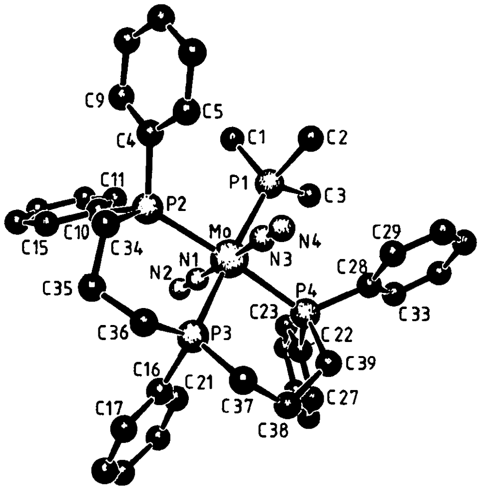

Fig. 1. Perspective view of the molecule $Mo(N_2)_2[PhP(CH_2CH_2CH_2PPh_2)_2](PMe_3)$ [*SCHAKAL* drawing (Keller, 1981)].

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Oligophosphine Ligands. XVIII.* Chlorohydrido[tris(3-dimethylphosphinopropyl)-phosphine]ruthenium(II)

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Abstract. $[Ru(Cl)(H)\{P[(CH_2)_3P(CH_3)_2]_3\}]$, $M_r = 477{\cdot}88$, trigonal, space group $P3_2$ (or its enantiomorph $P3_1$), $a = 9{\cdot}896\ (3)$, $c = 19{\cdot}589\ (5)$ Å, $V = 1661\ (1)$ Å^3, $Z = 3$, $D_x = 1{\cdot}433$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo}\ K\alpha) = 10{\cdot}05$ cm^{-1}, $F(000) = 744$, $T = 293$ K, $R = 0{\cdot}0495$ for 4168 observed reflexions. The X-ray analysis has revealed a *trans*-H—Ru—P(CH$_2$—)Me$_2$ moiety within the title complex, the overall geometry of which corresponds to distorted *cis*-octahedral. The Ru—P bond lengths vary considerably [2·217 (2)–2·343 (2) Å] and the Ru—Cl distance is 2·532 (2) Å.

Introduction. $Ru(Cl)(H)[P(CH_2CH_2CH_2PMe_2)_3]$ was prepared according to Antberg & Dahlenburg (1986). Since it was not possible from ^{1}H and ^{31}P NMR spectra to deduce whether the hydride ligand was *trans* to the bridging P(CH$_2$—)$_3$ fragment or *trans* to one of the terminal Me$_2$P substituents, we decided to establish this structural feature by means of a single-crystal diffraction study.

Experimental. Small, colourless crystals of the complex grew from hexane at room temperature, and a specimen of approximate dimensions 0·1 × 0·1 × 0·15 mm was chosen for X-ray work. Syntex $P2_1$ diffractometer; graphite-monochromated Mo $K\alpha$ radiation; crystal data from single-crystal diffractometry using 14 medium-angle reflexions within the range $15 < 2\theta < 22°$; collection of the intensity data by the $\theta/2\theta$ scan technique ($5 \leq 2\theta \leq 55°$, $0 \leq h \leq 12$, $-12 \leq k \leq 12$, $-26 \leq l \leq 26$); no unusual variation of intensity for three checks measured every 100 reflexions. 8323 data obtained, 5043 independent ($R_{\text{int}} = 0{\cdot}0163$), 4168 considered observed [$|F_o| > 4\sigma(F_o)$]. Lorentz and polarization corrections, no absorption correction. Laue symmetry ($\bar{3}$) and systematic absences ($00l$ with $l \neq 3n$) compatible with space group $P3_1$ or its enantiomorph $P3_2$. Structure solved by heavy-atom method and initially refined in $P3_1$ by full-matrix least-squares procedures on F assigning anisotropic thermal

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* Part XVII: Pietsch & Dahlenburg (1986).

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behaviour to all nonhydrogen atoms. Hydride ligand located on final difference maps and included in the refinement scheme with its positional and isotropic thermal parameters being varied. C-bonded H atoms placed on calculated positions assigning ideal geometry and a C—H distance of 0·96 Å. Convergence at $R = 0{\cdot}0514$ and $wR = 0{\cdot}0584$. The alternative space group $P3_2$ gave the marginally lower residuals $R = 0{\cdot}0495$ and $wR = 0{\cdot}0559$, and was thus preferred. Ratio of observations to number of variables >20; function minimized $\sum w(|F_o| - |F_c|)^2$ with weights $w = (\sigma^2|F_o| + 0{\cdot}0011|F_o|^2)^{-1}$. Maximum shift/e.s.d. in final cycle 0·04, maximum height on final difference map 0·8 e Å^{-3}. Computer program *SHELX* (Sheldrick, 1976). Complex neutral-atom scattering factors from *SHELX* and, for Ru, from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are given in Table 1, and selected bond lengths and angles in Table 2.* Fig. 1 shows the molecule, together with the atom-numbering scheme.

