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Crystal and Molecular Structure of Chlorotri(3-butenyl)phosphinerhodium(I), $RhClP(CH_2CH_2CH{=}CH_2)_3$

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The crystal and molecular structure of chlorotri(3-butenyl)phosphinerhodium(I) has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in space group $P2_1/c$ with $a = 14.637$ (4), $b = 13.986$ (6), $c = 14.887$ (5) Å, $\beta = 117.76$ (2)°, and $Z = 8$. The observed and calculated densities are 1.59 and 1.65 g/cm^3, respectively. The structure was solved by direct methods and refined to a residual of $R = 0.040$ for 2800 observed reflections. The two molecules in the crystallographic asymmetric unit are enantiomorphs and the molecular structures reveal trigonal-bipyramidal rhodium(I) compounds with nearly perfect threefold symmetry. In each molecule, the phosphorus, chlorine, and rhodium atoms lie on the pseudo-threefold axis, the carbon-carbon double bonds are inclined 13.7° (average) to the equatorial plane defined by the midpoints of the three carbon-carbon double bonds, and the rhodium atom is 0.1 Å out of this equatorial plane. The average rhodium-phosphorus bond length of 2.162 (2) Å is unusually short compared to previously determined values.

Introduction

A novel phosphorus ligand, $P(CH_2CH_2CH{=}CH_2)_3$, has been prepared and used in the synthesis of the five-coordinate complex chlorotri(3-butenyl)phosphinerhodium(I), $RhClP(CH_2CH_2CH{=}CH_2)_3$, by Clark and Hartwell.[1] Their infrared, Raman, and nuclear magnetic resonance studies indicate trigonal-bipyramidal coordination with the rhodium-carbon bonds in the equatorial positions. The compound RhP(*o*-vinylphenyl)$_3$Br, has recently been characterized and found to have trigonal-bipyramidal coordination.[2] The crystal and molecular structures of a few five-coordinate rhodium compounds such as $RhH(CO)(P(C_6H_5)_3)_3$,[3] $RhHCl(SiCl_3)(P(C_6H_5)_3)_2 \cdot xSiHCl_3$,[4] $RhCl(P(C_6H_5)_2CH_2CH_2CH{=}CH_2)_2$,[5] $RhCl(P(C_6H_5)_3)_2$[1,2-bis(phenylpropinoyl)benzol],[6] and $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$[7] have been determined but all of them exhibit distortion from regular trigonal-bipyramidal coordination.

The present study was undertaken to investigate the nature of the tetradentate phosphorus ligand and its bonding interaction with rhodium(I). The rhodium(I)-olefin interactions and the details of the proposed five-coordinate geometry are also of interest. According to the spectroscopic characterization[1] of the compound, the double bonds could be either perpendicular or parallel to the P-Rh-Cl axis of the molecule. Studies of other five-coordinate metal-olefin complexes such as (–)-(fumaric acid)Fe(CO)$_4$ indicate that the double bond can be inclined to the equatorial plane of the molecule.[8] Thus, the relative position of the double bond also served to motivate this investigation.

Experimental Section

Crystal Data. Crystals of $RhClP(CH_2CH_2CH{=}CH_2)_3$ were prepared and supplied by Clark and Hartwell.[1] The off-white rodlike crystals required no further purification from the reaction mixture. The principal faces observed were {100}, {010}, and {011}. Preliminary precession photographs using Mo Kα radiation established Laue symmetry of $2/m$ and the general conditions for nonextinction of $h0l$, $l = 2n$, and $0k0$, $k = 2n$, uniquely determined the space group as $P2_1/c$ ($C_{2h}{}^5$). The experimental density of 1.59 g/cm^3 obtained by flotation was in reasonable agreement with the value of 1.65 g/cm^3 calculated on the basis of eight molecules per unit cell. Thus there were two molecules per asymmetric unit with no molecular symmetry imposed by the space group. The lattice constants $a = 14.637$ (4), $b = 13.986$ (6), $c = 14.887$ (5) Å, and $\beta = 117.76$ (2)° were determined by a least-squares refinement using angular settings for 16 reflections which had been centered at both $\pm 2\theta$ on a Picker FACS-1 four-circle diffractometer.

Intensity Data Collection. A single crystal of dimensions 0.365 × 0.230 × 0.123 mm was mounted on an ultrastable goniometer head of our own design which has translations only. The data were collected with Mo Kα radiation obtained from the 002 reflection of a highly oriented graphite monochromator (λ 0.71069 Å). The crystal to source distance (target-monochromator-sample) was 23.5 cm and the crystal to detector distance was 24.9 cm. The takeoff angle was 2.2°. A scintillation detector with a pulse height discriminator using a window of 11.0–23.79 kV, together with the ω–2θ scan technique, a scan speed of 2°/min, a 2°+ dispersion scan width, 10-sec background counts, and counter aperture size of 2.5 × 2.5 mm, was used. ω scans indicated normal mosaicity. Data in the quadrant $h,k,\pm l$ were collected in the range $0 \leqslant 2\theta \leqslant 50°$. Some redundant data, $-h,k,\pm l$, were collected to compare intense reflections; however, due to time considerations they were limited to the range $0 \leqslant 2\theta \leqslant 20°$. All redundant data agreed to within 2σ (see below). During the data collection, three standard reflections, 061, 404, and $80\bar{6}$, were monitored after every 50 reflections and showed no systematic trends. The maximum variation was 4%. The absorption coefficient μ(Mo Kα) = 15.2 cm^{-1} and the maximum and minimum transmission factors were 0.85 and 0.70, respectively.

