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Crystal Structure of η^5 -Pentamethylcyclopentadienyltriphenylphosphineethylene-rhodium(I). A Case of Important π Component in a Metal-Olefin Bond

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Abstract: The crystal and molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{Rh}(\text{C}_2\text{H}_4)$ was determined from x-ray intensity data measured by a single-crystal automated diffractometer. Crystals are monoclinic, space group $P2_1/n$, with $a = 12.180$ (1), $b = 23.416$ (2), $c = 9.177$ (1) Å, $\beta = 96.60$ (2)°. The structure was solved by Patterson and Fourier methods and refined by least squares to a conventional R value of 0.037, based on 2359 observed reflections. In the molecule, of approximate C_s symmetry, the rhodium atom is coordinated to a $C_5\text{Me}_5$ ring, a triphenylphosphine molecule, and the ethylene ligand, with the approximate mirror plane passing through the Rh and P atoms and the middle point of the ethylene C-C bond. The geometry of the $C_5\text{Me}_5$ ligand is discussed also with reference to a partial localization of electron charge within the ring. The ethylene ligand, whose hydrogen atoms were clearly located in a Fourier difference map, is far from being planar and its conformation, which is characterized by a twist of 20° of the CH₂ groups about the C-C bond axis and by an almost tetrahedral geometry of the C atoms, suggests an important π component in the metal-ethylene bond.

The Chatt-Dewar description of the bonding between transition metals and olefins is now well accepted in the case of square-planar complexes of low oxidation state transition metals. However, this model, while being qualitatively successful in many other cases, does not give a satisfactory interpretation to the bonding mode in general. In the case of some Rh(I) complexes NMR spectra indicate that rotation of the olefinic ligand about the olefin-metal bond occurs at room temperature,^{1,2} thus implying a small or negligible π component in the bond.

A few crystal structures containing molecules with metal-olefin bonds have been solved by Guggenberger et al.;³⁻⁵ in the rhodium complex $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$ ³ the hydrogen atoms of the ethylenic ligand have been clearly located, showing a coordination geometry essentially identical with the one in the Zeise's salt, with the implication that also in this case the π component is not important.⁶

It seemed useful to us to solve and refine the crystal structure of the title compound, since it offered, in view of its similarity with $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$, the possibility of studying the influence of other ligands in determining the balance of the σ and π components in the metal-olefin bond. In this context, of particular interest appeared to be the high basicity of triphenylphosphine and the presence of the methyl substituents in the cyclopentadienyl ring, both factors suggesting a relatively important π component in this case, with a significant

electron back-donation from the metal and the establishment of a strong metal-olefin bond.

Experimental Section

Crystals suitable for x-ray diffraction measurements were obtained by crystallization from pentane of a product obtained by reacting $(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{RhI}_2$ and $(\text{CH}_2)_4\text{MgBr}_2$.⁷ The working conditions of the experiment, carried out on a Philips PW 1100 automatic four-circle diffractometer, and the crystal data are given in Table I.

The unit cell parameters and the space group symmetry were determined using the standard control program of the PW 1100 system,⁸ with a randomly oriented crystal. The cell parameters were refined by least squares, using the 2θ values of the reflections belonging to the $h00$, $0k0$, $00l$, and $h0h$ reciprocal lattice rows.

Intensity data were corrected for Lorentz and polarization effects but not for absorption, in view of the small crystal size and absorption coefficient (μ). The atomic positions were determined by the heavy-atom method and refined by least squares, minimizing $\sum w(F_o - F_c)^2$ with unitary weight factors, in the block-diagonal approximation.⁹ The atomic scattering factors given by Cromer and Mann¹⁰ were used; for the rhodium atom both the real and imaginary dispersion corrections¹¹ were taken into account.

The thermal vibration parameters were refined isotropically in a first stage (three cycles) and then anisotropically (three more cycles); at the end of this process, involving only the nonhydrogen atoms, the conventional R factor ($R = (\sum |KF_o - |F_c||) / \sum KF_o$) reached a value of 0.057 calculated on the basis of the 2359 observed reflections. At this point a Fourier difference map was calculated (with $F_o - F_c$

