

## X-ray Crystal Structure of *trans*-Dichloro(hexaphenyl-1,4,7,10-tetraphosphadecane)ruthenium(II)

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### Abstract

The synthesis and X-ray crystal structure of  $\text{RuCl}_2[(\text{Ph})_2\text{PC}_2\text{H}_4\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{P}(\text{Ph})_2]$  are reported. The crystals are monoclinic, space group  $P2_1/c$  with cell dimensions  $a = 10.389(2)$  Å,  $b = 27.815(5)$  Å,  $c = 14.377(3)$  Å,  $\beta = 109.17(1)^\circ$ . The structure was solved by the direct method; least-squares refinement converged to a final conventional  $R = 5.51\%$  for 3692 independent observed reflections collected by counter methods. The structure consists of discrete monomeric molecules. The central metal atom is octahedrally coordinated with the four phosphorus atoms of the ligand in the equatorial plane and with the two chlorine atoms in the axial positions. The  $\text{Ph}_2\text{P}-\text{Ru}$  and  $\text{PhP}-\text{Ru}$  pairs have an average distance of 2.392 Å and 2.295 Å, respectively.

### Introduction

Studies of metal complexes with polydentate phosphines are becoming increasingly important [1–6]. Compounds with the ligand  $(\text{Ph})_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})_2$  (TETRAPHOS 1) have been reported for several transition metal ions. The ligand can bond in several possible ways with one metal center or bridge several metal atoms. Thus the ligand can be: 1) monoligate monometallic as in  $\text{CH}_3\text{COFe}(\text{CO})(\text{TETRAPHOS 1})$  ( $\text{C}_5\text{H}_5$ ); 2) biligate monometallic in  $(\text{TETRAPHOS 1})\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}$ ),  $\text{CH}_3\text{Mn}(\text{CO})_3(\text{TETRAPHOS 1})$ ,  $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{TETRAPHOS 1})]\text{Cl}$ ,  $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{TETRAPHOS 1})$ ; 3) triligate monometallic:  $(\text{TETRAPHOS 1})\text{MCl}_3$  ( $\text{M} = \text{Rh}, \text{Re}$ ),  $(\text{TETRAPHOS 1})\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{Mo}$ ),  $(\text{TETRAPHOS 1})\text{Mn}(\text{CO})_2\text{Br}$  and  $[\text{C}_5\text{H}_5\text{Fe}(\text{TETRAPHOS 1})]^+$ ; 4) tetraligate monometallic as in  $[(\text{TETRAPHOS 1})\text{M}]^{2+}$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ),  $[(\text{TETRAPHOS 1})\text{CoCl}]^+$ , and  $[(\text{TETRAPHOS 1})\text{Rh}]^+$ ; 5) triligate bimetallic in  $[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})(\text{NO})_2(\text{TETRAPHOS 1})](\text{PF}_6)_2$ ; 6) tetraligate tetrametallic in  $(\text{TETRAPHOS 1})[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$  and  $(\text{TETRAPHOS 1})[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$  [7]. Sacconi and coworkers have reported the preparation of Fe(II), Co(II) and Ni(II) penta-coordinate complexes of general formula  $(\text{MLX})\text{BPh}_4$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) with  $\text{L} = (\text{TETRAPHOS 1})$  [8]. The X-ray structures of  $[\text{Fe}(\text{TETRAPHOS 1})\text{Br}](\text{BPh}_4 \cdot \text{CH}_2\text{Cl}_2)$  [9] and  $\text{FeH}(\text{N}_2)(\text{TETRAPHOS 1})\text{Br} \cdot \text{C}_5\text{H}_5\text{OH}$  [10] have been determined. For ruthenium the following complexes with their possible structures have been reported:  $[\text{RuCl}(\text{DMSO})(\text{TETRAPHOS 1})]\text{Cl}$  [11–13],  $[\text{RuCl}(\text{CO})(\text{TETRAPHOS 1})]\text{Cl}$  and  $\text{Ru}(\text{H})\text{Cl}(\text{TETRAPHOS 1})$  (tetraligate monometallic);  $\text{Ru}(\text{H})\text{Cl}(\text{DMSO})(\text{TETRAPHOS 1})$  (triligate monometallic) and  $[\text{RuCl}_2(\text{CO})_2]_2(\text{TETRAPHOS 1})$  (tetraligate bimetallic) [11]. In addition to the compounds of polyphosphines mentioned, Baacke [12] has reported a series of Ni, Pd, Pt and Mo complexes with tetradentate ligands analogous to (TETRAPHOS 1). These compounds are tetraligate monometallic of general formula  $[\text{MX}(\text{RR}'\text{P}(\text{CH}_2)_3\text{PR}''(\text{CH}_2)_3\text{PRR}')]\text{Y}$  ( $\text{M} = \text{Ni}$ ;  $\text{X} = \text{Y} = \text{Br}^-$ ;  $\text{R} = \text{R}'' = \text{Ph}, \text{Me}$ ;  $\text{R}' = \text{H}$ ;  $\text{R} = \text{R}' = \text{H}$ ;  $\text{R}'' = \text{Ph}, \text{Me}$ ;  $\text{R} = \text{R}'' = \text{Me}$ ;  $\text{R} = \text{CH}_2\text{OH}$ ;  $\text{M} = \text{Ni}$ ;  $\text{X} = \text{Br}$ ;  $\text{Y} = \text{BPh}_4, \text{PF}_6$ ;  $\text{R} = \text{R}'' = \text{Ph}$ ;  $\text{R}' = \text{H}$ ;  $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{X} = \text{Y} = \text{Cl}$ ;  $\text{R} = \text{R}'' = \text{Ph}$ ;  $\text{R}' = \text{H}$ ), and tetraligate bimetallic:  $[(\text{Mo}(\text{CO})_4)_2(\text{Ph}(\text{H})\text{P}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_3\text{P}(\text{H})\text{Ph})]$ .

