

PREPARATION OF OCTAHEDRAL HYDRIDO-AQUO-RUTHENIUM(II) COMPLEXES, AND STRUCTURAL CHARACTERISATION OF HYDRIDOQUODICARBONYLBIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II) TETRAFLUOROBORATE

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(Received August 22nd, 1980)

Summary

Reaction of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ with tetrafluoroboric acid/water gives $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$. Carbonylation of the latter compound yields $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$. In the IR spectra of these compounds, splitting of the asymmetric BF_4^- stretching band indicated the possibility of a coordinated tetrafluoroborato ligand, but an X-ray study of $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$ shows that the BF_4^- is not coordinated to the metal, but is involved in a network of hydrogen bonds with the coordinated water molecule and the ethanol molecule of crystallisation. The crystals are monoclinic, space group $P2_1$, with $Z = 2$ in a unit cell of dimensions $a = 9.3959(4)$, $b = 22.695(1)$, $c = 9.7878(3)$ Å, $\beta = 109.12(1)^\circ$. The observed and calculated densities are 1.39 and 1.404 g cm^{-3} respectively. The structure was solved by conventional methods and refined using the full-matrix least-squares equations to final residuals R and R_w of 0.048 and 0.064 respectively.

The ruthenium atom is in a distorted octahedral coordination geometry. The Ru—CO distances (1.83 and $1.97(2)$ Å) differ significantly, with the longer bond situated *trans* to the hydrido ligand. The Ru—P bonds (2.329 and $2.416(5)$ Å) are also significantly different, and the P—Ru—P angle is markedly non-linear at $165.1(2)^\circ$. This asymmetry can be attributed to crystal packing forces.

Introduction

Ionic tetrafluoroborates of T_d symmetry exhibit two triply degenerate IR active modes which absorb in the $1000\text{--}1100 \text{ cm}^{-1}$ region and around 525 cm^{-1} [1]. The latter is obscured in triphenylphosphine complexes by a very

strong phosphine band in the same region. Upon coordination to a metal in a monodentate fashion the original T_d symmetry is lowered to C_{3v} and, as a consequence, the asymmetric stretch at $1000\text{--}1100\text{ cm}^{-1}$ becomes split. The magnitude of the splitting is generally considered to be proportional to the degree of association of the ligand with the metal [2].

While seeking improved preparative routes to $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$, we have had occasion to prepare the complexes $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$ and $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$. The splitting patterns of the IR bands of the tetrafluoroborate groups are such that the complexes could be formulated as containing monodentate tetrafluoroborate ligands. In order to establish unequivocally the ruthenium stereochemistry and the mode of tetrafluoroborate coordination we have determined the crystal structure of $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$.

Experimental

Preparations and spectra

$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, chlorohydridocarbonyltris(triphenylphosphine)ruthenium(II). $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (3.0 g) and triphenylphosphine (23.0 g) in 2-methoxyethanol (methyl glycol) (350 ml) were heated under reflux for 48 h. If crystals did not form after 6 h, seed crystals were added. The mixture was allowed to cool to room temperature and the cream to pale pink crystalline solid was filtered, washed with ethanol and hexane and dried at room temperature (10.3 g). Physical properties were in agreement with previously reported data [3].

$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, dihydridocarbonyltris(triphenylphosphine)ruthenium(II). $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (2.0 g), triphenylphosphine (0.2 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxyethanol (50 ml) for 20 min. The mixture was cooled in an ice-bath and the white crystalline solid was collected and washed with ethanol, water and then ethanol again. The solid was dissolved in dichloromethane with triphenylphosphine (0.1 g) (and filtered through a celite pad if any undissolved NaCl was apparent) and ethanol was added. Removal of dichloromethane afforded white crystals (1.81 g, 94%). Physical properties were in agreement with previously reported data [4].

