

ligand" species $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2[\text{S}_2\text{C}_2(\text{CF}_3)_2]$ has $\phi = 38.3^\circ$.²³

Wentworth and coworkers²⁴ have shown that stabilization of octahedral (as opposed to trigonal-prismatic) coordination decreases in the series: low-spin $\text{Fe(II)} > \text{Ni(II)} > \text{high-spin Co(II)} > \text{Zn(II)}$ —or d^6 (low spin) $> d^8 > d^7$ (high spin) $> d^{10}$. These data are applicable to the $[\{\text{FB}(\text{ONCHC}_5\text{H}_5\text{N})_3\text{P}\}\text{M}^{\text{II}+}] \cdot [\text{BF}_4^-]$ species of Holm, for which magnetic moments (μ_{eff} in BM) are 0.4 for Fe(II) , 4.91 for Co(II) , 3.11 for Ni(II) , and ~ 0 for Zn(II) .²

Unfortunately, however, the covalent radii of these metals vary in the same order, *i.e.*, $\text{Fe(II)} < \text{Ni(II)} < \text{Co(II)} < \text{Zn(II)}$. It therefore appears that we will be unable to separate out electronic (ligand-field

(23) D. L. Johnston, W. L. Rohrbough, and W. D. Horrocks, *Inorg. Chem.*, **10**, 1474 (1971).

(24) W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *ibid.*, **9**, 1825 (1970).

stabilization) effects from size effects. We are, however, presently studying the crystal structures of $[\{\text{FB}(\text{ONCHC}_5\text{H}_5\text{N})_3\text{P}\}\text{Co}^{\text{II}+}]$ and $[\{\text{FB}(\text{ONCHC}_5\text{H}_5\text{N})_3\text{P}\}\text{Zn}^{\text{II}+}]$ derivatives, in order to ascertain the distortions that will occur when metal atoms *larger* than Ni(II) are encapsulated by the $[\text{FB}(\text{ONCHC}_5\text{H}_5\text{N})_3\text{P}^-]$ ligand.^{25,26}

Acknowledgments.—We thank Professor R. H. Holm, Dr. J. E. Parks, and Dr. B. E. Wagner for providing samples of the complex. This work was supported, in part, by National Science Foundation Grant No. GP-26293 (to M. R. C.).

(25) There are Co(II) and Zn(II) species which are isomorphous with the Ni(II) complex. Thus ϕ for the first two species will be close to the known value of 1.6° for Ni(II) but need not be identical.

(26) The Co(II) system is particularly difficult to study. The monoclinic modification undergoes a *single-crystal* transformation (of an unknown nature). We do, however, have a stable adduct— $[\{\text{FB}(\text{ONCHC}_5\text{H}_5\text{N})_3\text{P}\}\text{Co}^{\text{II}+}] \cdot [\text{BF}_4^-] \cdot \text{CH}_3\text{CN}$.

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The Structure of Bis(triphenylphosphine)bis(π -allyl)ruthenium, $(\text{C}_6\text{H}_5)_2\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$

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The structure of bis(triphenylphosphine)bis(π -allyl)ruthenium, $(\text{C}_6\text{H}_5)_2\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$, has been determined from three-dimensional data collected by counter methods using graphite-monochromatized Mo $K\alpha$ radiation. Attempts to establish the structure by both chemical and spectroscopic methods had been unsuccessful although nmr results suggested a tetrahedral structure. The unit cell is triclinic, with space group $P\bar{1}$, $a = 11.34$ (1) Å, $b = 9.813$ (4) Å, $c = 17.61$ (1) Å, $\alpha = 87.19$ (5)°, $\beta = 95.55$ (5)°, $\gamma = 108.99$ (5)°, and two molecules of $(\text{C}_6\text{H}_5)_2\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ per unit cell. A disordered solvent molecule (toluene) centered at $(0, 0, 1/2)$ is occluded in the unit cell. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least squares. The final R factors were $R = 0.051$ and $R_w = 0.047$ for 2349 reflections. The mean Ru-C distance [2.128 (16) Å] to the central carbon atoms of the allyl groups is significantly shorter than the Ru-C distances [2.239 (16) Å] to the end carbon atoms of the allyl groups. The bond angles between the central allyl carbons and the Ru and P atoms are all close to tetrahedral. The bond angles along with the shorter Ru-central allyl carbon distances indicate that the Ru is tetrahedrally coordinated to the central allyl carbon atoms and that a significant degree of σ bonding is involved.

