Crystal and Molecular Structure of Bis-(π-2-methylallyl)bis(trimethyl phosphite)ruthenium. An Example of Asymmetric π-Bonding Between Methylallyl Ligands and Ruthenium

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The crystal structure and molecular stereochemistry of the title compound have been determined from three-dimensional *X*-ray diffraction counter data by Patterson and Fourier methods. Crystals are monoclinic, $a = 15{\cdot}12$, $b = 17{\cdot}86$, $c = 8{\cdot}10$ Å, $\beta = 113{\cdot}4°$, space group $P2_1/a$, $Z = 4$. The structure has been refined by least-squares methods to R 0·051 for 677 independent reflections. The ruthenium atom is octahedrally co-ordinated and has the trimethyl phosphite ligands mutually *cis*; the methylallyl groups each occupy two adjacent sites. The bonding of each methylallyl group to the ruthenium atom is asymmetric: mean Ru–C(*trans* to P) 2·38(2); mean Ru–C(*trans* to C) 2·18(2) Å. The methylallyl groups are non-planar, the methyl group being bent out of the plane of the allyl moiety by some 12° away from the metal. The allyl plane is almost exactly perpendicular to the plane defined by the two outer carbon atoms and the ruthenium atom.

AMONGST the π-allyl structures which have been studied crystallographically, most are symmetric (*i.e.* they have closely similar metal–carbon bond lengths at each end of the allyl ligand). Bis(π-2-methylallyl)nickel [1] and (π-allyl)chloropalladium dimer [2,3] exhibit this feature. When, however, the environment at one end of the ligand is different from that at the other (usually because of a different *trans* ligand), the bonding of the allyl group to the metal may deviate from this symmetrical arrangement; $[(MeC_3H_4)PdCl(PPh_3)]$ [4] and $[(C_3H_5)_2RhCl]_2$ [5] are examples here. Further, the 2-methylallyl ligand may become non-planar when bonded to a transition metal. For example, in (π-2-methylallyl)chlorotriphenylphosphinepalladium [4] the 2-methyl group is bent out of the allyl plane towards the metal.

The ^{1}H n.m.r. spectrum of the title compound [6] is

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[1] R. Uttech and M. Dietrich, *Z. Krist.*, 1965, **122**, 60.

[2] A. E. Smith, *Acta Cryst.*, 1965, **18**, 331.

[3] W. E. Oberhansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 43.

[4] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.

[5] M. McPartlin and R. Mason, *Chem. Comm.*, 1967, 16.

[6] M. Cooke, R. J. Goodfellow, M. Green, and G. Parker, *J. Chem. Soc.* (*A*), 1971, 16.

consistent with the presence of mutually *cis* phosphite ligands, but the splittings suggest that each allyl group is asymmetrically bonded to the ruthenium atom. Information about the geometrical arrangement and bonding of the allyl ligands was sought, and as there has been no other crystallographic investigation of allylruthenium complexes, this study was undertaken.

EXPERIMENTAL

The crystals were prepared as in ref. 6 and were recrystallised from hexane as well formed colourless needles. In air they slowly decomposed on the surface and appeared black. Lattice parameters were measured from precession photographs by use of zirconium-filtered Mo-K_α radiation. Fourteen of the crystals examined were monoclinic, $P2_1/a$, and all were twinned on the (100) face. All the twins have their c axes parallel and their b axes antiparallel. One further crystal which was examined and which underwent the same surface decomposition was found to be orthorhombic. The lattice parameters of this crystal were characterised (see Crystal Data section), and from these it appeared that the crystal density is very close to that of the monoclinic form; no further structural studies were undertaken.