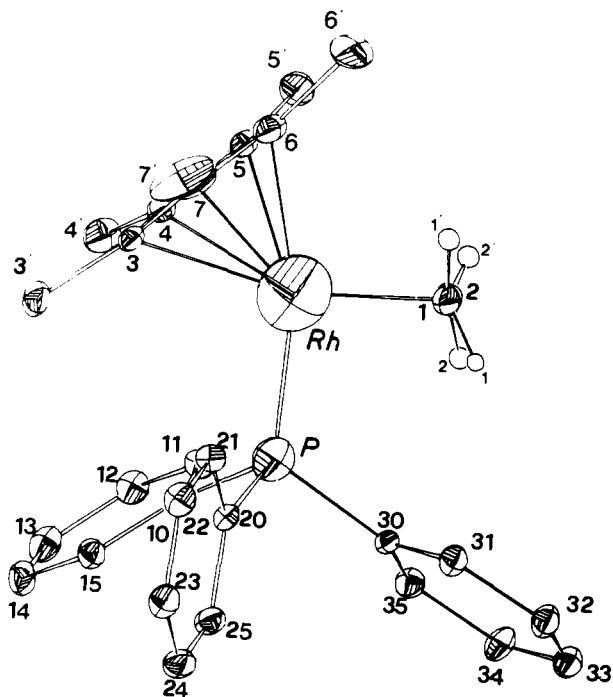


Figure 1. Computer drawing of (η^5 -C₅Me₅)Rh(C₂H₄)(PPh₃), projected along the C(1)-C(2) axis. Only the ethylene hydrogens are shown for clarity.

Table I. Working Conditions and Crystal Data

Scan method	$\omega - 2\theta$
Scan speed	3.0 deg/min
Scan width	1.0°
Background time (half-peak time)	2 × 10 s
θ range, (d min)	3-24° (0.87 Å)
Reciprocal space explored	$-h_{\max} \leq h \leq h_{\max};$ $k, l \geq 0$
Measured reflections	4082
Observed reflections ($I > 3.0 \sigma, \sigma^2 = \text{peak counts} + \text{total back-}$ grounds counts)	2359
Approximate crystal size (cylindrical shape)	0.08 × 0.15 mm
Power used	45 kV × 12 mA
Wavelength (graphite-monochromated Mo K α radiation)	0.710 69 Å
RhPC ₃₀ H ₃₄	Mol wt = 528.48
$a = 12.180$ (1) Å	$\beta = 96.60$ (2)°
$b = 23.416$ (2) Å	$V = 2600.0$ (3) Å ³
$c = 9.177$ (1) Å	Space group $P2_1/n$
$d_c = 1.35$ g/cm ³	$Z = 4$
$\mu = 7.20$ cm ⁻¹	$F(000) = 1096$

coefficients) and 19 electron density peaks were attributed to hydrogen atoms (peaks range 0.6-0.3 e Å⁻³).

Two more least-squares cycles, including the found hydrogen atoms as a fixed contribution in the calculations of the structure factors, were carried out giving a R value of 0.043. Another Fourier difference map showed all the remaining hydrogen atoms so clearly that the positional parameters of all the hydrogens were included in a further refinement in which the hydrogen thermal vibration parameters were kept fixed at the isotropic value of the corresponding carbon atoms multiplied by a factor of 1.2. Four cycles of this refinement brought to a R factor of 0.037, while when the ethylene hydrogens were excluded, the R value, at convergence, was 0.040 (hydrogen parameter final shifts were less than 0.5σ in the average and no final shift of the nonhydrogen atoms was larger than 0.25σ).

Statistical tests, according to Hamilton,¹² computed in the last stages of the described least-squares procedure, showed that the refinement of the hydrogen atoms was highly significant. In particular