In our laboratory we have been interested in the synthesis and catalytic properties of Ru complexes with polyphosphines, including those with (TETRAPHOS 1) [13]. In the present work we report the X-ray structure of one of the Ru compounds prepared using this ligand.

### Experimental

#### Synthesis

The synthesis of the compound was carried out under Ar atmosphere, using Schlenk glassware and syringes for transference. All solvents were dried appropriately and kept under argon. (TETRAPHOS 1) was obtained commercially from Strem & Co.

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*Trans*-Ru(pyr)<sub>4</sub>Cl<sub>2</sub> was synthesized as reported by Wilkinson [14] and Raichart [15].

In a typical reaction about  $5 \times 10^{-4}$  mol of Ru(pyr)<sub>4</sub>Cl<sub>2</sub> and an equimolar quantity of the polyphosphine are refluxed in toluene (40 ml) for 8 hours (1 at. pressure). After evaporating and cooling to  $-10^\circ\text{C}$  an orange solid precipitated (60% yield) which was slowly recrystallized in CHCl<sub>3</sub> to give orange-yellow crystals suitable for X-ray work.

#### Characterization

Elemental analysis: experimental\*, C = 60.16%, H = 5.24%, Cl, 7.61%; calculated for RuCl<sub>2</sub>(TETRAPHOS 1), C = 59.86%, H = 5.02%, Cl = 8.41%. UV-Visible (CHCl<sub>3</sub>) bands at 395 nm (str) ( $\epsilon = 1.7 \times 10^4$ ), UV(str). IR spectra show the bands of coordinated (TETRAPHOS 1). Cyclic voltammetry (in acetone, vs. Ag-AgCl reference electrode, 0.1 M (n-But<sub>4</sub>N)PF<sub>6</sub> supporting electrolyte, Pt working electrode) shows only one reversible wave at +0.62 V. NMR(<sup>31</sup>P) spectra\*\* (in CDCl<sub>3</sub>, Bruker HFX-10, vs. H<sub>3</sub>PO<sub>4</sub>, external) show the following (<sup>1</sup>H decoupled) A<sub>2</sub>B<sub>2</sub> pattern: +38.5, +46.4 ppm (external P) and +96.5, +104.4 ppm (internal P, forming part of two five-membered rings with the Ru),  $J_{PP} = 288$  Hz.

#### Unit Cell and Collection of Intensity Data

Precession and Weissenberg photographs taken at room temperature<sup>†</sup> with CuK<sub>α</sub> radiation showed the orange-yellow prismatic crystals of RuCl<sub>2</sub>(TETRAPHOS 1) to be monoclinic with  $P2_1/c$  (No. 14,  $C_{2h}^5$ ) [16] space group symmetry. A crystal of approximate dimensions 0.25 mm × 0.15 mm × 0.12 mm was mounted on a glass fibre and used for accurate cell parameters determination and the gathering of intensity data on an automated four-circle Philips PW 1100 diffractometer. By a least-squares procedure applied to the four angles of 25 strong reflections the following lattice parameters:  $a = 10.389(2)$  Å,  $b = 27.815(5)$  Å,  $c = 14.377(3)$  Å,  $\beta = 109.17(1)^\circ$ , and  $V = 3924$  Å<sup>3</sup>, were determined. The calculated density of 1.426 g/cm<sup>3</sup> for four molecules per unit cell is consistent with the experimental value of 1.43 g/cm<sup>3</sup>, determined by the flotation method in a solution of bromobenzene and benzene. Intensity data with  $6^\circ \leq 2\theta \leq 90^\circ$  were measured with graphite monochromated MoK<sub>α</sub> radiation and after Lp corrections the measured 3850 reflections were reduced to 3692 independent reflections with

$I > 3\sigma(I)$ . For MoK<sub>α</sub> radiation the linear absorption coefficient ( $\mu$ ) of  $6.49 \text{ cm}^{-1}$  results in a  $\mu R_{\text{max}}$  value of 0.08 for which the variations of absorption correction factors with  $\theta$  are negligible [17]. The weighted disagreement factor for the least-squares refinement was 3.4%.