Introduction

A crystalline yellow powder of composition corresponding to bis(triphenylphosphine)bis(π -allyl)ruthenium, $(\text{C}_6\text{H}_5)_2\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$, was prepared by Fuchs.¹ Little information could be obtained about the allyl groups from the ir spectrum because of overlapping by the $(\text{C}_6\text{H}_5)_3\text{P}$ bands. The nmr results were uncertain although they suggested a tetrahedral structure.²

Since it had not been possible to establish the structure by the usual chemical and physical methods, a single-crystal X-ray structure determination was undertaken.

Collection and Reduction of the Data

Crystals suitable for X-ray analysis were grown by the slow evaporation of a toluene solution in a stream of dry nitrogen. A pale green crystal of approximate dimensions $0.156 \times 0.171 \times 0.232$ mm was selected for structure determination and mounted in a thin-walled glass capillary in a nitrogen atmosphere.

A series of precession and Weissenberg photographs taken with Ni-filtered $\text{Cu } K\alpha$ radiation showed there were no systematic

extinctions suggesting space group $C_1^1-P_1$ or $C_1^1-P\bar{1}$. A triclinic cell was therefore assigned with unit cell dimensions as determined from diffractometer measurements using Zr-filtered Mo $K\alpha$ radiation (λ 0.71069 Å), $a = 11.34$ (1) Å, $b = 9.813$ (4) Å, $c = 17.61$ (1) Å, $\alpha = 87.19$ (5)°, $\beta = 95.55$ (5)°, and $\gamma = 108.99$ (5)°. A Delaunay reduction of the cell parameters failed to indicate any hidden symmetry; the reduced cell has dimensions $a = 20.002$ Å, $b = 9.8131$ Å, $c = 17.611$ Å, $\alpha = 92.812^\circ$, $\beta = 145.64^\circ$, and $\gamma = 98.12^\circ$. An approximate density of 1.30 ± 0.05 g/cm³ was obtained by flotation in a series of liquids of varying density. A calculated density of 1.278 g/cm³ was obtained for two molecules of $(\text{C}_6\text{H}_5)_2\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ per unit cell.

The crystal used for collecting the data was mounted in a thin-walled Lindemann glass capillary with the a axis of the crystal along the ϕ axis of the diffractometer to minimize the possibility of multiple reflections. The data were collected with a Picker four-circle card-controlled automatic diffractometer using a graphite monochromator crystal with a takeoff angle of 1.5° . The intensities were collected by the θ - 2θ scan technique at a scan rate of $0.5^\circ/\text{min}$. The scan range was -1.0° from $K\alpha_1$ to $+1.0^\circ$ from the 2θ value calculated for $K\alpha_2$. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan range. The scintillation counter was 27 cm from the crystal and had an aperture of 6×7 mm. Molybdenum-foil attenuators were inserted automatically when the intensity exceeded about 7000 counts/sec. A standard reference reflection was measured every 2–3 hr. There were no variations in the intensity beyond that expected from counting

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(1) G. A. Fuchs, personal communication.

(2) C. A. Reilly, personal communication.

