X-Ray Crystal Structure of Acetatohydridotris(triphenylphosphine)ruthenium(II): A Hydrogenation Catalyst with a Strained Octahedral Co-ordination

By **Andrzej C. Skapski** * and **Francis A. Stephens**, Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by Patterson and Fourier methods, and refined by least-squares techniques to *R* 0·089 for 4080 visually estimated independent reflections. Crystals are monoclinic, with unit-cell dimensions a = 20·68(4), b = 9·639(20), c = 26·59(4), β = 119·58(8), space group is $P2_1/c$ and Z = 4.

The complex is monomeric and the metal atom has a highly distorted octahedral co-ordination. The three triphenylphosphine ligands are meridional and the hydride hydrogen atom is *cis* to all three. Ru–P bond distances for the two approximately *trans* PPh_3 groups (2·363, 2·351 Å) are appreciably longer than the third (2·230 Å); Ru–H is *ca.* 1·7 Å. The acetate group is bidentate and weakly held, with two rather long Ru–O distances (2·198 and 2·210 Å). It subtends an angle of 57·6° at the ruthenium atom.

In view of the industrial importance of homogeneous hydrogenation of alkenes a considerable volume of work has been carried out on these processes and on the possible catalysts involved. One of the more efficient hydrogenation catalysts reported for alk-1-enes has been the title compound, $RuH(CO_2Me)(PPh_3)_3$.[1]

We determined the *X*-ray crystal structure of this complex in order to differentiate between possible mono- or bi-nuclear models, and to decide whether uni- or bi-dentate acetate groups were involved. We find that the complex is monomeric, with a bidentate acetate group and meridional triphenylphosphine ligands. The metal atom has a highly distorted octahedral co-ordination. Apart from the acetate group, the structure of this complex shows a striking similarity with that [2] of another hydrogenation catalyst,[3,4] $Ru(H)Cl(PPh_3)_3$.

Preliminary details of the title structure have been reported.[5] Since then further discussions of the reactions of this catalyst in various solutions have appeared.[6,7]

EXPERIMENTAL

Dark orange needles were crystallised from methanol–benzene. Unit-cell dimensions and space group were determined from preliminary Weissenberg and precession photographs.

Crystal Data.—$C_{56}H_{49}O_2P_3Ru$, M = 948·0, Monoclinic, a = 20·68(4), b = 9·636(20), c = 26·59(4) Å, β = 119·58(8)°, U = 4607·4 Å^3, D_m = 1·39 (by flotation), Z = 4, D_c = 1·37, $F(000)$ = 1960. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 42·4 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

The needles are elongated about the b axis. A crystal of size *ca.* 0·41 × 0·13 × 0·05 mm was selected and equi-inclination photographs were taken about [010] to record $h0$—$6l$ reflections (2—3 days exposure for each photograph). An $0kl$ layer was also recorded for scaling purposes. Intensities were estimated visually from multiple-film exposures and a total of 4080 observable independent reflections were measured. Lorentz and polarisation corrections were applied and at a later stage the data were corrected for absorption. This correction was calculated according to the method of Busing and Levy [8] using an 8 × 8 × 8 grid with crystal pathlengths determined by the vector analysis procedure of Coppens *et al.*[9]

Solution and Refinement of the Structure.—The structure was solved by Patterson and Fourier methods. The Crystal Structure Calculations System '*X*-ray '63' [10] and its updated version of July 1970 [11] were used for the calculations, which were carried out on the Imperial College IBM 7094 and the University of London CDC 7600 computers.

A three-dimensional Patterson synthesis gave a straightforward solution for the ruthenium atom, and a few cycles of least-squares refinement gave the standard agreement factor *R* 0·41. From subsequent difference-Fourier syntheses all the remaining 61 non-hydrogen atoms were located, and isotropic refinement gave *R* 0·122. Addition of the phenyl hydrogen atoms, as a fixed atom contribution with isotropic temperature factors of the parent carbon atoms, reduced *R* to 0·121. Correction for absorption and refinement as previously gave *R* 0·113. When all the non-hydrogen atoms were allowed to refine anisotropically *R* dropped to its final value of 0·089. The intermediate *R* factors quoted are only an approximate guide since for computational reasons the number of cycles had to be limited owing to the large number of parameters and observations involved: in later stages some 560, and over 4000 respectively.