$[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$, hydrido-aquocarbonyltris(triphenylphosphine)ruthenium(II) tetrafluoroborate. $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (1.81 g) was stirred in a degassed solution comprised of dichloromethane (70 ml), ethanol (10 ml) and tetrafluoroboric acid (ca. 40%) (1 ml) until dissolution had been effected. The slow evolution of hydrogen was evident. The dichloromethane was removed and water was added slowly until crystallisation was complete. Recrystallisation from dichloromethane-ethanol-water yielded large white crystals of the solvate $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4 \cdot \text{H}_2\text{O}$ (1.90 g, 93%). $^1\text{H NMR}$ (CDCl_3) shows τ , 7.97 [s (broad), 2 H, H_2O]. M.p. $126\text{--}128^\circ\text{C}$. Anal. Found: C, 63.73; H, 4.69; P, 9.30. $\text{C}_{55}\text{H}_{48}\text{BF}_4\text{O}_2\text{P}_3\text{Ru} \cdot \text{H}_2\text{O}$ calcd.: C, 63.53; H, 4.85; P, 8.94%. IR (Nujol mull, cm^{-1}) $\nu(\text{CO})$ 1940vs; $\nu(\text{OH})$ 3500w; $\delta(\text{OH})$ 1625w; (BF_4) 1110m, 1060s, 980m; $\delta(\text{RuH})$ 820w.

$[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$, hydrido-aquodicarbonylbis(triphenylphosphine)ruthenium(II) tetrafluoroborate. a) $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4 \cdot \text{H}_2\text{O}$ (1.0 g) was dissolved in dichloromethane-ethanol (50 ml, 1 : 1) and stirred un-

der an atmosphere of carbon monoxide (60 p.s.i.) for 1 h. The solvent was evaporated to 10 ml and the slow addition of water to the warm solution effected crystallisation. Recrystallisation from dichloromethane-ethanol-water gave the product as large colourless crystals of the water solvate $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{H}_2\text{O}$ (0.71 g, 91.6%). ^1H NMR (CDCl_3) shows τ , 8.30 [s (broad), 2 H, H_2O]. M.p. 122–125°C. Anal. Found: C, 56.85; H, 4.86; P, 6.72. $\text{C}_{38}\text{H}_{33}\text{BF}_4\text{O}_3\text{P}_2\text{Ru} \cdot \text{H}_2\text{O}$ calcd.: C, 56.66; H, 4.38; P, 7.69%. IR (Nujol mull, cm^{-1}) $\nu(\text{CO})$ 2070, 1995vs; $\nu(\text{OH})$ 3350w; $\delta(\text{OH})$ 1620w; (BF_4) 1100m, 1010s, 970s; $\delta(\text{RuH})$ 830w. b) This compound could be synthesized directly from $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ by following the instructions for the above two compounds without isolating $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3]\text{BF}_4 \cdot \text{H}_2\text{O}$. No triphenylphosphine was added to the solution.

X-ray structure

The crystals chosen for the diffraction study were recrystallised from dichloromethane-ethanol. The analysis showed that the non-coordinated water molecule had been replaced in the crystal lattice by an ethanol solvent molecule.

Crystal data

$[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_{38}\text{H}_{33}\text{O}_3\text{P}_2\text{Ru} \cdot \text{BF}_4 \cdot \text{C}_2\text{H}_6\text{O}$, $M = 833.88$. Colourless needles with diamond-shaped cross-section, monoclinic, space group $P2_1$, $a = 9.3959(4)$, $b = 22.695(1)$, $c = 9.7878(3)$ Å, $\beta = 109.12(1)^\circ$, $Z = 2$, d (flotation) = 1.39 g cm^{-3} , d (calcd.) = 1.404 g cm^{-3} , crystal dimensions $0.32 \times 0.32 \times 0.16 \text{ mm}$, $\mu = 45.11 \text{ cm}^{-1}$. Accurate unit cell parameters were obtained from a least-squares refinement of the setting angles of twelve high-theta reflections using a Hilger and Watts four-circle automatic diffractometer [5].