We were unable to find an untwinned crystal of the monoclinic group; the one chosen for X-ray investigation was of cross-section $0{\cdot}23 \times 0{\cdot}33 \times 1{\cdot}55$ mm. Though it was twinned, the ratio of major-to-minor twin was higher than in any other crystal, at *ca.* 16 : 1. No absorption corrections were made (μR *ca.* 0·59). The crystal was mounted on a glass rod with ' Araldite ', and with c as the rotation axis. Intensities were measured on a Buerger–Supper-Pace 0·01° incrementing two-circle auto-diffractometer, with equi-inclination geometry and a stationary-background–ω-scan–stationary-background system. The diffractometer settings ϒ and ϕ were input from punched paper tape prepared on an Atlas computer.[7] For each reflection hkl a scan interval of $(2{\cdot}0 + 0{\cdot}3/L)^{\circ}$ was used, where L is the Lorentz correction, at a scan speed of 1° min.$^{-1}$. During the scan (time t_s) a total count N_3 was recorded. The stability of the apparatus and of the crystal were monitored by measuring the intensity of a check reflection on each layer between every 20 measured intensities. No deviation $>3N_3^{\frac{1}{2}}$ was observed. The centring of ϕ was confirmed and checked on a chart recorder. Background counts for 0·5 min (t_b) were taken before and after the scan, giving counts N_1 and N_2 respectively. The intensity of reflection hkl is proportional to $[N_3 - t_s\,(N_1 + N_2)]$, and reflections for which $[\mathrm{N}_3 - \frac{t_s}{2t_b}(N_1 + N_2)]/[\mathrm{N}_3 + \frac{t_s}{2t_b}(N_1 + N_2)]^{\frac{1}{2}} \leqslant 2{\cdot}2$ were regarded as unobserved and were not included in the final refinement. The structure factor $F(hkl) = [I(hkl)^{\frac{1}{2}}](s/Lp)^{\frac{1}{2}}$, where s, the scale factor, was arbitrarily fixed at 100·0 and p is the polarisation factor. The standard deviation $\sigma_{F(hkl)}$ is given by $\frac{s}{Lp}[N_3 + \left(\frac{t_s}{2t_b}\right)^2 (N_1 + N_2)]^{\frac{1}{2}}/2|F(hkl)|$. Reflections for which N_1 and N_2 differed by $>(3\sigma_{N_1} + 3\sigma_{N_2})$ were re-measured.

RESULTS

Crystal Data.—$C_{14}H_{32}O_6P_2Ru$, $M = 460$.

Type (1): Monoclinic, space group $P2_1/a$, $a = 15{\cdot}12(1)$, $b = 17{\cdot}86(1)$, $c = 8{\cdot}11(2)$ Å, $\beta = 113° \; 21'(15')$, D_m (by flotation) 1·50, $Z = 4$, $D_c = 1{\cdot}52$, $F(000) = 952$. Mo-K_α X-radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 16·3 cm^{-1}.

Type (2): Orthorhombic, space group $Pca2_1$ or $Pcam$, $a = 27{\cdot}28(3)$, $b = 8{\cdot}01(2)$, $c = 18{\cdot}43(2)$ Å, $D_c = 1{\cdot}52$, $Z = 8$, $F(000) = 1904$.

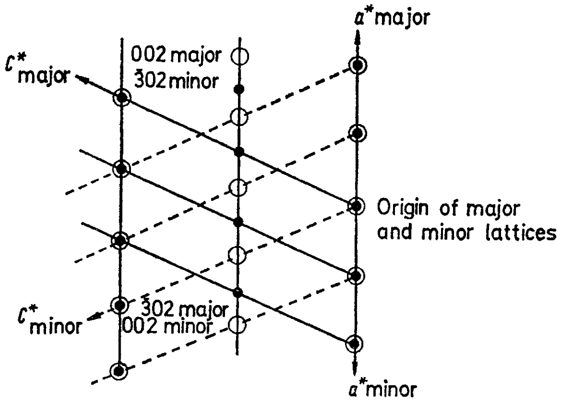

FIGURE 1 A view of the $h0l$ reciprocal lattices showing overlap of the major twin-lattice points (full circles) with those of the minor twin (open circles) on layers hkl for which $l = 2n$