Towards the end of refinement a weighting scheme of the type suggested by Hughes [12] was used, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 52$ being the final value. The application of the weighting scheme had negligible influence of the value of *R*, but the estimated standard deviations decreased on average by *ca.* 10%. The hydride hydrogen atom could be clearly located in difference-Fourier maps as the dominant remaining peak of *ca.* 1·5 eÅ^{-3}, although its exact location and its height may be to

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[5] A. C. Skapski and F. A. Stephens, *Chem. Comm.*, 1969, 1008.

[6] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

[7] R. W. Mitchell, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 846.

[8] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[9] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[10] '*X*-ray '63' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

[11] Ref. 10, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[12] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

some extent affected by the presence of a ' ripple ' of up to 0·7 eÅ^{-3} around the ruthenium atom.

TABLE 1

Fractional co-ordinates, with estimated standard deviations in parentheses

	x	y	z
Ru(1)	0·23250(4)	0·03278(11)	0·24447(3)
P(1)	0·27105(15)	0·0762(4)	0·34276(13)
P(2)	0·14841(15)	0·0350(4)	0·14452(12)
P(3)	0·33566(14)	0·0998(3)	0·24436(12)
O(1)	0·2397(4)	−0·1949(10)	0·2481(3)
O(2)	0·1459(4)	−0·0990(9)	0·2457(4)
C(1)	0·1779(7)	−0·2100(15)	0·2463(5)
C(2)	0·1486(9)	−0·3488(17)	0·2490(8)
C(11)*	0·3535(7)	0·1785(15)	0·3903(5)
C(12)	0·4094(7)	0·1321(18)	0·4453(6)
C(13)	0·4723(8)	0·2133(22)	0·4776(6)
C(14)	0·4793(9)	0·3379(23)	0·4563(8)
C(15)	0·4267(10)	0·3862(18)	0·4025(8)
C(16)	0·3626(7)	0·3015(17)	0·3702(6)
C(21)	0·2810(7)	−0·0732(17)	0·3899(5)
C(22)	0·2613(8)	−0·0643(20)	0·4338(7)
C(23)	0·2669(10)	−0·1763(28)	0·4666(7)
C(24)	0·2889(11)	−0·2996(29)	0·4572(9)
C(25)	0·3124(9)	−0·3113(21)	0·4141(9)
C(26)	0·3065(8)	−0·1961(19)	0·3821(6)
C(31)	0·1950(7)	0·1663(19)	0·3441(5)
C(32)	0·1957(9)	0·3088(22)	0·3541(7)
C(33)	0·1328(11)	0·3742(20)	0·3468(7)
C(34)	0·0686(10)	0·3081(29)	0·3311(8)
C(35)	0·0656(9)	0·1648(34)	0·3225(8)
C(36)	0·1289(7)	0·0954(19)	0·3290(6)
C(41)	0·0658(6)	0·1358(15)	0·1284(5)
C(42)	0·0504(8)	0·1692(19)	0·1726(6)
C(43)	−0·0107(8)	0·2466(21)	0·1617(7)
C(44)	−0·0618(8)	0·2903(19)	0·1055(7)
C(45)	−0·0471(7)	0·2563(17)	0·0606(6)
C(46)	0·0144(8)	0·1814(16)	0·0717(5)
C(51)	0·1703(6)	0·1084(17)	0·0898(5)
C(52)	0·1645(8)	0·0292(16)	0·0441(5)
C(53)	0·1821(9)	0·0901(23)	0·0038(6)
C(54)	0·2018(10)	0·2256(25)	0·0090(7)
C(55)	0·2086(9)	0·3018(20)	0·0562(7)
C(56)	0·1915(8)	0·2427(18)	0·0956(6)
C(61)	0·1074(6)	−0·1338(15)	0·1130(5)
C(62)	0·0334(7)	−0·1664(17)	0·0906(6)
C(63)	0·0101(8)	−0·2996(23)	0·0732(7)
C(64)	0·0561(11)	−0·4011(20)	0·0768(7)
C(65)	0·1309(10)	−0·3698(20)	0·0992(7)
C(66)	0·1566(8)	−0·2373(17)	0·1178(6)
C(71)	0·3483(5)	0·0235(13)	0·1852(4)
C(72)	0·3653(6)	0·1016(15)	0·1488(5)
C(73)	0·3794(7)	0·0297(22)	0·1080(6)
C(74)	0·3765(7)	−0·1084(21)	0·1039(5)
C(75)	0·3547(7)	−0·1829(16)	0·1372(6)
C(76)	0·3434(6)	−0·1169(14)	0·1794(5)
C(81)	0·3602(6)	0·2781(12)	0·2419(5)
C(82)	0·4309(6)	0·3104(16)	0·2482(5)
C(83)	0·4515(7)	0·4470(18)	0·2493(6)
C(84)	0·4040(8)	0·5533(15)	0·2448(6)
C(85)	0·3340(8)	0·5199(18)	0·2353(6)
C(86)	0·3126(7)	0·3825(16)	0·2349(5)
C(91)	0·4199(6)	0·0262(17)	0·3088(5)
C(92)	0·4808(6)	0·1041(15)	0·3474(5)
C(93)	0·5421(7)	0·0382(20)	0·3935(6)
C(94)	0·5437(7)	−0·1014(21)	0·4011(6)
C(95)	0·4817(8)	−0·1786(15)	0·3640(6)
C(96)	0·4213(6)	−0·1145(18)	0·3178(5)

