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Structure of (Carbonyl)chloro(hydrido)tris(methyldiphenylphosphine)ruthenium(II)

By Majid Motevalli and Michael B. Hursthouse*

Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS, England

and Andrew R. Barron and Geoffrey Wilkinson*

Chemistry Department, Imperial College, South Kensington, London SW7 2AY, England

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Abstract. $[RuClH(C_{13}H_{13}P)_3(CO)]$, $M_r = 766·1$, triclinic, $P\bar{1}$, $a = 10·125$ (2), $b = 11·364$ (4), $c = 17·312$ (3) Å, $\alpha = 99·38$ (3), $\beta = 88·41$ (2), $\gamma = 110·06$ (2)°, $U = 1845·21$ Å^3, $Z = 2$, $D_x = 1·38$ Mg m^{-3}, $F(000) = 788$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 26·46$ mm^{-1}, room temperature, final $R = 0·027$ for 5647 counter reflections with $F_o > 4\sigma(F_o)$. Coordination about Ru is octahedral with a meridional arrangement of the phosphines and a *trans* arrangement for the chloro and the carbonyl ligands. The hydrido appears to exert a strong *trans* influence with the Ru—P bond *trans* to it 0·08 Å longer than the others.

Introduction. A wide range of carbonyl, dicarbonyl and hydrido carbonyl complexes of ruthenium(II) containing tertiary phosphine and halogen ligands has been reported in the literature (Bennett, Bruce & Matheson, 1982). In the formation of these carbonyl complexes from Ru halides, the CO ligand is obtained by the decarbonylation of oxygen-containing organic solvents (*e.g.* alcohol). This process often coincides with the replacement of a halide ligand with a hydrido species. An example of this is the formation of (carbonyl)-chloro(hydrido)tris(triphenylphosphine)ruthenium(II) from ruthenium trichloride and triphenylphosphine refluxed in methanol (Vaska & DiLuzio, 1961). A *mer* configuration has been proposed for this complex from ^{1}H and ^{31}P nuclear magnetic resonance data. As is common for hydrido complexes stabilized by tertiary phosphines the coupling between H and P is greater in the *trans* than in the *cis* position. However, the above complex exhibits a greater than usual *trans* coupling, $J(\text{P—H}) = 109$ Hz (Lupin & Shaw, 1968). *Trans* couplings for other hydridophosphine ruthenium complexes are in the region of 70–80 Hz (*e.g.* Hallman, McGarvey & Wilkinson, 1968). In order to ascertain the structural significance of this enlarged coupling we now report the crystal structure of the methyldiphenylphosphine complex.

Experimental. (Carbonyl)chloro(hydrido)tris(triphenylphosphine)ruthenium(II) prepared according to the literature method (Stephenson & Wilkinson, 1966) and refluxed in toluene in the presence of excess methyldiphenylphosphine gave on cooling to 253 K colourless crystals of the title compound.

Crystals mounted under argon in thin-walled glass capillaries. Specimen with dimensions 0·8 × 0·5 × 0·2 mm used for X-ray work. Lattice parameters determined by least-squares fitting of setting angles of reflections, $10 \leq \theta \leq 20°$, automatically centred on CAD-4 diffractometer. Intensities collected with graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\omega/2\theta$ scan mode, scan rate 1·2–6·6° min^{-1}, scan width $(0·8 + 0·15 \tan\theta)°$, aperture setting 4 mm, $1·5 \leq \theta \leq 25°$, 6699 reflections measured, 6480 unique, $R_{\text{int}} = 0·0002$, 5647 $[F_o > 4\sigma(F_o)]$ used in refinement, index range h −12/12, k −13/13, l 0/20. Three intensity control reflections, monitored after every hour of data collection, showed no decay. Structure solved by heavy-atom method.

Least-squares anisotropic refinement (based on F) of positions of non-hydrogen atoms and free isotropic refinement of hydrogens (except H atoms on the phenyl rings, fixed using C—H = 0·96 Å) gave final $R = 0·027$, $wR = 0·037$, $w = 1/[\sigma^2(F_o) + 0·00005F_o]$. $\Delta/\sigma(\text{max.}) = 0·024$, residual electron density $-0·36 \leq \Delta\rho \leq +0·46$ e Å^{-3}. Scattering factor data from *International Tables for X-ray Crystallography* (1974). No corrections for absorption or secondary extinction. Final atomic parameters are listed in Table 1.† Computer programs used: *SHELX76* (Sheldrick, 1976); *SNOOPY* (Davies, 1983).