Structure Solution and Refinement.—All preliminary work on the structure was done assuming that the crystal was untwinned (*i.e.*, that the intensities from the major component would sufficiently override those of the minor component, which interfere only on layers for which $l = 2n$, to give a working solution). Indeed, the ruthenium atom was readily located from the composite three-dimensional Patterson synthesis, and the twenty-two non-hydrogen atoms were located by successive electron-density difference syntheses. At this stage one methylallyl group, C(1)—(4), was much more clearly defined than the other, C(5)—(8); R was 0·22, and R' 0·26. A few cycles of least-squares refinement with anisotropic thermal parameters for Ru, P(1), and P(2), isotropic thermal parameters for all other atoms, and separate reciprocal layer scale-factors, gave R 0·16. The quantity minimised was $\Sigma\{w(|F_o| - |F_c|)^2\}$ and for each reflection $\sqrt{w} = 1/\sigma_{F(hkl)}$. An approximate solution to the structure was thus obtained, but in order to improve it some account of the twinning of the crystals had to be taken. It is apparent from the geometry of the Bravais lattice that the major and minor reciprocal lattices coincide on layers hkl for which $l = 2n$. The condition for exact coincidence (see Figure 1) is that $2c^* \cos \beta^* = ma^*$, where m is an integer. For this crystal $m = 3$, giving $\beta^* = 66° \; 18'$. The measured value of β^* (66° 45′) is sufficiently different to give inexact coincidence on $hk2$ and $hk4$, and distinct double reflections on $hk6$. This form of twinning, where major and minor twins share a common face containing the unique axis, occurs not infrequently in the monoclinic system,[8] and the possibility of superimposing points in reciprocal space when the lattices are placed with two of their axes coincident is a

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[7] J. Cuppola, TAPSET, a Fortran program for computation of ϒ, ϕ, and Lp corrections, adapted for used on an Atlas computer by S. F. Watkins.

[8] W. L. Bragg, 'The Atomic Structure of Minerals,' Cornell University Press, New York, 1937, p. 243.

condition very favourable to twinning.[9] As shown in Figure 1 for layers with $l = 2n$ the general reflection hkl for the major twin nearly coincides with $-(h + 3l/2), k, l$ for the minor twin, and each of these reflections will have been measured on the diffractometer as single intensity. The contribution of each component for such a pair of multiple reflections can be deduced knowing that the intensity of the major : minor twin (x) is, in the present instance, 16 : 1. This proportion was estimated visually from the layers hkl with $l = 2n + 1$, on which the twinned lattices do not overlap. It turns out that

$$I_{\mathrm{corr}(hkl)} = \frac{x}{x^2 - 1}\,[I_{\mathrm{m}(hkl)} \cdot x - I_{\mathrm{m}(-(h + 3l/2),\, k,\, l)}]$$

where $I_{\mathrm{corr}(hkl)}$ is the corrected intensity for reflection hkl, and I_{m} is the intensity measured by the diffractometer for the two superimposed reflections. Corrected intensities, which should now apply to the major twin only, were thus calculated for all reflections hkl with $l = 2n$. The effects of random fluctuations in the background intensities were also minimised by replacing measured values with those interpolated from a plot of the variation in average background count with sin θ in every case where $(N_2 - N_1) > (3\sigma_{N_1} + 3\sigma_{N_2})$. Least-squares refinement on all reflections then gave R 0·101 (R' 0·143). Finally, individual weights were reassessed according to the scheme: $1/w = \sigma^2_{F(hkl)} + 0{\cdot}026|F|^2$, the constant 0·026 having been chosen to keep $w(\Delta F)^2$ as constant as possible over ranges of $|F|$ and $\sin\theta/\lambda$.[10] Least-squares refinement with this improved weighting scheme gave R 0·064 (R' 0·097), while deletion of a few reflections for which spurious peaks had been evident on the chart recorder gave a final R 0·050 (R' 0·043) for 677 independent reflections. A final electron-density difference synthesis showed no peaks greater than +0·6 nor less than −0·6 e Å^{-3}. Positional and thermal parameters are in Table 1, interatomic distances and angles in Table 2, and some appropriate least-squares planes in Table 3. The atomic scattering factors used were those of ref. 11. All computational work was carried out with the '*X*-Ray '63' System on an Atlas computer.[12] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20621 (3 pp., 1 microfiche).*