#### Determination and Refinement of the Structure

The best E-map obtained by multisolution  $\Sigma_2$  sign expansion [18] led to the set of coordinates for the independent ruthenium, chlorine and phosphorus atoms. From subsequent difference maps the remaining nonhydrogen atoms were located. Several cycles of isotropic least-squares refinement with unitary weights gave a discrepancy value of  $R = [\sum \|F_o\| - |F_c|] / \sum F_o \times 100 = 8.82\%$ . Additional cycles of least-squares refinement with anisotropic thermal parameters for the ruthenium, chlorine and phosphorus and isotropic for all carbons reduced the discrepancy factor to  $R = 5.62\%$ . Finally all hydrogen atoms were placed in geometrically calculated positions and refined as rigid groups with the constraint that all C-H bonds were 1.00 Å, which is the usual C-H refined distance in organic compounds. The final refinement was done by introducing two additional isotropic factors for the hydrogens, namely, one for the Ph-ring's and a different one for the ethylenics. The final weights used were  $w = 1.38/\sigma^2(F)$  and the refinement converged to  $R = 5.51\%$  and  $R_w = [\sum w \|F_o\| - |F_c|]^2 / \sum w |F_o|^2]^{1/2} \times 100 = 5.53\%$ . The atomic scattering factors were taken from the usual source [19]. The effects of anomalous dispersion were included in  $F_c$  for all atoms using  $\Delta f'$  and  $\Delta f''$  given by Cromer [20]. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ . All the calculations were done with the SHELX system [18] on a Burroughs B5900 computer at the Universidad de Los Andes. Tables of weighted least-squares planes and the distance of the atoms from their respective planes, root-mean-squares amplitudes of thermal vibrations and observed and calculated structure factors are available from the Editor. A difference map based on final thermal and positional parameters showed no electron density peaks greater than 0.6 e/Å<sup>3</sup>. Final positional parameters are given in Tables I-II and the derived bond lengths and angles in Tables III-IV. Figure 1 shows two different views of the molecule with the atomic labelling and the torsional angles.

## Results and Discussion

#### Description of the Structure

The RuCl<sub>2</sub>(TETRAPHOS 1) complex exists in the solid state as discrete monomeric molecules. The closest intermolecular approaches are H(122)⋯H(422) = 2.683 Å and H(115)⋯H(413) = 2.736

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<sup>†</sup>Photographs taken by Lic. Alicia Játem, Departamento de Química, Facultad de Ciencias, ULA, Mérida, Venezuela.