Integrated intensities, I, and standard errors, $\sigma(I)$, for the 6707 reflections scanned were calculated as

$$I = C - 0.5(t_c/t_b)(B_1 + B_2)$$

$$\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$$

where C is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are the background counts obtained in time t_b, and ρ is an empirical coefficient.[9] A value of 0.05 was assigned to ρ. Lorentz and polarization corrections were made in the usual manner. The unique set contained 4987 independent reflections of which 2800 had $F_o{}^2 \geqslant 2.33\sigma(F_o{}^2)$ and were considered observed. Preliminary scale and overall temperature factors were determined by Wilson's method.[10]

Solution of Structure and Refinement. Direct methods were used to determine the phases of the largest 618 normalized structure factors, E, and a three-dimensional E map revealed the positions of the rhodium, chlorine, and phosphorus atoms.[11] A sharpened three-dimensional Patterson function confirmed the positions of these heavy atoms. An electron density map, calculated with phases due to the heavy atoms, revealed the positions of all nonhydrogen atoms. Scattering factors for rhodium, chlorine, phosphorus, and carbon were

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Table II. Final Positional Parameters and Anisotropic Thermal Parameters for Nonhydrogen Atoms of $RhClP(CH_2CH_2CH{=}CH_2)_3$[a,b]

Atom	10^4x	10^4y	10^4z	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Rh(1)	329.8 (6)	6934.3 (5)	2037.3 (5)	292 (5)	234 (4)	260 (4)	26 (4)	126 (4)	25 (3)
Cl(1)	−1427 (2)	7656 (2)	1192 (2)	446 (19)	535 (16)	496 (16)	204 (14)	194 (14)	142 (14)
P(1)	1840 (2)	6281 (2)	2763 (2)	296 (18)	310 (14)	320 (14)	51 (12)	133 (13)	28 (11)
Rh(2)	4627.0 (6)	2200.8 (5)	2758.3 (5)	304 (5)	267 (4)	267 (4)	−4 (4)	128 (4)	1 (3)
Cl(2)	6298 (2)	3111 (2)	3488 (2)	443 (19)	470 (16)	620 (18)	−103 (14)	245 (15)	−111 (14)
P(2)	3189 (2)	1414 (2)	2074 (2)	321 (18)	309 (14)	318 (14)	−2 (12)	110 (13)	−2 (11)
C(1)	2230 (7)	6041 (7)	1783 (7)	327 (73)	325 (55)	511 (67)	52 (49)	221 (57)	−43 (50)
C(2)	1241 (8)	5889 (8)	787 (7)	518 (81)	449 (62)	401 (64)	23 (57)	275 (60)	−77 (53)
C(3)	418 (8)	6637 (7)	604 (6)	500 (80)	458 (65)	210 (54)	63 (55)	127 (52)	26 (45)
C(4)	657 (8)	7584 (7)	849 (6)	466 (74)	368 (60)	230 (52)	83 (52)	78 (50)	96 (44)
C(5)	2719 (8)	7086 (8)	3726 (7)	366 (71)	708 (81)	362 (60)	−19 (62)	105 (56)	−153 (62)
C(6)	2359 (9)	8102 (7)	3346 (8)	652 (90)	409 (65)	534 (72)	−226 (62)	264 (66)	−291 (59)
C(7)	1215 (8)	8240 (7)	2971 (8)	639 (89)	331 (58)	510 (69)	−43 (58)	290 (66)	−114 (50)
C(8)	672 (9)	7828 (8)	3411 (8)	574 (87)	486 (72)	458 (66)	48 (62)	223 (64)	−146 (57)
C(9)	1752 (9)	5168 (8)	3365 (9)	607 (92)	433 (67)	663 (86)	181 (64)	355 (74)	239 (58)
C(10)	894 (9)	5327 (8)	3661 (8)	569 (89)	486 (72)	613 (81)	115 (61)	313 (71)	225 (59)
C(11)	−44 (8)	5774 (7)	2844 (8)	555 (87)	355 (60)	638 (79)	−33 (55)	364 (70)	125 (55)
C(12)	−425 (9)	5539 (8)	1838 (10)	476 (86)	304 (59)	829 (106)	−57 (62)	252 (78)	72 (63)
C(13)	3219 (9)	548 (7)	2996 (8)	476 (84)	371 (61)	621 (78)	−48 (60)	250 (69)	108 (57)
C(14)	3866 (9)	967 (8)	4042 (8)	563 (90)	576 (76)	410 (68)	14 (64)	219 (64)	205 (57)
C(15)	4876 (8)	1377 (7)	4168 (7)	465 (81)	490 (69)	300 (60)	31 (59)	114 (58)	115 (49)
C(16)	5450 (9)	978 (8)	3759 (8)	442 (81)	501 (70)	458 (74)	168 (66)	112 (65)	183 (57)
C(17)	2143 (8)	2266 (7)	1760 (8)	344 (73)	471 (66)	522 (70)	70 (56)	176 (58)	12 (59)
C(18)	2507 (8)	3228 (7)	1562 (8)	527 (82)	286 (57)	492 (68)	198 (54)	162 (63)	28 (51)
C(19)	3575 (8)	3497 (6)	2346 (8)	542 (81)	199 (51)	568 (77)	42 (52)	228 (63)	−20 (49)
C(20)	3966 (9)	3331 (7)	3365 (8)	425 (79)	395 (63)	533 (74)	−21 (54)	228 (60)	−139 (53)
C(21)	3071 (8)	799 (8)	946 (7)	523 (86)	385 (62)	424 (68)	−6 (58)	194 (63)	−83 (51)
C(22)	4170 (9)	634 (8)	1114 (7)	614 (90)	493 (69)	326 (64)	111 (63)	211 (62)	−109 (52)
C(23)	4870 (8)	1474 (8)	1548 (7)	440 (77)	524 (70)	448 (69)	12 (64)	252 (63)	−55 (56)
C(24)	4537 (8)	2408 (8)	1245 (7)	471 (81)	493 (71)	390 (64)	−30 (60)	208 (59)	52 (54)

