data errors. All calculations were carried out with the program system *SHELXTL* (Sheldrick, 1983).

Bond lengths of the complex are shown in Fig. 1, main bond angles are given in Table 2. From these the distortion from an ideal square-pyramidal coordination of the W atoms with the terminal S atoms in axial position can be seen. The four S atoms forming the base of the two pyramids are planar within 0·05 Å. The axes W1—S3 and W2—S4 of the pyramids are tilted by 18·9°. The torsion angle S3—W1—W2—S4 is −1·0 (1)° which means that the two terminal S atoms are in an exact *syn* configuration as already postulated by spectroscopy (Keck, Kuchen & Mathow, 1986). There are three groups of W—S distances, and the C—C distances are shortened by large displacement parameters caused by the data errors. The complex is close to the point symmetry *m* with atoms W1, W2, S3, S4, P1, P2, C1 to C5, and C7 planar within 0·09 Å. Atoms C6 and C8 deviate 0·18 and 1·18 Å, respectively, from this least-squares plane.

Related literature. Crystal structures of two modifications of $W_2S_4[S_2P(OEt)_2]_2$ have been reported (Drew, Hobson, Mumba, Rice & Turp, 1987) and reveal similar geometries although the comparison is limited by the low accuracy of these structures. The main core *syn*-$W_2S_2(\mu\text{-}S)_2^{2+}$ itself has been characterized in several crystal structures as in $[N(C_2H_5)_2]_2W_2S_2(\mu\text{-}S)_2(S_4)_2$ (Cohen & Stiefel, 1985, and literature cited therein).

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Structure of *mer*-Trichlorotris(pyridyl)osmium(III)

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Abstract. $[OsCl_3(C_5H_5N)_3]$, $M_r = 533·86$, monoclinic, $P2_1/n$, $a = 9·0837\ (20)$, $b = 12·521\ (4)$, $c = 15·550\ (3)$ Å, $\beta = 91·170\ (17)°$, $V = 1768·3$ Å^3, $Z = 4$, $D_x = 2·005$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 7·678$ mm^{-1}, $F(000) = 1012$, $T = 298$ K, $R = 0·0199$ for 2356 unique observed reflections. The Os occupies an octahedral environment, coordinated by three chloride and three pyridyl ligands in a meridional arrangement. The reaction mechanism which leads to this product involves the stepwise substitution of chloride ligands in $[OsCl_6]^{2-}$ by pyridine: the first bound pyridine directs the substitution of the *trans* Cl by the second, thereby ensuring the meridional rather than the facial isomer of $OsCl_3(py)_3$. The mutually *trans* Os—N and Os—Cl distances are 2·086 (3) and 2·3761 (10) Å respectively, compared with 2·090 (4), 2·097 (4) Å for the *trans* Os—N bonds and 2·3569 (11), 2·3590 (11) Å for the *trans* Os—Cl bonds. The pyridyl ligands are twisted out of the mean $OsN_3Cl(3)$ plane by 52·6 (3), 48·6 (3) and 43·5 (3)°: the limiting contacts appear to involve the Cl and α-H atoms, at distances of about 2·8 Å.

Experimental. Compound prepared by electroreduction of $[Pr_4N]_2[OsCl_6]$ in pyridine at room temperature and recrystallized from chloroform/diethyl ether (Heath, Sharp, Smith & Yellowlees, 1988). Dark red crystal, 0·28 × 0·32 × 0·40 mm, AED2 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radia-