TABLE 1

Atomic parameters with standard deviations in parentheses

Atom	x/a	y/b	z/c	B
Ru	0·7255(1)	0·4080(1)	0·3726(2)	*
P(1)	0·8566(4)	0·3687(3)	0·5974(7)	*
P(2)	0·6694(5)	0·2964(4)	0·2526(8)	*
O(11)	0·955(1)	0·376(1)	0·589(2)	5·3(4)
O(12)	0·867(1)	0·280(1)	0·656(2)	4·2(4)
O(13)	0·878(1)	0·404(1)	0·795(2)	6·1(4)
O(21)	0·588(1)	0·259(1)	0·305(1)	2·2(3)
O(22)	0·631(1)	0·287(1)	0·035(2)	5·2(4)
O(23)	0·746(1)	0·224(1)	0·297(2)	5·5(4)
C(11)	0·045(2)	0·352(1)	0·712(3)	8·3(8)
C(12)	0·792(1)	0·256(1)	0·742(2)	2·9(5)
C(13)	0·876(1)	0·489(1)	0·839(2)	2·9(5)
C(21)	0·538(2)	0·189(1)	0·212(3)	6·6(7)
C(22)	0·557(2)	0·333(1)	−0·087(3)	5·1(6)
C(23)	0·847(2)	0·225(1)	0·272(3)	7·7(7)
C(1)	0·609(1)	0·461(1)	0·406(2)	1·6(5)
C(2)	0·636(1)	0·401(1)	0·518(3)	4·7(6)
C(3)	0·559(1)	0·433(1)	0·233(2)	2·7(5)
C(4)	0·616(1)	0·542(1)	0·487(2)	1·9(4)
C(5)	0·803(1)	0·420(1)	0·188(2)	2·6(5)
C(6)	0·767(1)	0·493(1)	0·234(2)	2·2(5)
C(7)	0·817(1)	0·521(1)	0·424(2)	1·4(4)
C(8)	0·701(1)	0·539(1)	0·064(2)	3·9(6)

* Anisotropic thermal parameters (×10^4) for Ru and P atoms in the form $-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	54(1)	26(1)	126	−2(1)	66(2)	5(2)
P(1)	44(5)	21(3)	55	7(3)	34(7)	21(5)
P(2)	37(5)	33(3)	112	4(3)	44(6)	−17(6)

DISCUSSION

The compound $(\pi\text{-}C_4H_7)_2Ru[P(OMe)_3]_2$ has the central ruthenium atom in a distorted octahedral co-ordination and the phosphite groups mutually *cis*. The two methylallyl ligands are equivalent, but each is asymmetrically bonded to the metal. There is a natural (noncrystallographic) C_2 axis bisecting the P(1)–Ru–P(2) angle. The molecular geometry and numbering are

TABLE 2

Bond lengths (Å) and bond angles (deg.)

(*a*) Distances

(i) Trimethyl phosphite groups

Ru–P(1)	2·210(5)	Ru–P(2)	2·233(7)
P(1)–O(11)	1·52(2)	P(2)–O(21)	1·60(2)
P(1)–O(12)	1·63(2)	P(2)–O(22)	1·63(2)
P(1)–O(13)	1·63(2)	P(2)–O(23)	1·66(2)
O(11)–C(11)	1·39(3)	O(21)–C(21)	1·51(3)
O(12)–C(12)	1·60(3)	O(22)–C(22)	1·42(3)
O(13)–C(13)	1·56(3)	O(23)–C(23)	1·63(4)

(ii) Methyl allyl groups

Ru–C(1)	2·11(2)	Ru–C(5)	2·25(2)
Ru–C(2)	2·12(2)	Ru–C(6)	2·12(2)
Ru–C(3)	2·36(2)	Ru–C(7)	2·39(2)
C(1)–C(2)	1·36(3)	C(6)–C(5)	1·51(3)
C(1)–C(3)	1·39(3)	C(6)–C(7)	1·51(3)
C(1)–C(4)	1·58(3)	C(6)–C(8)	1·58(3)

