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Dichlorotris[dimethyl(phenyl)phosphine]nitridorhenium(V), $ReNCl_2(Me_2PhP)_3$

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Abstract. $[Re(C_8H_{11}P)_3Cl_2N]$, $C_{24}H_{33}Cl_2NP_3Re$, $M_r = 686$, orthorhombic, space group *Pcab*, $a = 16{\cdot}673$ (5), $b = 16{\cdot}754$ (5), $c = 19{\cdot}200$ (6) Å, $V = 5364$ (3) Å^3, $D_x = 1{\cdot}70$ Mg m^{-3} for $Z = 8$, $\mu = 4{\cdot}7$ mm^{-1} (Mo $K\alpha$). The structure was solved by standard methods from X-ray diffractometer intensities and refined by full-matrix least squares to a final R of 0·034 for 2816 observed reflexions. The Re atom is in a distorted octahedral-coordination geometry and the Re—N bond length is 1·660 (8) Å.

Introduction. $ReNCl_2(Me_2PhP)_3$ was prepared following the method of Chatt, Falk, Leigh & Paske (1969).

A suspension of potassium perrhenate and hydrazine dihydrochloride in ethanol was mixed with dimethyl(phenyl)phosphine and heated under reflux for 72 h. The resultant yellow solution was filtered off and evaporated under low pressure to give a yellow product which was then crystallized from ethanol.

A regular prismatic specimen with a maximum dimension of 0·2 mm was chosen for the determination of the cell constants by least squares from 25 reflexions, and to collect intensities up to $\theta = 25°$ on a Philips PW 1100 diffractometer with Mo $K\alpha$ radiation. Intensities were recorded by the $\theta/2\theta$ scan technique at a rate of 2° min^{-1}. The 2816 unique reflexions above background (3σ) were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by Patterson and Fourier techniques, with full-matrix least-squares refinement. The ring C atoms were treated as rigid bodies together with the attached H atoms (C—H = 0·95 Å; $U_{\rm iso} = 0{\cdot}06$ Å^2). Difference syntheses permitted the location of the methyl H atoms. Only Re, Cl, P and N were treated anisotropically. The final conventional R was 0·034. Calculations were performed mainly with *SHELX* (Sheldrick, 1975); weighted least-squares planes were calculated using the program of Nardelli, Musatti, Domiano & Andreetti (1965). Atomic scattering factors for Re were taken from *International Tables for X-ray Crystallography* (1974), and for H from Stewart, Davidson & Simpson (1965). Those for Cl, P, C, and N were supplied internally by *SHELX*. The effects of anomalous dispersion for Re were taken in account.

Table 1. *Atomic coordinates of the bonded atoms and isotropic thermal parameters* (Å^2)