Intensity data, structure determination and refinement

Intensity data were recorded using CuK_α radiation to a θ limit of 56.5° using a symmetric $2\theta/\omega$ scan of 0.80° in θ at a scan speed of 0.01° per second. The background was recorded for 15 s at each end of the scan range. The data were averaged and corrected for Lorentz, polarisation and absorption effects, to yield 2493 observed reflections with I greater than $3\sigma(I)$.

The x and z coordinates of the ruthenium atom were determined from a Patterson map. Although the subsequent electron density map contained a false mirror plane, the two carbonyl ligands were found to lie within the mirror plane, and the two phosphorus atoms were symmetrically disposed above and below it. There was no indication from the shapes of these peaks that the atoms were not truly mirror related, and initial structure solution and refinement assumed the space group to be $P2_1/m$. One further atom lay in the mirror plane, approximately 2 Å from the ruthenium atom, and this was assumed to be the oxygen atom of a coordinated water molecule. The phenyl rings of the triphenylphosphine groups also closely followed the mirror symmetry. However, the tetrafluoroborate anion and ethanol solvate molecule did not refine satisfactorily in the centrosymmetric space group, and further refinement was carried out assuming the space group to be $P2_1$. The final residuals R and R_w were 0.048 and 0.064, respectively.

Final atomic positions are listed in Table 1. The atomic numbering scheme is

TABLE I

ATOMIC POSITIONS FOR $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{CH}_3\text{CH}_2\text{OH}$

Atom	x/a	y/b	z/c
Ru	0.1630(1)	0.2520	0.02860(1)
P(1)	0.1263(6)	0.3575(2)	0.0180(6)
P(2)	0.1306(6)	0.1502(2)	0.0216(6)
C(1)	0.1344(10)	0.2499(3)	0.2044(10)
C(2)	0.3846(11)	0.2475(10)	0.0985(13)
C(3)	0.8298(23)	0.2276(19)	0.4713(22)
C(4)	0.8290(32)	0.2851(15)	0.4223(36)
O(1)	0.1106(11)	0.2570(11)	0.3114(9)
O(2)	0.5138(8)	0.2528(11)	0.1372(11)
O(3)	0.1556(7)	0.2531(10)	0.8065(6)
O(4)	0.8823(13)	0.2314(7)	0.6300(11)
B	0.4941(16)	0.2480(19)	0.6489(16)
F(1)	0.4229(11)	0.2551(11)	0.7488(12)
F(2)	0.6359(13)	0.2629(14)	0.7120(16)
F(3)	0.4324(15)	0.2624(16)	0.5191(15)
F(4)	0.5344(22)	0.1940(6)	0.6434(18)
H	-0.026(13)	0.245(11)	0.957(13)
Ph1			
C(11)	0.2758(11)	0.3986(5)	0.1601(11)
C(12)	0.3692(11)	0.3757(5)	0.2886(11)
C(13)	0.4792(14)	0.4054(5)	0.3859(14)
C(14)	0.4948(12)	0.4694(5)	0.3376(12)
C(15)	0.4011(13)	0.4965(5)	0.1993(14)
C(16)	0.2973(10)	0.4598(4)	0.1203(11)
Ph2			
C(21)	0.1142(11)	0.3868(5)	0.8485(12)
C(22)	-0.0249(16)	0.4159(6)	0.7658(15)
C(23)	-0.0026(15)	0.4312(6)	0.6090(15)
C(24)	0.1315(16)	0.4198(7)	0.5775(17)
C(25)	0.2637(17)	0.3999(7)	0.6728(18)
C(26)	0.2480(14)	0.3810(5)	0.8075(14)
Ph3			
C(31)	0.9592(13)	0.3763(5)	0.0607(13)
C(32)	0.9423(9)	0.4200(4)	0.1447(9)
C(33)	0.8115(13)	0.4288(6)	0.1715(13)
C(34)	0.6836(15)	0.4006(6)	0.0898(15)
C(35)	0.6789(15)	0.3628(6)	-0.0123(16)
C(36)	0.8251(11)	0.3485(5)	-0.0149(12)
Ph4			
C(41)	0.2727(9)	0.1029(4)	0.1372(9)
C(42)	0.3570(12)	0.1253(5)	0.2706(12)
C(43)	0.4711(13)	0.0877(5)	0.3696(13)
C(44)	0.5041(16)	0.0354(7)	0.3480(17)
C(45)	0.4169(13)	0.0150(5)	0.2280(13)
C(46)	0.2934(15)	0.0454(6)	0.1077(15)
Ph5			
C(51)	0.1123(11)	0.1162(4)	0.8416(11)
C(52)	-0.0125(12)	0.0938(5)	0.7490(12)
C(53)	-0.0414(16)	0.0714(6)	0.6216(16)
C(54)	0.0805(13)	0.0752(5)	0.5709(13)
C(55)	0.2156(11)	0.1030(4)	0.6565(11)
C(56)	0.2298(12)	0.1212(5)	0.7919(12)
Ph6			
C(61)	0.9534(9)	0.1254(4)	0.0472(9)
C(62)	0.9697(15)	0.0805(6)	0.1606(15)
C(63)	0.8241(14)	0.0644(6)	0.1828(14)
C(64)	0.6911(13)	0.0953(6)	0.1108(14)
C(65)	0.6944(14)	0.1423(6)	0.0110(14)
C(66)	0.8168(14)	0.1561(6)	-0.0372(14)