TABLE I. Atom Co-ordinates ( $\times 10^4$ ) and Isotropic Temperature Factors ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U
Ru	3808(1)	3480(1)	2116(1)	
Cl(1)	4024(2)	3140(1)	3708(2)	
Cl(2)	3576(2)	3853(1)	516(2)	
P(1)	1820(2)	3913(1)	2106(2)	
P(2)	2245(2)	2927(1)	1225(2)	
P(3)	5298(2)	2959(1)	1769(2)	
P(4)	5791(2)	3968(1)	2817(2)	
C(111)	961(9)	3477(4)	3565(7)	60(3)
C(112)	803(11)	3454(4)	4500(8)	73(3)
C(113)	1174(11)	3830(4)	5110(9)	80(3)
C(114)	1566(11)	4265(4)	4844(9)	84(4)
C(115)	1712(10)	4296(4)	3884(8)	66(3)
C(116)	1384(9)	3906(3)	3247(7)	49(2)
C(121)	247(9)	4768(3)	1659(7)	54(3)
C(122)	-10(10)	5245(4)	1332(7)	59(3)
C(123)	955(9)	5501(4)	1094(7)	57(3)
C(124)	2187(9)	5291(3)	1161(7)	54(3)
C(125)	2453(9)	4808(3)	1478(6)	43(2)
C(126)	1473(8)	4545(3)	1722(6)	39(2)
C(211)	2409(9)	2161(3)	2517(7)	53(2)
C(212)	1878(10)	1779(4)	2931(8)	65(3)
C(213)	495(11)	1705(4)	2624(8)	70(3)
C(214)	-385(12)	1969(4)	1916(8)	81(3)
C(215)	132(10)	2352(4)	1486(7)	60(3)
C(216)	1521(8)	2449(3)	1790(6)	39(2)
C(311)	6524(8)	2491(3)	3565(6)	45(2)
C(312)	6974(10)	2099(4)	4187(8)	62(3)
C(313)	6894(11)	1641(4)	3790(8)	75(3)
C(314)	6382(11)	1571(4)	2796(8)	79(3)
C(315)	5896(9)	1964(3)	2157(8)	61(3)
C(316)	5970(8)	2433(3)	2548(6)	43(2)
C(411)	5396(9)	4174(3)	4593(6)	45(2)
C(412)	5813(11)	4324(4)	5594(8)	65(3)
C(413)	7142(11)	4388(4)	6088(9)	76(3)
C(414)	8135(12)	4327(4)	5675(8)	76(3)
C(415)	7743(10)	4181(3)	4657(7)	57(3)
C(416)	6381(8)	4109(3)	4142(6)	35(2)
C(421)	6235(9)	4612(3)	1422(6)	46(2)
C(422)	6377(9)	5060(3)	1046(7)	53(3)
C(423)	6298(10)	5470(4)	1553(7)	59(3)
C(424)	6075(10)	5440(4)	2450(8)	65(3)
C(425)	5941(9)	4983(3)	2837(7)	52(3)
C(426)	6013(8)	4561(3)	2328(6)	35(2)
C(1)	320(9)	3596(3)	1191(6)	46(2)
C(2)	765(8)	3278(3)	489(6)	44(2)
C(3)	2980(8)	2577(3)	404(6)	44(2)
C(4)	4437(8)	2731(3)	520(6)	42(2)
C(5)	6826(8)	3293(3)	1766(6)	42(2)
C(6)	7273(8)	3633(3)	2656(6)	42(2)

$\text{\AA}$  which are greater than the corresponding van der Waals distances, indicating that in the crystalline state the arrangement of the four molecules per unit cell has no unusual intermolecular interactions. The ruthenium atom is hexa-coordinated by the four phosphorus atoms of the ligand and by the two

TABLE II. Hydrogen Atom Co-ordinates ( $\times 10^4$ ) and Isotropic Temperature Factors ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U
H(111)	772(9)	3187(4)	3129(7)	111(7)
H(112)	417(11)	3159(4)	4707(8)	111(7)
H(113)	1166(11)	3792(4)	5799(9)	111(7)
H(114)	1742(11)	4549(4)	5296(9)	111(7)
H(115)	2052(10)	4600(4)	3675(8)	111(7)
H(121)	-459(9)	4587(3)	1849(7)	111(7)
H(122)	-906(10)	5397(4)	1273(7)	111(7)
H(123)	771(9)	5843(4)	870(7)	111(7)
H(124)	2893(9)	5480(3)	985(7)	111(7)
H(125)	3346(9)	4656(3)	1525(6)	111(7)
H(211)	3411(9)	2225(3)	2744(7)	111(7)
H(212)	2503(10)	1565(4)	3440(8)	111(7)
H(213)	127(11)	1443(4)	2943(8)	111(7)
H(214)	-1384(12)	1898(4)	1695(8)	111(7)
H(215)	-511(10)	2553(4)	959(7)	111(7)
H(311)	6600(8)	2821(3)	3853(6)	111(7)
H(312)	7354(10)	2147(4)	4916(8)	111(7)
H(313)	7214(11)	1359(4)	4238(8)	111(7)
H(314)	6352(11)	1239(4)	2520(8)	111(7)
H(315)	5501(9)	1910(3)	1431(8)	111(7)
H(411)	4411(9)	4116(3)	4220(6)	111(7)
H(412)	5120(11)	4382(4)	5927(8)	111(7)
H(413)	7416(11)	4485(4)	6796(9)	111(7)
H(414)	9114(12)	4382(4)	6068(8)	111(7)
H(415)	8448(10)	4133(3)	4330(7)	111(7)
H(421)	6292(9)	4318(3)	1039(6)	111(7)
H(422)	6538(9)	5085(3)	399(7)	111(7)
H(423)	6403(10)	5792(4)	1276(7)	111(7)
H(424)	6009(10)	5739(4)	2820(8)	111(7)
H(425)	5791(9)	4961(3)	3488(7)	111(7)
H(11)	-336(9)	3842(3)	799(6)	50(7)
H(12)	-140(9)	3391(3)	1560(6)	50(7)
H(21)	6(8)	3057(3)	129(6)	50(7)
H(22)	1021(8)	3483(3)	5(6)	50(7)
H(31)	2396(8)	2629(3)	-296(6)	50(7)
H(32)	2982(8)	2228(3)	571(6)	50(7)
H(41)	4951(8)	2448(3)	395(6)	50(7)
H(42)	4413(8)	2990(3)	32(6)	50(7)
H(51)	6612(8)	3485(3)	1146(6)	50(7)
H(52)	7578(8)	3062(3)	1804(6)	50(7)
H(61)	7719(8)	3440(3)	3263(6)	50(7)
H(62)	7940(8)	3870(3)	2559(6)	50(7)