[a] The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Errors in parentheses throughout this paper refer to the least significant figures.

taken from Cromer and Waber.[12] The anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ calculated by Cromer[13] were used for rhodium, chlorine, and phosphorus. The scattering factors for hydrogen were those of Stewart, Davidson, and Simpson.[14]

The positional parameters of the 30 nonhydrogen atoms were refined for two cycles by least squares yielding residuals of $R_1 = 0.083$ and $R_2 = 0.170$ where $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$ where $w = 1/[\sigma(F_o^2)]^2$. Two cycles of isotropic least-squares refinement reduced the residuals to $R_1 = 0.064$ and $R_2 = 0.14$.

Corrections for anomalous dispersion effects of the rhodium, chlorine, and phosphorus atoms were then introduced and anisotropic refinement was begun. Due to computer limitations the positional and anisotropic temperature parameters of all 30 nonhydrogen atoms could not be refined simultaneously. Least-squares refinement computations were iterated in which the parameters for all six heavy atoms plus the twelve carbon atoms of one molecule at a time were varied. After refining until the shifts of all the parameters were less than their standard errors, $R_1 = 0.051$ and $R_2 = 0.120$.

A difference Fourier synthesis was next computed and coordinates of the 42 hydrogen atoms were assigned. Hydrogen coordinates only were then refined until all shifts were less than their standard deviations. The residuals were $R_1 = 0.044$ and $R_2 = 0.097$.

The data were corrected for absorption according to the numerical method of Coppens, *et al.*[15] After further refinement, the final residuals were $R_1 = 0.040$ and $R_2 = 0.092$ for the observed data. The residuals for all 4987 independent reflections were $R_1 = 0.081$ and

Table III. Final Positional Parameters for Hydrogen Atoms of $RhClP(CH_2CH_2CH{=}CH_2)_3$

Atom	10^3x	10^3y	10^3z	Atom	10^3x	10^3y	10^3z
H(1)	259 (7)	659 (7)	177 (6)	H(22)	255 (7)	35 (6)	281 (6)
H(2)	267 (7)	548 (6)	183 (6)	H(23)	348 (7)	−4 (7)	290 (6)
H(3)	101 (7)	525 (7)	77 (6)	H(24)	401 (7)	45 (6)	448 (6)
H(4)	139 (7)	591 (6)	28 (7)	H(25)	344 (7)	144 (6)	418 (6)
H(5)	−18 (7)	647 (6)	11 (6)	H(26)	522 (7)	177 (6)	470 (6)
H(6)	17 (7)	803 (6)	54 (6)	H(27)	611 (8)	103 (6)	407 (6)
H(7)	145 (8)	776 (6)	119 (6)	H(28)	526 (7)	38 (6)	338 (6)
H(8)	347 (8)	700 (6)	390 (6)	H(29)	201 (7)	228 (6)	234 (7)
H(9)	272 (7)	698 (6)	430 (7)	H(30)	155 (7)	205 (6)	121 (6)
H(10)	253 (7)	826 (6)	279 (6)	H(31)	204 (7)	368 (6)	154 (6)
H(11)	270 (7)	855 (6)	385 (6)	H(32)	242 (7)	320 (6)	86 (7)
H(12)	92 (7)	879 (6)	251 (6)	H(33)	385 (7)	396 (6)	208 (6)
H(13)	1 (7)	815 (6)	326 (6)	H(34)	352 (7)	309 (6)	358 (6)
H(14)	107 (7)	752 (6)	397 (7)	H(35)	458 (7)	368 (6)	382 (6)
H(15)	160 (7)	463 (6)	293 (6)	H(36)	270 (7)	18 (7)	83 (6)
H(16)	239 (7)	495 (6)	388 (6)	H(37)	270 (7)	119 (6)	41 (6)
H(17)	120 (7)	569 (6)	426 (7)	H(38)	419 (7)	48 (6)	53 (7)
H(18)	81 (7)	474 (6)	397 (6)	H(39)	447 (7)	12 (6)	153 (6)
H(19)	−55 (7)	596 (6)	298 (6)	H(40)	552 (7)	137 (6)	181 (6)
H(20)	−3 (7)	499 (7)	170 (6)	H(41)	388 (7)	255 (6)	74 (6)
H(21)	−99 (7)	560 (6)	148 (7)	H(42)	503 (7)	287 (6)	135 (6)

