Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

V—F	1·933 (4)	F—V—F"	92·9 (1)
V—O	1·985 (4)	F—V—O	88·5 (1)
O—H	0·66 (2)	O—V—F"	177·9 (2)
H···F'	1·96 (2)	O—V—O"	90·0 (2)
O···F'	2·620 (3)	H—O—H"'	112 (5)
		O—H···F'	176 (3)

Symmetry code: (i) $x + \frac{1}{3}$, $x - y + \frac{2}{3}$, $z - \frac{1}{3}$; (ii) $-y$, $-x$, z; (iii) x, $x - y$, z.

parameter for the H atom and anisotropic ones for the non-H atoms, the refinement resulted in $R = 0\cdot019$, $wR = 0\cdot017$ and $S = 1\cdot077$ with $\Delta/\sigma < 0\cdot004$ in the last cycle. A final difference map yielded $\Delta\rho_{min}$ and $\Delta\rho_{max}$ values of $-0\cdot34$ and $0\cdot36$ e Å^{-3}, respectively. The atomic parameters are listed in Table 1.* The polarity of the crystal specimen as defined by these was slightly preferred in the refinement, the inversed one yielding $R = 0\cdot020$, $wR = 0\cdot018$ and $S = 1\cdot150$. Table 2 contains interatomic distances and angles and Fig. 1 shows the complex octahedral molecule and its complete hydrogen-bonding environment in the crystal.

Related literature. Related compounds $M\mathrm{F}_3(\mathrm{OH}_2)_3$ have been reported to crystallize either in a rhombohedral ($R\bar{3}m$) structure with ligand and orientational disorder of discrete complex octahedral molecules or in a tetragonal ($P4/n$) structure with chains of edge-sharing octahedra, bridged by hydrogen-bonded water molecules (Herbstein, Kapon & Reisner, 1985). A representative of the latter is also another form of VF$_3$.3H$_2$O itself (Maak, Eckerlin & Rabenau, 1961).

Fig. 1. The complex octahedral molecule VF$_3$(OH$_2$)$_3$ with all intermolecular hydrogen bonds O—H···F and F···H—O. Projection down the c axis, z coordinates of V atoms as noted, 50% probability ellipsoids.

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53889 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetracarbonyl-μ-(diphenylphosphanido)-di-μ-iodo-iodo(iododiphenylphosphine)-dirhenium(II)(*Re–Re*) Chloroform Solvate

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Abstract. [Re$_2$I$_3$\{P(C$_6$H$_5$)$_2$\}(CO)$_4$\{P(C$_6$H$_5$)$_2$I\}].CHCl$_3$, $M_r = 1481\cdot1$, monoclinic, $P2_1$, $a = 11\cdot823$ (3), $b = 13\cdot641$ (2), $c = 12\cdot150$ (3) Å, $\beta = 103\cdot56$ (2)°, $V = 1904\cdot8$ Å^3, $Z = 2$, $D_x = 2\cdot583$ g cm^{-1}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 98\cdot9$ cm^{-1}, $F(000) = 1310$, $T = 298$ (1) K, $R = 0\cdot027$, $wR = 0\cdot025$ for 2593 unique intensities ($F > 4\sigma F$). The molecule is a 34 valence electron cluster with two face-sharing octahedrally