chlorine atoms in a distorted octahedral arrangement, with all four phosphorus in the equatorial plane and the two chlorine in the axial positions (see Fig. 1). Deviations from the octahedral geometry can be considered significant on the P-Ru-P angles. Thus, the axial Cl-Ru-Cl angle is  $178^\circ$ , all P atoms are within 0.002  $\text{\AA}$  on its least-squares plane and the angles between the axial chlorines and the equatorial plane are  $90^\circ$  and  $88^\circ$ , respectively, where Cl(1), the bent chlorine, corresponds to that surrounded by four phenyl rings. The Cl(1) displacement from the Ru-Cl(2) bond direction

TABLE III. Bond Lengths (Å).

Cl(1)–Ru	2.417(4)
Cl(2)–Ru	2.463(4)
P(1)–Ru	2.388(4)
P(2)–Ru	2.298(4)
P(3)–Ru	2.292(4)
P(4)–Ru	2.395(4)
C(116)–P(1)	1.839(11)
C(126)–P(1)	1.841(10)
C(1)–P(1)	1.896(10)
C(216)–P(2)	1.843(10)
C(2)–P(2)	1.837(10)
C(3)–P(2)	1.873(10)
C(316)–P(3)	1.835(11)
C(4)–P(3)	1.836(10)
C(5)–P(3)	1.841(10)
C(416)–P(4)	1.842(10)
C(426)–P(4)	1.838(10)
C(6)–P(4)	1.877(10)
C(1)–C(2)	1.522(13)
C(3)–C(4)	1.528(12)
C(5)–C(6)	1.535(13)
C(111)–C(112)	1.409(14)
C(112)–C(113)	1.338(15)
C(113)–C(114)	1.370(16)
C(114)–C(115)	1.439(15)
C(115)–C(116)	1.388(13)
C(116)–C(111)	1.400(13)
C(121)–C(122)	1.402(13)
C(122)–C(123)	1.363(13)
C(123)–C(124)	1.382(13)
C(124)–C(125)	1.417(13)
C(125)–C(126)	1.390(12)
C(126)–C(121)	1.394(12)
C(211)–C(212)	1.417(13)
C(212)–C(213)	1.373(14)
C(213)–C(214)	1.342(14)
C(214)–C(215)	1.423(14)
C(215)–C(216)	1.390(12)
C(216)–C(211)	1.396(12)
C(311)–C(312)	1.391(13)
C(312)–C(313)	1.385(14)
C(313)–C(314)	1.367(15)
C(314)–C(315)	1.410(14)
C(315)–C(316)	1.413(13)
C(316)–C(311)	1.393(13)
C(411)–C(412)	1.423(13)
C(412)–C(413)	1.340(14)
C(413)–C(414)	1.359(14)
C(414)–C(415)	1.443(14)
C(415)–C(416)	1.379(12)

TABLE III. (continued)

C(416)–C(411)	1.392(12)
C(421)–C(422)	1.385(12)
C(422)–C(423)	1.371(13)
C(423)–C(424)	1.386(14)
C(424)–C(425)	1.413(13)
C(425)–C(426)	1.398(12)
C(426)–C(421)	1.402(12)

TABLE IV. Bond Angles (deg.)

Cl(2)–Ru–Cl(1)	178.0(1)
P(1)–Ru–Cl(1)	90.8(2)
P(1)–Ru–Cl(2)	87.8(2)
P(2)–Ru–Cl(1)	95.5(2)
P(2)–Ru–Cl(2)	85.8(2)
P(2)–Ru–P(1)	83.3(2)
P(3)–Ru–Cl(1)	95.8(2)
P(3)–Ru–Cl(2)	85.9(2)
P(3)–Ru–P(1)	164.3(1)
P(3)–Ru–P(2)	81.9(2)
P(4)–Ru–Cl(1)	91.4(2)
P(4)–Ru–Cl(2)	87.8(2)
P(4)–Ru–P(1)	109.8(2)
P(4)–Ru–P(2)	165.2(1)
P(4)–Ru–P(3)	84.3(2)
C(116)–P(1)–Ru	117.0(4)
C(126)–P(1)–Ru	124.6(4)
C(126)–P(1)–C(116)	101.3(5)
C(1)–P(1)–Ru	106.3(4)
C(1)–P(1)–C(116)	103.1(5)
C(1)–P(1)–C(126)	101.6(5)
C(216)–P(2)–Ru	123.6(4)
C(2)–P(2)–Ru	105.6(4)
C(2)–P(2)–C(216)	104.6(5)
C(3)–P(2)–Ru	109.8(4)
C(3)–P(2)–C(216)	102.4(5)
C(3)–P(2)–C(2)	110.5(5)
C(316)–P(3)–Ru	121.3(4)
C(4)–P(3)–Ru	106.5(4)
C(4)–P(3)–C(316)	106.7(5)
C(5)–P(3)–Ru	108.9(4)
C(5)–P(3)–C(316)	104.4(5)
C(5)–P(3)–C(4)	108.4(5)
C(416)–P(4)–Ru	120.3(4)
C(426)–P(4)–Ru	123.2(4)
C(426)–P(4)–C(416)	99.3(5)
C(6)–P(4)–Ru	107.1(4)
C(6)–P(4)–C(416)	103.0(5)
C(6)–P(4)–C(426)	100.8(5)
C(2)–C(1)–P(1)	111.7(7)
C(1)–C(2)–P(2)	107.9(7)

