fluorides, the different fluorine atoms on the tungsten atom are not resolved in $F_5W-N(CH_2CF_3)_2$ in the temperature range of −90 to +25°C and in different solvents.

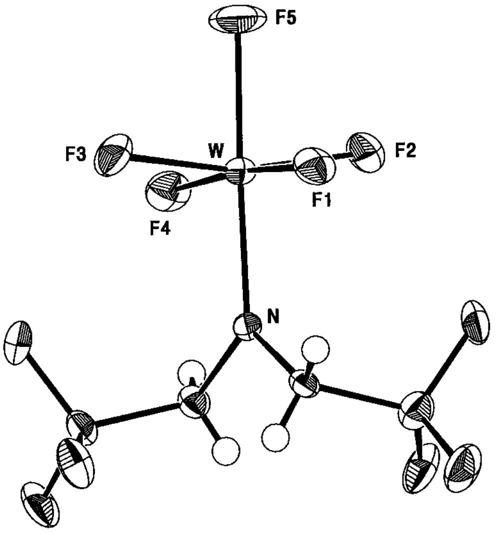

Figure 3. Structure of $F_5W-N(CH_2CF_3)_2$ in the crystal modification (1); ORTEP plot with 50% ellipsoids; overall structure and atomic numbering of modification (2) is the same

Attempts to treat $F_5W-N(CH_2CF_3)_2$ with a second equivalent of $HN(CH_2CF_3)_2$, and the reaction of WF_6 with two equivalents $HN(CH_2CF_3)_2$, do not yield the expected *cis*-$F_4W[N(CH_2CF_3)_2]_2$. Instead we obtained a red-brown compound in the form of needles or platelets; these contain an anion formed by deprotonation according to the single-crystal structure determinations, done as before on two modifications. The structure is in agreement with the complete set of ^1H-, ^{19}F-, and ^{13}C-NMR data. One remarkable feature is its tetragonal pyramidal WF_5 group, attached to a CN linkage, which forms a three-membered WNC ring (Figure 4 and Table 1). Thus, it also has a seven-coordinate tungsten atom. The counterion is $[H_2N(CH_2CF_3)_2]^+$. The anion could also be regarded as a π complex between WF_5^- and $CF_3-CHN-CH_2-CF_3$. In addition to its peculiar structure the spontaneous formation of a W−C bond with help of the weak base $HN(CH_2CF_3)_2$ is another remarkable finding.

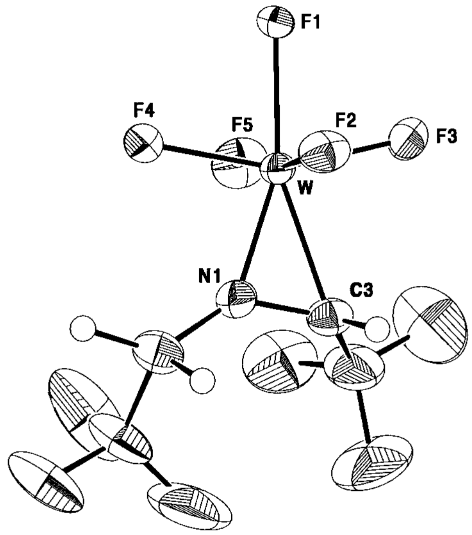

Figure 4. Structure of the anion of $[(CF_3CH_2)_2NH_2]^+[F_5W\eta_2$-$(CF_3-CHN-CH_2CF_3]^-$, ORTEP plot with 50% ellipsoids; overall structure and atomic numbering of modification (2) is the same

The existence of highly oxidized organometallic compounds with certain heavy transition-metal elements as central atoms, especially from Re $\{(CH_3)ReO_3$, Cp^*ReO_3 $[Cp^* = \text{cyclo-}(CH_3)_5C_5]\}$ is, of course, well known.[40] In the tungsten series recently the compounds Cp^*WF_4 and Cp^*WF_5 have been reported[41]; these may most closely resemble the tungstaazacyclopropane compound presented in this paper.

Experimental Section

General: All materials were handled in a drybox or in glass or metal vacuum systems in order to avoid hydrolysis. Reaction vessels made of FEP tubing (Perfluoro ether/propene copolymer) were often used. WF_6 and CsF were purchased from Aldrich Co.; MoF_6 and CF_3CH_2OH were purchased from Merck GmbH. $HN(CH_2CF_3)_2$ was prepared from $H_2N-CH_2CF_3$ and $C_4F_9-SO_2-O-CH_2CF_3$. Solvents were carefully dried and degassed before use.