TABLE 2

INTERATOMIC DISTANCES (Å) FOR [Ru(H)(H₂O)(CO)₂(PPh₃)₂]BF₄ · CH₃CH₂OH

Ru—P(1)	2.416(5)	Ru—C(1)	1.827(18)
Ru—P(2)	2.329(5)	Ru—C(2)	1.970(15)
Ru—O(3)	2.153(14)	C(1)—O(1)	1.151(24)
Ru—H	1.69(17)	C(2)—O(2)	1.153(22)
P(1)—C(11)	1.870(11)	P(2)—C(41)	1.797(9)
P(1)—C(21)	1.756(11)	P(2)—C(51)	1.878(10)
P(1)—C(31)	1.803(12)	P(2)—C(61)	1.851(9)
C(11)—C(12)	1.378(14)	C(41)—C(42)	1.383(13)
C(12)—C(13)	1.337(15)	C(42)—C(43)	1.461(15)
C(13)—C(14)	1.548(15)	C(43)—C(44)	1.263(18)
C(14)—C(15)	1.486(15)	C(44)—C(45)	1.279(18)
C(15)—C(16)	1.335(14)	C(45)—C(46)	1.279(18)
C(16)—C(11)	1.457(13)	C(46)—C(41)	1.363(15)
C(21)—C(22)	1.452(16)	C(51)—C(52)	1.326(13)
C(22)—C(23)	1.653(18)	C(52)—C(53)	1.291(16)
C(23)—C(24)	1.415(19)	C(53)—C(54)	1.392(17)
C(24)—C(25)	1.364(20)	C(54)—C(55)	1.420(14)
C(25)—C(26)	1.439(18)	C(55)—C(56)	1.352(13)
C(26)—C(21)	1.445(15)	C(56)—C(51)	1.349(13)
C(31)—C(32)	1.330(13)	C(61)—C(62)	1.477(15)
C(32)—C(33)	1.353(14)	C(62)—C(63)	1.499(17)
C(33)—C(34)	1.365(16)	C(63)—C(64)	1.405(17)
C(34)—C(35)	1.307(17)	C(64)—C(65)	1.455(17)
C(35)—C(36)	1.420(16)	C(65)—C(66)	1.413(17)
C(36)—C(31)	1.387(15)	C(66)—C(61)	1.456(14)
B—F(1)	1.363(31)	B—F(3)	1.255(35)
B—F(2)	1.316(34)	B—F(4)	1.290(31)
C(3)—C(4)	1.390(41)	C(4)—O(4)	1.471(31)
<i>Hydrogen bonding and short intermolecular approaches</i>			
O(3)—O(4)	2.630(18)	O(2)—C(4)	3.418(33)
O(3)—F(1)	2.750(21)	O(4)—F(2)	2.781(24)
O(1)—F(3)	3.044(28)	O(4)—F(4)	3.421(19)
O(1)—C(4)	3.235(33)		