TABLE I
ATOMIC COORDINATES^a

Atom	x	y	z
Ru	0.02845 (10)	0.41501 (10)	0.28946 (8)
P(1)	0.17623 (29)	0.59232 (29)	0.22279 (24)
P(2)	-0.17237 (29)	0.43157 (28)	0.25694 (24)
C(1)	0.0060 (13)	0.2663 (14)	0.1920 (11)
C(2)	0.0270 (13)	0.2047 (13)	0.2632 (13)
C(3)	-0.0642 (14)	0.1826 (11)	0.3163 (10)
C(4)	0.0459 (11)	0.5580 (12)	0.3885 (8)
C(5)	0.0817 (13)	0.4371 (13)	0.4085 (9)
C(6)	0.1840 (15)	0.4191 (12)	0.3788 (9)
C(7)	0.1311 (10)	0.6961 (10)	0.1421 (8)
C(8)	0.0288 (11)	0.6249 (11)	0.0947 (9)
C(9)	-0.0093 (12)	0.6912 (13)	0.0296 (9)
C(10)	0.0517 (12)	0.8357 (13)	0.0154 (9)
C(11)	0.1519 (11)	0.9073 (12)	0.0628 (9)
C(12)	0.1946 (11)	0.8401 (12)	0.1262 (9)
C(13)	0.2978 (11)	0.7357 (12)	0.2781 (8)
C(14)	0.2656 (12)	0.8462 (13)	0.3054 (9)
C(15)	0.3579 (15)	0.9538 (15)	0.3515 (10)
C(16)	0.4686 (15)	0.9366 (16)	0.3677 (11)
C(17)	0.5037 (14)	0.8345 (16)	0.3431 (10)
C(18)	0.4169 (13)	0.7279 (13)	0.2959 (9)
C(19)	0.2739 (11)	0.5104 (11)	0.1744 (10)
C(20)	0.3140 (12)	0.4042 (13)	0.2113 (9)
C(21)	0.3759 (13)	0.3270 (14)	0.1734 (12)
C(22)	0.3954 (13)	0.3611 (14)	0.0995 (12)
C(23)	0.3594 (14)	0.4657 (16)	0.0611 (10)
C(24)	0.2994 (13)	0.5426 (14)	0.0995 (11)
C(25)	0.7170 (10)	0.2939 (10)	0.1948 (10)
C(26)	0.6327 (10)	0.1744 (10)	0.2243 (8)
C(27)	0.5564 (11)	0.0624 (11)	0.1776 (11)
C(28)	0.5668 (11)	0.0695 (12)	0.1006 (11)
C(29)	0.6514 (11)	0.1892 (12)	0.0693 (9)
C(30)	0.7259 (10)	0.3000 (11)	0.1164 (11)
C(31)	0.8103 (11)	0.6001 (11)	0.2137 (8)
C(32)	0.7088 (12)	0.6060 (12)	0.1649 (9)
C(33)	0.6990 (13)	0.7374 (14)	0.1367 (9)
C(34)	0.7898 (13)	0.8616 (14)	0.1589 (9)
C(35)	0.8894 (13)	0.8573 (13)	0.2076 (9)
C(36)	0.9002 (11)	0.7262 (12)	0.2349 (8)
C(37)	0.7326 (11)	0.4083 (11)	0.3385 (8)
C(38)	0.7523 (12)	0.3311 (12)	0.4029 (10)
C(39)	0.6772 (13)	0.3068 (13)	0.4640 (9)
C(40)	0.5811 (14)	0.3567 (15)	0.4599 (10)
C(41)	0.5564 (14)	0.4342 (15)	0.3984 (11)
C(42)	0.6324 (14)	0.4625 (14)	0.3365 (10)

^a The standard deviation of the least significant figure is given in parentheses.

statistics. The mean of the observed F_o for the 63 (002) reference reflections was 159.5 electrons with a standard deviation of 0.81.

Data were collected up to $2\theta = 57^\circ$. Since there were very few reflections above background beyond $2\theta \approx 42^\circ$, the data used for the structure determination were restricted to $2\theta \leq 42^\circ$. The data were corrected for Lorentz and polarization effects. The $(LP)^{-1}$ factor used for the monochromator in the configuration of the Picker monochromator was

$$(LP)^{-1} = \sin 2\theta \left(\frac{1 + \cos^2 2\theta_m}{\cos^2 2\theta + \cos^2 2\theta_m} \right)$$

where θ_m is the Bragg angle setting of the monochromator crystal. The $2\theta_m$ value for the graphite monochromator crystal was 20.45° . The linear absorption coefficient for this complex for Mo $K\alpha$ radiation is 5.28 cm^{-1} . The μR values for the crystal ranged from 0.042 to 0.093; therefore, no absorption corrections were applied. The weighting scheme and expression for $\sigma(I)$ were similar to those of Busing and Levy³ and those of Corfield, *et al.*,⁴ with $p = 0.01$. Of the 2610 reflections collected, 2349 with $I \geq 3\sigma(I)$ were given $w > 0$. $\sigma(F)$ was taken equal to $[S_1\sigma(F_o)^2]^{1/2}/2F_o$ where S_1 is a scale factor.