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}
Re(1)	4751 (1)	9106	2388 (1)	27 (1)
Re(2)	2644 (1)	8705 (1)	732 (1)	29 (1)
I(1)	7428 (1)	10822 (1)	1905 (1)	45 (1)
I(2)	4688 (1)	7698 (1)	724 (1)	41 (1)
I(3)	1829 (1)	8439 (1)	−1579 (1)	50 (1)
I(4)	4057 (1)	10330 (1)	482 (1)	39 (1)
P(1)	2791 (3)	9097 (3)	2621 (3)	29 (2)
P(2)	6854 (3)	9288 (3)	2687 (3)	31 (2)
C(1)	4811 (14)	10250 (13)	3341 (14)	35 (4)
O(1)	4899 (13)	10928 (12)	3892 (12)	60 (4)
C(2)	5099 (14)	8118 (13)	3503 (14)	32 (4)
O(2)	5398 (14)	7461 (14)	4132 (14)	73 (4)
C(3)	1991 (15)	7458 (15)	953 (15)	41 (4)
O(3)	1618 (12)	6713 (12)	1025 (12)	57 (4)
C(4)	1154 (16)	9382 (14)	504 (15)	41 (4)
O(4)	313 (14)	9781 (13)	369 (13)	70 (4)
C(11)	2337 (9)	8241 (8)	3592 (8)	33 (4)
C(12)	1224	7836	3282	42 (4)
C(13)	810	7258	4051	40 (4)
C(14)	1509	7086	5129	59 (5)
C(15)	2622	7491	5438	40 (4)
C(16)	3036	8069	4670	33 (4)
C(21)	2222 (11)	10264 (8)	3026 (10)	34 (4)
C(22)	1921	10311	4069	64 (6)
C(23)	1478	11178	4407	89 (8)
C(24)	1336	12000	3704	72 (7)
C(25)	1637	11953	2662	66 (6)
C(26)	2080	11085	2323	59 (5)
C(31)	7728 (8)	9369 (10)	4155 (8)	43 (4)
C(32)	8938	9335	4354	39 (4)
C(33)	9619	9470	5447	46 (5)
C(34)	9090	9638	6342	60 (5)
C(35)	7880	9672	6144	65 (6)
C(36)	7199	9537	5050	58 (5)
C(41)	7591 (11)	8300 (8)	2108 (10)	39 (4)
C(42)	7554	7371	2579	63 (6)
C(43)	8049	6572	2150	68 (6)
C(44)	8582	6701	1250	61 (6)
C(45)	8619	7630	779	65 (5)
C(46)	8123	8429	1208	57 (5)
C(5)	4829 (18)	4275 (18)	2107 (18)	57 (5)
Cl(1)	3551 (7)	4823 (6)	1308 (7)	90 (2)
Cl(2)	4534 (8)	3148 (7)	2633 (8)	102 (2)
Cl(3)	5460 (8)	5041 (8)	3225 (8)	114 (3)

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

Re(1)—Re(2)	2·864 (1)		Re(1)—I(2)	2·777 (1)
Re(1)—I(4)	2·815 (1)		Re(1)—P(1)	2·400 (3)
Re(1)—P(2)	2·439 (3)		Re(2)—I(2)	2·783 (1)
Re(2)—I(3)	2·770 (1)		Re(2)—I(4)	2·834 (1)
Re(2)—P(1)	2·323 (4)			

Re(2)—Re(1)—I(2)	59·1 (1)		Re(2)—Re(1)—I(4)	59·9 (1)
Re(2)—Re(1)—P(1)	51·5 (1)		I(2)—Re(1)—I(4)	81·9 (1)
I(2)—Re(1)—P(1)	102·7 (1)		I(4)—Re(1)—P(1)	89·8 (1)
Re(1)—Re(2)—I(2)	58·9 (1)		Re(1)—Re(2)—I(4)	59·2 (1)
Re(1)—Re(2)—P(1)	53·9 (1)		I(2)—Re(2)—I(4)	81·4 (1)
I(2)—Re(2)—P(1)	104·7 (1)		I(4)—Re(2)—P(1)	91·0 (1)
Re(1)—I(2)—Re(2)	62·0 (1)		Re(1)—I(4)—Re(2)	60·9 (1)
Re(1)—P(1)—Re(2)	74·6 (1)			

distorted polyhedra at the Re atoms as the central molecular fragment. The Re—Re bond distance is 2·864 (1) Å, bridged by two I atoms and one PPh_2 group. Both μ_2-I ligands have nearly equal Re—I bond lengths and are *trans* to the CO ligands. The μ_2-PPh_2 bridge has an asymmetric shape and is *trans* to the terminal ligands I and PPh_2I, respectively.