(*b*) Angles

P(1)–Ru–P(2)	97·9(2)	Ru–P(2)–O(21)	116·9(6)
Ru–P(1)–O(11)	120·9(6)	Ru–P(2)–O(22)	118·1(7)
Ru–P(1)–O(12)	119·8(6)	Ru–P(2)–O(23)	118·9(6)
Ru–P(1)–O(13)	116·9(7)	O(21)–P(2)–O(22)	105·3(9)
O(11)–P(1)–O(12)	96·5(9)	O(21)–P(2)–O(23)	99·5(8)
O(11)–P(1)–O(13)	100·7(9)	O(22)–P(2)–O(23)	94·3(9)
O(12)–P(1)–O(13)	97·4(9)	P(2)–O(21)–C(21)	120(2)
P(1)–O(11)–C(11)	130(2)	P(2)–O(22)–C(22)	123(2)
P(1)–O(12)–C(12)	113(1)	P(2)–O(23)–C(23)	125(2)
P(1)–O(13)–C(13)	126(1)	C(5)–C(6)–C(7)	117(2)
C(2)–C(1)–C(3)	107(2)	C(5)–C(6)–C(8)	113(2)
C(2)–C(1)–C(4)	120(2)	C(7)–C(6)–C(8)	127(2)
C(3)–C(1)–C(4)	132(2)	C(5)–Ru–C(7)	67·5(8)
C(2)–Ru–C(3)	58·7(8)	P(2)–Ru–C(7)	157·6(8)
P(1)–Ru–C(3)	153·4(6)	C(2)–Ru–C(5)	172·5(7)
C(1)–Ru–C(6)	100·6(9)		

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1972, Issue No. 24. Items less than 10pp. are sent as full size copies.

[9] M. J. Buerger, 'Crystal Structure Analysis,' Wiley, London, p. 54.

[10] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, *B*, **25**, 374.

[11] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[12] J. M. Stewart and D. High, '*X*-Ray '63', compiled by B. W. Brown, Oak Ridge National Laboratory Technical Report TR 64 6; and further edited by J. C. Baldwin, Atlas Computer Laboratory, Chilton, Didcot, Berkshire.

shown in Figure 2; the molecular packing within the unit cell, as seen in projection down *a*, is shown in Figure 3.

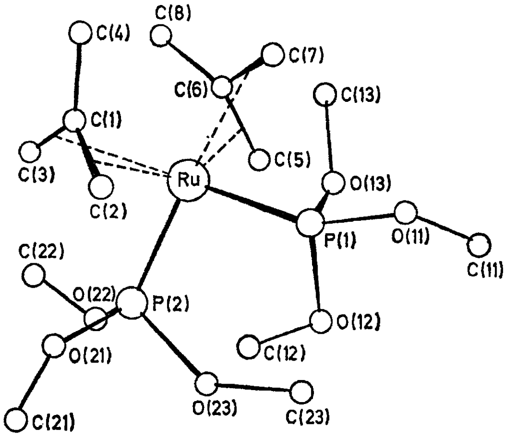

FIGURE 2 A perspective view of the molecule

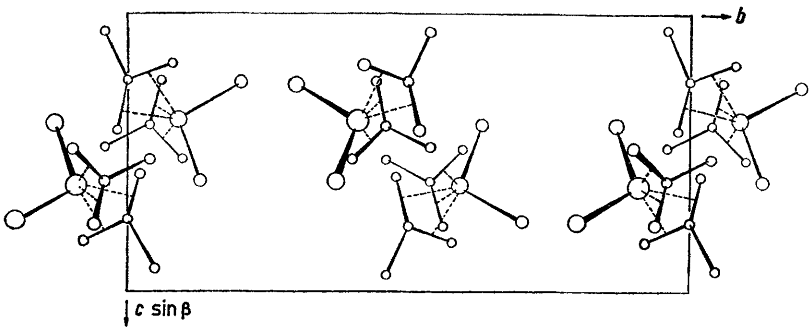

FIGURE 3 The contents of the unit cell viewed down *a* showing the molecular packing

The Methylallyl Ligands.—The methylallyl ligands each bridge two co-ordination positions on the ruthenium atoms, with the 2-methyl groups pointing in a direction away from the phosphite ligands in each case. The ruthenium–allyl carbon distances show that the carbon atoms *trans* to phosphite groups {Ru–C(3)[*trans* to P(1)] 2·36(2), Ru–C(7)[*trans* to P(2)] 2·39(2) Å} are significantly more weakly bonded to the metal than the remainder of the allyl group in each case: [Ru–C(1) 2·11(2), Ru–C(2) 2·12(3), Ru–C(5) 2·25(2), Ru–C(6) 2·12(2) Å] Values of *ca.* 2·20 Å have been observed in $HRu_3(CO)_9(C_{12}H_{15})$ between the three symmetrically π-bonded carbon atoms of the ring and one ruthenium atom of the cluster.[13] No other asymmetrically bonded allylruthenium complexes have been studied to afford direct comparison, but in [chloro(methylallyl)(triphenylphosphine)palladium] values for the metal–carbon bond lengths are: Pd–C(*trans* to Cl) 2·14(3), Pd–C(*trans* to P) 2·28(3) Å.[4]