(3) W. R. Busing and H. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(4) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

TABLE II
PRINCIPAL INTERATOMIC DISTANCES^a

Atoms	Dist, Å	Atoms	Dist, Å
RU-P(1)	2.342 (4)	C(15)-C(16)	1.319 (23)
RU-P(2)	2.344 (3)	C(16)-C(17)	1.298 (22)
RU-C(1)	2.249 (17)	C(17)-C(18)	1.417 (21)
RU-C(2)	2.131 (13)	C(19)-C(20)	1.377 (18)
RU-C(3)	2.226 (11)	C(19)-C(24)	1.377 (26)
RU-C(4)	2.245 (13)	C(20)-C(21)	1.412 (21)
RU-C(5)	2.125 (16)	C(21)-C(22)	1.349 (29)
RU-C(6)	2.236 (16)	C(22)-C(23)	1.352 (22)
P(1)-C(7)	1.836 (13)	C(23)-C(24)	1.400 (22)
P(1)-C(13)	1.853 (13)	C(25)-C(26)	1.365 (16)
P(1)-C(19)	1.850 (14)	C(25)-C(30)	1.391 (27)
P(2)-C(25)	1.835 (14)	C(26)-C(27)	1.401 (18)
P(2)-C(31)	1.847 (11)	C(27)-C(28)	1.370 (28)
P(2)-C(37)	1.837 (14)	C(28)-C(29)	1.380 (18)
C(1)-C(2)	1.398 (27)	C(29)-C(30)	1.391 (19)
C(2)-C(3)	1.417 (25)	C(31)-C(32)	1.381 (18)
C(4)-C(5)	1.393 (17)	C(31)-C(36)	1.363 (16)
C(5)-C(6)	1.380 (21)	C(32)-C(33)	1.393 (18)
C(7)-C(8)	1.366 (17)	C(33)-C(34)	1.359 (19)
C(7)-C(12)	1.390 (15)	C(34)-C(35)	1.360 (21)
C(8)-C(9)	1.392 (20)	C(35)-C(36)	1.390 (17)
C(9)-C(10)	1.382 (18)	C(37)-C(38)	1.374 (20)
C(10)-C(11)	1.353 (20)	C(37)-C(42)	1.398 (18)
C(11)-C(12)	1.394 (20)	C(38)-C(39)	1.398 (22)
C(13)-C(14)	1.372 (17)	C(39)-C(40)	1.326 (20)
C(13)-C(18)	1.380 (18)	C(40)-C(41)	1.352 (24)
C(14)-C(15)	1.436 (20)	C(41)-C(42)	1.414 (25)

^a The standard deviation of the least significant figure is given in parentheses.

Structure Determination

The structure was solved by standard Patterson, Fourier, and least-squares calculations. The Ru and both phosphorus atoms were located from a three-dimensional map of the Patterson functions. A series of Fourier and difference Fourier syntheses interspersed with least squares using the identified atoms to calculate the phases for the successive Fourier syntheses led to the location of all nonhydrogen atoms.

The quantity minimized in the least-squares calculations was $\sum w |F_o| - |F_c|^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w , were taken equal to the reciprocals of the variances $\sigma^2(F_o^2)$. The atomic scattering factors were taken from Cromer and Waber's⁵ values with the exception of those for hydrogen which were taken from the values of Stewart, *et al.*,⁶ The anomalous scattering factors for Ru, P, and C were applied throughout the refinement. Cromer's^{7,8} values for $\Delta f'$ and $\Delta f''$ were used.⁹

Three cycles of full-matrix, least-squares refinement of the atomic positions and individual isotropic thermal parameters for the Ru, 2 P, and all 42 carbon atoms decreased the values of R and R_w from 0.40 and 0.47 to 0.15 and 0.18, respectively, where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \left[\frac{\sum w (|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2}$$

The 30 phenyl hydrogens and the 10 allyl hydrogens were then included at the calculated theoretical positions and two additional cycles of least squares were carried out keeping the H positional and thermal parameters constant but applying anisotropic temperature factors to the Ru and two P atoms. The factors R and R_w decreased to 0.127 and 0.130, respectively, but were not further reduced by an additional cycle of least squares.

(5) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3172 (1965).

(7) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(8) D. T. Cromer, personal communication.

(9) In addition to various local programs, the programs used in refinement were Busing and Levy's ORFLS program, Zalkin's FORDAP FOURIER, LSLONG least-squares, and DISTAN distance and angle programs, and Johnson's ORTEP thermal ellipsoid program. Hope's program HPOSN was used to calculate the hydrogen positions.

