

Triphenylphosphineiminato-substituted Tungsten(VI) Fluorides. Crystal Structure of Tetrafluorobis(triphenylphosphineiminato)tungsten(VI)*

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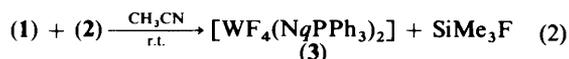
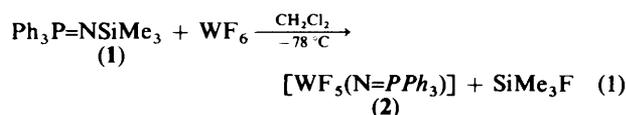
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The complexes $[WF_5L]$ and $[WF_4L_2]$ ($L = Ph_3P=N$) have been prepared from WF_6 and $LSiMe_3$; they are crystalline solids with high kinetic stability. A crystal structure determination of $[WF_4L_2]$ [space group $Fdd2$, $a = 33.832(8)$, $b = 18.933(4)$, $c = 9.926(2)$ Å, $Z = 8$; $R = 0.021$] showed it to be the *cis* isomer with crystallographic 2 symmetry. The W–N bond length of 1.825 Å suggests multiple-bond character. There is appreciable deviation from linearity at nitrogen (W–N–P 157.2°).

Dialkylaminotungsten(VI) fluorides are known¹ in the form of polymeric viscous oils. In general, transition-metal fluoro complexes are characterized by fluoro bridges between the metal atoms. We recently showed² that $SeCl_4$ reacts with $Ph_3P=NSiMe_3$ (1) with elimination of $SiMe_3Cl$ to give kinetically stable mono- and bis-substituted products (a series of transition-metal chloro complexes with $R_3P=N$ ligands is also known³) and it seemed worthwhile to attempt to extend this reaction type to fluorides of Group 6A elements.

Results and Discussion

Hexafluorotungsten(VI) reacts with (1) to give (depending on molar ratio, temperature, and solvent) pentafluoro(triphenylphosphineiminato)tungsten(VI), (2), and tetrafluorobis(triphenylphosphineiminato)tungsten(VI), (3): equations (1) and (2) (r.t. = room temperature).



Compounds (2) and (3) are crystalline solids with moderate to good solubility in polar solvents. Their kinetic stability is remarkable; (2) hydrolyses only slowly in moist air, while (3) is not noticeably affected by boiling water. The ¹⁹F n.m.r. spectrum of (3) indicates the presence of the *cis* isomer in solution; this is confirmed in the solid state by a single-crystal X-ray structure analysis.

Phosphineiminato complexes generally show linear MNP ($M =$ transition metal) units,^{3a-c} which are described as $M=N=PR_3$ with *sp*-hybridized nitrogen; however, bent geometry is also observed and has been ascribed to favourable overlap of an occupied *p* orbital of nitrogen with the vacant

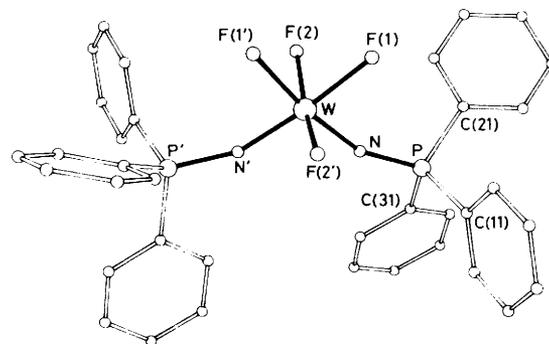


Figure. The molecule of (3) in the crystal. The tungsten atom lies on the two-fold axis $\frac{1}{2}, \frac{1}{2}, z$. Selected bond lengths (Å) and angles (°): N–W 1.825(6), F(1)–W 1.935(6), F(2)–W 1.891(6), N–P 1.594(6); N–W–F(1) 89.7(3), N–W–F(2) 93.9(3), F(1)–W–F(2) 84.6(3), N–W–N' 98.5(4), N–W–F(1') 171.6(3), F(1)–W–F(1') 82.1(4), N–W–F(2') 96.3(3), F(1)–W–F(2') 83.5(3), F(2)–W–F(2') 164.3(3), W–N–P 157.2(4). Primed atoms are at $\frac{1}{2} - x, \frac{1}{2} - y, -z$

$d_{x^2-y^2}$ orbital of phosphorus.^{3d} The current structure lies between these two extreme forms (W–N–P 157.2°). The W–N bond length (1.825 Å) corresponds to some multiple-bonding character {cf. 1.776 Å in the nitrene complex $[WCl_2(NSO_2Ph)_2 \cdot (CH_3CN)_2]^{4+}$ } and the consequent neutralization of the high nuclear charge of tungsten may explain the high kinetic stability. The high *trans* influence of the phosphineiminato ligand is seen in the long W–F(1) bond (1.935 Å).