(continued on facing page)

TABLE IV. (continued)

C(4)–C(3)–P(2)	112.4(7)
C(3)–C(4)–P(3)	110.5(7)
C(6)–C(5)–P(3)	109.5(7)
C(5)–C(6)–P(4)	111.8(7)
C(113)–C(112)–C(111)	119.4(12)
C(114)–C(113)–C(112)	123.8(13)
C(115)–C(114)–C(113)	117.0(13)
C(116)–C(115)–C(114)	120.5(11)
C(115)–C(116)–C(111)	119.0(10)
C(111)–C(116)–P(1)	119.8(8)
C(115)–C(116)–P(1)	120.1(8)
C(126)–C(121)–C(122)	120.9(10)
C(123)–C(122)–C(121)	120.3(10)
C(124)–C(123)–C(122)	120.1(10)
C(125)–C(124)–C(123)	120.2(10)
C(126)–C(125)–C(124)	119.9(9)
C(125)–C(126)–C(121)	118.6(9)
C(121)–C(126)–P(1)	122.0(8)
C(125)–C(126)–P(1)	119.4(7)
C(216)–C(211)–C(212)	119.5(10)
C(213)–C(212)–C(211)	119.2(11)
C(214)–C(213)–C(212)	122.8(12)
C(215)–C(214)–C(213)	118.7(12)
C(216)–C(215)–C(214)	120.6(11)
C(215)–C(216)–C(211)	119.2(9)
C(211)–C(216)–P(2)	118.5(7)
C(215)–C(216)–P(2)	122.2(8)

TABLE IV. (continued)

C(316)–C(311)–C(312)	121.3(10)
C(313)–C(312)–C(311)	119.6(11)
C(314)–C(313)–C(312)	120.8(12)
C(315)–C(314)–C(313)	120.2(12)
C(316)–C(315)–C(314)	119.7(11)
C(315)–C(316)–C(311)	118.3(9)
C(311)–C(316)–P(3)	119.4(8)
C(315)–C(316)–P(3)	122.2(8)
C(416)–C(411)–C(412)	118.9(9)
C(413)–C(412)–C(411)	119.6(11)
C(414)–C(413)–C(412)	123.4(12)
C(415)–C(414)–C(413)	118.4(12)
C(416)–C(415)–C(414)	118.9(10)
C(415)–C(416)–C(411)	120.8(9)
C(411)–C(416)–P(4)	117.6(7)
C(415)–C(416)–P(4)	121.4(7)
C(426)–C(421)–C(422)	121.7(10)
C(423)–C(422)–C(421)	120.5(10)
C(424)–C(423)–C(422)	120.2(11)
C(425)–C(424)–C(423)	119.2(11)
C(426)–C(425)–C(424)	121.4(10)
C(425)–C(426)–C(421)	117.0(9)
C(421)–C(426)–P(4)	121.7(7)
C(425)–C(426)–P(4)	121.3(7)