Discussion. A diagram of the molecular structure is given in Fig. 1; selected bond lengths and angles are given in Table 2. The three phosphines are arranged in a

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* Authors to whom correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43347 (41 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. *Fractional coordinates* ($\times 10^5$ *for* Ru, P, Cl; $\times 10^4$ *for* O, C, H) *and equivalent isotropic temperature factors* [$Å^2 \times 10^4$; U_{iso} ($Å^2 \times 10^3$) *for* H *atom*] *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}*
Ru(1)	24324 (2)	13735 (2)	26022 (1)	288
P(1)	37431 (7)	8584 (6)	35878 (4)	320
P(2)	42483 (7)	31586 (6)	22629 (4)	343
P(3)	2258 (7)	−1866 (6)	26888 (4)	353
Cl(1)	18842 (7)	28599 (7)	36761 (4)	471
O(1)	2770 (2)	−392 (2)	1207 (1)	577
C(1)	2688 (3)	300 (2)	1754 (2)	376
C(2)	2717 (3)	326 (3)	4435 (2)	460
C(3)	4485 (2)	−381 (1)	3226 (1)	344
C(4)	5057 (2)	−374 (1)	2484 (1)	402
C(5)	5604 (2)	−1315 (1)	2168 (1)	491
C(6)	5578 (2)	−2263 (1)	2595 (1)	558
C(7)	5005 (2)	−2270 (1)	3337 (1)	576
C(8)	4459 (2)	−1329 (1)	3653 (1)	470
C(9)	5281 (2)	2104 (2)	4117 (1)	348
C(10)	5052 (2)	3070 (2)	4651 (1)	443
C(11)	6187 (2)	4030 (2)	5060 (1)	494
C(12)	7552 (2)	4023 (2)	4935 (1)	547
C(13)	7781 (2)	3057 (2)	4401 (1)	625
C(14)	6646 (2)	2097 (2)	3992 (1)	492
C(15)	5271 (4)	4417 (3)	3033 (2)	402
C(16)	3667 (2)	4145 (2)	1698 (1)	520
C(17)	4565 (2)	4847 (2)	1183 (1)	504
C(18)	4143 (2)	5659 (2)	805 (1)	613
C(19)	2823 (2)	5770 (2)	942 (1)	684
C(20)	1925 (2)	5069 (2)	1457 (1)	708
C(21)	2347 (2)	4256 (2)	1835 (1)	542
C(22)	5615 (2)	2797 (2)	1655 (1)	438
C(23)	5243 (2)	2149 (2)	893 (1)	561
C(24)	6246 (2)	1828 (2)	419 (1)	812
C(25)	7620 (2)	2156 (2)	707 (1)	1053
C(26)	7992 (2)	2805 (2)	1469 (1)	1038
C(27)	6989 (2)	3125 (2)	1943 (1)	737
C(28)	−1053 (3)	464 (4)	3166 (2)	533
C(29)	−631 (2)	−986 (2)	1724 (1)	437
C(30)	−855 (2)	−242 (2)	1210 (1)	671
C(31)	−1457 (2)	−808 (2)	467 (1)	860
C(32)	−1835 (2)	−2118 (2)	237 (1)	859
C(33)	−1610 (2)	−2862 (2)	751 (1)	928
C(34)	−1008 (2)	−2296 (2)	1494 (1)	697
C(35)	51 (2)	−1558 (2)	3159 (1)	412
C(36)	−986 (2)	−1969 (2)	3698 (1)	648
C(37)	−1110 (2)	−3049 (2)	4020 (1)	895
C(38)	−196 (2)	−3718 (2)	3803 (1)	849
C(39)	841 (2)	−3307 (2)	3263 (1)	644
C(40)	965 (2)	−2227 (2)	2941 (1)	483
H(1)	1485 (25)	1827 (23)	2076 (14)	36 (7)

* $U_{eq} = \frac{1}{3}$(trace **U**).

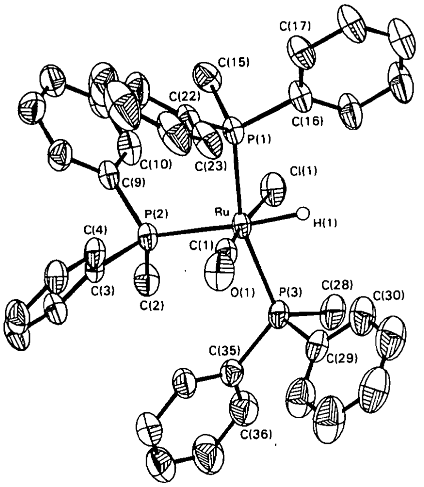

Fig. 1. The molecular structure of the title compound. Only the hydrogen bound to ruthenium is shown.