Table II. Fractional Atomic Coordinates of (η^5 -C₅Me₅)Rh(C₂H₄)(PPh₃)^a

Atom	x/a	y/b	z/c
Rh	85 752 (5)	16 551 (2)	6391 (6)
P	73 530 (15)	9509 (8)	2430 (18)
C(1)	9525 (8)	1389 (5)	-991 (11)
C(2)	8704 (10)	1771 (5)	-1593 (9)
C(3)	8461 (7)	1866 (3)	2987 (7)
C(3')	7905 (11)	1543 (4)	4098 (9)
C(4)	8019 (6)	2346 (3)	2158 (8)
C(4')	6887 (7)	2592 (4)	2261 (11)
C(5)	8845 (7)	2567 (3)	1429 (8)
C(5')	8729 (10)	3098 (4)	471 (10)
C(6)	9827 (6)	2250 (4)	1766 (9)
C(6')	10 943 (9)	2401 (6)	1302 (15)
C(7)	9623 (7)	1834 (3)	2794 (9)
C(7')	10 454 (12)	1452 (5)	3653 (15)
C(10)	5972 (5)	1162 (3)	674 (7)
C(11)	5520 (6)	1658 (4)	16 (7)
C(12)	4507 (6)	1862 (4)	303 (9)
C(13)	3930 (6)	1573 (4)	1285 (9)
C(14)	4356 (6)	1095 (4)	1992 (9)
C(15)	5378 (6)	889 (3)	1683 (8)
C(20)	7657 (6)	288 (3)	1278 (7)
C(21)	8643 (6)	248 (3)	2183 (8)
C(22)	8937 (7)	-254 (4)	2935 (9)
C(23)	8258 (8)	-720 (3)	2780 (8)
C(24)	7271 (7)	-690 (3)	1874 (9)
C(25)	6970 (7)	-189 (3)	1131 (8)
C(30)	7069 (5)	637 (3)	-1622 (7)
C(31)	7815 (6)	250 (3)	-2064 (8)
C(32)	7669 (7)	20 (4)	-3476 (8)
C(33)	6780 (8)	176 (4)	-4433 (8)
C(34)	6026 (7)	554 (4)	-4004 (8)
C(35)	6179 (6)	786 (4)	-2604 (8)
H(1)	9408 (74)	1067 (39)	-1431 (96)
H(1')	1228 (75)	1479 (38)	-529 (94)
H(2)	8061 (71)	1671 (40)	-2208 (94)
H(2')	9069 (74)	2062 (38)	-1813 (97)
H(3'.1)	7964 (67)	1756 (38)	4998 (89)
H(3'.2)	8365 (71)	1110 (36)	4305 (94)
H(3'.3)	7056 (68)	1507 (37)	3697 (89)
H(4'.1)	6949 (61)	2907 (32)	3132 (80)
H(4'.2)	6310 (60)	2246 (32)	2508 (80)
H(4'.3)	6677 (61)	2747 (32)	1395 (79)
H(5'.1)	9101 (62)	3455 (33)	1087 (82)
H(5'.2)	7955 (63)	3112 (33)	99 (83)
H(5'.3)	9315 (63)	3048 (33)	-256 (83)
H(6'.1)	11 271 (83)	2744 (44)	1896 (112)
H(6'.2)	10 791 (82)	2497 (46)	233 (111)
H(6'.3)	11 452 (84)	1986 (43)	1267 (110)
H(7'.1)	1866 (81)	1612 (44)	4406 (108)
H(7'.2)	11 050 (86)	1317 (43)	2959 (111)
H(7'.3)	9806 (87)	1114 (44)	4182 (110)
H(11)	5961 (46)	1844 (24)	-582 (62)
H(12)	4199 (51)	2191 (27)	-224 (67)
H(13)	3359 (52)	1775 (28)	1659 (70)
H(14)	3945 (54)	858 (28)	2716 (71)
H(15)	5634 (49)	546 (25)	2102 (65)
H(21)	9120 (46)	536 (24)	2213 (61)
H(22)	9577 (52)	-271 (27)	3397 (68)
H(23)	8352 (53)	-1077 (27)	3319 (69)
H(24)	6763 (54)	-1053 (28)	1745 (71)
H(25)	6234 (49)	-163 (26)	495 (66)
H(31)	8418 (49)	103 (26)	-1378 (63)
H(32)	8226 (52)	-236 (27)	-3753 (69)
H(33)	6734 (54)	142 (28)	-5309 (70)
H(34)	5345 (52)	674 (28)	-4702 (69)
H(35)	5562 (50)	997 (26)	-2361 (65)

^a Estimated standard deviations are in parentheses. The values are ×10⁵ for rhodium and phosphorus and ×10⁴ for all the other atoms.