Physical Measurements: The IR spectra were recorded with a Perkin Elmer 883 instrument, the Raman spectra with a Type 1403 of Spex Industries, 1064 nm, 300 mW; and the NMR spectra with a JEOL JNM-LA 400 instrument for ^1H, ^{19}F, and ^{13}C. Chemical shifts are given for $CFCl_3$ and tetramethylsilane as standards. Dryboxes for the use of water-sensitive compounds were obtained from Brown GmbH, Munich, Germany. Elemental analyses were performed by the Beller Co., Göttingen, Germany.

X-ray Crystallographic Procedures: When necessary, suitable single crystals were obtained as described in the experimental procedures. A suitable single crystal was cut, then mounted on an Enraf-Nonius CAD 4 four-cycle diffractometer with help of a special device (a simplified version of the one previously described).[41] Mo-K_α radiation with a graphite monochromator was used. Lattice constants were obtained by fine adjustment of 25 reflections with θ values between 20 and 25°. X-ray intensities were measured with the ω-scan method, with maximal 60 s/reflection, allowing 25% of this time for background measurements. A Lorentz polarization and ψ absorption corrections were applied. The structures were solved and refined with the SHELX procedures.[42] All atoms were refined anisotropically, and hydrogen atoms were refined isotropically with a single vibrational parameter for all hydrogen atoms. Most hydrogen atoms could be located in difference Fourier analyses, missing hydrogen atoms were refined using a riding model. Table 2 lists further crystallographic details, while Table 1 lists selected bond lengths and angles. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102175. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

$F_5W-OCH_2CF_3$: 1.44 g (14.5 mmol) of CF_3CH_2OH and 5.34 g (17.9 mmol) of WF_6 are condensed at −196°C with the help of a metal vacuum line into an FEP tube equipped with a metal valve. The mixture is warmed to room temperature, and a slightly pink solution is formed. HF and excess WF_6 are removed by pumping all volatile material through an NaOH/CaO containing FEP tube, and pure $F_5W-OCH_2CF_5$ is trapped in a −40°C cold FEP trap. The result is 4.2 g (76% yield) of $F_5W-OCH_2CF_3$ as a colorless liquid. − IR (liquid): ṽ = 3024 w, 2967 w (C-H), 1438 m, 1395 s, 1285 vs, 1173 vs, 1113 s, 1043 s, 995 m, 951 s, 912 w, 846 w, 840 s, 712 s, 633 vs, 531 w, 486 w, 434 w cm^{-1}. − Raman (liquid): ṽ = 3020 (8), 2969 (12), 1438 (9), 1395 (5), 1279 (12), 1143 (35), 1043 (1), 951 (6), 841 (40), 771 (5), 734 (100), 638 (10), 618 (35), 529 (30), 364 (30), 306 (60), 247 (5), 185 (4), 122 (20) cm^{-1}. − ^1H NMR (400 MHz, CD_3CN): δ = 6.29 (q, $^3J_{FH}$ = 8 Hz). − ^{13}C NMR (100.4 MHz, CD_3CN): δ = 123.82 (q, $^1J_{CF}$ = 279 Hz). 80.40 (q, $^2J_{CF}$ = 39 Hz). − ^{19}F NMR: (376.0 MHz, CD_3CN): δ = 128.36 (d, $^2J_{FF}$ = 65 Hz), 102.69 (qt, $^2J_{FF}$ = 63 Hz), −72.15 (t, $^3J_{HF}$ = 8 Hz). − MS (70 eV, EI), for ^{186}W); *m/z* (%): 361 (35) $[M^+ - F]$, 341 (20) $[M^+ - H - 2\ F]$, 311 (40) $[F_5W-OCH_2^+]$, 281 (100) $[F_5W^+]$, and smaller fragments. − $C_2H_2F_8OW$ (377.9): calcd. C 6.36, H 0.71, F 39.3; found C 7.01, H 0.71, F 40.2.

F_5Mo-OCH_2CF_3: 210 mg (2.1 mmol) of CF_3CH_2OH and 530 mg (2.5 mmol) of MoF_6 are treated and purified as described above. Obtained is a yellow liquid. − ^{19}F NMR: δ = 239.10 (d, $^2J_{FF}$ = 82 Hz). 223.99 (qt, $^2J_{FF}$ = 86 Hz), -69.96 (t, $^3J_{HF}$ = 8 Hz).