TABLE 3

Least squares planes defined by atomic positions and, in square brackets, distances of atoms (Å) from these planes *

Plane (i):		
C(1)—(3)	$15{\cdot}003x - 0{\cdot}785y - 4{\cdot}053z - 7{\cdot}127 = 0$	[Ru 1·928, C(4) −0·273]
Plane (ii):		
C(5)—(7)	$12{\cdot}203x + 9{\cdot}049y - 4{\cdot}848z - 12{\cdot}656 = 0$	[Ru −1·915, C(8) 0·430]
Plane (iii):		
C(2), C(3), Ru	$1{\cdot}464x + 17{\cdot}186y + 1{\cdot}575z - 8{\cdot}662 = 0$	[C(1) 0·800]
Plane (iv):		
C(5), C(7), Ru	$8{\cdot}859x - 8{\cdot}344y + 3{\cdot}044z - 4{\cdot}157 = 0$	[C(6) −0·767]

* x, y, z are fractional crystal co-ordinates

The carbon–carbon bond lengths within the allyl fragments of the ruthenium complex are not very accurately determined: C(1)–C(2) 1·36(3), C(1)–C(3) 1·37(3), C(6)–C(5) 1·51(3), C(6)–C(7) = 1·51(3) Å; these values do not differ significantly from those found for other π-allyl complexes.[2-5,14] It has also been observed[4,5] that the carbon atoms which are furthest from the metal tend to be closer to one another, but significant differences in the C–C bond lengths can be established only in the most accurately determined structures. Likewise the angle at the central carbon atom tends to be rather less than the 120° expected for trigonal hybrid bonds.

The dihedral angle between the allyl C_3 plane and the plane defined by the ruthenium atom and the terminal allyl-carbon atoms (=χ, see Figure 4) is 88·6° for C(2)–C(1)–C(3) and 88·0° for C(5)–C(6)–C(7). For most other allyl complexes this angle is significantly greater than 90°: in bis(π-2-methylallyl)nickel[1] and in $[(C_3H_5)_2RhCl]_2$[5] the dihedral angles are 110·3 and 105·5°. Furthermore, the methylallyl groups deviate from the planarity found in the free ligand; the 2-methyl groups have been shown to bend out of the plane of the allyl moiety away from the ruthenium atom by some 12° [Figure 4]. This complex is unique in that other methylallyl transition metal complexes show deviation of the methyl group towards the metal. Values for bis-(π-2-methylallyl)nickel[1] and for (π-2-methylallyl)-palladium chloride dimer[14] are 12·0 and 11·8°.

The Phosphite Ligands.—The ruthenium–phosphorus distances [Ru–P(1) 2·210(5), and Ru–P(2) 2·233(7) Å] suggest considerable back-donation from the ruthenium

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[13] A. Cox and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3599.

[14] R. Mason and A. G. Wheeler, *J. Chem. Soc.* (*A*), 1968, 2549.

atom to the methyl phosphite ligand. In Ru(H)-(AcO)(PPh_3)$_3$,[15] two of the triphenylphosphine ligands exhibit a mutually *trans*-influence and have a mean Ru–P distance of 2·355 Å, while the third triphenylphosphine ligand, which is *trans* to an oxygen atom of the acetate ligand, has Ru–P 2·229 Å. The phosphorus co-ordination is close to tetrahedral (mean Ru–P–O 118·6°) and the mean P–O–C angle is 122·7°.