	x	y	z	$U_{\rm eq}$ or U ($\times 10^3$)
Re	0·67482 (2)	0·03049 (2)	0·92046 (2)	27 (0)*
Cl(1)	0·8315 (1)	0·0494 (1)	0·9244 (1)	44 (1)*
Cl(2)	0·7015 (2)	−0·0827 (1)	0·9972 (1)	46 (2)*
N	0·5758 (5)	0·0297 (5)	0·9113 (4)	45 (3)*
P(1)	0·6909 (2)	−0·0677 (1)	0·8258 (1)	35 (1)*
P(2)	0·6946 (1)	0·1446 (1)	0·8451 (1)	31 (1)*
P(3)	0·6633 (1)	0·1093 (1)	1·0287 (1)	31 (1)*
C(1)	0·6374 (3)	−0·0497 (4)	0·7448 (3)	34 (2)
C(2)	0·5550 (3)	−0·0357 (4)	0·7492 (3)	45 (2)
C(3)	0·5103 (3)	−0·0239 (4)	0·6887 (3)	54 (3)
C(4)	0·5478 (3)	−0·0261 (4)	0·6238 (3)	53 (3)
C(5)	0·6302 (3)	−0·0401 (4)	0·6194 (3)	50 (3)
C(6)	0·6749 (3)	−0·0519 (4)	0·6799 (3)	41 (2)
C(7)	0·7921 (7)	−0·0921 (8)	0·8016 (6)	60 (3)
C(8)	0·6478 (8)	−0·1640 (7)	0·8489 (7)	62 (3)
C(9)	0·6033 (4)	0·1844 (4)	0·8065 (3)	35 (2)
C(10)	0·5578 (4)	0·2398 (4)	0·8436 (3)	47 (3)
C(11)	0·4866 (4)	0·2693 (4)	0·8154 (3)	57 (3)
C(12)	0·4609 (4)	0·2434 (4)	0·7501 (3)	58 (3)
C(13)	0·5064 (4)	0·1879 (4)	0·7130 (3)	62 (3)
C(14)	0·5776 (4)	0·1584 (4)	0·7412 (3)	45 (2)
C(15)	0·7594 (7)	0·1289 (6)	0·7710 (5)	46 (3)
C(16)	0·7414 (6)	0·2333 (6)	0·8827 (5)	41 (2)
C(17)	0·5954 (3)	0·1949 (3)	1·0253 (3)	33 (2)
C(18)	0·6224 (3)	0·2730 (3)	1·0347 (3)	37 (2)
C(19)	0·5687 (3)	0·3366 (3)	1·0293 (3)	50 (3)
C(20)	0·4881 (3)	0·3221 (3)	1·0146 (3)	55 (3)
C(21)	0·4611 (3)	0·2440 (3)	1·0052 (3)	50 (3)
C(22)	0·5148 (3)	0·1804 (3)	1·0106 (3)	44 (3)
C(23)	0·7560 (6)	0·1478 (6)	1·0647 (5)	43 (2)
C(24)	0·6206 (7)	0·0535 (6)	1·1012 (5)	46 (3)

* Asterisks indicate $U_{\rm eq}$ values: $U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3$.

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Table 2. *Distances* (Å) *and angles* (°)

(*a*) Bond distances (Å)

Coordination

Re—N	1·660 (8)	Re—P(1)	2·467 (2)
Re—Cl(1)	2·633 (2)	Re—P(2)	2·421 (2)
Re—Cl(2)	2·442 (2)	Re—P(3)	2·469 (2)

Me_2PPh_3

P(1)—C(1)	1·82 (1)	P(2)—C(16)	1·83 (1)
P(1)—C(7)	1·80 (1)	P(3)—C(17)	1·83 (1)
P(1)—C(8)	1·82 (1)	P(3)—C(23)	1·81 (1)
P(2)—C(9)	1·82 (1)	P(3)—C(24)	1·82 (1)
P(2)—C(13)	1·81 (1)		

(*b*) Bond angles (°)

Coordination

N—Re—Cl(1)	172·2 (3)	Cl(1)—Re—P(3)	89·4 (1)
N—Re—Cl(2)	103·8 (3)	Cl(2)—Re—P(1)	84·6 (1)
N—Re—P(1)	91·4 (3)	Cl(2)—Re—P(2)	161·6 (1)
N—Re—P(2)	94·5 (3)	Cl(2)—Re—P(3)	85·5 (1)
N—Re—P(3)	91·0 (3)	P(1)—Re—P(2)	94·1 (1)
Cl(1)—Re—Cl(2)	84·0 (1)	P(1)—Re—P(3)	170·2 (1)
Cl(1)—Re—P(1)	89·6 (1)	P(2)—Re—P(3)	95·2 (1)
Cl(1)—Re—P(2)	77·7 (1)		

Me_2PPh_3

Re—P(1)—C(1)	117·8 (2)	C(1)—P(1)—C(7)	106·1 (4)
Re—P(1)—C(7)	116·4 (4)	C(1)—P(1)—C(8)	99·3 (5)
Re—P(1)—C(8)	111·6 (4)	C(7)—P(1)—C(8)	103·4 (6)
Re—P(2)—C(9)	114·8 (2)	C(9)—P(2)—C(15)	103·5 (4)
Re—P(2)—C(15)	116·0 (3)	C(9)—P(2)—C(16)	102·7 (4)
Re—P(2)—C(16)	117·7 (3)	C(15)—P(2)—C(16)	100·0 (5)
Re—P(3)—C(17)	115·9 (2)	C(17)—P(3)—C(23)	105·2 (4)
Re—P(3)—C(23)	116·4 (3)	C(17)—P(3)—C(24)	100·8 (4)
Re—P(3)—C(24)	113·5 (3)	C(23)—P(3)—C(24)	103·0 (5)

