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Structure of a Trinuclear Rhodium(I) Fluorophosphine Complex, $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$

By Joel T. Mague and Marie P. Johnson

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, *USA*

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Abstract. Tris[μ-bis(difluorophosphino)methylamine]-tri-μ-chloro-trirhodium, $M_r = 916\cdot06$, monoclinic, $C2/c$, $a = 17\cdot323$ (2), $b = 10\cdot998$ (2), $c = 23\cdot226$ (3) Å, $\beta = 93\cdot03$ (1)°, $V = 4419$ Å^3, $Z = 8$, $D_x = 2\cdot76$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0\cdot70930$ Å, $\mu = 30\cdot8$ cm^{-1}, $F(000) = 3456$, $T = 298$ K. Final $R = 0\cdot030$ for 3811 observed data. The final product of the reaction of $[Rh_2Cl_2(CO)_4]$ with two equivalents of $H_3CN(PF_2)_2$ is shown to contain a triangular Rh_3 moiety with three edge-bridging chloride and three edge-bridging fluorophosphine ligands. The structure, in the shape of a truncated triangular pyramid, is a new type for closed trinuclear clusters. The coordination about each Rh atom is essentially square planar and the whole molecule possesses approximate C_{3v} symmetry. Although differing significantly, the Rh—Rh distances span a rather narrow range [3·0755 (4)–3·1180 (4) Å] and are considered non-bonding. The mean planes of the ligating atoms about each metal atom are inclined with respect to the plane of the three metal atoms by an average angle of 120·81 (4)°.

Experimental. Dark red-orange crystals of the title compound were obtained directly from the reaction mixture as previously described (Mague, Johnson & Lloyd, 1989). Enraf–Nonius CAD-4 diffractometer, crystal size 0·25 × 0·30 × 0·45 mm, cell dimensions from setting angles of 25 widely distributed reflections ($11\cdot53 \leq \theta \leq 25\cdot81$°), graphite-monochromated Mo $K\alpha$ radiation, 9046 reflections scanned, $\omega/2\theta$ mode, $3 \leq \theta \leq 26$°, index range h 0 to 21, k −13 to 13, l −28 to 28, scan speed 1·5–16·5° min^{-1}, scan range $(0\cdot80 + 0\cdot20\tan\theta)$°, 13% linear decay (average) from three intensity standards monitored every 7200 s, linear decay correction applied, orientation stable from three monitor reflections checked every 200 reflections, empirical absorption correction (North, Phillips & Mathews, 1968), transmission-factor range 0·741–1·000, hkl and $h\bar{k}l$ reflections averaged to give 4322 unique data, agreement on F for averaged reflections is 0·017, 3811 data with $I \geq 3\sigma(I)$ used in analysis, 15 reflections (marked by negative σ_F) excluded from final refinement because of highly asymmetric backgrounds, structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined by full-matrix least squares, non-H atoms refined anisotropically, 271 variables, H atoms located in difference map and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1·3 times those of the respective C atoms. $\sum w(\Delta F)^2$ minimized, final shifts all $\leq 0\cdot11\sigma$, $w = 1/\sigma_F^2$, $\sigma_F = \sigma_{F^2}/2F$, $\sigma_{F^2} = [\sigma_I^2 + (0\cdot04F^2)^2]^{1/2}$, residual electron density within 0·43 to −0·38 e Å^{-3}, $R = 0\cdot030$, $wR = 0\cdot038$, GOF = 2·72. Computations made on a PDP 11/73 with Enraf–Nonius *SDP* (Frenz, 1985) using complex neutral-atom scattering factors (Cromer & Waber, 1974; Cromer, 1974). Final atomic coordinates for non-H atoms are given in Table 1,* selected bond distances and interbond angles in Table 2. Figs. 1 and 2 show the full molecule viewed perpendicular to the Rh_3 plane and a perspective view of the inner coordination sphere, respectively.