Table III. Thermal Vibration Parameters of $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{PPh}_3)^{a,b}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	355 (2)	364 (2)	295 (2)	-49 (2)	86 (1)	-82 (2)
P	350 (8)	352 (8)	273 (7)	12 (13)	10 (12)	-20 (13)
C(1)	74 (6)	124 (8)	87 (6)	-99 (11)	97 (10)	-135 (12)
C(2)	142 (9)	106 (8)	39 (4)	-130 (14)	68 (10)	-21 (9)
C(3)	77 (5)	42 (4)	26 (3)	-40 (7)	10 (6)	-12 (5)
C(3')	159 (9)	61 (6)	41 (4)	-65 (12)	64 (10)	-14 (8)
C(4)	44 (4)	39 (3)	43 (3)	-4 (6)	7 (6)	-17 (6)
C(4')	50 (5)	74 (6)	83 (6)	8 (8)	16 (8)	-59 (9)
C(5)	59 (4)	39 (4)	38 (4)	-14 (6)	7 (6)	-19 (6)
C(5')	120 (8)	50 (4)	56 (5)	-52 (10)	32 (10)	2 (8)
C(6)	39 (4)	62 (5)	63 (5)	-10 (7)	1 (7)	-48 (8)
C(6')	52 (5)	141 (10)	158 (10)	-89 (12)	96 (12)	-154 (17)
C(7)	74 (5)	47 (4)	48 (4)	24 (7)	-72 (7)	-30 (6)
C(7')	140 (10)	81 (7)	128 (9)	76 (14)	-177 (16)	-74 (14)
C(10)	33 (3)	39 (3)	34 (3)	-8 (5)	6 (5)	-17 (5)
C(11)	41 (3)	46 (3)	42 (3)	6 (7)	-2 (5)	14 (7)
C(12)	45 (4)	63 (5)	48 (4)	26 (7)	-15 (6)	-1 (7)
C(13)	39 (4)	79 (6)	55 (4)	29 (8)	-5 (6)	-38 (8)
C(14)	41 (4)	84 (6)	47 (4)	-4 (7)	24 (6)	-14 (8)
C(15)	43 (4)	56 (4)	38 (3)	-5 (6)	9 (6)	-1 (6)
C(20)	41 (3)	35 (3)	30 (3)	10 (5)	1 (5)	-13 (5)
C(21)	39 (3)	35 (3)	46 (4)	5 (5)	-1 (5)	8 (6)
C(22)	58 (4)	53 (4)	43 (4)	18 (7)	-9 (6)	10 (7)
C(23)	79 (5)	39 (4)	43 (4)	10 (7)	12 (7)	8 (6)
C(24)	74 (5)	36 (4)	59 (5)	-16 (7)	9 (8)	-6 (7)
C(25)	62 (4)	36 (4)	46 (4)	-7 (6)	-2 (6)	-9 (6)
C(30)	34 (3)	40 (3)	31 (3)	-13 (5)	5 (5)	-16 (5)
C(31)	55 (4)	47 (4)	36 (4)	6 (6)	8 (6)	-5 (6)
C(32)	69 (5)	52 (4)	38 (4)	7 (7)	16 (7)	-10 (7)
C(33)	79 (5)	60 (5)	30 (3)	-17 (8)	7 (7)	-5 (6)
C(34)	66 (5)	72 (5)	27 (3)	-3 (8)	-28 (6)	-27 (7)
C(35)	38 (4)	57 (4)	44 (4)	5 (6)	-3 (6)	-5 (7)

^a Estimated standard deviations are in parentheses. The thermal function is $T = \exp[-(\beta_{11}h^2a^*{}^2 + \beta_{22}k^2b^*{}^2 + \beta_{33}l^2c^*{}^2 + \beta_{12}hka^*b^* + \beta_{13}hla^*c^* + \beta_{23}klb^*c^*)/4]$. The values (in \AA^2) are $\times 10^2$ for rhodium and phosphorus and $\times 10$ for all the other atoms. ^b For the thermal parameters of the hydrogen atoms see text.

Table IV. Selected Interatomic Distances of $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{PPh}_3)^a$

Rh-C(1)	2.089(11)	C(5)-C(6)	1.410(11)
Rh-C(2)	2.096(9)	C(6)-C(7)	1.398(12)
Rh-P	2.223(2)	C(10)-C(11)	1.393(10)
Rh-C(3)	2.230(7)	C(10)-C(15)	1.394(10)
Rh-C(4)	2.288(7)	C(11)-C(12)	1.377(11)
Rh-C(5)	2.266(7)	C(12)-C(13)	1.381(12)
Rh-C(6)	2.230(8)	C(13)-C(14)	1.367(13)
Rh-C(7)	2.266(8)	C(14)-C(15)	1.394(11)
P-C(10)	1.839(7)	C(20)-C(21)	1.382(9)
P-C(20)	1.835(7)	C(20)-C(25)	1.393(10)
P-C(30)	1.859(7)	C(21)-C(22)	1.389(11)
C(1)-C(2)	1.408(16)	C(22)-C(23)	1.367(12)
C(3)-C(3')	1.494(13)	C(23)-C(24)	1.383(12)
C(4)-C(4')	1.507(12)	C(24)-C(25)	1.385(11)
C(5)-C(5')	1.520(12)	C(30)-C(31)	1.377(10)
C(6)-C(6')	1.513(14)	C(30)-C(35)	1.373(9)
C(7)-C(7')	1.504(15)	C(31)-C(32)	1.395(10)
C(3)-C(4)	1.427(10)	C(32)-C(33)	1.364(11)
C(3)-C(7)	1.448(12)	C(33)-C(34)	1.365(13)
C(4)-C(5)	1.372(11)	C(34)-C(35)	1.389(10)