outlined in Fig. 1. Bond distances and bond angles are listed in Tables 2 and 3 respectively. Tables of thermal parameters and observed and calculated structure factors are available on request from the authors (G.R.C.).

Description and discussion of the crystal structure

The unit cell consists of monomeric ions linked in a hydrogen-bonded network by solvent molecules. The octahedral coordination about the ruthenium atom is shown in Fig. 1. The ligands are disposed such that the two triphenylphosphine groups occupy *trans* positions, whilst the hydride, water molecule and *cis* carbonyl ligands occupy the equatorial sites. Consequently the tetrafluoroborate anion is not coordinated to the ruthenium. Instead, it is hydrogen-bonded to the cation through the coordinated water molecule, and is further hydrogen-bonded through another fluorine atom to the ethanol solvate molecule, which is itself hydrogen-bonded to the coordinated water molecule. This hydrogen-bonding network is illustrated in Fig. 2 which shows a projection of the participating atoms onto the plane at $y = \frac{1}{4}$. The overall molecular packing

TABLE 3

INTERATOMIC ANGLES ($^{\circ}$) FOR $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{CH}_3\text{CH}_2\text{OH}$

P(1)—Ru—P(2)	165.1(2)	P(2)—Ru—H	78(6)
P(1)—Ru—O(3)	89.3(4)	O(3)—Ru—C(1)	170.2(7)
P(1)—Ru—C(1)	90.1(6)	O(3)—Ru—C(2)	91.8(6)
P(1)—Ru—C(2)	100.7(5)	O(3)—Ru—H	84(6)
P(1)—Ru—H	88(6)	C(1)—Ru—C(2)	97.9(10)
P(2)—Ru—O(3)	91.2(4)	C(1)—Ru—H	86(6)
P(2)—Ru—C(1)	86.8(6)	C(2)—Ru—H	171(6)
P(2)—Ru—C(2)	94.1(5)		
Ru—C(1)—O(1)	170.2(8)	Ru—C(2)—O(2)	170.9(8)
Ru—P(1)—C(11)	113.6(3)	Ru—P(2)—C(41)	120.7(3)
Ru—P(1)—C(21)	112.3(3)	Ru—P(2)—C(51)	113.9(3)
Ru—P(1)—C(31)	110.3(3)	Ru—P(2)—C(61)	114.3(2)
C(11)—C(12)—C(13)	125.0(12)	C(41)—C(42)—C(43)	118.7(11)
C(12)—C(13)—C(14)	112.6(6)	C(42)—C(43)—C(44)	127.2(8)
C(13)—C(14)—C(15)	125.5(7)	C(43)—C(44)—C(45)	112.0(12)
C(14)—C(15)—C(16)	111.4(11)	C(44)—C(45)—C(46)	130.1(13)
C(15)—C(16)—C(11)	125.8(7)	C(45)—C(46)—C(41)	113.2(6)
C(16)—C(11)—C(12)	119.7(6)	C(46)—C(41)—C(42)	118.4(8)
C(21)—C(22)—C(23)	104.4(6)	C(51)—C(52)—C(53)	132.1(8)
C(22)—C(23)—C(24)	123.7(8)	C(52)—C(53)—C(54)	112.5(7)
C(23)—C(24)—C(25)	126.1(9)	C(53)—C(54)—C(55)	119.9(7)
C(24)—C(25)—C(26)	112.4(12)	C(54)—C(55)—C(56)	119.8(12)
C(25)—C(26)—C(21)	126.0(13)	C(55)—C(56)—C(51)	119.9(14)
C(26)—C(21)—C(22)	126.3(13)	C(56)—C(51)—C(52)	115.5(15)
C(31)—C(32)—C(33)	122.0(8)	C(61)—C(62)—C(63)	113.7(10)
C(32)—C(33)—C(34)	120.0(7)	C(62)—C(63)—C(64)	120.6(8)
C(33)—C(34)—C(35)	124.0(8)	C(63)—C(64)—C(65)	119.5(8)
C(34)—C(35)—C(36)	112.0(14)	C(64)—C(65)—C(66)	125.8(15)
C(35)—C(36)—C(31)	127.0(15)	C(65)—C(66)—C(61)	111.5(12)
C(36)—C(31)—C(32)	113.4(12)	C(66)—C(61)—C(62)	127.7(13)
F(1)—B—F(2)	107.0(11)	F(2)—B—F(3)	118.0(14)
F(1)—B—F(3)	121.6(13)	F(2)—B—F(4)	89.9(12)
F(1)—B—F(4)	111.2(10)	F(3)—B—F(4)	104.5(13)
C(3)—C(4)—O(4)	105.8(13)		