Related literature. The ligand bis(difluorophosphino)methylamine has been previously found to form a number of complexes with unusual structures (King, Shimura & Brown, 1984; Newton, King, Chang, Pantaleo & Gimeno, 1977; Newton, King, Lee, Nørskov-Lauritsen & Kumar, 1982; Dulebohn, Ward & Nocera, 1988). In our studies of binuclear, 'A-frame'-type complexes we attempted to prepare such a complex of rhodium with this ligand (Mague *et al.*, 1989). Unexpectedly the product obtained proved to be the trinuclear complex $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$. Other examples of non-bonding Rh–Rh separations comparable to those found here are ones of 3·1520 (8) and 3·155 (4) Å found in the 'A-frame' complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$ (Cowie & Dwight, 1979) and $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (Kubiak & Eisenberg, 1977) [DPM =

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* Tables of structure factors, anisotropic thermal parameters, r.m.s. amplitudes of displacement, H-atom positions, torsion angles, non-essential bond distances and angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52128 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters and equivalent isotropic thermal parameters*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
Rh(1)	0·24652 (3)	0·09148 (5)	0·56580 (2)	2·633 (9)
Rh(2)	0·30537 (3)	0·20952 (5)	0·68204 (2)	2·544 (9)
Rh(3)	0·13253 (3)	0·15240 (5)	0·65991 (2)	2·514 (9)
Cl(1)	0·3230 (1)	0·2703 (2)	0·58458 (7)	3·63 (3)
Cl(2)	0·1953 (1)	0·3406 (2)	0.68583 (8)	3·75 (3)
Cl(3)	0·1308 (1)	0·2138 (2)	0·56119 (7)	3·90 (3)
P(11)	0·1751 (1)	−0·0625 (2)	0·54524 (7)	3·10 (3)
P(12)	0·3531 (1)	−0·0049 (2)	0·56578 (8)	3·31 (3)
P(21)	0·4021 (1)	0·0905 (2)	0·67899 (7)	2·92 (3)
P(22)	0·2899 (1)	0·1863 (2)	0·77171 (7)	2·88 (3)
P(31)	0·0645 (1)	0·0016 (2)	0·63020 (7)	3·35 (4)
P(32)	0·1314 (1)	0·1079 (2)	0·74931 (7)	2·90 (3)
F(111)	0·1476 (3)	−0·0735 (5)	0·4810 (2)	5·8 (1)
F(112)	0·2078 (3)	−0·1938 (4)	0·5504 (2)	5·3 (1)
F(121)	0·3551 (3)	−0·1448 (4)	0·5559 (3)	6·4 (1)
F(122)	0·4051 (3)	0·0245 (6)	0·5153 (2)	6·3 (1)
F(211)	0·4162 (3)	−0·0074 (4)	0·7268 (2)	4·8 (1)
F(212)	0·4830 (2)	0·1509 (5)	0·6869 (2)	4·7 (1)
F(221)	0·3493 (2)	0·1179 (4)	0·8110 (2)	4·28 (9)
F(222)	0·2938 (3)	0·3077 (4)	0·8074 (2)	5·0 (1)
F(311)	0·0389 (3)	−0·0993 (5)	0·6720 (2)	5·2 (1)
F(312)	−0·0186 (3)	0·0361 (6)	0·6073 (2)	5·9 (1)
F(321)	0·1062 (3)	−0·0194 (5)	0·7689 (2)	5·7 (1)
F(322)	0·0709 (3)	0·1778 (6)	0·7834 (2)	5·8 (1)
N(1)	0·4175 (3)	0·0071 (6)	0·6210 (3)	3·5 (1)
N(2)	0·2093 (3)	0·1269 (5)	0·7933 (2)	2·9 (1)
N(3)	0·0913 (3)	−0·0833 (6)	0·5759 (2)	3·6 (1)
C(1)	0·4923 (5)	−0·0623 (9)	0·6190 (4)	5·8 (2)
C(2)	0·2008 (4)	0·1064 (8)	0·8574 (3)	3·9 (2)
C(3)	0·0387 (5)	−0·183 (1)	0·5536 (4)	6·1 (2)