(*c*) Contact distances (Å)

N···P(1)	3·007 (9)	Cl(1)···P(3)	3·589 (3)
N···P(2)	3·041 (8)	Cl(1)···Cl(2)	3·399 (3)
N···P(3)	2·998 (8)	Cl(2)···P(1)	3·305 (3)
N···Cl(2)	3·265 (9)	Cl(2)···P(3)	3·335 (3)
Cl(1)···P(1)	3·596 (3)	P(1)···P(2)	3·578 (3)
Cl(1)···P(2)	3·174 (3)	P(2)···P(3)	3·612 (3)

Final atomic positions are given in Table 1.* Bond lengths and angles and selected mean planes are given in Tables 2 and 3.

Table 3. *Weighted least-squares planes and distances* (Å) *of atoms from the plane*

The equation of a plane is expressed as $AX + BY + CZ = D$ in orthogonal ångström space. Average e.s.d. on the displacements from the planes is 0·003 Å.

Plane I: N, Cl(1), Cl(2), P(2)

$$0\cdot104X - 0\cdot603Y - 0\cdot791Z = -13\cdot096 \text{ Å}$$

[N −0·046, Cl(1) −0·002, Cl(2) 0·002, P(2) 0·003, Re* −0·001]

Plane II: N, Cl(1), P(1), P(3)

$$-0\cdot142X + 0\cdot779Y - 0\cdot610Z = -12\cdot171 \text{ Å}$$

[N 0·520, Cl(1) 0·017, P(1) −0·024, P(3) −0·023, Re* 0·188]

Plane III: P(1), P(2), P(3), Cl(2)

$$-0\cdot991X - 0\cdot063Y - 0\cdot118Z = -13\cdot489 \text{ Å}$$

[P(1) 0·265, P(2) −0·066, P(3) 0·071, Cl(2) −0·284, Re* 0·211]

Angles between the planes (°)

I–II	90·1 (1)	I–III	88·3 (1)	II–III	80·6 (1)

* Atom not included in the plane calculation.

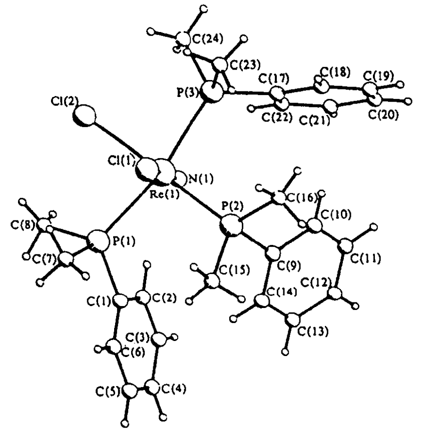

Fig. 1. The molecule $ReNCl_2(Me_2PhP)_3$ with atom numbering.

Discussion. As shown in Fig. 1 the compound is monomeric with the Re atom in a distorted octahedral-coordination geometry, with meridional Me_2PhP groups, *cis* halogen atoms, and N *trans* to Cl(1). The atoms Cl(1), Cl(2), P(2), and N are essentially coplanar, together with Re. There are significant deviations of atoms from the other two planes of Table 3. The lengths of the two *trans* Re—P bonds agree very well and are about 0·05 Å longer than Re—P(2) which is *trans* to Re—Cl(2).

The Re—Cl(1) distance of 2·633 (2) Å *trans* to N is *ca* 0·2 Å longer than Re—Cl(2), in accordance with the very strong *trans* effect the N atom exerts on the Cl atom. The Re—N distance of 1·660 (8) Å compares favourably with 1·709 (4) and 1·690 (5) Å in $ReCl_3(NC_6H_4OCH_3)(PEt_2Ph)_2$ and $ReCl_3(NC_6H_4COCH_3)(PEt_2Ph)_2$ (Bright & Ibers, 1968), with 1·685 (11) Å in $ReCl_3(NCH_3)(PEtPh_2)_2$ (Bright & Ibers, 1969), with 1·614 (13) Å in K_2OsNCl_5 (Bright & Ibers, 1969), and with 1·602 (9) Å in $ReNCl_2(PPh_3)_2$ in which the Re atom is five-coordinate (Doedens & Ibers, 1967), but significantly differs from 1·788 (11) Å found in

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38030 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$ReNCl_2(PEt_2Ph)_3$ (Corfield, Doedens & Ibers, 1967). In this case, however, the authors suggested that this 'rather long' distance could be attributed to steric effects.