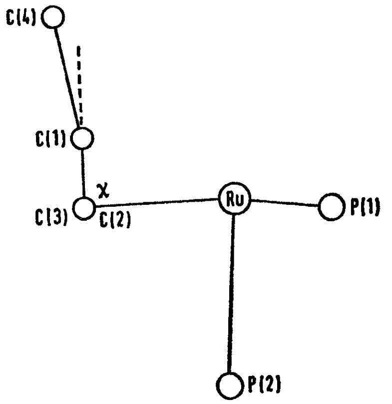

FIGURE 4 Part of the molecule showing both the dihedral angle, χ, between the allyl plane and that defined by the two outer carbon atoms and the ruthenium atom, and the non-planarity of the 2-methylallyl ligand

The Bonding Situation.—From energy considerations [16,17] it is likely that the molecular orbitals of the allyl group which are of symmetry $b_1(1)$ and a_2 (bonding, and non-bonding, respectively, in the free radical) will become bonding with respect to the metal atom, while the molecular orbital of symmetry $b_1(2)$ (which is antibonding in the free radical) will contribute very little to the bonding situation. Back-donation of electrons from the ruthenium atom to the phosphite ligands can be assumed if the length of the Ru–P bond is a reliable indication. The metal–allyl bonds, on the other hand, are likely to involve only a negligible back-bonding component. This *trans*-influence due to phosphorus is in general greater than that due to chlorine or to ethylenic carbon, and the observed asymmetry of the allyl attachment is consistent with this.[18] In [(MeC_3H_4)PdCl(PPh_3)] a similar effect is observed,[4] the more weakly bonded carbon atom of the allyl fragment being *trans* to the phosphorus atom.

The expected magnitude of the angle between the plane of the allyl moiety and that defined by the two outer carbon atoms and the metal has been discussed in relation to the nature of the bonding.[17] According to which orbitals contribute dominantly, the dihedral angle will vary from 90 to 180°. The value of 88° recorded here for the title compound is the lowest yet observed, and even if allowance were made for the asymmetry of the bonding by imagining the more distant carbon atom to be shifted closer to the metal, the dihedral angle would still be not greater than 95°. We have, therefore, an example of one extreme situation being preferred to the exclusion of situations which are favoured in other similar compounds.

The distortion from planarity in the 2-methylallyl ligand itself has been observed in many methylallyl complexes and has been discussed for [(MeC_3H_4)PdCl]$_2$.[14] In bonding with transition metals, electron density is depleted from the ends of the allyl fragment and builds up at the central carbon atom. The hybridisation state of the central atom is between sp^2 and sp^3, and hence tends towards non-planarity. In the present compound, however, where the direction of distortion is opposite to that found in all other allyl complexes so far, the reasons may be primarily steric. The hydrogen atoms of the 2-methyl group [*e.g.* those attached to C(4)] may approach within 2·35 Å of the nearest hydrogen atom on the terminal carbon atom of the other allyl group, C(7); and likewise for the H atoms on C(8) with the terminal hydrogen atom on C(**3**). If the 2-methyl group were bent in the opposite direction (towards the metal) the closest approach would be reduced to 1·70 Å, which is much less than twice the van der Waals radius of hydrogen. In other complexes where such a structural feature has been observed, the deviation is towards the metal and no unfavourable steric interactions have been present.[19]

Intermolecular Forces.—The closest approach between molecules in the crystal is some 3·5 Å. The crystal is therefore reasonably regarded as an almost close-packed array of molecules. The two optical isomers, because of the space-group symmetry, occur in equal numbers.

The Orthorhombic Crystal Form.—No further structural work was carried out on the single orthorhombic crystal found in the original sample, but it seems possible that a close structural relationship may exist. The volume

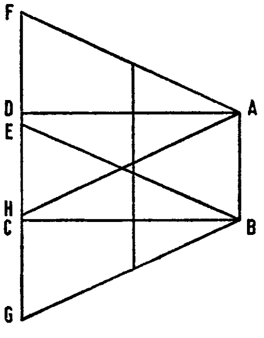

FIGURE 5 Projection down *b* of the unstable orthorhombic form, ABCD, shearing to give two unit cells of the monoclinic form as ABEF and its twin ABGH

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of the unit cell (4013·8 Å^3) is almost exactly twice that of the monoclinic unit (2011·2 Å^3), so that a shear mechanism of the type postulated for 1,2,4,5-tetrachlorobenzene[20] might explain the interconversion here (Figure 5). The idealised parameters of the unit cell would then be: $a = 27{\cdot}78$, $b = 8{\cdot}11$, $c = 17{\cdot}86$ Å, compared with the actual values: $a = 27{\cdot}28$, $b = 8{\cdot}01$, $c = 18{\cdot}43$ Å. The orthorhombic form of the crystal was notably less stable than the monoclinic form and decomposed in the X-ray beam.

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