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

Rh(1)—Cl(1)	2·398 (1)	Rh(3)—Cl(3)	2·389 (1)
Rh(1)—Cl(3)	2·412 (1)	Rh(3)—P(31)	2·128 (1)
Rh(1)—P(11)	2·136 (1)	Rh(3)—P(32)	2·134 (1)
Rh(1)—P(12)	2·129 (1)	P(11)—N(3)	1·666 (4)
Rh(2)—Cl(1)	2·395 (1)	P(12)—N(1)	1·661 (4)
Rh(2)—Cl(2)	2·396 (1)	P(21)—N(1)	1·662 (4)
Rh(2)—P(21)	2·131 (1)	P(22)—N(2)	1·644 (3)
Rh(2)—P(22)	2·129 (1)	P(31)—N(3)	1·655 (3)
Rh(3)—Cl(2)	2·400 (1)	P(32)—N(2)	1·663 (3)
Cl(1)—Rh(1)—Cl(3)	90·01 (4)	Cl(3)—Rh(3)—P(31)	86·02 (5)
Cl(1)—Rh(1)—P(11)	176·82 (4)	Cl(3)—Rh(3)—P(32)	176·58 (4)
Cl(1)—Rh(1)—P(12)	86·43 (4)	P(31)—Rh(3)—P(32)	95·94 (4)
Cl(3)—Rh(1)—P(11)	87·84 (5)	Rh(1)—Cl(1)—Rh(2)	81·16 (3)
Cl(3)—Rh(1)—P(12)	175·18 (5)	Rh(2)—Cl(2)—Rh(3)	79·78 (3)
P(11)—Rh(1)—P(12)	95·57 (5)	Rh(1)—Cl(3)—Rh(3)	80·29 (3)
Cl(1)—Rh(2)—Cl(2)	90·46 (4)	Rh(1)—P(11)—N(3)	121·3 (1)
Cl(1)—Rh(2)—P(21)	90·02 (4)	Rh(1)—P(12)—N(1)	120·5 (1)
Cl(1)—Rh(2)—P(22)	170·67 (4)	Rh(2)—P(21)—N(1)	121·7 (1)
Cl(2)—Rh(2)—P(21)	179·09 (4)	Rh(2)—P(22)—N(2)	119·9 (1)
Cl(2)—Rh(2)—P(22)	83·97 (4)	Rh(3)—P(31)—N(3)	120·9 (1)
P(21)—Rh(2)—P(22)	95·66 (4)	Rh(3)—P(32)—N(2)	121·4 (1)
Cl(2)—Rh(3)—Cl(3)	88·82 (4)	P(12)—N(1)—P(21)	122·6 (2)
Cl(2)—Rh(3)—P(31)	171·57 (5)	P(22)—N(2)—P(32)	122·5 (2)
Cl(2)—Rh(3)—P(32)	88·91 (4)	P(11)—N(3)—P(31)	122·3 (2)
Rh(1)···Rh(2)	3·1180 (4)	Rh(1)—Rh(2)—Rh(3)	59·97 (1)
Rh(1)···Rh(3)	3·0956 (4)	Rh(1)—Rh(3)—Rh(2)	60·69 (1)
Rh(2)···Rh(3)	3·0755 (4)	Rh(2)—Rh(1)—Rh(3)	59·33 (1)

bis(diphenylphosphino)methane], respectively. Also, the Rh—Cl—Rh angles compare well with the values typically observed (*ca* 80–95°) where no formal Rh—Rh bond exists (Dahl, Martell & Wampler, 1961; Ibers & Snyder, 1962; Bonnet, Jeannin, Kalck, Maisonnat & Poilblanc, 1975; Coetzer & Gafner, 1970) and contrasts with the value of 66·51 (4)° found in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]BPh_4$ (Cowie, Mague & Sanger, 1978) where an Rh—Rh single bond is proposed.

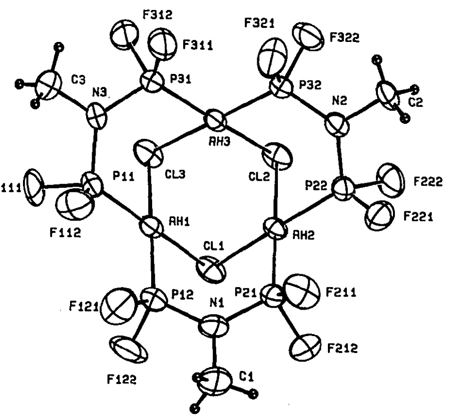

Fig. 1. View of $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$ perpendicular to the Rh_3 plane. Non-H-atom thermal ellipsoids drawn at the 30% probability level. H atoms drawn artificially small for clarity.