can be seen in the stereopair diagram of Fig. 3.

The ruthenium—carbonyl distances of 1.83 and 1.97(2) Å are not equivalent but lie within the wide range of distances found in other complexes [6–9]. The longer bond is situated *trans* to the hydrido ligand, and the lengthening of the Ru—C distance can be attributed to a much greater structural *trans* influence of a hydrido ligand over that of a coordinated water molecule.

The Ru—H bond length of 1.7(2) Å is comparable to values observed in other ruthenium complexes, e.g. 1.66(5) Å in $\text{RuH}(\text{N}_2)(\text{PPh-t-Bu}_2)_2$ [10].

The Ru—OH₂ distance of 2.15(1) Å is significantly longer than the value of 1.99 Å predicted from the sum of the covalent radii [11].

The Ru—P distances of 2.329 and 2.416(5) Å differ by 17 sigma. The longer bond lies within the range of values normally found in ruthenium-bis(triphenylphosphine) complexes (approximately 2.37–2.45 Å), but the shorter bond appears to be abnormally short. There is no obvious electronic reason for any difference in the two Ru—P bond lengths, and it is likely that crystal packing effects are responsible. The molecules pack into the unit cell in such a manner that the shortest intermolecular contact is 3.42 Å between C(14) and C(44)'. If