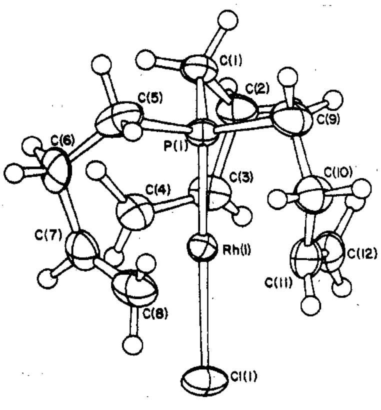

Figure 1. Perspective view of molecule one.

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(11) All computations were performed on CDC 3400-3600 and CDC 6600 computers. For phase determination, a local version of Long's program was used. Gvildy's B-149 was used to compute Fourier summations. Refinement was carried out with Gvildy's ANLFLS, a modification of the least-squares program of Busing, Martin, and Levy. Gvildy's ANLFFE was used to compute bond distances and angles and their standard errors. Least-squares planes and lines were calculated with Norment's program. Figures were produced using Johnson's ORTEP. Absorption correction was made using the DATAPH program by Coppens and Hamilton.

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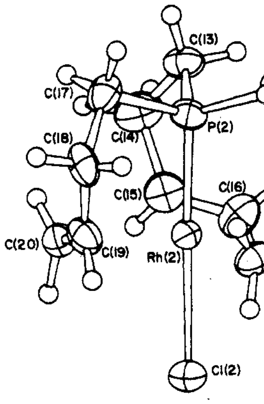

Figure 2. Perspective view of molecule two.

Table IV. Selected Distances (Å) and Angles (deg)

	Distances		
Rh(1)-P(1)	2.160 (2)	Rh(1)-Cl(1)	2.490 (3)
Rh(2)-P(2)	2.165 (3)	Rh(2)-Cl(2)	2.512 (3)
	Angles		
P(1)-Rh(1)-Cl(1)	178.9 (1)	P(2)-Rh(2)-Cl(2)	177.8 (1)
Molecule 1		Molecule 2	
C(1)-P(1)-C(5)	112.1 (5)	C(13)-P(2)-C(17)	110.7 (5)
C(1)-P(1)-C(9)	110.7 (5)	C(13)-P(2)-C(21)	109.9 (5)
C(5)-P(1)-C(9)	109.1 (5)	C(17)-P(2)-C(21)	111.4 (5)
Average	110.6	Average	110.7
CC(1)[a]-Rh(1)-CC(2)	117.5	CC(4)-Rh(2)-CC(5)	117.9
CC(1)-Rh(1)-CC(3)	122.3	CC(4)-Rh(2)-CC(6)	121.8
CC(2)-Rh(1)-CC(3)	119.5	CC(5)-Rh(2)-CC(6)	119.5
Average	119.8	Average	119.7

[a] CC notation refers to the midpoint of a carbon-carbon double bond; 1, 2, 3 refer to ligands of molecule 1; 4, 5, 6 refer to ligands of molecule 2.

R_2 = 0.111. The standard deviation of an observation of unit weight was 0.619. This low value indicates that our errors are somewhat overestimated and ρ should have been assigned a value less than 0.05.

The observed and calculated structure factors are listed in Table I.[16] The final positional parameters and anisotropic thermal parameters for the 30 nonhydrogen atoms are given in Table II. Table III lists the positional parameters for the 42 hydrogen atoms. The isotropic thermal parameter used for the hydrogen atoms was the Wilson plot value of 3.715.

A final difference Fourier revealed no positive maxima greater than 0.73 e/Å^3 and many of the peaks appeared to be due to the residuals from heavy atoms when compared to the corresponding regular Fourier.

Results and Discussion

The crystal structure revealed that the two molecules in the asymmetric unit were enantiomorphs. Perspective views of the two molecules and the numbering scheme are given in Figures 1 and 2. Figure 3 shows a stereoscopic view of molecule one. Figure 4 is a stereoscopic view of the contents of the unit cell. The structure shows a five-coordinate rhodium atom of trigonal-bipyramidal geometry. The phosphorus and chlorine atoms are in the apical positions with the midpoints of the three carbon-carbon double bonds occupying equatorial positions. Bond distances and angles for the two molecules are given in Tables IV-VIII and the notations used are shown in Figures 5 and 6.