Table 2. *Bond lengths* (Å) *and angles* (°)

P(1)–Ru(1)	2·449 (3)	P(2)–Ru(1)	2·369 (3)
P(3)–Ru(1)	2·347 (3)	Cl(1)–Ru(1)	2·486 (3)
C(1)–Ru(1)	1·823 (5)	H(1)–Ru(1)	1·598 (26)
C(2)–P(1)	1·836 (5)	C(3)–P(1)	1·831 (4)
C(9)–P(1)	1·847 (4)	C(15)–P(2)	1·826 (5)
C(16)–P(2)	1·845 (4)	C(22)–P(2)	1·833 (4)
C(28)–P(3)	1·818 (5)	C(29)–P(3)	1·848 (4)
C(35)–P(3)	1·827 (4)		
C(1)–O(1)	1·150 (4)		

P(2)–Ru(1)–P(1)	98·5 (2)	P(3)–Ru(1)–P(1)	99·1 (2)
P(3)–Ru(1)–P(2)	162·3 (1)	Cl(1)–Ru(1)–P(1)	87·0 (2)
Cl(1)–Ru(1)–P(2)	87·2 (2)	Cl(1)–Ru(1)–P(3)	91·4 (2)
C(1)–Ru(1)–P(1)	98·8 (2)	C(1)–Ru(1)–P(2)	93·4 (2)
C(1)–Ru(1)–P(3)	86·2 (2)	C(1)–Ru(1)–Cl(1)	174·0 (1)
H(1)–Ru(1)–P(1)	170·8 (9)	H(1)–Ru–P(2)	82·7 (9)
H(1)–Ru(1)–P(3)	79·5 (9)	H(1)–Ru(1)–Cl(1)	83·9 (10)
H(1)–Ru(1)–C(1)	90·3 (10)	C(3)–P(1)–Ru(1)	114·9 (2)
C(2)–P(1)–Ru(1)	114·4 (2)	C(9)–P(1)–Ru(1)	120·1 (2)
C(3)–P(1)–C(2)	105·0 (2)	C(9)–P(1)–C(3)	101·3 (2)
C(9)–P(1)–C(2)	98·7 (2)	C(16)–P(2)–Ru(1)	115·2 (2)
C(15)–P(2)–Ru(1)	119·7 (2)	C(22)–P(2)–Ru(1)	115·3 (2)
C(16)–P(2)–C(15)	98·3 (2)	C(22)–P(2)–C(16)	102·9 (2)
C(22)–P(2)–C(15)	102·7 (2)	C(29)–P(3)–Ru(1)	113·3 (2)
C(28)–P(3)–Ru(1)	112·7 (2)	C(35)–P(3)–Ru(1)	120·9 (2)
C(29)–P(3)–C(28)	102·9 (2)	C(35)–P(3)–C(29)	100·6 (6)
C(35)–P(3)–C(28)	104·3 (2)		
O(1)–C(1)–Ru(1)	176·0 (2)		

meridional configuration, and of the other three ligands the carbonyl and chlorine are *trans* to each other. The most notable geometrical feature of the structure is the large *trans* influence exerted by the hydrido ligand, where the Ru—P bond *trans* to it is some 0·08 Å longer than the other two mutually *trans* Ru—P distances. This is somewhat larger than the difference found for other ruthenium hydride complexes, *e.g.* *cis*-$RuH_2(dppe)_2$ where the difference is only 0·03 Å (Pertici, Vitulli, Porzio & Zocchi, 1979). The large *trans* effect implied by the ^1H NMR spectrum is thus present in the molecular structure. It is also worth drawing attention to the fact that the P—C distances do not reflect the expected differences between P—C(sp^3) and P—C(sp^2) bonds and that, indeed, the values found vary considerably, from 1·818 (5) to 1·847 (4) Å. We can only presume that this variation, if real (and we have found similar variations in many of the structures of metal–phosphine complexes determined in our laboratory), is a feature of the packing environment, which may also be responsible for the variation in the angles at the P atoms, *e.g.* Ru—P—C = 112·7 (2)–120·9 (2)°, C—P—C = 98·3 (2)–105·0 (2)°.