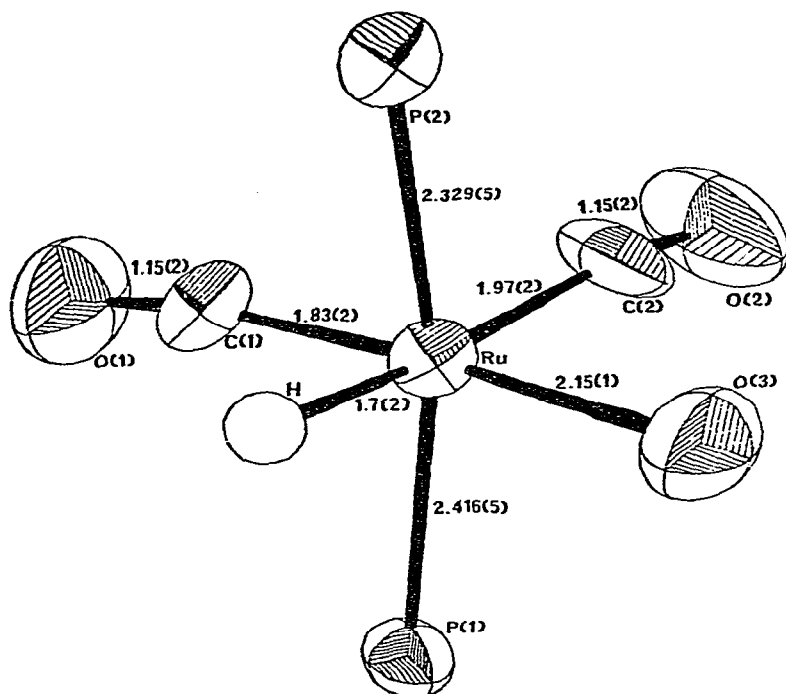


Fig. 1. The coordination geometry and anisotropic thermal ellipsoids for $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{CH}_3\text{CH}_2\text{OH}$. The atoms are drawn as 50% probability ellipsoids.

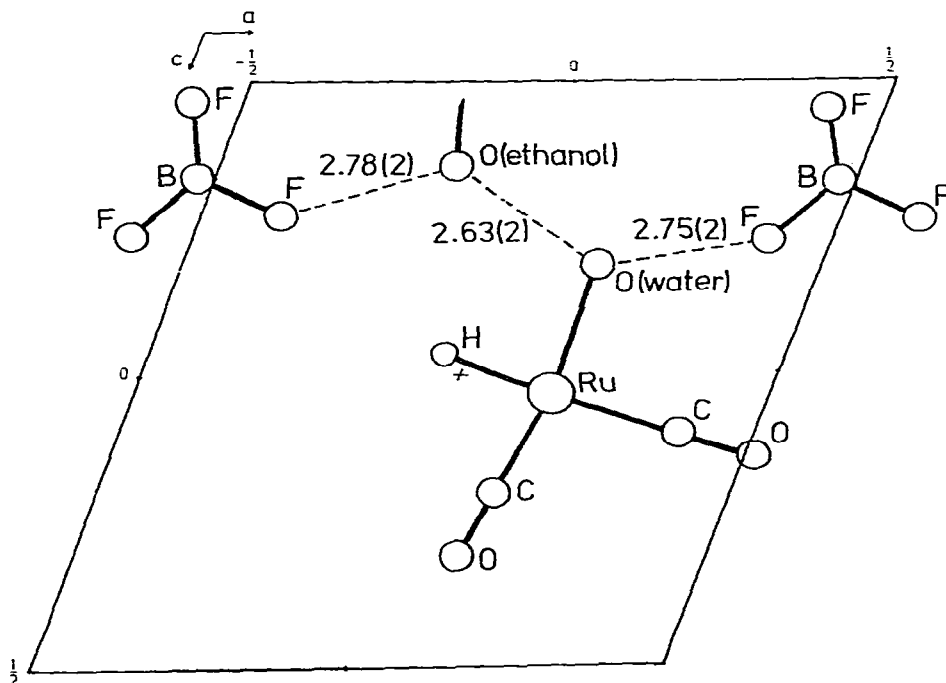


Fig. 2. The hydrogen-bonding network. The participating atoms are projected onto the equatorial plane of the molecule.