* Ring carbon atoms are numbered C(*mn*) where *m* is ring no. and *n* is the atom no. in the ring; *n* is such that C(*m*1) is attached to P and other atoms are numbered in succession such that C(*m*4) is *para* to C(*m*1).

TABLE 2

Anisotropic thermal parameters

	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ru(1)	253(6)	354(9)	323(6)	−10(4)	164(4)	−4(4)
	10^4U_{11}	10^3U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
P(1)	320(15)	49(3)	397(16)	4(14)	217(12)	−19(15)
P(2)	325(14)	42(3)	376(15)	−2(14)	194(12)	−24(15)
P(3)	249(13)	29(3)	358(16)	14(12)	180(11)	−9(13)
	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
O(1)	29(4)	53(7)	42(4)	−8(4)	10(3)	0(4)
O(2)	46(4)	43(7)	60(5)	−0(4)	29(4)	2(4)
C(1)	63(8)	36(11)	39(6)	1(7)	17(6)	5(6)
C(2)	79(10)	30(13)	107(13)	−16(8)	42(9)	12(9)
C(11)	52(7)	24(11)	56(7)	−3(6)	27(6)	9(6)
C(12)	52(8)	92(14)	44(7)	−5(8)	15(6)	−3(8)
C(13)	53(8)	98(17)	57(9)	−8(9)	22(7)	−10(9)
C(14)	77(11)	97(18)	76(11)	−27(10)	38(9)	−32(11)
C(15)	103(13)	49(14)	98(13)	−2(10)	70(11)	−3(10)
C(16)	49(7)	58(13)	59(8)	−14(7)	26(6)	−8(8)
C(21)	44(6)	56(13)	39(6)	−2(7)	16(5)	11(6)
C(22)	65(9)	103(17)	67(9)	5(9)	38(8)	21(10)
C(23)	83(12)	121(23)	52(9)	−15(12)	27(8)	26(11)
C(24)	75(12)	121(24)	77(13)	−33(13)	9(10)	37(13)
C(25)	71(10)	70(17)	99(14)	−3(10)	14(10)	25(12)
C(26)	72(9)	53(15)	47(7)	11(8)	26(7)	13(8)
C(31)	57(8)	80(15)	39(7)	23(7)	36(6)	18(7)
C(32)	85(11)	88(17)	73(10)	21(10)	63(9)	18(9)
C(33)	115(14)	82(15)	90(12)	44(11)	79(11)	20(10)
C(34)	72(11)	148(23)	81(12)	44(13)	53(10)	16(13)
C(35)	46(9)	224(29)	69(11)	14(13)	32(8)	8(15)
C(36)	45(7)	109(15)	60(9)	8(8)	28(6)	−9(8)
C(41)	50(7)	53(11)	40(6)	−7(6)	26(5)	−4(6)
C(42)	56(8)	99(15)	59(9)	9(8)	33(7)	2(8)
C(43)	50(8)	138(18)	74(10)	40(9)	35(8)	2(10)
C(44)	54(8)	93(15)	78(11)	23(9)	26(8)	−0(10)
C(45)	47(7)	63(13)	67(9)	10(7)	11(7)	6(8)
C(46)	62(8)	66(13)	51(8)	8(7)	31(7)	3(7)
C(51)	36(6)	38(13)	46(7)	13(6)	16(5)	11(6)
C(52)	72(8)	57(12)	53(7)	1(7)	44(7)	0(7)
C(53)	88(11)	85(17)	64(9)	12(10)	52(9)	15(9)
C(54)	98(13)	104(20)	69(11)	9(12)	57(10)	36(11)
C(55)	79(11)	90(16)	66(10)	−8(10)	32(8)	17(10)
C(56)	70(9)	40(13)	57(8)	−2(8)	32(7)	18(7)
C(61)	45(6)	42(11)	46(7)	−9(6)	19(5)	−4(6)
C(62)	53(7)	35(13)	66(9)	−12(7)	27(7)	−0(7)
C(63)	56(9)	70(18)	78(11)	−31(10)	21(8)	−9(10)
C(64)	83(12)	49(15)	82(11)	−17(10)	32(9)	−13(9)
C(65)	107(13)	30(14)	74(10)	5(10)	41(9)	−10(9)
C(66)	64(9)	32(13)	60(8)	−3(8)	27(7)	−6(7)
C(71)	27(5)	45(10)	33(5)	7(5)	10(4)	2(5)
C(72)	35(6)	75(12)	46(7)	−2(6)	26(5)	−1(6)
C(73)	59(8)	73(16)	53(8)	−0(8)	33(6)	1(8)
C(74)	63(8)	50(14)	48(7)	4(8)	27(6)	−4(7)
C(75)	56(7)	55(12)	56(8)	9(7)	31(6)	−8(7)
C(76)	48(7)	41(10)	45(7)	8(6)	24(5)	1(6)
C(81)	46(6)	16(9)	41(6)	9(5)	24(6)	−2(5)
C(82)	42(6)	39(13)	57(7)	−5(6)	32(5)	−2(6)
C(83)	50(7)	41(13)	69(8)	−1(8)	35(6)	6(7)
C(84)	64(8)	22(12)	84(10)	−9(7)	38(7)	0(8)
C(85)	71(8)	39(13)	61(8)	19(8)	35(7)	0(7)
C(86)	52(7)	17(12)	59(8)	4(6)	26(6)	6(6)
C(91)	45(6)	32(12)	49(6)	4(6)	27(5)	10(7)
C(92)	40(6)	43(11)	45(7)	−4(6)	14(5)	−5(6)
C(93)	60(8)	38(15)	61(8)	−8(7)	29(6)	−17(8)
C(94)	56(8)	34(14)	79(10)	−0(7)	31(7)	2(8)
C(95)	63(8)	23(11)	71(9)	2(7)	28(7)	7(7)
C(96)	44(7)	27(12)	50(7)	0(6)	18(5)	8(6)