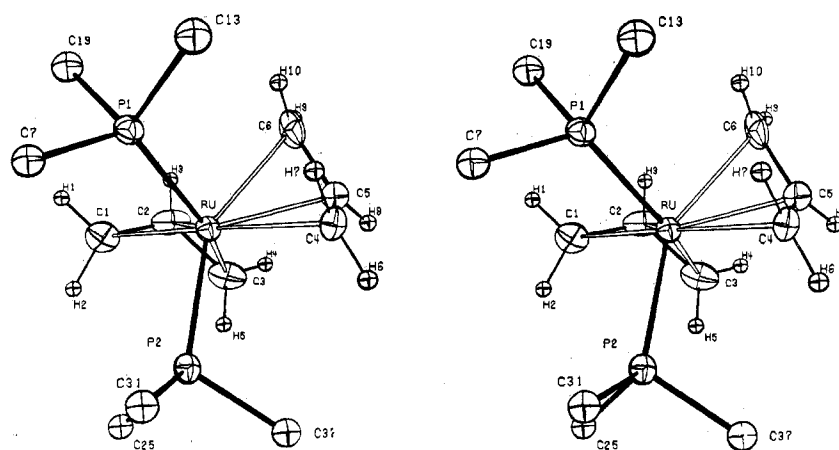


Figure 1.—ORTEP stereoscopic drawing of inner coordination sphere of $(C_6H_5)_2Ru[P(C_6H_5)_3]_2$, 50% probability ellipsoids.

Since the quality of the data would indicate that the R factor should converge to a considerably lower value, it was suspected that solvent molecules might be occluded in the crystal. The density at this point had only been very approximately measured. A difference Fourier was therefore computed which indicated the presence of a disordered toluene solvent molecule centered around $(0, 0, 1/2)$. This was included and three additional cycles of least squares were computed using anisotropic temperature factors on the Ru, P, and allyl carbon atoms and individual isotropic temperature factors on the phenyl C atoms. The 40 hydrogen atoms were included but their isotropic temperature factors and positional parameters were not varied. The discrepancy factors R and R_w decreased to 0.069 and 0.061, respectively. No parameter except those for the solvent molecule had shifted by more than about one-tenth of its estimated standard deviation. A difference Fourier synthesis was again computed and the diffuse electron density of the occluded solvent molecule was more accurately determined. Anisotropic temperature factors were applied to the carbon atoms of the occluded solvent molecule and two more cycles of least squares were computed varying only the positional and temperature factors of the solvent molecule. The R factors decreased to $R_0 = 0.0506$ for the 2349 reflections of nonzero weight and $R_w = 0.047$ and $R = 0.0576$ for 2610 reflections. The standard deviation of unit weight was 0.940, close to the expected value of unity.

The positional parameters derived from the last cycle of least squares are presented in Table I along with the associated standard deviations in these parameters estimated from the inverse matrix. The principal interatomic distances and bond angles of $(C_6H_5)_2Ru[P(C_6H_5)_3]_2$ are given in Tables II and III. The final values of $5F_0$ and $5F_c$ are given in Table IV for the 2610 reflections used in the refinement.¹⁰

Description of the Structure

The crystal structure of $(C_6H_5)_2Ru[P(C_6H_5)_3]_2$ consists of discretely packed molecules with an occluded molecule of solvent (toluene) occupying a hole centered at $(0, 0, 1/2)$. The geometry of the inner coordination sphere is illustrated in ORTEP, Figure 1. The ruthenium-carbon distances of the central carbon atoms of both allyl groups, 2.131 (13) and 2.125 (16) Å, respectively, are significantly shorter at the 7σ level than the Ru-C distances of the end carbon atoms (mean 2.239 (16) Å). Although the Ru-C distances for the end carbon atoms in both allyl groups differ which might suggest asymmetric bonding, the differences are not significant at the 3σ level. In addition, the C-C bonds in the allyl groups do not differ significantly. Evidence

TABLE III

PRINCIPAL BOND ANGLES^a

Atoms	Angle, deg	Atoms	Angle, deg
P(1)-Ru-P(2)	109.9 (1)	C(1)-C(2)-C(3)	118.2 (1.3)
P(1)-Ru-C(2)	111.0 (5)	C(4)-C(5)-C(6)	120.4 (1.3)
P(1)-Ru-C(5)	109.2 (4)	Ru-P(1)-C(7)	122.5 (4)
P(2)-Ru-C(2)	108.8 (4)	Ru-P(1)-C(13)	118.4 (5)
P(2)-Ru-C(5)	112.4 (4)	Ru-P(1)-C(19)	110.2 (4)
C(2)-Ru-C(5)	105.5 (7)	Ru-P(2)-C(25)	118.3 (4)
C(1)-Ru-C(4)	178.17 (5)	Ru-P(2)-C(31)	119.8 (4)
P(1)-Ru-C(1)	91.2 (4)	Ru-P(2)-C(37)	113.9 (4)
P(1)-Ru-C(3)	87.6 (4)	C(7)-P(1)-C(19)	101.6 (5)
P(1)-Ru-C(4)	88.1 (3)	C(13)-P(1)-C(19)	101.3 (6)
P(1)-Ru-C(6)	149.2 (4)	C(25)-P(2)-C(31)	102.3 (6)
P(2)-Ru-C(1)	88.1 (4)	C(25)-P(2)-C(37)	98.6 (6)
P(2)-Ru-C(4)	93.7 (3)	C(31)-P(2)-C(37)	100.6 (5)
P(2)-Ru-C(6)	87.5 (4)		
P(2)-Ru-C(3)	148.9 (4)		