^a The given values are in \AA units and the estimated standard deviations are in parentheses.

the inclusion of the ethylene hydrogens brought an improvement in the R value which was significant at the level $\alpha = 0.001$, with $R_q/R_0 > R_{b,n-m,\alpha} = 1.0084$, where $b = 12$, $n = 2359$, and $m = 424$ (for the meaning of these symbols see ref 12). Moreover, in a final Fourier difference map, for which only the ethylene hydrogens were not included in the structure factor calculations, the ethylene hydrogen peaks showed up in positions whose coordinates did not differ from the ones obtained from the refinement by more than 2σ , while the

Table V. Selected Interatomic Angles of $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{PPh}_3)^a$

C(1)-Rh-C(2)	39.3 (4)	P-C(20)-C(25)	123.0 (6)
C(1)-Rh-P	94.4 (3)	P-C(30)-C(31)	118.2 (5)
C(2)-Rh-P	93.4 (3)	P-C(30)-C(35)	123.5 (6)
Rh-C(1)-C(2)	70.6 (6)	C(10)-C(11)-C(12)	121.7 (6)
Rh-C(2)-C(1)	70.1 (6)	C(11)-C(12)-C(13)	119.3 (6)
P-Rh-C(3)	102.0 (2)	C(12)-C(13)-C(14)	121.1 (8)
P-Rh-C(4)	112.6 (2)	C(13)-C(14)-C(15)	119.1 (7)
P-Rh-C(5)	145.1 (3)	C(14)-C(15)-C(10)	121.4 (7)
P-Rh-C(6)	161.6 (3)	C(15)-C(10)-C(11)	117.4 (7)
P-Rh-C(7)	125.4 (5)	C(20)-C(21)-C(22)	120.9 (6)
Rh-P-C(10)	112.2 (2)	C(21)-C(22)-C(23)	120.4 (7)
Rh-P-C(20)	116.8 (2)	C(22)-C(23)-C(24)	119.7 (8)
Rh-P-C(30)	119.6 (2)	C(23)-C(24)-C(25)	120.1 (7)
C(4)-C(3)-C(7)	106.9 (6)	C(24)-C(25)-C(20)	120.7 (7)
C(3)-C(4)-C(5)	107.7 (6)	C(25)-C(20)-C(21)	118.3 (6)
C(4)-C(5)-C(6)	110.2 (6)	C(30)-C(31)-C(32)	120.6 (7)
C(5)-C(6)-C(7)	107.6 (7)	C(31)-C(32)-C(33)	120.1 (7)
C(6)-C(7)-C(3)	107.3 (7)	C(32)-C(33)-C(34)	120.0 (8)
C(10)-P-C(20)	104.6 (3)	C(33)-C(34)-C(35)	119.8 (7)
C(10)-P-C(30)	103.1 (3)	C(35)-C(30)-C(31)	118.2 (7)
C(20)-P-C(30)	98.5 (3)	C(34)-C(35)-C(30)	121.3 (7)
P-C(10)-C(11)	117.2 (5)		
P-C(10)-C(15)	125.3 (7)		
P-C(20)-C(21)	118.6 (5)		

^a The reported values are in degrees and the estimated standard deviations are in parentheses.

shapes of the contour lines were almost identical with the ones of the difference map calculated at the R -value level of 0.043.