Atomic scattering factors used were those of ref. 13, except those for hydrogen which were from ref. 14. Correction for the effects of the real and the imaginary parts of anomalous dispersion correction for ruthenium were made according to ref. 15. Table 1 lists the fractional co-

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[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[15] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 3

Fractional co-ordinates of the hydrogen atoms. Except for H(1), these are numbered according to the carbon atom to which they are attached

	x	*y*	*z*
H(1)	0·230	0·207	0·245
H(12)	0·403	0·035	0·462
H(13)	0·515	0·177	0·519
H(14)	0·527	0·401	0·482
H(15)	0·434	0·482	0·386
H(16)	0·320	0·338	0·328
H(22)	0·241	0·032	0·441
H(23)	0·254	−0·167	0·501
H(24)	0·290	−0·389	0·481
H(25)	0·333	−0·408	0·407
H(26)	0·323	−0·202	0·350
H(32)	0·246	0·368	0·368
H(33)	0·134	0·484	0·354
H(34)	0·020	0·363	0·325
H(35)	0·015	0·107	0·311
H(36)	0·127	−0·015	0·323
H(42)	0·087	0·133	0·216
H(43)	−0·020	0·274	0·197
H(44)	−0·111	0·348	0·097
H(45)	−0·085	0·289	0·017
H(46)	0·024	0·157	0·036
H(52)	0·147	−0·077	0·039
H(53)	0·180	0·029	−0·031
H(54)	0·212	0·274	−0·023
H(55)	0·227	0·408	0·062
H(56)	0·196	0·303	0·131
H(62)	−0·006	−0·087	0·087
H(63)	−0·048	−0·324	0·056
H(64)	0·036	−0·505	0·062
H(65)	0·169	−0·450	0·102
H(66)	0·215	−0·214	0·136
H(72)	0·368	0·213	0·152
H(73)	0·393	0·089	0·080
H(74)	0·391	−0·160	0·075
H(75)	0·346	−0·292	0·130
H(76)	0·330	−0·178	0·207
H(82)	0·468	0·228	0·252
H(83)	0·505	0·471	0·254
H(84)	0·421	0·660	0·248
H(85)	0·296	0·603	0·228
H(86)	0·258	0·360	0·229
H(92)	0·481	0·215	0·342
H(93)	0·589	0·099	0·423
H(94)	0·592	−0·151	0·435
H(95)	0·480	−0·288	0·371
H(96)	0·374	−0·177	0·288

ordinates of the non-hydrogen atoms with their estimated standard deviations.† Table 2 contains the coefficients in the expression for the anisotropic Debye–Waller factor $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, while the unrefined co-ordinates of the hydrogen atoms are given in Table 3. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20879 (8 pp., 1 microfiche).‡