^a The standard deviation of the least significant figure is given in parentheses.

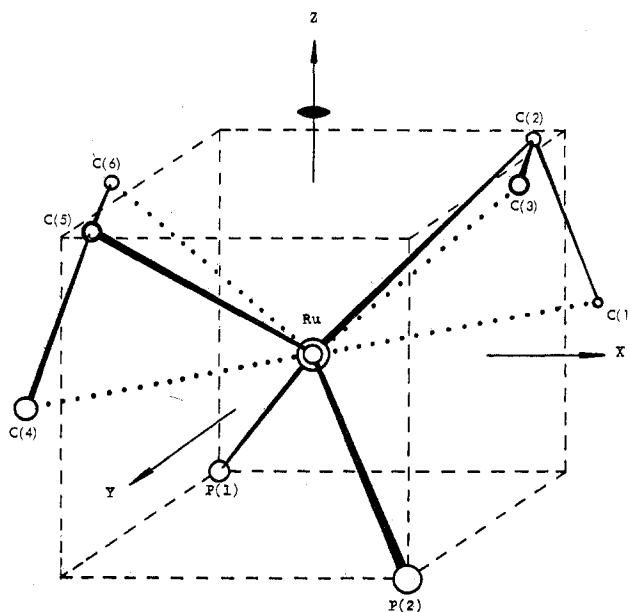


Figure 2.—Schematic drawing of inner coordination sphere— x , y , and z axes indicated.

(10) Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2306. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

for asymmetrical bonding in ruthenium allyl complexes based on nmr data has been reported by Powell and Shaw.¹¹ However, in dichloro(dodeca-2,6,10-triene-

(11) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 159 (1968).

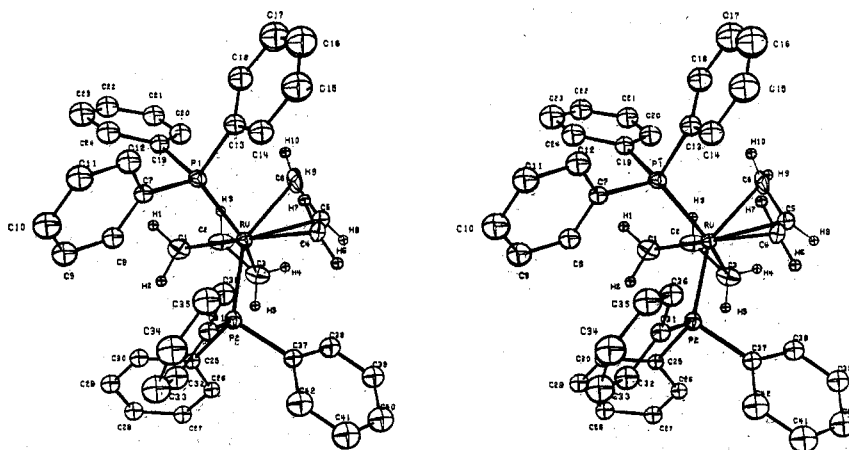


Figure 3.—ORTEP stereoscopic drawing of the entire $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$ molecule. Phenyl hydrogen atoms are not shown for clarity