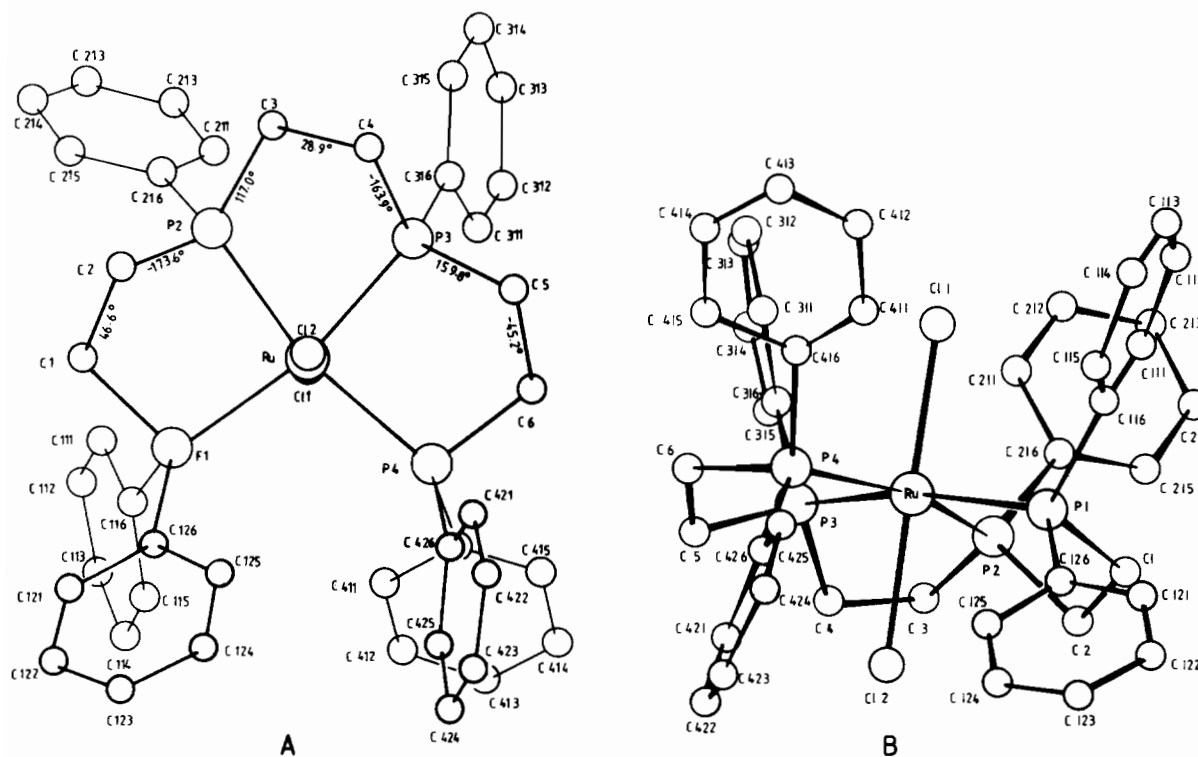


Fig. 1. RuCl<sub>2</sub>(TETRAPHOS 1) perspective views. A) Onto the plane containing all four P atoms, showing the torsional angles around the chelate rings. B) Onto the plane containing the Ru and the two Cl atoms.

TABLE V. (TETRAPHOS 1) as Tetradentate Monometallic Ligand.

		Hexacoordinate		
		Pentacoordinate	Hexacoordinate	
		Fe(TETRAPHOS 1)BrBPh <sub>4</sub>	FeH(N <sub>2</sub> )(TETRAPHOS 1)Br	RuCl <sub>2</sub> (TETRAPHOS 1)
Bonds (Å)	M–P	2.300	2.238	2.388
		2.180	2.213	2.298
		2.246	2.199	2.292
		2.215	2.239	2.395
Bond Angles (°)	P(1)–M–P(2)	80.7	85.9	83.3
	P(1)–M–P(3)	164.1	153.9	164.3
	P(1)–M–P(4)	97.2	101.4	109.8
	P(2)–M–P(3)	83.7	82.5	81.9
	P(2)–M–P(4)	105.0	165.1	165.2
	P(3)–M–P(4)	84.1	85.4	84.3
Dihedral Angles (°) between Phenyl Planes	Ph(a)–Ph(b)	90.9	59.6	71.4
	Ph(e)–Ph(f)	89.0	95.1	80.7
	Ph(b)–Ph(c)	159.2	90.5	103.9
	Ph(c)–Ph(d)	121.6	53.2	71.2
	Ph(d)–Ph(e)	116.2	107.5	82.3
	Ph(e)–Ph(b)	153.1	69.2	66.3
Angles between Phenyl Planes and its Attached M–P Bond (°)	M–P(1)–Ph(a)	21.9	3.5	4.8
	M–P(1)–Ph(b)	59.5	63.0	66.4
	M–P(2)–Ph(c)	8.6	40.3	37.4
	M–P(3)–Ph(d)	26.7	35.7	43.17
	M–P(4)–Ph(e)	10.6	33.1	25.8
	M–P(4)–Ph(d)	65.2	61.7	53.4
M–P <sub>4</sub> (Plane) Distance (Å)		0.7872	0.3426	0.1246