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the molecular structure of the monomeric complex. The central metal atom has a distorted octahedral co-ordination geometry in which the three triphenylphosphine groups are meridional with the hydride hydrogen atom *cis* to all three, and the acetate group is bidentate.§ The immediate environment of the ruthenium atom is shown in Figure 2. The more important bond lengths and bond angles are quoted in Tables 4 and 5 respectively.

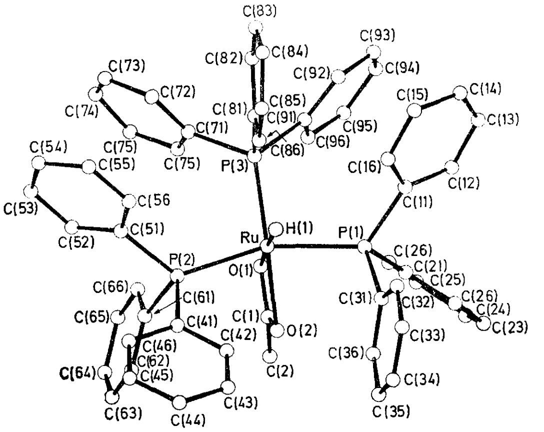

FIGURE 1 The molecular structure

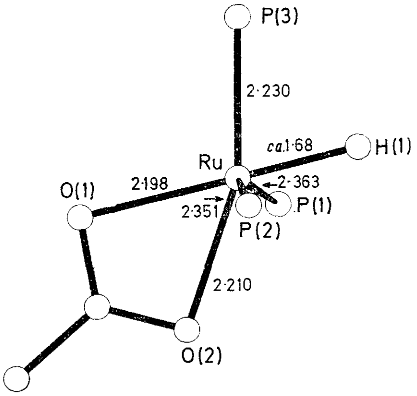

FIGURE 2 Co-ordination about the ruthenium atom

TABLE 4

Selected bond lengths (Å), with estimated standard deviations in parentheses

Ru(1)–P(1)	2·363(5)	Ru(1)–O(1)	2·198(13)
Ru(1)–P(2)	2·351(5)	Ru(1)–O(2)	2·210(10)
Ru(1)–P(3)	2·230(4)	Ru(1)–H(1)	1·68
C(1)–O(1)	1·263(18)	C(1)–O(2)	1·255(18)
C(1)–C(2)	1·485(24)		
P(1)–C(11)	1·829(12)	P(2)–C(61)	1·844(15)
P(1)–C(21)	1·853(17)	P(3)–C(71)	1·870(14)
P(1)–C(31)	1·811(17)	P(3)–C(81)	1·802(14)
P(2)–C(41)	1·817(14)	P(3)–C(91)	1·879(11)
P(2)–C(51)	1·860(16)		
Mean P–C	1·841		

Mean phenyl C–C

Ring		Ring	
C(1*n*)	1·389	C(6*n*)	1·372
C(2*n*)	1·381	C(7*n*)	1·385
C(3*n*)	1·384	C(8*n*)	1·385
C(4*n*)	1·393	C(9*n*)	1·384
C(5*n*)	1·382	Overall mean	1·384

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† In the final stages of refinement the least-squares program CRYLSQ[11] was used employing large partial matrices. The standard deviations thus obtained are more realistic than those from a simple block-diagonal program such as BLOKLS,[10] but may still be a slight underestimate of the true deviations.

‡ For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

§ *Note added in proof:* In a recent publication (I. S. Kolomnikov, A. I. Gusev, G. G. Aleksandrov, T. S. Lobeeva, Yu. T. Struchkov, and M. E. Vol'pin, *J. Organometallic Chem.*, 1973, **59**, 349) preliminary details are reported of the structure of the formato-analogue, $RuH(CO_2H)(PPh_3)_3$. The co-ordination geometry is essentially similar to that in the acetato-complex, although the hydride hydrogen atom was not located.