The complex adopts a considerably distorted pseudo-octahedral coordination with the hydride ligand *trans* to one of the terminal Me$_2$P substituents of the tetrakis-(tertiary) phosphine. As a consequence of the different *trans*-bond weakening influences of the ligated H, P and Cl donors, the Ru—P bond lengths exhibit significant variations: *trans*-atom Cl 2·217 (2) *trans*-group PMe$_2$ 2·310 (2), and *trans*-ligand H 2·343 (2) Å. The Ru—Cl distance of 2·532 (2) Å is comparable with that found in RuCl$_2$[P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$] for the Ru—Cl moiety *trans* to the bridging P(CH$_2$—)$_3$ group [2·521 (1) Å] (Antberg & Dahlenburg, 1986). The position of the hydride ligand is 1·38 (12) Å from the metal atom. In view of the limited accuracy of this structural parameter it is difficult to compare the Ru—H bond distance of the complex under discussion with those of other hydro derivatives of Ru^{II}. For the structurally related inner coordination spheres of the dimer μ-[CH$_2$P(Me)CH$_2$CH$_2$PMe$_2$]$_2$[HRu(Me$_2$PCH$_2$CH$_2$PMe$_2$)]$_2$ the Ru—H separations amount to 1·47 (7) and 1·83 (7) Å (Cotton, Hunter & Frenz, 1975), whereas in the monomeric naphthyl compound, *cis*-Ru(H)(C$_{10}$H$_7$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$, *d*(Ru—H) measures 1·7 Å (Gregory, Ibekwe, Kilbourn & Russell, 1971).

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Table 1. *Positional and thermal parameters*

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} tensor).

	x	y	z	U_{eq}(Å^2)
Ru	1·00440 (5)	0·49795 (5)	1·00000 (0)	0·0305 (4)
P(1)	1·1948 (2)	0·7583 (2)	1·0005 (1)	0·0421 (18)
P(2)	0·7975 (2)	0·5173 (2)	1·0475 (1)	0·0480 (18)
P(3)	0·8857 (3)	0·2351 (2)	0·9746 (1)	0·0438 (18)
P(4)	1·0877 (2)	0·4719 (2)	1·1016 (1)	0·0412 (17)
Cl	0·9225 (3)	0·5222 (3)	0·8802 (1)	0·0545 (20)
C(11)	1·186 (1)	0·913 (1)	1·046 (1)	0·086 (14)
C(12)	1·247 (1)	0·848 (1)	0·916 (1)	0·067 (11)
C(13)	1·386 (1)	0·787 (1)	1·025 (1)	0·103 (18)
C(14)	1·401 (1)	0·720 (2)	1·086 (1)	0·083 (13)
C(15)	1·298 (1)	0·548 (1)	1·106 (1)	0·066 (10)
C(21)	0·741 (1)	0·642 (1)	1·001 (1)	0·091 (13)
C(22)	0·607 (1)	0·346 (1)	1·060 (1)	0·071 (11)
C(23)	0·830 (1)	0·604 (1)	1·133 (1)	0·068 (10)
C(24)	0·887 (1)	0·530 (1)	1·186 (1)	0·060 (9)
C(25)	1·055 (1)	0·567 (1)	1·176 (1)	0·054 (8)
C(31)	0·698 (1)	0·140 (1)	0·929 (1)	0·069 (11)
C(32)	1·000 (1)	0·188 (1)	0·915 (1)	0·084 (13)
C(33)	0·849 (1)	0·096 (1)	1·043 (1)	0·057 (9)
C(34)	0·986 (1)	0·146 (1)	1·092 (1)	0·079 (12)
C(35)	1·013 (1)	0·276 (1)	1·140 (1)	0·058 (8)
H	1·116 (14)	0·489 (13)	0·961 (5)	0·10 (4)

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

P(1)—Ru	2·310 (2)	P(4)—Ru	2·217 (2)
P(2)—Ru	2·343 (2)	Cl—Ru	2·532 (2)
P(3)—Ru	2·310 (2)	H—Ru	1·38 (12)
P(2)—Ru—P(1)	99·5 (1)	Cl—Ru—P(3)	84·3 (1)
P(3)—Ru—P(1)	158·3 (1)	Cl—Ru—P(4)	175·9 (1)
P(3)—Ru—P(2)	101·8 (1)	H—Ru—P(1)	81 (5)
P(4)—Ru—P(1)	89·0 (1)	H—Ru—P(2)	170 (4)
P(4)—Ru—P(2)	92·5 (1)	H—Ru—P(3)	78 (5)
P(4)—Ru—P(3)	94·1 (1)	H—Ru—P(4)	97 (4)
Cl—Ru—P(1)	91·1 (1)	H—Ru—Cl	79 (4)
Cl—Ru—P(2)	91·5 (1)		

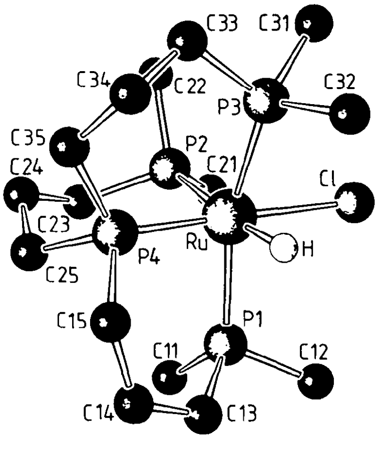

Fig. 1. *SCHAKAL* drawing (Keller, 1981) of the molecule Ru(H)(Cl)[P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$].