Experimental

$[WF_5(N=PPh_3)]$ (2).—Compound (1) (3 g, 8.6 mmol) in CH_2Cl_2 (30 cm^3) was run dropwise into a stirred solution of WF_6 (3 g, 10 mmol) in CH_2Cl_2 (50 cm^3) at $-78^\circ C$. The mixture was allowed to warm to room temperature and evaporated to dryness *in vacuo*. Yield: 4.3 g (90%) of (2) as a yellow solid. Recrystallization from CH_3CN gave a white crystalline product. No melting or decomposition occurred below $300^\circ C$. Field desorption (f.d.) mass spectrum: molecular ion, *m/e* 555, 100%. ¹⁹F n.m.r. ($CH_3CN, -45^\circ C$): double doublet with ¹⁸³W satellite peaks, 75.2 p.p.m. [*cis* to iminato ligand; ¹*J*(¹⁹F–¹⁸³W) 39, ³*J*(³¹P–¹⁹F) 3.5, ²*J*(¹⁹F–¹⁹F) 68 Hz]; quintet, -24.3 p.p.m. [*trans*; poor resolution prevented calculation of further coupling constants].

* Tetrafluorobis(triphenylphosphorane-diylimido)tungsten(VI). Additional crystallographic material (structure factors, thermal parameters, complete bond lengths and angles, H-atom co-ordinates) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Please quote reference number CSD 51597 and the full literature citation.

Table. Atomic co-ordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
W	2 500	2 500	7 500	C(22)	1 118(1)	3 896(3)	6 924(5)
N	2 178(1)	2 950(2)	6 299(5)	C(23)	769(1)	3 789(3)	7 579(7)
P	1 831.3(4)	3 458(1)	5 804(1)	C(24)	690(2)	3 141(3)	8 175(6)
F(1)	2 214(1)	2 935(3)	8 970(4)	C(25)	959(2)	2 602(3)	8 048(6)
F(2)	2 147(1)	1 738(2)	7 761(3)	C(26)	1 308(2)	2 703(3)	7 367(8)
C(11)	1 987(1)	4 368(3)	5 885(5)	C(31)	1 708(2)	3 278(3)	4 066(6)
C(12)	2 071(2)	4 741(3)	4 729(6)	C(32)	1 358(2)	3 485(4)	3 497(6)
C(13)	2 216(1)	5 433(3)	4 822(7)	C(33)	1 289(2)	3 377(4)	2 140(7)
C(14)	2 269(2)	5 734(3)	6 061(8)	C(34)	1 563(2)	3 062(4)	1 361(7)
C(15)	2 185(2)	5 364(3)	7 206(7)	C(35)	1 915(2)	2 841(4)	1 908(7)
C(16)	2 038(2)	4 679(3)	7 116(6)	C(36)	1 996(2)	2 956(3)	3 272(7)
C(21)	1 387(1)	3 351(3)	6 788(5)				

[WF₄(N=PPh₃)₂] (3).—Compound (1) (1.9 g, 5.4 mmol) in CH₃CN (30 cm³) was run dropwise into a stirred solution of (2) (3 g, 5.4 mmol) in CH₃CN (50 cm³). After 4 h the precipitated (3) was filtered off. Yield: 3.2 g (72%) (decomp. 275 °C). F.d. mass spectrum: molecular ion, *m/e* 812, 100%. ¹⁹F N.m.r. (Me₂SO): two triplets at -3.5, -21.5 p.p.m. [²J(¹⁹F-¹⁹F) 70 Hz; again low solubility causes poor resolution].

X-Ray Structure Determination of (3).—Crystal data. C₃₆H₃₀F₄N₂P₂W, *M* = 812.4, orthorhombic, space group *Fdd2*, *a* = 33.832(8), *b* = 18.933(4), *c* = 9.926(2) Å, *U* = 6 358 Å³, *Z* = 8, *D*_c 1.70 g cm⁻³, Mo-*K*_α radiation, λ = 0.710 69 Å, crystal size 0.5 × 0.3 × 0.3 mm, μ = 3.9 mm⁻¹, *F*(000) = 3 200.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-*K*_α radiation, 2 077 unique profile-fitted⁵ reflections (2θ_{max} 45°), 1 964 with *F* > 4σ(*F*) used for all calculations. Absorption correction based on ψ scans (transmissions 0.35–0.51). No crystal decay.

Structure solution and refinement. Heavy-atom method for W and P, other non-H atoms from difference syntheses. Least-squares refinement on *F* to *R* 0.021, *R'* 0.021 [non-H atoms anisotropic, H atoms incorporated using riding model with C–H 0.96 Å, *U*(H) = 1.2 *U*_{eq}(C); weighting scheme *w*⁻¹ = σ²(*F*) + 0.000 15 *F*²; 203 parameters]. Absolute structure⁶ by η refinement;⁷ η = +1.04(2). Program system SHELXTL (written by G. M. S.). Final atomic co-ordinates are given in the Table. The molecular structure, with selected bond lengths and angles, is given in the Figure.

Acknowledgements

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