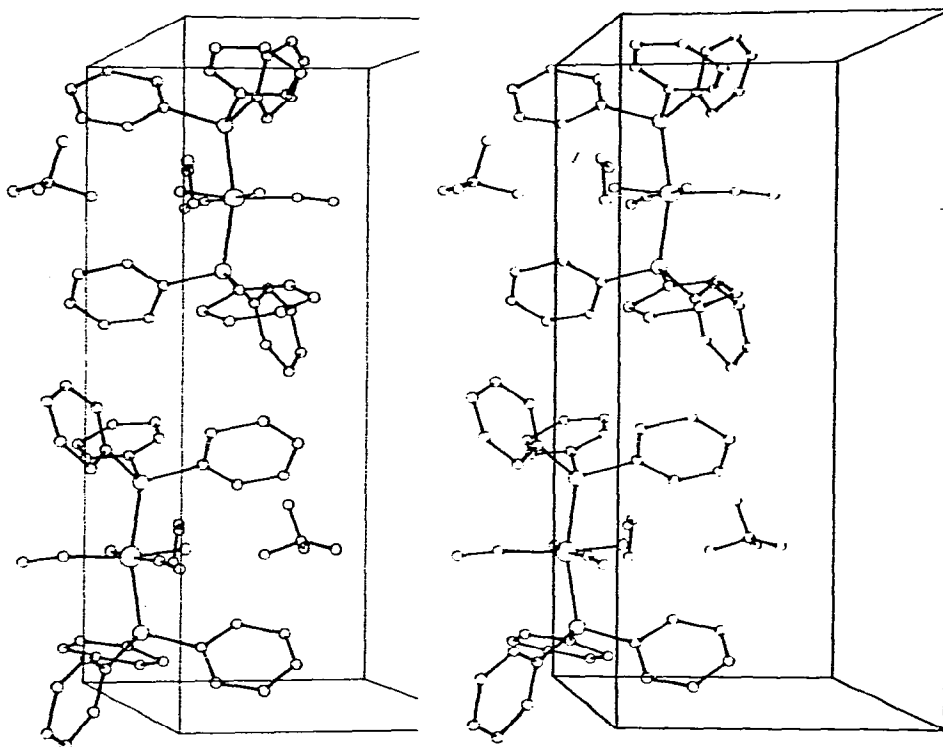


Fig. 3. A stereoscopic view of the contents of the unit cell of $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{CH}_3\text{CH}_2\text{OH}$.

the distance Ru—P(2) is increased to approximately the same distance as Ru—P(1), the C(14)—C(44)' contact decreases to 3.37 Å, but this would still be the only intermolecular contact shorter than 3.5 Å. Further insight into the influence of packing forces on the molecular geometry can be found by observing that the P(1)—Ru—P(2) angle of 165.1(2)° shows a considerable deviation from linearity. If atomic sites are calculated for a linear P—Ru—P arrangement, there is a significant increase in the number of intermolecular contacts less than 3.5 Å, [C(22)—C(63) 3.45 Å, C(25)—C(44) 3.3 Å, C(25)—C(45) 3.3 Å]. The co-aligning of these bonds also brings phenyl ring 1 closer to the carbonyl oxygen atom O(2), which is bent away from P(2). A further increase in the number of close intermolecular contacts occurs when the Ru—P(2) distance is lengthened to be the same as Ru—P(1) and the P—Ru—P bonds are simultaneously made linear. It is likely, therefore, that the deviation from ideal octahedral coordination geometry results from an attempt by the molecules to minimise steric interactions during the process of crystallisation. The easiest way to minimise strain is by a bending of a triphenylphosphine group towards that corner of the octahedron which has the least bulk occupancy, i.e. the corner occupied by the hydrido ligand.

Of particular interest in this compound is the hydrogen bonding between the tetrafluoroborate ion and the solvent molecules. Initially it appeared on the basis of IR evidence that the tetrafluoroborate ion might be coordinated

directly to the ruthenium atom, since the IR spectrum indicated a reduction in the symmetry of the ion. However, it can be seen that in the crystal, the symmetry of the ion is lowered by the hydrogen bonding of fluorine atoms F(1) and F(2) to the coordinated water molecule and ethanol solvent molecules respectively. The F—O distances of 2.75 and 2.78(2) Å lie within the range of 2.56—2.86 Å measured for a number of metal fluoride hydrates [12]. It is clear from this study that deductions about the coordination of tetrafluoroborate (or perchlorate) ions to metal centres based solely on splitting patterns in the IR spectrum may be inconclusive, and should be reinforced, wherever possible, by crystal structure determinations.

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