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* Tables of structure factors, anisotropic thermal parameters, and H-atom positional and isotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42900 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Aqua[(1*SR*,4*RS*,8*SR*,11*RS*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) Perchlorate Monohydrate

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Abstract. $[Cu(C_{14}H_{32}N_4)(H_2O)](ClO_4)_2.H_2O$, $M_r = 554{\cdot}91$, monoclinic, $P2_1/c$, $a = 9{\cdot}784\,(3)$, $b = 14{\cdot}081\,(3)$, $c = 16{\cdot}958\,(5)$ Å, $\beta = 91{\cdot}26\,(3)°$, $U = 2335{\cdot}85$ Å^3, $Z = 4$, $D_x = 1{\cdot}5785$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}258$ mm^{-1}, $F(000) = 1166{\cdot}0$, $T = 296\,(4)$ K, $R(F) = 0{\cdot}060$ for 2240 observed reflections $[I > 3\sigma(I)]$. The coordination geometry about the Cu^{II} atom is a buckled square-based pyramid. This complex has the (1*SR*,4*RS*,8*SR*,11*RS*) configuration at the chiral N centers, with the four attached methyl groups on the same side of the macrocyclic plane. The two six-membered chelate rings exhibit a chair form, and the two five-membered rings take distorted eclipsed forms.

Introduction. Preparations of divalent transition-metal complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) have been reported by Barefield & Wagner (1973). An X-ray structure determination of $[Ni(tmc)N_3]ClO_4$ prepared by combining the Ni^{II} ion with the free ligand has shown that the macrocyclic ligand is coordinated in a planar fashion with all four methyl groups on the same side of the metal–nitrogen plane. In this work, the crystal structure of $[Cu(tmc)H_2O](ClO_4)_2.H_2O$ obtained by direct interaction of the Cu^{II} ion with tmc is reported.

Experimental. The tmc was prepared according to a previously described procedure (Barefield & Wagner, 1973). Aqueous solutions of $Cu(ClO_4)_2.6H_2O$ (1·8 g in 20 ml) and tmc (1·25 g in 30 ml) were mixed and the mixture was filtered. The blue solution was evaporated under a gentle stream of air to give dark-blue crystals. The single crystals used in the X-ray analysis were obtained by recrystallization from an aqueous solution at room temperature, and were sealed in a capillary tube containing some moisture. The crystals thus grown are plate-like and blue and deteriorate gradually on exposure to the air.

Experimental data and structure solution parameters together with standard refinement procedures are listed in Table 1.

Table 1. *Experimental data and structure-refinement parameters*

Crystal size (mm)	0·3 × 0·3 × 0·35
Diffractometer and data-collection technique used	ω–2θ scan, four-circle diffractometer (Nonius CAD-4) with graphite monochromator
Scan width (2θ)	2 (0·7 + 0·35 tanθ)°
Number and θ range used for measuring lattice parameters	25 reflections with 11 < 2θ < 20°
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Transmission factor	0·632
Max. (sinθ)/λ in intensity measurement	0·5947 Å^{-1}
Range of *hkl*	0,0,–23 to 5,19,23
Standard reflections and intensity variation	$0\bar{8}0$, $\bar{4}49$, $53\bar{5}$; < 4%
Number of reflections measured	5741
Number of unique reflections	2240 $[I > 3\sigma(I)]$
Method used to solve the structure	Patterson and Fourier methods
Max. height in final difference Fourier synthesis	0·39 e Å^{-3}
Parameters refined, nonhydrogen atoms	Coordinates, occupancies and anisotropic temperature factors (281 parameters)
hydrogen atoms	Coordinates and isotropic temperature factor (144 parameters)
Quantity minimized	$\sum w(\Delta F)^2$; $w = 1/\sigma_F^2$
Atomic scattering factors, f' and f''	*International Tables for X-ray Crystallography* (1974)
Number of reflections per parameter	6
$R(F)$ and wR	0·060 and 0·058
S	2·769
R_{int}	0·032
Average, max. Δ/σ	0·58, 0·96
Programs used	*THUCP* (Hsieh & Lee, 1985); *XTAL*83 (Stewart, Hall, Alden, Olthof-Hazekamp, Doherty, Pagoaga & Norden, 1983); *ORTEP*II (Johnson, 1976)
Computer	CDC Cyber-840 and IBM PC-XT

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