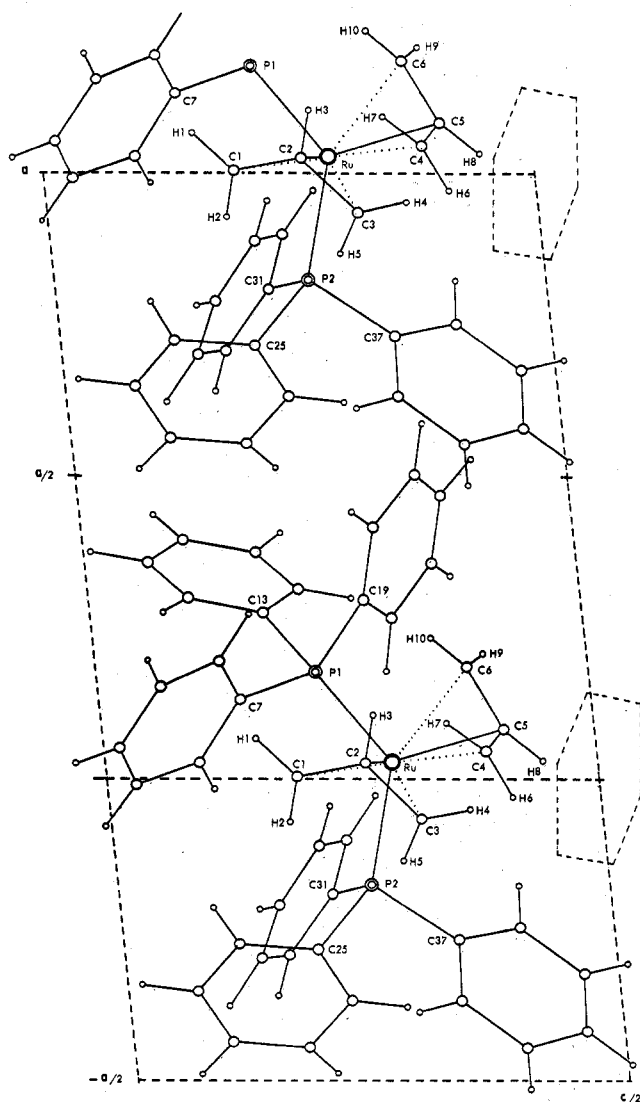


Figure 4.—Packing arrangement of the $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$ molecule projected along the b axis. The occluded solvent molecules are indicated by dotted lines.

1,12-diyl)ruthenium(IV) ($RuCl_2C_{12}H_{18}$)¹² one allyl group is clearly symmetric and the other questionably asymmetric (difference in bond length 2.7σ).

The coordination of the Ru atom relative to P(1) and

(12) J. E. Lydon and M. R. Truter, *J. Chem., Soc. A*, 362 (1968).

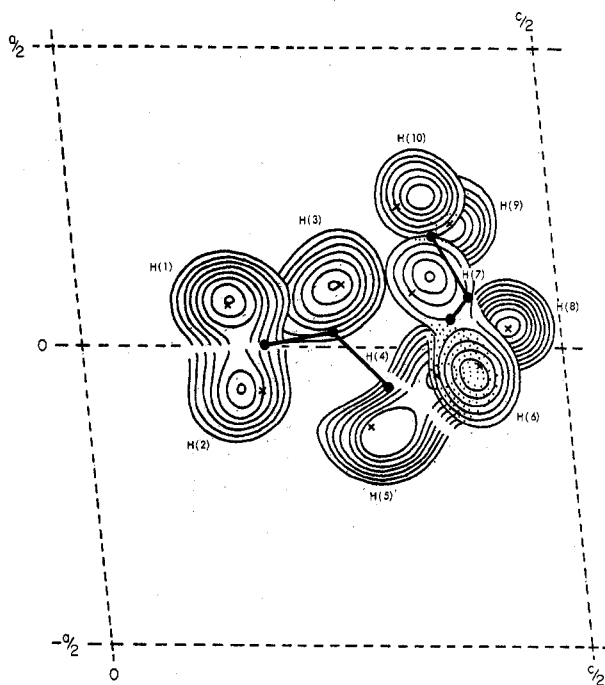


Figure 5.—Composite sections of a difference map indicating the location of allyl hydrogen atoms. The contours are evenly spaced on an arbitrary scale.

P(2) and the central atoms of the allyl groups C(2) and C(5) is tetrahedral. The respective bond angles are (Table III) $P(1)-Ru-P(2) = 109.9(1)$, $P(1)-Ru-C(2) = 111.0(5)$, $P(1)-Ru-C(5) = 109.2(4)$, $P(2)-Ru-C(2) = 108.8(4)$, and $P(2)-Ru-C(5) = 112.4(4)^\circ$. Since the allyl central carbon atom-ruthenium distances are significantly shorter than the end allyl C-Ru distances and allyl central carbon-Ru-P angles are close to 109° , this would indicate that there is a significant degree of σ bonding between the central allyl carbon atom and the ruthenium atom.