Two of the Ru–P distances [Ru–P(1) 2·363 and Ru–P(2) 2·351 Å], are appreciably longer than the third [Ru–P(3) 2·230 Å]. The two PPh_3 groups associated with the longer Ru–P bonds are approximately *trans* to each other (P–Ru–P *ca.* 155°). A similar triplet of PPh_3 groups is found in two five-co-ordinate complexes: in $RuHCl(PPh_3)_3$ there is one short Ru–P distance of 2·202 Å and two longer ones of 2·330 and 2·364 Å,[2] while in the precursor of both the hydrido-complexes $RuCl_2(PPh_3)_3$ the distances are 2·230, and 2·374 and 2·412 Å respectively.[16,*]

TABLE 5

Selected bond angles (°), with estimated standard deviations in parentheses

P(1)–Ru(1)–P(3)	98·59(13)	P(2)–Ru(1)–P(3)	99·72(15)
P(1)–Ru(1)–O(2)	85·3(3)	P(2)–Ru(1)–O(2)	82·7(2)
P(1)–Ru(1)–O(1)	98·6(2)	P(2)–Ru(1)–O(1)	93·4(2)
O(1)–Ru(1)–O(2)	57·6(4)	P(3)–Ru(1)–O(1)	104·2(3)
P(1)–Ru(1)–H(1)	79	P(2)–Ru(1)–H(1)	89
P(3)–Ru(1)–H(1)	75	O(2)–Ru(1)–H(1)	123
O(1)–Ru(1)–H(1)	177	O(2)–Ru(1)–P(3)	161·8(3)
P(1)–Ru(1)–P(2)	154·89(14)		
Ru(1)–P(1)–C(11)	123·4(6)	C(11)–P(1)–C(21)	101·3(6)
Ru(1)–P(1)–C(21)	118·4(5)	C(11)–P(1)–C(31)	104·5(7)
Ru(1)–P(1)–C(31)	106·5(4)	C(21)–P(1)–C(31)	99·6(8)
Ru(1)–P(2)–C(41)	111·0(4)	C(41)–P(2)–C(51)	100·4(7)
Ru(1)–P(2)–C(51)	124·0(4)	C(41)–P(2)–C(61)	101·2(6)
Ru(1)–P(2)–C(61)	114·8(4)	C(51)–P(2)–C(61)	102·2(7)
Ru(1)–P(3)–C(71)	114·8(4)	C(71)–P(3)–C(81)	100·7(6)
Ru(1)–P(3)–C(81)	124·2(5)	C(71)–P(3)–C(91)	99·7(6)
Ru(1)–P(3)–C(91)	110·3(5)	C(81)–P(3)–C(91)	104·0(6)
Mean Ru–P–C	116·4	Mean C–P–C	101·5
Ru(1)–O(1)–C(1)	93·9(8)	Ru(1)–O(2)–C(1)	93·6(9)
O(1)–C(1)–O(2)	114·9(1·3)		
O(1)–C(1)–C(2)	122·1(1·4)	O(2)–C(1)–C(2)	122·9(1·5)

Since the title complex is six-co-ordinate, this close resemblance merits further consideration. The first and most obvious reason for the difference in the Ru–P lengths is the existence of a mutual *trans*-influence between the approximately opposed PPh_3 groups. However, the difference between the shorter Ru–P distance and the mean of the other two (0·127 Å), is appreciably longer than would be expected. A comparison can be made with another d^6 complex *mer*-$RhCl_3(PPhEt_2)_3$,[17] where the difference between mean Rh–P(*trans* to P) and Rh–P(*trans* to Cl) is 0·074 Å. Furthermore, there the *trans*-PPh_3 groups are more nearly opposed, with P–Rh–P 168°, than in the title complex, and hence one would expect a stronger *trans*-influence. In Ru^{II} complexes where PPh_3 groups are *cis*, Ru–P distances *ca.* 2·32 Å are found, *cf.* means of 2·318 Å in $Rh_3Cl_6(PPhEt_2)_9$,[18] and 2·326 Å in $Ru(PPh_3)_2(pyS)_2$.[19] Therefore, apart from *trans*-influence a further factor must be invoked to explain the short Ru–P(3) distance.

It has been suggested [20-24] that in some circumstances a bidentate group may be considered as occupying one co-ordination site about a metal atom. Such a concept clearly has its limitations; nevertheless an assumption that the title complex has a pseudo-five-co-ordinate geometry makes more understandable the differentiation of Ru–P bond lengths, and the similarity with $Ru(H)Cl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$. The bidentate acetate group, owing to its small 'bite', subtends an angle of only 57·6° at the ruthenium atom. In both the title complex and in $Ru(H)Cl(PPh_3)_3$, the $RuH(PPh_3)_3$ portion is almost identical. If one now takes C(1) as representing the centre of the acetate group then the angle P(3)–Ru–C(1) is *ca.* 128° compared to the equivalent angle P–Ru–Cl of 121·5° in $RuHCl(PPh_3)_3$[2].