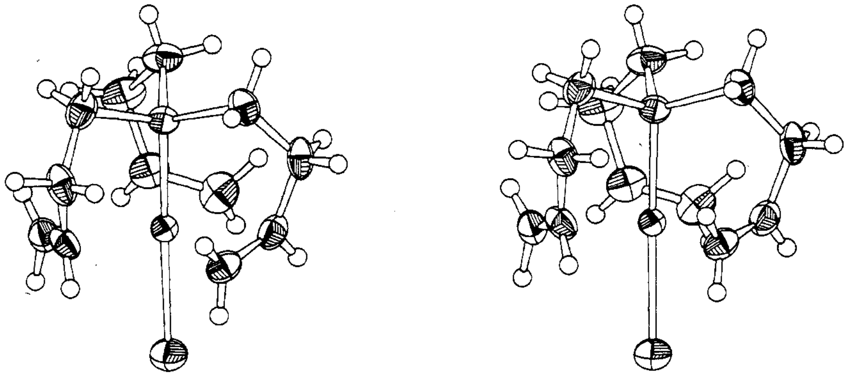

Figure 3. Stereoscopic view of molecule one, RhClP(CH$_2$CH$_2$CH=CH$_2$)$_3$. The thermal ellipsoids are drawn at 50% probability in all figures. The ellipsoids for hydrogen atoms are based on an artificial scale.

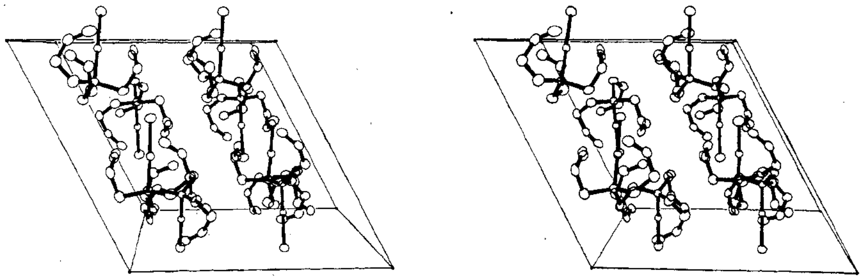

Figure 4. Stereoscopic packing diagram of RhClP(CH$_2$CH$_2$CH=CH$_2$)$_3$ viewed normal to the *xz* plane. Hydrogen atoms have been omitted for clarity.

Although several structures of five-coordinate rhodium with either trigonal-bipyramidal or square-based-pyramidal coordination have been reported, most of them are slightly distorted from ideal five-coordinate geometries.[2-7,17-20] The present structure appears to be a nearly perfect example of trigonal-bipyramidal coordination. Molecular C_3 symmetry is evidenced by the values of the CC-RH-CC angles (Table IV), 117.5-122.3°, which are all close to the ideal value of 120°, where

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(16) See paragraph at end of paper regarding supplementary material.

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Table V. Ligand Bond Distances[a] (Å)

	A	*B*	*C*	*D*	*E*	*F*	*G*
C(1)	1.829 (10)	1.530 (13)	1.521 (13)	1.376 (13)	2.236 (9)	2.124	2.230 (9)
C(5)	1.805 (10)	1.530 (15)	1.512 (15)	1.370 (14)	2.295 (9)	2.165	2.246 (9)
C(9)	1.829 (10)	1.530 (14)	1.482 (14)	1.373 (14)	2.234 (9)	2.104	2.193 (10)
Molecule 1[b]	1.821	1.530	1.505	1.373	2.255	2.131	2.223
C(13)	1.816 (10)	1.515 (14)	1.514 (14)	1.366 (14)	2.270 (9)	2.138	2.219 (10)
C(17)	1.819 (10)	1.526 (14)	1.499 (14)	1.369 (13)	2.270 (9)	2.154	2.251 (10)
C(21)	1.823 (10)	1.525 (14)	1.495 (14)	1.393 (14)	2.236 (10)	2.113	2.214 (10)
Molecule 2[b]	1.819	1.522	1.503	1.376	2.259	2.135	2.228

[a] See Figure 5 for notation. [b] Average value for molecule.

Table VI. Ligand Bond Angles[a] (deg)

	β_1	β_2	β_3	β_4	α_1	α_2	α_3
C(1)	107.8 (3)	107.0 (6)	113.0 (8)	122.1 (10)	84.2 (2)	87.6	91.2 (3)
C(5)	108.5 (4)	106.9 (7)	112.7 (9)	124.0 (10)	82.9 (3)	87.4	91.3 (1)
C(9)	108.4 (4)	105.8 (7)	113.3 (9)	123.0 (10)	82.7 (3)	86.9	91.4 (3)
Molecule 1[b]	108.2	106.6	113.0	123.0	83.3	87.3	91.3
C(13)	107.9 (4)	107.6 (7)	112.4 (9)	124.0 (10)	83.0 (3)	87.2	91.7 (3)
C(17)	107.8 (4)	107.5 (7)	113.7 (8)	124.5 (10)	83.7 (3)	87.9	92.3 (3)
C(21)	109.0 (4)	106.3 (6)	114.2 (8)	122.1 (9)	82.8 (3)	86.3	90.2 (3)
Molecule 2[b]	108.2	107.1	113.4	123.5	83.2	87.1	91.4

[a] See Figure 5 for notation. [b] Average for one molecule.