Experimental. The compound was prepared by reaction of $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-}PPh_2)]$ (Haupt, Balsaa & Flörke, 1987) and iodine in boiling xylene solution under reflux and recrystallized from $CHCl_3$/pentane. Red crystal, size $0·08 \times 0·10 \times 0·41$ mm. Lattice

parameters refined from 25 reflections $8 \le 2\theta \le 25°$. Nicolet *R3m/V* diffractometer, graphite monochromator, Mo $K\alpha$ radiation. ω–2θ scan, 2946 intensities $3 \le 2\theta \le 46°$, $0 \le h \le 13$, $0 \le k \le 15$, $-13 \le l \le 13$, 3 standard reflections monitored every 400 reflections showed only random deviations, Lp correction, empirical absorption correction *via* ψ scans, min./max. transmission 0·100/0·139, 2790 unique intensities after merging, $R_{int} = 0·016$, 2593 with $F > 4\sigma(F)$. Structure solved by direct methods and subsequent ΔF maps; full-matrix least-squares refinement based on F; 167 parameters with anisotropic refinement for Re, I and P atoms. H atoms fixed from geometrical considerations with isotropic displacement parameters, phenyl groups treated as rigid bodies (C—C 1·395 Å); one enclosed $CHCl_3$ solvent molecule per asymmetric unit; $R = 0·027$, $wR = 0·025$, $w^{-1} = \sigma^2(F) + 0·0001F^2$, $S = 1·443$; max. $(\Delta/\sigma) = 0·001$; max. height in final ΔF map 0·9 e Å^{-3} near Re, min. height in refined ΔF map $-0·8$ e Å^{-3}. Scattering factors, structure solution and refinement: *SHELXTL-Plus*88 (Sheldrick, 1988). Atomic parameters are given in Table 1, selected bond lengths and angles in Table 2.* Fig. 1 shows the molecular structure.

Related literature. Other triple-bridged Re—Re bonds with two μ_2-I ligands have been described for the anion $[Re_2(CO)_6(\mu\text{-I})_2(\mu\text{-H})]^-$ (Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983), for

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53739 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
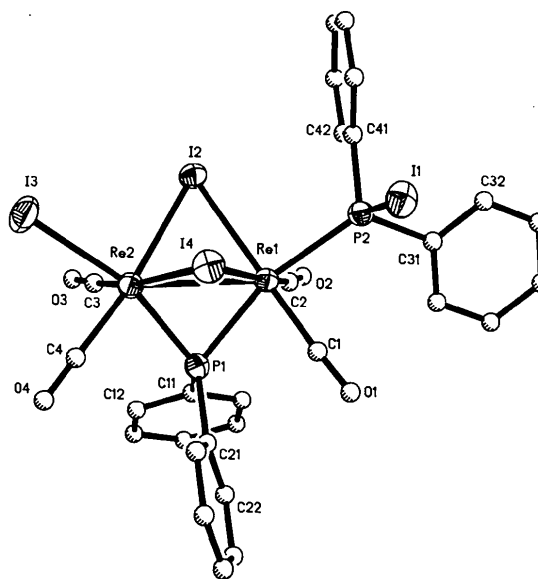

Fig. 1. Molecular structure of the title compound.

[Re$_2$(CO)$_8$(μ-I)$_2$(μ_4-In)][Re$_2$(CO)$_6$(μ-I)] (Haupt & Flörke, 1989) and [Re$_2$(CO)$_4\mu$-I)$_2$(PPh$_3$)$_2$][μ-Ga{Re(CO)$_4$PPh$_3$}] (Ph = phenyl) (Flörke, Balsaa & Haupt, 1986).