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Structure du Complexe Diperchlorate de μ-[Fumarato(2−)-O',O'',O''',O'''']-bis{[N,N-bis(diéthylaminoéthyl)-éthylamine]cuivre(II)}

PAR P. CHARPIN, G. CHEVRIER, M. LANCE ET D. VIGNER

CEA-CEN/SACLAY-IRDI/DESICP/DPC/SCM, 91191 *Gif sur Yvette CEDEX, France*

ET F. TINTI

Laboratoire de Spectrochimie des Eléments de Transition, Bâtiment 420, *UA* 420, *Université Paris Sud*, 91405 *Orsay CEDEX, France*

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Abstract. $[Cu_2(C_4H_2O_4)(C_{14}H_{33}N_3)_2](ClO_4)_2$, $M_r = 926{\cdot}92$, monoclinic, $P2_1/n$, $a = 8{\cdot}6808\ (9)$, $b = 14{\cdot}892\ (2)$, $c = 16{\cdot}679\ (3)$ Å, $\beta = 90{\cdot}52\ (1)°$, $V = 2156{\cdot}0\ (9)$ Å^3, $Z = 2$, $D_x = 1{\cdot}428$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}1727$ mm^{-1}, $F(000) = 980$, $T = 295$ K, $R = 0{\cdot}052$ for 1970 independent reflections $[I > 3\sigma(I)]$. The Cu atom is 4 + 1* coordinated by the three N atoms of the complex ligand [Cu—N: 2·087 (7), 2·008 (7) and 2·061 (6) Å] and the O atoms O(1) [Cu—O(1): 1·969 (5) Å] and O(2) [Cu—O(2): 2·424 (6) Å] of the bridging fumaric acid molecule in the dimeric unit; the distance between the two Cu atoms is 6·313 (2) Å.

Introduction. Les acides carboxyliques peuvent former des complexes de coordination binucléaires avec les ions cuivriques Cu^{II} (Deacon & Philips, 1980; Doedens, 1976; Kato, Jonassen & Fanning, 1964; Melnik, 1981).

En modifiant la stéréochimie des complexes, on peut moduler le couplage antiferromagnétique entre ions métalliques (Hendrickson & Kahn, 1985; Julve, Verdaguer, Kahn, Gleizes & Philoche-Levisalles, 1983, 1984).

En augmentant la distance Cu^{II}–Cu^{II}, on peut explorer la limite supérieure de l'interaction antiferromagnétique possible entre centres paramagnétiques (Tinti, Julve, Verdaguer & Solans, 1986; Verdaguer, Gouteron, Jeannin, Jeannin & Kahn, 1984).

Nous utilisons ici l'acide fumarique, à la place de l'acide oxalique, en vue d'augmenter la distance Cu^{II}—Cu^{II} en ajoutant formellement une double liaison C=C entre les groupements carboxylates.

Partie expérimentale. La solution mère est préparée à partir d'un mélange de $Cu(ClO_4)_2.6H_2O$ (2 mmol) et de N,N-bis(diéthylaminoéthyl)-éthylamine (2 mmol) en solution aqueuse, filtrée puis additionnée d'une solution aqueuse d'un sel disodium d'acide fumarique (1 mmol). Les monocristaux sont obtenus par évaporation lente à la température ambiante de la solution bleu foncé résultante.

Cristal, de couleur bleu-violet, de forme prismatique (250 × 600 × 250 µm). Groupe centrosymétrique $P2_1/n$ imposé par les conditions d'extinction $h0l$: $h + l = 2n$, $0k0$: $k = 2n$ et par les tests statistiques. Intensités mesurées à l'aide d'un diffractomètre automatique Enraf–Nonius CAD-4 équipé d'un monochromateur graphite. Paramètres cristallins obtenus à partir de 25 réflexions indépendantes ($8 < \theta < 12°$); corrections de Lorentz–polarisation, d'absorption empirique fonction de $\sin\theta/\lambda$ (max., min. correction = 1,162, 0,777); facteurs de diffusion des atomes neutres des *International Tables for X-ray Crystallography* (1974) corrigés de f' et f'' (respectivement 0,263 et 1,266 pour le cuivre); facteurs de température des atomes du Cu, Cl, O et N rendus anisotropes; atomes d'H introduits en position calculée dans le dernier affinement avec un facteur d'agitation thermique fixé à 5 Å^2, et contraints de suivre leurs atomes de carbone. Les programmes utilisés sont les programmes *SDP*/Enraf–Nonius (Frenz, 1983); mesures effectuées entre 1 et 25° (θ);

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