Table VII. Carbon–Hydrogen Bond Lengths[a] (Å)

	a	*b*	*c*	*d*	*e*	*f*	*g*
C(1)	0.93 (9)	0.98 (9)	0.87 (9)	0.96 (9)	0.87 (9)	1.06 (9)	0.90 (9)
C(5)	0.86 (9)	1.01 (10)	1.00 (9)	0.93 (9)	0.99 (8)	0.88 (9)	1.00 (9)
C(9)	0.95 (9)	0.94 (9)	0.93 (9)	0.97 (9)	0.89 (9)	1.03 (9)	0.75 (9)
Molecule 1[b]	0.91	0.98	0.93	0.95	0.92	0.99	0.88
C(13)	0.94 (9)	0.93 (9)	0.99 (9)	0.93 (9)	0.90 (8)	0.98 (9)	0.86 (9)
C(17)	0.96 (9)	0.92 (9)	1.00 (9)	0.92 (9)	0.94 (9)	0.92 (9)	0.97 (9)
C(21)	0.91 (2)	0.99 (9)	0.92 (1)	0.90 (1)	0.85 (1)	0.92 (1)	0.93 (1)
Molecule 2[b]	0.94	0.95	0.97	0.92	0.90	0.94	0.92

[a] See Figure 6 for notation. [b] Average for one molecule.

Table VIII. Carbon–Hydrogen Bond Angles[a] (deg)

	ν_1	ν_2	ν_3	δ_1	δ_2	*e*	*n*
C(1)	120.7 (73)	119.8 (57)	116.1 (49)	121.2 (60)	111.2 (60)	104.2 (73)	109.3 (74)
C(5)	126.1 (79)	114.9 (52)	112.4 (63)	120.0 (55)	113.9 (54)	105.9 (72)	103.0 (73)
C(9)	118.4 (88)	120.1 (76)	114.3 (50)	110.6 (58)	119.4 (58)	96.9 (67)	97.3 (70)
Molecule 1[b]	121.7	118.3	114.3	117.3	114.8	102.3	103.2
C(13)	109.5 (77)	119.9 (63)	122.3 (57)	115.6 (60)	116.9 (59)	109.8 (72)	98.1 (72)
C(17)	121.5 (76)	117.4 (54)	117.0 (57)	122.6 (56)	110.2 (56)	105.4 (68)	107.8 (75)
C(21)	114.5 (11)	118.3 (11)	122.9 (11)	116.7 (11)	117.5 (11)	103.5 (10)	108.3 (61)
Molecule 2[b]	115.2	118.5	120.7	118.3	114.9	106.2	104.7

[a] See Figure 6 for notation. [b] Average for one molecule.

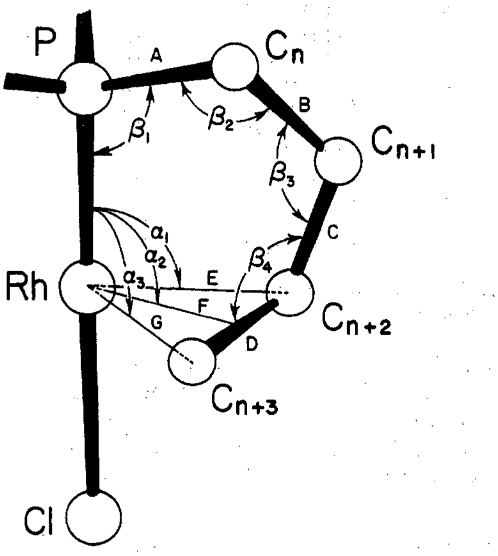

Figure 5. Schematic view showing notation used in Tables V and VI.

CC is the midpoint of the carbon–carbon double bond. Bond distances and angles for the olefin portions of the ligand further illustrate the threefold symmetry (see Tables IV–VIII). The rhodium atoms are 0.1 Å out of (toward chlorine) the equatorial planes defined by the CC midpoints. Table IX gives the data on the planes.