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Table 1. *Fractional coordinates of atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
Os	−0·00595 (1)	0·08816 (1)	0·24652 (1)	0·0336 (1)
Cl(1)	0·05610 (12)	0·24909 (8)	0·31703 (7)	0·0515 (6)
Cl(2)	−0·07343 (12)	−0·06990 (9)	0·17317 (7)	0·0497 (6)
Cl(3)	0·12260 (11)	−0·01028 (8)	0·35496 (7)	0·0488 (6)
N(1)	0·1875 (4)	0·09749 (23)	0·1764 (3)	0·0405 (19)
C(12)	0·2650 (4)	0·0083 (3)	0·1573 (3)	0·0441 (22)
C(13)	0·3929 (5)	0·0118 (4)	0·1113 (3)	0·0517 (25)
C(14)	0·4471 (6)	0·1093 (4)	0·0834 (4)	0·058 (3)
C(15)	0·3681 (4)	0·2003 (3)	0·1019 (3)	0·0517 (25)
C(16)	0·2417 (4)	0·1919 (3)	0·1485 (3)	0·0466 (22)
N(2)	−0·2005 (4)	0·08034 (25)	0·31654 (25)	0·0414 (20)
C(22)	−0·3295 (4)	0·0510 (4)	0·2787 (3)	0·0507 (24)
C(23)	−0·4587 (5)	0·0482 (4)	0·3224 (3)	0·061 (3)
C(24)	−0·4607 (6)	0·0747 (4)	0·4087 (4)	0·067 (3)
C(25)	−0·3285 (6)	0·1029 (4)	0·4484 (3)	0·064 (3)
C(26)	−0·2011 (5)	0·1048 (4)	0·4017 (3)	0·0513 (25)
N(3)	−0·1162 (3)	0·17683 (24)	0·15165 (20)	0·0383 (17)
C(32)	−0·0972 (4)	0·1567 (3)	0·06640 (24)	0·0446 (22)
C(33)	−0·1655 (5)	0·2133 (4)	0·0029 (3)	0·0512 (24)
C(34)	−0·2606 (5)	0·2967 (4)	0·0256 (3)	0·055 (3)
C(35)	−0·2824 (4)	0·3168 (3)	0·1109 (3)	0·0497 (24)
C(36)	−0·2076 (4)	0·2576 (3)	0·1720 (3)	0·0442 (21)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

Os—Cl(1)	2·3569 (11)	N(2)—C(22)	1·351 (6)
Os—Cl(2)	2·3590 (11)	N(2)—C(26)	1·360 (6)
Os—Cl(3)	2·3761 (10)	C(22)—C(23)	1·369 (6)
Os—N(1)	2·090 (4)	C(23)—C(24)	1·382 (8)
Os—N(2)	2·097 (4)	C(24)—C(25)	1·385 (8)
Os—N(3)	2·086 (3)	C(25)—C(26)	1·379 (7)
N(1)—C(12)	1·357 (5)	N(3)—C(32)	1·364 (5)
N(1)—C(16)	1·356 (5)	N(3)—C(36)	1·350 (5)
C(12)—C(13)	1·377 (6)	C(32)—C(33)	1·355 (6)
C(13)—C(14)	1·390 (7)	C(33)—C(34)	1·404 (6)
C(14)—C(15)	1·380 (7)	C(34)—C(35)	1·369 (6)
C(15)—C(16)	1·375 (6)	C(35)—C(36)	1·374 (6)

Cl(1)—Os—Cl(2)	178·18 (4)	C(13)—C(14)—C(15)	118·1 (5)
Cl(1)—Os—Cl(3)	90·23 (4)	C(14)—C(15)—C(16)	119·4 (4)
Cl(1)—Os—N(1)	89·95 (10)	N(1)—C(16)—C(15)	123·3 (4)
Cl(1)—Os—N(2)	89·68 (10)	Os—N(2)—C(22)	121·3 (3)
Cl(1)—Os—N(3)	88·90 (9)	Os—N(2)—C(26)	121·0 (3)
Cl(2)—Os—Cl(3)	91·55 (4)	C(22)—N(2)—C(26)	117·7 (4)
Cl(2)—Os—N(1)	90·44 (10)	N(2)—C(22)—C(23)	122·4 (4)
Cl(2)—Os—N(2)	89·91 (10)	C(22)—C(23)—C(24)	120·3 (5)
Cl(2)—Os—N(3)	89·33 (9)	C(23)—C(24)—C(25)	117·7 (5)
Cl(3)—Os—N(1)	89·59 (10)	C(24)—C(25)—C(26)	119·9 (5)
Cl(3)—Os—N(2)	90·83 (10)	N(2)—C(26)—C(25)	122·0 (4)
Cl(3)—Os—N(3)	178·98 (9)	Os—N(3)—C(32)	121·39 (25)
N(1)—Os—N(2)	179·45 (14)	Os—N(3)—C(36)	121·40 (25)
N(1)—Os—N(3)	89·88 (13)	C(32)—N(3)—C(36)	117·2 (3)
N(2)—Os—N(3)	89·70 (13)	N(3)—C(32)—C(33)	123·1 (4)
Os—N(1)—C(12)	120·9 (3)	C(32)—C(33)—C(34)	118·7 (4)
Os—N(1)—C(16)	122·0 (3)	C(33)—C(34)—C(35)	118·8 (4)
C(12)—N(1)—C(16)	117·0 (4)	C(34)—C(35)—C(36)	119·4 (4)
N(1)—C(12)—C(13)	122·3 (4)	N(3)—C(36)—C(35)	122·7 (4)
C(12)—C(13)—C(14)	119·9 (4)		