Deviations from the idealized geometry in the coordination octahedron appear to be largely determined by repulsions between N and ligands. All P atoms, but especially the highly electronegative *cis* Cl atom, are bent away from the N atom until the $N\cdots L$ (*cis*) distances are at the optimum values (about 3·0 Å for $N\cdots P$ but 3·26 Å for $N\cdots Cl$). The bending away of the *cis* Cl atom in turn forces the *trans* Cl atom toward P(2), as can be appreciated from the values of the bond angles.

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Tri-μ-chloro-bis[(η-*p*-cymene)ruthenium(II)] Tetraphenylborate Methanol Solvate

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Abstract. $[Ru_2Cl_3\{p\text{-}CH_3.C_6H_4.CH(CH_3)_2\}_2]BPh_4.MeOH$, $C_{44}H_{48}BCl_3Ru_2.CH_3OH$, $M_r = 928$, monoclinic, $I2$ (non-standard setting of $C2$), $a = 27{\cdot}331\ (5)$, $b = 9{\cdot}765\ (5)$, $c = 16{\cdot}923\ (2)$ Å, $\beta = 112{\cdot}748\ (14)°$, $U = 4165$ Å^3, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}48$ g cm^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 9·3 cm^{-1}. $R = 0{\cdot}064$ for 2783 observed data with $I > 2{\cdot}5\sigma(I)$. There are two crystallographically independent Ru–Ru dimers each lying across a twofold rotation axis. Ru and Cl atoms were refined anisotropically, all benzene rings were constrained to have ideal geometries. Both $Ru\cdots Ru$ distances are 3·283 Å; $Ru\cdots Cl$ distances lie between 2·41 and 2·45 Å with Ru—Cl—Ru angles in the range 84·1 to 86·1°.

Introduction. The title compound was prepared during studies of binuclear triply bridged arene ruthenium(II) complexes (Arthur & Stephenson, 1981). A number of binuclear triply bridged ruthenium compounds have been examined by X-ray crystallography (Laing & Pope, 1976) and show $Ru\cdots Ru$ distances between 3·44 and 3·08 Å depending on the oxidation state of the Ru atoms and also the nature of the bridging ligands. NMR studies indicated a binuclear diamagnetic complex in which bridging ligands were Cl and terminal ligands π-bonded arenes with both Ru atoms in oxidation state (II). This structure determination is the first to show the nature of the binuclear Ru^{II}–π-arene interaction.

Experimental. Dark-red needles were grown from a 313–333 K petroleum ether–methylene chloride mixture. Preliminary photography showed that the space group was $I2$ or $I2/m$ (alternative settings for $C2$ and $C2/m$; the symmetry operators for $I2$ are x,y,z; $\bar{x},y,\bar{z}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$). A crystal of dimensions 0·15 × 0·15 × 0·25 (needle) mm was mounted along the needle axis. Data were collected in the ω–2θ scan mode using a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation for θ out to 25°. Of the 3869 unique reflections measured, 2783 had $I > 2{\cdot}5\sigma(I)$. No crystal decay was observed and no absorption correction was applied. The two Ru atoms were located from a Patterson map and all remaining non-H atoms were found from subsequent Fourier maps. The structure consists of two crystallographically unrelated dimers. Each $Ru\cdots Ru$ bond is bisected by a twofold rotation axis which also runs through one of the bridging chlorides. One of these molecules was found to show a significant oscillation about the $Ru\cdots Ru$ axis. Disorder was also apparent in one of the phenyl rings of the tetraphenylborate anion and also in the position of the methanol solvent

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