Multiple phosphorus-metal bonding is evidenced by the unusually short average rhodium–phosphorus distance of 2.162 (2) Å. For other five-coordinate structures containing the rhodium–phosphorus bond, the distance varies from 2.176 (10) Å in $RhP(o\text{-vinylphenyl})_3Br$[2] to 2.40 Å.[3-6,17,20,21] Rhodium–phosphorus bond lengths as short as 2.14 Å have been reported, but these are in compounds of four-coordinate rhodium.[22,23] The Rh–P–C and C–P–C angles have average values of 108.2 (4) and 110.6 (5)°, respectively, more nearly tetrahedral than C–P–C angles of 104° for other five-coor-

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Table IX

Plane of the Form $AX + BY + CZ = D$

Atoms	Plane no.	A	B	C	D
CC(1), CC(2), CC(3)	1	11.63	−5.862	0.2810	−3.522
CC(4), CC(5), CC(6)	2	11.18	7.000	0.08077	6.627

Distances of Rh Atoms to Planes

Rh(1)	0.10 Å	Rh(2)	0.11 Å

Lines[a]

Atoms	Line no.	A	B	C	D	E	F
C(3), C(4)	1	0.05375	0.01744	0.7111	0.06886	0.07266	0.01784
C(7), C(8)	2	0.09436	0.03958	0.8034	0.03006	0.3191	−0.03216
C(11), C(12)	3	−0.02344	0.02775	0.5657	0.01708	0.2341	0.07330
C(15), C(16)	4	0.5163	0.04207	0.1178	−0.02920	0.3964	−0.02993
C(19), C(20)	5	0.3771	0.02856	0.3414	−0.01216	0.2856	0.07443
C(23), C(24)	6	0.4704	−0.02390	0.1941	0.06701	0.1397	−0.02175

Dihedral Angles between Planes and Lines

Molecule 1			Molecule 2		
Line no.	Plane no.	Angles, deg	Line no.	Plane no.	Angles, deg
1	1	11.3	4	2	15.3
2	1	16.0	5	2	13.9
3	1	14.1	6	2	11.5
		Av 13.8			Av 13.6

[a] Parametric equations of the line: $X = A + BT$; $Y = C + DT$; $Z = E + FT$.

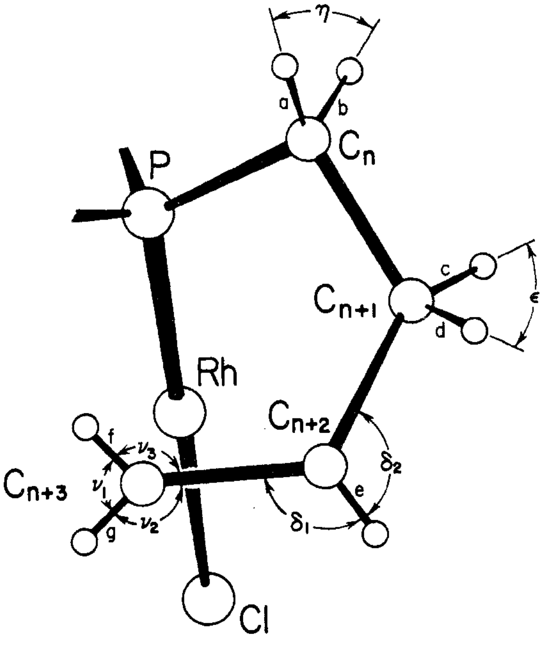

Figure 6. Schematic view showing notation used in Tables VII and VIII.

Table X

Planes

Atoms	Plane no.	A	B	C	D
C(2), C(3), C(4)	3	−5.424	−2.407	14.59	−0.9424
C(6), C(7), C(8)	4	−1.473	11.12	8.580	11.53
C(10), C(11), C(12)	5	10.13	9.993	−6.163	3.9724
C(14), C(15), C(16)	6	1.851	−7.624	10.04	4.038
C(18), C(19), C(20)	7	−6.446	12.46	4.509	3.111
C(22), C(23), C(24)	8	−10.09	1.035	14.27	−2.551

Angles between C–H Bonds and Planes

Plane no.	C–H Bond	Hydrogen	Angle,[a] deg
3	C(3)-H(5)	H_C	24.2
3	C(4)-H(6)	H_B	19.0
3	C(4)-H(7)	H_A	1.2
4	C(7)-H(12)	H_C	15.3
4	C(8)-H(13)	H_B	19.0
4	C(8)-H(14)	H_A	5.0
5	C(11)-H(19)	H_C	27.5
5	C(12)-H(20)	H_A	3.2
5	C(12)-H(21)	H_B	23.0
6	C(15)-H(26)	H_C	19.9
6	C(16)-H(27)	H_B	27.2
6	C(16)-H(28)	H_A	2.7
7	C(19)-H(33)	H_C	17.1
7	C(20)-H(34)	H_A	5.8
7	C(20)-H(35)	H_B	14.2
8	C(23)-H(40)	H_C	19.8
8	C(24)-H(41)	H_A	2.8
8	C(24)-H(42)	H_B	18.4

[a] Angle between line and plane. All are directed away from the rhodium atom.

dinate Rh and Ni compounds.[4,24] This is further evidence for multiple phosphorus-metal bonding.