Cl(1)—Os—N(1)—C(12)	143·1 (3)	Os—N(1)—C(12)—C(13)	179·9 (3)
Cl(1)—Os—N(1)—C(16)	−36·5 (3)	C(16)—N(1)—C(12)—C(13)	−0·4 (6)
Cl(2)—Os—N(1)—C(12)	−38·7 (3)	Os—N(1)—C(16)—C(15)	−179·6 (3)
Cl(2)—Os—N(1)—C(16)	141·7 (3)	C(12)—N(1)—C(16)—C(15)	0·8 (6)
Cl(3)—Os—N(1)—C(12)	52·9 (3)	N(1)—C(12)—C(13)—C(14)	0·6 (7)
Cl(3)—Os—N(1)—C(16)	−126·7 (3)	C(12)—C(13)—C(14)—C(15)	−1·2 (7)
N(3)—Os—N(1)—C(12)	−128·0 (3)	C(13)—C(14)—C(15)—C(16)	1·5 (7)
N(3)—Os—N(1)—C(16)	52·4 (3)	C(14)—C(15)—C(16)—N(1)	−1·4 (7)
Cl(1)—Os—N(2)—C(22)	138·0 (3)	Os—N(2)—C(22)—C(23)	−178·1 (3)
Cl(1)—Os—N(2)—C(26)	−41·9 (3)	C(26)—N(2)—C(22)—C(23)	1·8 (6)
Cl(2)—Os—N(2)—C(22)	−40·3 (3)	Os—N(2)—C(26)—C(25)	178·3 (3)
Cl(2)—Os—N(2)—C(26)	139·8 (3)	C(22)—N(2)—C(26)—C(25)	−1·6 (6)
Cl(3)—Os—N(2)—C(22)	−131·8 (3)	N(2)—C(22)—C(23)—C(24)	−0·7 (7)
Cl(3)—Os—N(2)—C(26)	48·3 (3)	C(22)—C(23)—C(24)—C(25)	−0·5 (8)
N(3)—Os N(2)—C(22)	49·1 (3)	C(23)—C(24)—C(25)—C(26)	0·7 (8)
N(3)—Os—N(2)—C(26)	−130·8 (3)	C(24)—C(25)—C(26)—N(2)	0·4 (7)
Cl(1)—Os—N(3)—C(32)	133·4 (3)	Os—N(3)—C(32)—C(33)	−179·2 (3)
Cl(1)—Os—N(3)—C(36)	−45·6 (3)	C(36)—N(3)—C(32)—C(33)	−0·2 (6)
Cl(2)—Os—N(3)—C(32)	−47·0 (3)	Os—N(3)—C(36)—C(35)	−179·5 (3)
Cl(2)—Os—N(3)—C(36)	134·0 (3)	C(32)—N(3)—C(36)—C(35)	1·4 (5)
N(1)—Os—N(3)—C(32)	43·5 (3)	N(3)—C(32)—C(33)—C(34)	−0·1 (6)
N(1)—Os—N(3)—C(36)	−135·5 (3)	C(32)—C(33)—C(34)—C(35)	−0·9 (6)
N(2)—Os—N(3)—C(32)	−136·9 (3)	C(33)—C(34)—C(35)—C(36)	2·1 (6)
N(2)—Os—N(3)—C(36)	44·1 (3)	C(34)—C(35)—C(36)—N(3)	−2·4 (6)

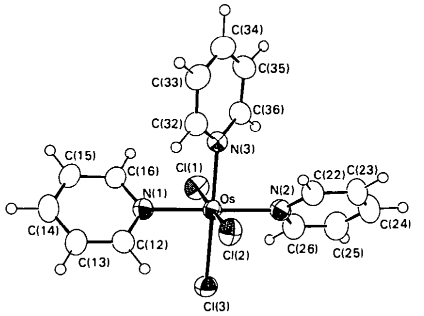

Fig. 1. View of the molecule showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, excepting those of H which have artificial radii of 0·10 Å for clarity.