***cis*-$F_4W(OCH_2CF_3)_2$:** 378 mg (1.0 mmol) F_5W-OCH_2CF_3 is weighed into an FEP tube, equipped with a metal valve. With help of a glass vacuum line 250 mg (2.5 mmol) CF_3CH_2OH is condensed on it at −196°C. Warming to room temperature gives a light brown solution. Volatile HF is pumped off at room temperature. Obtained is 320 mg of *cis*-$F_4W(OCH_2CF_3)_2$ as a colorless liquid at room temperature, mp −5°C. − IR (liquid, KBr, νCH): ṽ = 1441 s, 1397 s, 1373 m, 1284 vs, 1167 vs, 1105 vs, 1050 m, 952 vs, 839 s, 3024 w, 2967 w, 712 s, 681 vs, 632 vs, 533 m cm^{-1}. − Raman (liquid): ṽ = 3010 (12), 2962 (30), 2869 (4), 2777 (4), 1440 (25), 1398 (12), 1280 (20), 1156 (50), 1031 (2), 962 (10), 839 (100), 732 (75), 667 (55), 649 (10), 619 (50), 531 (65), 360 (55), 307 (80), 250 (20), 183 (15) cm^{-1}. − ^1H NMR (CD_3CN): δ = 5.94 (q, $^3J_{HF}$ = 8 Hz). − ^{19}F NMR (CD_3CN): δ = 91.37 (t, $^2J_{FF}$ = 66 Hz), 76,68 (t, $^2J_{FF}$ = 66 Hz), −73.19 (t, $^3J_{HF}$ = 9 Hz). − MS (70 eV, EI for ^{186}W); *m/z* (%): 441 (15) $[M^+ - F]$, 421 (8) $[M^+ - H - 2\ F]$, 391 (55) $[M^+ - CF_3]$, 361 (100) $[F_4W - OCH_2CF_3{}^+]$, and smaller fragments.

$C_4H_4F_{10}O_2W$ (457.9): calcd. C 10.49, H 0.88, F 41.49, W 40.1; found C 10.51, H 0.95, F 41.00, W 39.3. Single crystals are obtained by recrystallization at −30°C without solvent.

$Cs^+[F_6WOCH_2CF_3]^-$: In a dry-box 152 mg (1 mmol) of CsF and 275 mg (0.7 mmol) of F_5W-OCH_2CF_3 are weighed into an FEP tube. The tube is sealed and heated for 24 h to 60°C. The liquid phase disappears, and a light brown solid is formed. Recrystallisation from CH_3CN at -30°C affords $Cs^+F_6W(OCH_2CF_3)^-$ as colorless crystals. Under the microscope these appear as thin platelets. − IR (Nujol): ṽ = 1282 s, 1168 s, 1084 m, 1035 m, 983 s, 946 m, 916 w, 888 w, 830 w, 683 m, 598 vs, 502 s, 435 w cm^{-1}. − Raman (solid): ṽ = 1296 (10), 1112 (20), 983 (100, br), 841 (30), 733 (80), 711 (75), 663 (100) cm^{-1}. − ^1H NMR (CD_3CN): δ = 5.56 (q, $^3J_{HF}$ = 9 Hz). − ^{13}C NMR (CD_3CN): δ = 126.44 (q, $^1J_{CF}$ = 278 Hz), 73.91 (q, $^2J_{CF}$ = 36 Hz). − ^{19}F NMR (CD_3 CN): δ = 106.40 (s), −73.71 (t, J_{HF} = 8 Hz).

Table 2. Crystal data and structure refinements

	cis-$F_4W(OCH_2CF_3)_2$	$Cs^+[F_6WOCH_2CF_3]^-$	$F_5W-N(CH_2CF_3)_2$		$[(CF_3CH_2)NH_2]^+$ $[F_5W\eta^2(CF_3-CHN-CH_2CF_3)]^-$	
			(1)	(2)	(1)	(2)
formula weight [g mol^{-1}]	457.92	570.85	458.93	458.93	640.15	640.15
temperature [°C]	−143	−143	−143	−143	−143	−143
space group	*Pbnm*	*P*1	$P2_1/n$	$P2_12_12_1$	*P*4/*n*	$P2_1/c$
a [pm]	494.4(1)	530.6(1)	804.4(1)	546.4(1)	1822.5(1)	1007.5(4)
b [pm]	961.6(1)	727.1(1)	910.6(2)	1292.5(1)	1822.5(1)	1347.4(4)
c [pm]	2100.0(2)	1518.7(2)	1367.5(2)	1346.7(2)	1033.8(1)	1227.6(4)
α [°]	90	93.69(1)	90	90	90	90
β [°]	90	94.95(1)	95.13(1)	90	90	91.69(3)
γ [°]	90	94.46(1)	90	90	90	90
V [$10^6 pm^3$]	998.4(2)	580.5(1)	997.7(2)	951.0(2)	3433.6(4)	1665.7(10)
Z	4	2	4	4	8	4
$\rho_{calcd.}$ [Mgm^{-3}]	3.046	3.266	3.055	3.205	2.476	2.552
μ [mm^{-1}]	11.71	13.14	11.72	12.29	6.89	7.11
Transmission, max/min	0.95/0.84	0.85/0.62	0.98	0.99/0.89	0.98/0.82	
reflections						
collected	660	3613	35.30	1627	2618	3053
unique	600	3293	3443	1622	2477	2874
θ_{max} [°]	25	30	35	30	25	25
parameters	82	141	171	149	281	276
R_1 [$I > 2\sigma(I)$]	0.053	0.068	0.038	0.044	0.031	0.039
wR_2 (all data)	0.113	0.206	0.107	0.109	0.073	0.103