The average carbon-carbon double bond length of 1.374 (14) Å can be compared to 1.49 (2) Å in RhP(o-vinylphenyl)$_3$Br,[2] to 1.38–1.45 Å in other rhodium-olefin compounds,[5,18,25,26] and to 1.354 (15) Å for the ethylene double bond in the neutron diffraction study of K[PtCl$_3$·C$_2$H$_4$].[27]

For each ligand, the double bond was found to be inclined to the equatorial plane of the molecule defined by the midpoints of the double bonds. The average values for the angles of inclination are 13.8 and 13.6° for molecules one and two, respectively.[28] Similar behavior has been observed

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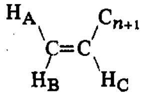
(28) As a reviewer suggested, the inclination of the double bond to the equatorial plane could be a consequence of the structural constraints on the butene group.

in the monoolefin compound (−)-(fumaric acid)$Fe(CO)_4$ where two of the three crystallographically independent molecules have a carbon-carbon double bond inclined to the equatorial plane at an angle of 17°.[8]

The hydrogen atoms of the double-bond carbon atoms are of considerable interest since they appear to be directed away from the rhodium atom. If the double bond remains olefinic, these hydrogen atoms are expected to be coplanar with the C=C bond. In order to investigate the olefin hydrogens further, the plane C_{n+1}, C_{n+2}, and C_{n+3} (see Figure 5) was calculated and the angles between the respective C-H bonds and the plane were computed. Table X gives the planes, lines, and angles. The angles can be summarized as follows for the structure



H_A-C ranges from 1.2 to 5.8°, H_B-C from 14.2 to 27.2°, and H_C-C from 17.1 to 27.5° out of the plane. Although hydrogen atoms are determined poorly at best in a structure containing heavy atoms, there would seem to be significant nonplanarity of the olefin and this would be consistent with a change from sp^2 toward a more complex hybrid due to metal-carbon bonding.

Selected intermolecular contacts[29] and the appropriate symmetry operations are listed in Table XI.

Table XI. Selected Intermolecular Distances

Carbon ref[a]	Atoms	Distance, Å	Symmetry operation
C(17)	H(29)-Cl(1)	2.75 (9)	$\bar{x}, y - 1/2, 1/2 - z$
C(1)	H(1)-Cl(2)	2.82 (9)	$1 - x, 1/2 + y, 1/2 - z$
C(21)	Cl(1)-H(37)	2.76 (3)	$\bar{x}, 1 - y, \bar{z}$
C(18)	Cl(1)-H(32)	2.95 (9)	$\bar{x}, 1 - y, \bar{z}$
C(10)	Cl(1)-H(18)	3.09 (9)	$\bar{x}, 1/2 + y, 1/2 - z$
C(7)	H(12)-C(12)	2.84 (9)	$\bar{x}, 1/2 + y, 1/2 - z$
C(9)	C(21)-H(16)	2.94 (9)	$x, 1/2 - y, -1/2 + z$
C(14)	H(41)-H(25)	2.53 (9)	$x, 1/2 - y, -1/2 + z$
C(15)	H(42)-H(26)	2.65 (8)	$x, 1/2 - y, -1/2 + z$

[a] Carbon atom to which the hydrogen atom is bonded. Hydrogen atoms are numbered consecutively starting with carbon atom 1; *i.e.*, H(1) and H(2) are attached to C(1), H(3) and H(4) are attached to C(2), etc.

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Registry No. (+)-$RhClP(CH_2CH_2CH=CH_2)_3$, 50276-25-0; (−)-$RhClP(CH_2CH_2CH=CH_2)_3$, 50276-26-1.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm editon of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$7.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-792).

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Crystal and Molecular Structure of *trans*-[(Methyl)(methyl-*N*,*N*-dimethylaminocarbene)bis(dimethylphenylphosphine)platinum(II)] Hexafluorophosphate

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The crystal and molecular structure of *trans*-[(methyl)(methyl-*N*,*N*-dimethylaminocarbene)bis(dimethylphenylphosphine)-platinum(II)] hexafluorophosphate has been determined from three-dimensional X-ray data collected on an automatic four-circle diffractometer using Cu radiation. The compound crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with unit cell dimensions $a = 8.515$ (2), $b = 10.934$ (2), and $c = 28.549$ (7) Å with $\beta = 93.93$ (1)°. The observed and calculated densities are 1.77 (1) and 1.76 g cm^{-3}, respectively. Full-matrix least-squares refinement on F gave a final conventional R factor of 0.041 for 1865 reflections with $I > 3\sigma(I)$. The coordination geometry about the Pt atom is square planar, with the carbene ligand lying perpendicular to the plane. The average Pt-P bond distance is 2.294 (3) Å, the Pt-C(methyl) bond length is 2.147 (11) Å, and the Pt-C(sp^2) bond length is 2.079 (13) Å. The C(sp^2)-N bond distance is 1.266 (15) Å. The Pt-C bond lengths are discussed in terms of the trans influences of the methyl and carbene ligands.

Introduction

Square-planar Pt(II) carbene complexes have been prepared in several ways,[1-3] notably by nucleophilic addition to coordinated isocyanides[1,4-7] and by the cleavage of electron-rich olefins in the presence of Pt(II).[2] Both methods yield carbene ligands which contain a C(sp^2) atom stabilized by two adjacent nucleophilic atoms such as O, N, or S. The structures of several of the complexes of this type have been determined by X-ray diffraction methods.[6,8-10]

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