tion, cell parameters from 11 reflections with $14 < \theta < 15°$. For data collection, ω–2θ scans with ω scan width $(0{\cdot}99 + 0{\cdot}347\tan\theta)°$, $2\theta_{max} = 50°$, h −10→10, k 0→14, l 0→17, no significant crystal movement or decay, initial absorption correction using ψ scans (min. and max. transmission factors 0·0346, 0·0649), 3227 unique reflections, giving 2356 with $F > 6\sigma(F)$ for structure solution [from a Patterson synthesis (Os) followed by iterative cycles of least-squares refinement and difference Fourier synthesis] and refinement [using full-matrix least squares on F (Sheldrick, 1976)]. At isotropic convergence, final absorption correction applied empirically using *DIFABS* (Walker & Stuart, 1983). Anisotropic thermal parameters for all non-H atoms, H atoms in fixed, calculated positions. At convergence, $R = 0{\cdot}0199$, $wR = 0{\cdot}0277$, $w = [\sigma^2(F_o) + 0{\cdot}0016F_o^2]^{-1}$, $S = 0{\cdot}625$ for 199 parameters, max. shift/e.s.d. in final cycle 0·03, max. and min. residues in final difference Fourier synthesis 0·66, $-1{\cdot}30$ e Å^{-3} respectively. Scattering factors were inlaid (Sheldrick, 1976) except for Os (Cromer & Mann, 1968). Atom coordinates and equivalent isotropic thermal parameters are given in Table 1 while selected geometry parameters appear in Table 2.* The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51104 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

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Structures of Spirocyclic Phosphathiazenes: $(Ph_6P_3N_4)S(S_2N_3)$

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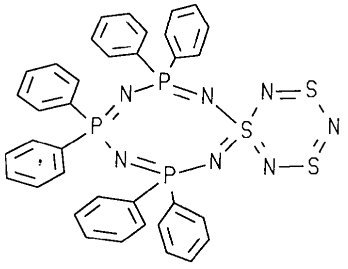
Abstract. 3,5,7-Triphenyl-$1\lambda^6$,2,4,6,8,$3\lambda^5$,$5\lambda^5$,$7\lambda^5$-thiatetraazatriphosphocine-1-spiro-1′-$1'\lambda^6$,2′,4′,6′-thiatriazadiphosphorine, $C_{36}H_{30}N_7P_3S_3$, $M_r = 749.8$, triclinic, $P\bar{1}$, $a = 9.547$ (2), $b = 12.554$ (3), $c = 15.330$ (3) Å, $\alpha = 92.01$ (2), $\beta = 102.77$ (2), $\gamma = 92.31$ (2)°, $V = 1789$ (1) Å^3, $Z = 2$, $D_x = 1.39$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.7$ cm^{-1}, $F(000) = 776$, $T = 293$ K, $R = 0.069$ for 2881 unique observed reflections. The molecule is composed of a six-membered S_3N_3 ring and an eight-membered $(PPh_2)_3SN_4$ ring joined by an S atom which is common to both rings. In the S_3N_3 ring one of the N atoms (N5) adjacent to the unique S atom is 0.746 (7) Å out of the plane of the rest of the S_3N_2 unit, which is planar within 0.05 Å. The P_3SN_4 ring adopts a distorted tub configuration with the tub 'end' atoms (P1,N2,P3,N4) displaced 0.79–1.08 Å from the other four atoms which are planar within 0.05 Å.

Experimental. Crystals of (I) obtained from acetonitrile solutions. Dark-blue platelet data crystal 0.14 × 0.38 × 0.42 mm mounted on glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4 to 16° min^{-1} in θ. Unit cell determined from least-squares analysis of angle data for 25 reflections with $16 < 2\theta < 19°$. Analytical absorption correction based on crystal shape varied from 0.90 to 1.00. Data collected to $(\sin\theta)/\lambda$ of 0.60 Å^{-1}, $-11 < h < 11$, $-14 < k < 14$, $-18 < l < 0$. Four standard reflections ($\bar{1}\bar{1}\bar{6}$, $23\bar{5}$, $\bar{3}3\bar{1}$, $3\bar{3}0$) decreased less than 0.9% over 50.9 h of data collection. 6533 reflections measured, 6277 unique ($R_{\rm int} = 0.02$), 2657 reflections with $I < 3\sigma(I)$ considered unobserved.



(I)

Solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms were constrained to idealized positions (C—H = 0.95 Å) with isotropic thermal parameters, $B = 12.0$ Å^2. One phenyl group (C31) showed a rotational disorder which was best modeled by four isotropic half-occupancy C atom positions along with the P-bonded C atom and the *trans* C—H group; all other non-H atoms refined anisotropically for a total of 438 variables. The C25 phenyl ring has very high thermal parameters indicating extensive thermal motion and/or disorder; high thermal parameters rather than our attempts at disorder models gave the best refinement. $R = 0.069$, $wR = 0.088$, $S = 2.21$, where non-Poisson $w^{-1} = [\sigma^2(I) + 0.0025I^2]/4F^2$. Final $(\Delta/\sigma)_{\max} < 0.5$, $\Delta\rho_{\max} = 0.55$ (3)