F_5W-$N(CH_2CF_3)_2$: 970 mg (5.3 mmol) of $HN(CH_2CF_3)_2$ is weighed into an FEP tube equipped with a metal valve. 1.7 g (5.7 mol) of WF_6 is condensed into the tube with help of a glass vacuum line at −196°C. After warming to room temperature a yellow solution and a colorless solid is formed. Excess WF_6 is pumped off, and the solution turns red. Addition of 12 mL of isopentane, centrifugation and cooling to −40°C affords red, needle-shaped crystals, yield 1.2 g (49%). − Raman (solid): $\tilde{\nu}$ = 3052 (5), 3003 (11), 1377 (12), 1022 (60), 827 m, 720 (100), 689 (35), 292 (70) cm^{-1}. − ^{19}F NMR ($CDCl_3$, r.t.): $\delta = -66.8$ (CF_3), 143 (br., F_5W).

$H_2N(CH_2CF_3)_2{}^+[F_5W$-$\eta^2(CF_3CH_2{-}NCH{-}CF_3)]^-$: 325 mg (1.8 mol) of $HN(CH_2CF_3)_2$ is weighed into a 10-mm (inner diameter) glass tube, equipped with a teflon valve. With help of a glass vacuum line 1 mL of $CHCl_3$ as solvent and 175 mg (0.6 mmol) of WF_6 are condensed into the glass tube at −196°C. The tube is sealed and warmed to room temperature. The solution turns yellow, then orange and red due to formation of $F_5W{-}N(CH_2CF_3)_2$, and colorless powder precipitates. After shaking for 8 h at room temperature the color changes to yellow orange. The entire reaction mixture is kept at room temperature for 2 weeks. Brown crystals of $H_2N(CH_2CF_3)_2{}^+[F_5W(\eta^2CF_3CH_2{-}NCH{-}CF_3)]^-$ are formed. − Raman (solid, only peaks with at least medium intensity): $\tilde{\nu}$ = 2997 (12), 2948 (8), 1432 (10), 1413 (7), 1044 (20), 978 (10), 934 (7), 874 (30), 834 (30), 679 (28), 665 (80), 635 (10), 618 (25), 502 (35), 460 (15), 378 (15), 363 (20), 329 (25), 293 (75), 281 (75), 255 (100), 119(40) cm^{-1}. − ^1H NMR (CD_3CN, r.t.): δ = 5.24 (m, J_{HF} = 9 HZ, 1 H, $-CH_ACF_3$), 5.64 (m, J_{HF} = 9 Hz, 1 H, CH_BCF_3, J_{HH} = 14.7 Hz), 3.55 (s, $-CHCF_3$), 8.5 (s, $-NH_2$), 4.00 (q, $-CH_2$). − ^{13}C NMR (CD_3CN): δ = 128.9 (q, $^1J_{CF}$ = 279.5 Hz, $^2J_{CH}$ = 7 Hz, $-CH_AH_BCF_3$), 128,6 (q, $^1J_{CF}$ = 275.8 Hz, $^2J_{CH}$ = 7 Hz, $-CHCF_3$), 58.7 (q, $^2J_{CF}$ = 33.9 Hz, $^1J_{CH}$ = 146 Hz, $-CH_AH_BCF_3$), 81.7 (q, $^2J_{CF}$ = 40,5 Hz, $-CHCF_3$), 50.1 (q, $^2J_{CF}$ = 36 Hz, $^1J_{CH}$ = 149 Hz, $-CH_2CF_3$, cation), 124.1 (q, $^1J_{CF}$ = 277.8 Hz, $^2J_{CH}$ = 7 Hz, $-CH\ CF_3$ cation). − ^{19}F NMR (CF_3CN): δ = 57.5 (d, J_{FF} = 80.6 Hz, $-WF_4$), 1,2 (qt, J_{FF} = 80.6 Hz, $-WF$), −68.3 (t, J_{FH} = 8 Hz, $-CH_AH_BCF_3$), −62.8 (s, $-CHCF_3$), −67.8 (t, J_{FH} = 9 Hz, $-CH_2CF_3$, cation).

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