If one assumes that the ruthenium atom is in the oxidation state II (the nmr results^{1,2} eliminate $Ru(0)$ which would be paramagnetic), there are 18 electrons in the valence orbitals of the molecule, four from each allyl group, two from each $P(C_6H_5)_3$ group, and six from the d shell of the ruthenium. If the $5s, 5p^3$ orbitals form sp^3 tetrahedral hybrids to the central allyl carbon atoms and to the phosphorus atoms and the d_{xy} , d_{xz} , and d_{yz} orbitals are considered to be involved in forming

π bonds to the allyl groups, 14 electrons would be accommodated. Examination of the structure (Figure 2) shows, however, that although the d_{xy} and d_{xz} orbitals would overlap with the π orbitals of C(1), C(4) and C(3), C(6), respectively, the d_{yz} as well as the d_{z^2} and $d_{x^2-y^2}$ would not overlap appreciably. Six electrons can then be accommodated in the d_{xz} , d_{z^2} , and $d_{x^2-y^2}$ orbitals associated mainly with the ruthenium atom.

The relative arrangement of the allyl groups including the hydrogens with respect to each other and the Ru, as well as the orientation of the thermal ellipsoids for the ruthenium, phosphorus, and allyl carbon atoms, is illustrated in Figure 1. The molecule possesses approximate C_2 symmetry (Figure 2). The dihedral angle between planes C(2)-Ru-C(5) and P(1)-Ru-P(2) is 90.4° . An ORTEP stereoscopic drawing of the entire molecule is shown in Figure 3. The packing arrangement of the molecules projected along the b axis is shown in Figure 4. The Ru-P distances 2.342 (4) and 2.344 (3) Å are shorter than the basal Ru-P distances 2.374 (6) and 2.412 (6) Å reported for the distorted square-pyramidal $\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_3$ complex¹³ but are comparable to those reported¹⁴ for the equatorial distances 2.329 and 2.361 Å for the distorted pyramidal complex $\text{RuClH}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ and for the diruthenium complex $\text{Ru}_2\text{Cl}_3[(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{P}]_6 + [\text{RuCl}_3((\text{C}_2\text{H}_5)_2\text{PC}_6\text{H}_5)_3]^-$ 2.259–2.389 (7) Å (mean 2.326 (7) Å).¹⁵ The P-C₆H₅ distances ranged from 1.835 to 1.850 (14) Å (mean 1.843 (13) Å) close to the mean value 1.848 Å (range 1.823–1.864 Å) reported¹³ for the $\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$ complex and the approximate mean value reported¹⁵ for the binuclear Ru complex.

The final hydrogen coordinates used in the structure factor and least-squares calculations were the theoretical values calculated from the last carbon atom coordinates using normal bond distances and angles. Calculations of the allyl hydrogen-Ru distances showed that four of the distances involving H(2), H(5), H(7), and H(10)

were shorter than the expected sum of the van der Waals radii of about 2.59 Å. In view of the unusual coordination and of the reported¹³ filling of the vacant octahedral site by one of the hydrogen atoms of one of the phenyl rings in $\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$, a difference Fourier was calculated to determine the hydrogen coordinates. All of the hydrogens including those of the allyl group were readily located (Figure 5). The four hydrogens, whose theoretically assumed coordinates indicated by crosses in Figure 5 gave short Ru-H distances, had moved away from the Ru atom to give normal Ru-H van der Waals distances of 2.6–2.8 Å. The coordinates of the other hydrogens were not significantly different from the theoretically calculated values. The planes through the carbon atoms of the allyl groups (based on triclinic coordinates) are (I) $0.1581x + 0.81644y + 0.36347z + 7.18296 = 0$ and (II) $0.38738x + 0.35186y + 0.73917z + 7.18296 = 0$. The distances of the hydrogen atoms from the allyl planes, using the coordinates from the difference Fourier, are given in Table V. The angle between the planes of the allyl

TABLE V
DISTANCES (Å) OF HYDROGENS FROM ALLYL PLANES

Atom	Distance to plane I	Atom	Distance to plane II
C(1)	0.000	C(4)	0.000
C(2)	0.000	C(5)	0.000
C(3)	0.000	C(6)	0.000
H(1)	0.028	H(6)	-0.116
H(2)	-0.489	H(7)	0.376
H(3)	0.044	H(8)	0.015
H(4)	-0.037	H(9)	-0.078
H(5)	-0.388	H(10)	0.369

groups I and II is 35.7° and the angles between allyl groups I and II and the P(1)-Ru-P(2) planes are 32.15° and 31.58° , respectively.

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