Both the Ru–O(AcO) distances (2·198 and 2·210 Å) are long, suggesting that this group is only loosely held. This agrees with the finding [1] that in solution it is easily replaced by CO. The two distances are not significantly different [because of the method of data collection the *y* co-ordinates are least accurately determined in the structure; this affects especially Ru–O(1) which lies in the *b* direction]. It is difficult to find a strictly comparable Ru–O distance, but in $[Ru_3O(CO_2Me)_6(PPh_3)_3]$ [25] the mean Ru–O(μ-AcO) distance is 2·06 Å, and in $(NH_4)_2[RuCl_4(NO)(OH)]$ [26] the Ru–O distance is 2·03 Å. The bond lengths we find are some 0·2 Å longer than the sum of Pauling's covalent radii (1·99 Å).[27]

Although the position of the hydride hydrogen atom has been determined with only limited accuracy the Ru–H distance found agrees very well with that [2] of 1·68 Å in $RuHCl(PPh_3)_3$ and of 1·67 Å in Ru–H(naphthyl)(dmpe), [dmpe = 1,2-bis(dimethylphosphino)ethane].[28,29] The mean P–C distance (1·841 Å) can be compared to the means in $RuHCl(PPh_3)_3$ (1·841) and in $Ru(PPh_3)_2(pyS)_2$ (1·845 Å).[19] P–C(Ph) distances are appreciably shorter when the fourth bond is to an organic entity rather than to a transition metal, *viz.* a mean of 1·790 Å in the benzyltriphenylphosphonium ion.[30] Also in this context departures from perfect sp^3 geometry at the phosphorus atom are much more marked in metal complexes, especially where these bulky ligands are crowded. This leads to an appreciable spread in tetrahedral angles, but the mean values

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[*] Although these two five-co-ordinate complexes have been described as distorted trigonal-bipyramidal and distorted square-pyramidal respectively, in fact the distortions in each case are such that the geometries are as close to each other as to the idealised polyhedron.

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of 116·4° for Ru–P–C and of 101·5° for C–P–C may be considered as typical for this class of compound.

The molecular structure shows approximate *m* symmetry, where the ' mirror plane ' can be taken as that containing Ru, P(3), the acetate group, and the hydride hydrogen atom. Phenyl ring C(8*n*) lies almost on this plane, while P(1) is approximately mirror-related to P(2), as are the following pairs of phenyl rings: C(7*n*) and C(9*n*), C(1*n*) and C(5*n*), and C(2*n*) and C(6*n*) (Table 6). The remaining pair of rings, C(3*n*) and C(4*n*), however, drastically break this pseudo-symmetry. A possible reason for this is that ring C(4*n*) swivels out of position such that its α-hydrogen blocks the most open gap in the ruthenium co-ordination, that between O(2) and H(1). This is by far the nearest non-bonded hydrogen atom and is *ca.* 2·88 Å from the metal atom. The classic example of such a behaviour exists in $RuCl_2(PPh_3)_3$,[16] where an α-hydrogen blocks the sixth co-ordination site in this five-co-ordinate complex. There the hydrogen atom is as close as 2·59 Å from ruthenium, and La Placa and Ibers were able to show that the marked distortion at the phosphorus atom, where P–C(1)–C(4) angle is 169·5°, was consistent with repulsion of the α-hydrogen atoms. In our structure, where the α-hydrogen is further away, we find no such distortion for this ring, in that the phosphorus atom is within 0·01 Å of the least-squares plane. That it is ring C(4*n*) rather than C(3*n*) which is ' out of position ' can be inferred from the fact that while C(3*n*) could not be rotated to mirror C(4*n*), since this would produce a clash between them, there is no reason due to intramolecular packing why C(4*n*) could not mirror C(3*n*). Clearly, an Ru · · · H(42)

TABLE 6

Planarity of groups of atoms in the molecule and distances (Å) from least-squares planes. Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space