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Structure of 3,4-Bis(1,2-ethanedithiolato)-1,2-bis(triphenylphosphine)-1,2,3;1,3,4;1,2,4;2,3,4-tetra-μ_3-sulfido-dicopperditungsten(4 Cu–W, 1 W–W)

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Abstract. [Cu$_2$W$_2$(C$_{18}$H$_{15}$P)$_2$(C$_2$H$_4$S$_2$)$_2$S$_4$], M_r = 1331·96, orthorhombic, $P2_12_12_1$, a = 12·362 (9), b = 31·57 (1), c = 11·682 (8) Å, V = 4559 (4) Å^3, Z = 4, D_x = 1·94 g cm^{-3}, λ(Mo $K\alpha$) = 0·710690 Å, μ = 65·13 cm^{-1}, $F(000)$ = 2568, T = 296 K, R = 0·039 for 3977 unique reflections with $I \geq 3\sigma(I)$. The molecule contains a cubane-like cluster core (W$_2$Cu$_2$S$_4$)$^{4+}$ which has approximate C_{2v} symmetry [W(1)—W(2) 2·851 (1) Å, mean W—Cu 2·823 (2) Å]. Each W atom has a tetragonal-pyramidal coordination formed by three bridging sulfido ligands [one W—S 2·202 (4) Å, other two average 2·345 (4) Å] and one bidentate 1,2-ethanedithiolato ligand [mean W—S 2·346 (4) Å]; a PPh$_3$ ligand and three sulfido ligands complete the coordination of each Cu atom [Cu—S 2·284 (4), 2·383 (4) and 2·426 (4) Å]. The bond lengths and bond angles of the W$_2$S$_4$(SCH$_2$CH$_2$S)$_2$ moiety are almost the same as in the isolated starting material, except that the W=S double bonds elongate slightly from 2·143 (2) and 2·156 (2) Å to 2·201 (4) and 2·202 (4) Å.

Experimental. The synthetic procedure is described by Zhu, Zheng & Wu (1990). A dark orange crystal measuring 0·40 × 0·60 × 0·90 mm was mounted in a random orientation on a glass fiber. Data were collected using a Rigaku AFC5R diffractometer (*CONTROL* software; Molecular Structure Corporation, 1986) using Mo $K\alpha$ radiation at *ca* 296 K. Cell constants were obtained by least-squares analysis of

20 diffraction maxima (20 < 2θ < 26°), $\omega/2\theta$ scan, scan speed varied between 2, 4 and 8° min^{-1} (in ω) with scan width (0·798 + 0·35 tanθ)°, 2$\theta \leq$ 50° (0 $\leq h \leq$ 15, 0 $\leq k \leq$ 38, 0 $\leq l \leq$ 14). 4525 unique reflections were collected. Three standard reflections, remeasured periodically, showed only random variations in intensity. Intensity was defined as $C - \frac{1}{2}(t_c/t_b)(b_1 + b_2)$, where C is the total number of counts, t_c is the time spent counting peak intensity, t_b is the time spent counting one side of the background, b_1 represents the high-angle background counts and b_2 represents the low-angle background counts; $\sigma(I) = [C + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + pI)^2]^{1/2}$, where I is the intensity and p was taken to be 0·05. An empirical absorption correction, based on azimuthal scans of three reflections, was applied (transmission factor ranges from 0·6540 to 1·000). A decay correction was not applied. The data were corrected for Lorentz and polarization factors. 3977 reflections with $I \geq 3\sigma(I)$ were considered observed, and were all used in the refinement.

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983); the W atoms were located in the E map. The Cu atoms and most non-H atoms were located using *DIRDIF* (Beurskens, 1984); the remaining non-H atoms were located in the succeeding difference Fourier syntheses (H atoms were placed in geometrically calculated positions with C—H = 0·95 Å, but not included in the refinement). The structure was refined by full-matrix least squares on F with anisotropic thermal parameters for W, Cu, S, P, and the four C atoms of the 1,2-ethanedithiolato ligands, and isotropic ther-

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