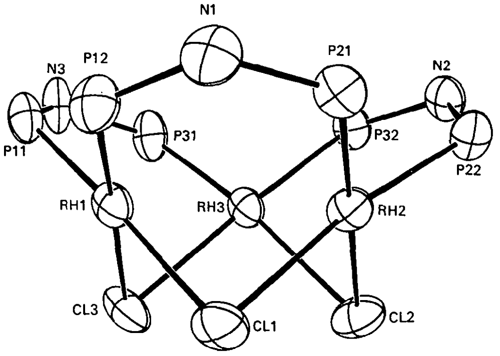

Fig. 2. Perspective view of the inner coordination sphere of $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$. Thermal ellipsoids drawn at the 50% probability level.

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Structure of $(CO)_5Cr[\overline{P(Me_3SiNH)NSNSNH}]$: the Chromium Pentacarbonyl Complex of a $P^{III}N_3S_2$ Ring

By Tristram Chivers, James F. Fait and Cees Lensink

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

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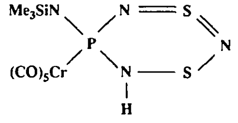
Abstract. Pentacarbonyl(5-trimethylsilylamino-4,5-dihydro-1λ^4,3-dithia-2,4,6-triaza-5-phosphorine)chromium, $[Cr(CO)_5(C_3H_{11}N_4PS_2Si)]$, $M_r = 418{\cdot}38$, monoclinic, $P2_1/n$, $a = 6{\cdot}266\,(2)$, $b = 13{\cdot}739\,(4)$, $c = 19{\cdot}959\,(5)$ Å, $\beta = 101{\cdot}97\,(3)°$, $V = 1680{\cdot}9\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}65$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}47$ cm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0{\cdot}065$ for 1810 unique observed reflections. The molecule is an octahedral chromium complex in which the $Cr(CO)_5$ group occupies the axial position at the P atom of a six-membered $P^{III}N_3S_2$ ligand. The ring adopts a half-boat conformation with the N(H) nitrogen out of the plane of the other five ring atoms. The ring contains two short [1·560 (6) and 1·571 (7) Å] and two long [1·654 (7) and 1·684 (6) Å] S—N bonds. The corresponding bond angles at sulfur are 119·4 (4) (N=S=N) and 107·6 (3)° (N—S—N).

Experimental. The title compound (I) was obtained from the reaction of $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$ with S_4N_4 followed by treatment of the product with 2-propanol (Chivers, Dhathathreyan, Lensink, Meetsma, van de Grampel & de Boer, 1989). A dark orange crystal (0·32 × 0·24 × 0·19 mm) obtained from a pentane solution was mounted on a glass fiber. Enraf–Nonius CAD-4 diffractometer, Mo radiation, graphite monochromator, ω–2θ scans. Unit-cell dimensions from 25 reflections $6 < \theta < 16°$. No indication of any higher metric symmetry or crystal decomposition. Data collected to $(\sin\theta)/\lambda$ of 0·59 Å^{-1}, $-7 < h < 7$, $0 < k < 16$, $0 < l < 23$. 3420 reflections measured, 2952 unique, 1810 reflections with $F > 4\sigma(F)$ considered observed. Two standard reflections, 3·5% intensity variation.



(I)

Solved by a combination of heavy-atom techniques and direct methods to give a partial structure of the $Cr\overline{PNSNSN}$ system. Remaining non-H atoms located in difference maps after refining the scale and thermal parameters. All H atoms bonded to carbon were located in difference Fourier maps; the hydrogens on N(1) and N(4) were not found. Corrected for absorption using *DIFABS* (Walker & Stuart, 1983). All non-H atoms refined anisotropically, with the H atoms riding on the C atom to which they are bonded with a common isotropic factor for all H atoms. Final cycles of least squares were performed with weights of $1/\sigma(F)^2$ with a maximum Δ/σ of 0·003, and $(\Delta\rho)_{max} = 0{\cdot}534$, $(\Delta\rho)_{min} = -0{\cdot}516$ e Å^{-3}, $R = 0{\cdot}065$, $wR = 0{\cdot}055$, $S = 2{\cdot}502$.

Neutral-atom scattering factors used with anomalous-dispersion corrections applied from *International Tables for X-ray Crystallography* (1974). No extinction corrections. Programs used were *XTAL* (Hall & Stewart, 1988) and *SHELX* (Sheldrick, 1976). Table 1 gives the atom coordinates for non-H atoms and Table 2 lists bond distances and angles.

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