				Deviation (Å) of atoms from plane	
P	*Q*	*R*	*S*	Defining plane	Not defining plane
−0·22	0·32	23·25	5·64	Ru(1) 0·001, P(3) −0·003, O(1) 0·012, O(2) 0·008, C(1) −0·022, C(2) 0·004	P(1) 2·292 P(2) −2·303 H(1) 0·07
16·09	4·45	20·05	2·93	C(11) 0·003, C(12) −0·001, C(13) −0·006, C(14) 0·010, C(15) −0·008, C(16) 0·001	P(1) −0·079
14·44	2·43	6·33	6·36	C(21) −0·013, C(22) 0·001, C(23) 0·018, C(24) −0·024, C(25) 0·013, C(26) 0·006	P(1) −0·092
−4·33	−1·55	25·05	7·53	C(31) −0·014, C(32) 0·012, C(33) 0·001, C(34) −0·012, C(35) 0·009, C(36) 0·004	P(1) −0·237
10·47	8·16	−2·86	1·42	C(41) 0·004, C(42) −0·011, C(43) 0·011, C(44) −0·006, C(45) 0·000, C(46) 0·001	P(2) 0·010
16·18	−2·68	2·62	2·70	C(51) −0·002, C(52) −0·003, C(53) 0·013, C(54) −0·017, C(55) 0·012, C(56) −0·003	P(2) −0·019
−6·82	−2·16	25·53	2·45	C(61) −0·004, C(62) −0·001, C(63) 0·002, C(64) 0·001, C(65) −0·006, C(66) 0·007	P(2) 0·154
15·02	−0·76	6·25	6·36	C(71) 0·014, C(72) −0·017, C(73) −0·005, C(74) 0·030, C(75) −0·032, C(76) 0·010	P(3) 0·136
−2·71	0·21	24·64	5·02	C(81) 0·019, C(82) −0·012, C(83) −0·012, C(84) 0·029, C(85) −0·022, C(86) −0·002	P(3) 0·109
−16·59	1·31	23·96	0·48	C(91) −0·009, C(92) 0·007, C(93) 0·007, C(94) −0·019, C(95) 0·017, C(96) −0·003	P(3) −0·059

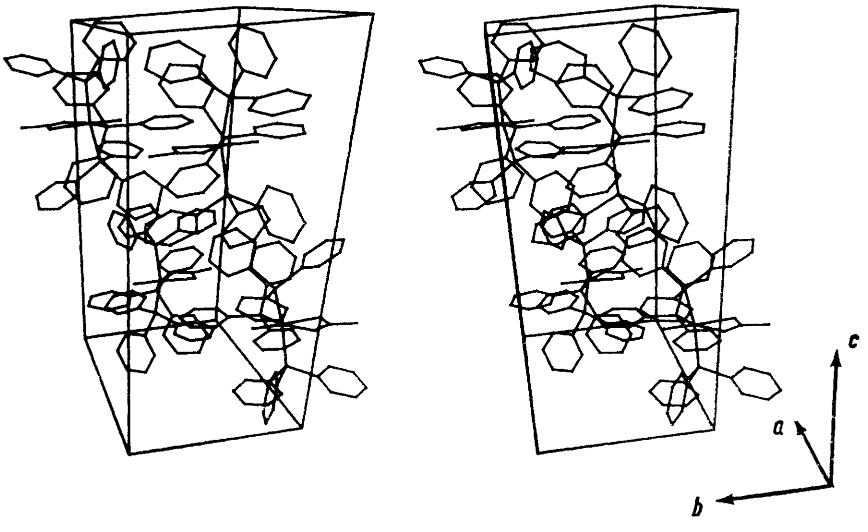

FIGURE 3 A stereoscopic view showing the packing of the molecules

distance of *ca.* 2·88 Å cannot in any sense be considered as constituting a bond, however, it may be that a weak long-range attraction is responsible for this orientation of C(4*n*).

Figure **3** shows a stereoscopic view of the arrangement of the molecules in the unit cell.[31] Intermolecular distances are not particularly noteworthy, the shortest is 3·48 Å and involves an oxygen atom of the acetate group.

The hydrogenation catalysis behaviour of the title complex in benzene [6] and acidified methanol solution [7] has been found to be different. In the latter the first stage involves a loss of both the acetate group and the hydride hydrogen to give a cation of the type $[Ru(PPh_3)_3 n MeOH]^{2+}$, followed by the loss of a triphenylphosphine group in the presence of alkene under hydrogen. In the former case the acetate group and the hydride hydrogen remain, and a triphenylphosphine group is lost in the first step. In both cases the specificity of this complex for alk-1-enes is thought to be due to steric hindrance of the bulky triphenylphosphine groups limiting the approach of alkenes other than of the terminal variety.

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