is toward the Ph<sub>2</sub>P–Ru–PPh<sub>2</sub> area in such a way that its projection on the equatorial plane is closer to the Ru–P(1) than to the Ru–P(4) bond projection. The Ru–Cl(1) distance of 2.418(4) Å is significantly shorter than the Ru–Cl(2) distance of 2.463(4) Å. The ruthenium atom is 0.12 Å from the equatorial plane, displaced towards Cl(1) and the values of the P–Ru–P angles are 81.9° in the central chelate ring, 83.3° and 84.3° in the external chelate rings and 109.8° for the Ph<sub>2</sub>P–Ru–PPh<sub>2</sub> angle. The P–Ru–P chelate rings angles are in the same range of values reported so far for the tetraligand monometallic (TETRAPHOS 1) metal complexes X-ray studied: 80.7°, 83.7° and 84.1° in [Fe(TETRAPHOS 1)Br](BPh<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>) [9], and 86.0°, 82.5° and 85.4° in FeH(N<sub>2</sub>)(TETRAPHOS 1)Br·C<sub>5</sub>H<sub>5</sub>OH [10], while the Ph<sub>2</sub>P–Ru–PPh<sub>2</sub> angle is significantly larger than the reported ones: 97.2° [9] and 101.4° [10].

#### Tetradentate Monometallic (TETRAPHOS 1) Ligand

(TETRAPHOS 1) as tetradentate monometallic behaves as a flexible ligand which can present different coordination geometries with a nonplanar MP<sub>4</sub> moiety. The nonplanarity observed in [Fe(TETRAPHOS 1)Br](BPh<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>) [9], a distorted

trigonal bipyramid compound, has been proposed to be a consequence of the penta-coordination geometry, while in FeH(N<sub>2</sub>)(TETRAPHOS 1)Br·C<sub>5</sub>H<sub>5</sub>OH [10], a distorted octahedral complex, the nonequivalence of the axial groups (N<sub>2</sub> and H) and the angular requirements of the linear ligand are supposed to be responsible for the observed bending of the MP<sub>4</sub> fragment towards the hydride. However, the nonplanarity observed in the compound *trans*-dichloro (TETRAPHOS 1)ruthenium reported here, which presents two identical axial groups, indicates that the angular requirements of the linear ligand with a tetrahedral P and C atoms chain, could be the main factor determining the MP<sub>4</sub> configuration.

Table V gives a comparison of the known geometrical details of the (TETRAPHOS 1) as a tetradentate monometallic ligand. It can be observed that the four M–P distances in (TETRAPHOS 1) as tetraligand monometallic are either similar or significantly different. The reported anisotropy of the M–P bond distances in Fe(TETRAPHOS 1)Br(BPh<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>) has been ascribed [9] to a possible formation of a partially conjugated system in two different planar arrangements (each involving one phenyl ring, one P and the metal atom) which are present in this

structure. In *trans*-dichloro(TETRAPHOS 1) ruthenium the four Ru–P distances can be considered equivalent in pairs, with mean values of 2.295 Å for those bonding two adjacent chelate rings and 2.392 Å for those belonging to only one ring. However, a similar explanation to that given for the shortening of the Ru–P bonds in Fe(TETRAPHOS 1)Br(BPh<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>) cannot be given for the Ru–P(2) and Ru–P(3) shortening observed in the present compound. In fact, c and d phenyl rings (Fig. 1) are not coplanar with the metal atom, they are at about 40° from its attached Ru–P bond. Moreover, in *trans*-dichloro-(TETRAPHOS 1)ruthenium, contrary to what has been suggested, the observed near coplanarity is between the longest Ru–P bonds and one of their attached phenyl rings. These facts point out that coplanarity between a phenyl ring and its joined M–P bond by itself does not account for the anisotropy of the M–P distances present in some tetraligand monometallic (TETRAPHOS 1) complexes.

The coordination around the P atoms is distorted tetrahedral with angles between 99.4–124.6° with a mean value of 109.21°, where the (Ph)C–P–C(Ph) angles are the narrowest with an average value of 100.4° and (Ph)C–P–Ru the widest with a mean value of 121.7°. All phenyl rings are planar with a deviation less than 0.01 Å, the C–C distances in the range of 1.339–1.442 Å with a mean value of 1.391 Å, and the angles centered on C atoms bonded to P, except for C(416), presenting its usual characteristic [21] of being less than 120°. The displacement of the attached phosphorus atoms from the least-squares planes of the phenyl rings do not exceed 0.13 Å. The dihedral angle between the two phenyl rings in each PPh<sub>2</sub> moiety, 99° and 101°, are in the range reported for other diphenylphosphinoethane complexes (73.5–107.6°) [22]. The six (Ph)C–P distances can be considered identical with a mean value of 1.840 Å, and the (Eth)C–P bonds in the range of 1.836–1.895 Å. The (Eth)C–(Eth)C–P angles and the (Eth)C–(Eth)C distances can be considered identical with average values of 110.7° and 1.529 Å, respectively.

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