The fractional coordinates of all the refined atoms and the anisotropic thermal parameters of the nonhydrogen atoms are given in

Table VI. Selected Best Planes through Groups of Atoms in the Structure

Groups	Plane equations	δ^a
Phenyl ring <i>n</i> .1	$0.454\ 99x + 0.557\ 68y + 0.694\ 58z - 4.663\ 32 = 0$	0.009
Phenyl ring <i>n</i> .2	$-0.461\ 09x + 0.313\ 44y + 0.830\ 15z + 3.977\ 47 = 0$	0.002
Phenyl ring <i>n</i> .3	$-0.527\ 40x - 0.752\ 86y + 0.393\ 76z + 6.607\ 18 = 0$	0.004
Cyclopentadienyl ring	$0.254\ 14x + 0.619\ 73y + 0.742\ 53z - 6.492\ 91 = 0$	0.022

^a δ is the mean square displacement in Å units.

Table VII. C-H Distances (Å)^a

C(3')-H(3'.1)	0.96 (8)	C(11)-H(11)	0.90 (6)
C(3')-H(3'.2)	1.16 (9)	C(12)-H(12)	0.97 (6)
C(3')-H(3'.3)	1.06 (8)	C(13)-H(13)	0.97 (7)
C(4')-H(4'.1)	1.09 (7)	C(14)-H(14)	1.08 (7)
C(4')-H(4'.2)	1.11 (8)	C(15)-H(15)	0.96 (6)
C(4')-H(4'.3)	0.89 (7)	C(21)-H(21)	0.89 (6)
C(5')-H(5'.1)	1.08 (8)	C(22)-H(22)	0.85 (7)
C(5')-H(5'.2)	0.97 (8)	C(23)-H(23)	0.95 (7)
C(5')-H(5'.3)	1.04 (8)	C(24)-H(24)	1.04 (7)
C(6')-H(6'.1)	1.03 (10)	C(25)-H(25)	1.05 (6)
C(6')-H(6'.2)	1.00 (10)	C(31)-H(31)	0.98 (6)
C(6')-H(6'.3)	1.16 (10)	C(32)-H(32)	1.00 (6)
C(7')-H(7'.1)	0.89 (10)	C(33)-H(33)	0.78 (7)
C(7')-H(7'.2)	1.07 (11)	C(34)-H(34)	0.99 (7)
C(7')-H(7'.3)	1.26 (11)	C(35)-H(35)	0.92 (6)

^a Estimated standard deviations are in parentheses.

Tables II and III, respectively. A list of observed and calculated structure factors is available.¹⁹

Results and Discussion

The crystal structure is based on the packing of molecules $(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{Rh}(\text{C}_2\text{H}_4)$ with no intermolecular distance smaller than the sum of the commonly accepted van der Waals radii.

As shown in Figure 1, in the molecule, of approximate C_s symmetry, the rhodium atom is coordinated to a pentamethylcyclopentadienyl ring (hereafter indicated as Me_5Cp), a triphenylphosphine molecule, and the ethylene ligand, with the approximate mirror plane passing through the Rh and P atoms and the middle point of the olefinic C-C bond.

The nonhydrogen atom distances and angles are given in Tables IV and V and the equations of some best planes through groups of atoms are reported in Table VI. The C-H distances are given in Table VII.

We feel that the small dispersion of the phosphine C-C distances about their average value of 1.382 (10) Å (very close to the theoretical value) and the small mean square displacements of the C atoms from the best planes computed for the phenyl rings constitute a proper basis for assessing the reliability of this structure determination.

It may be interesting to compare the general features of the present structure with the ones of π -cyclopentadienylethylenetetrafluoroethylenerhodium, $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$,³ and the ones of π -tetraphenylchlorocyclopentadienylbis(ethylene)rhodium, $(\eta^5\text{-C}_5(\text{C}_6\text{H}_5)_4\text{Cl})\text{Rh}(\text{C}_2\text{H}_4)_2$,¹³ which were solved and refined with comparable accuracy and precision. Also in these cases the molecular symmetry is close to being the one of point group C_s with the pseudo-mirror plane passing through the middle point of the C-C bond of the ethylenic ligand (or ligands). This plane is also a pseudo-symmetry element for the cyclopentadienyl ring, lying perpendicularly to it and passing close to one of its carbon atoms.

The Rh-C(Cp) bonds can be grouped in two sets, one containing three values and averaging 2.273 Å and the other (two values) for which the mean value is 2.230 Å. In the ring only one C-C distance (1.372 Å) is significantly different from the

Table VIII. Bond Distances (Å), Angles (deg), and Torsion Angles (deg) Describing the Conformation of the Ethylene Ligand^a

C(1)-H(1)	0.86 (9)	C(2)-H(2)	0.94 (8)
C(1)-H(1')	0.94 (9)	C(2)-H(2')	0.85 (9)
C(2)-C(1)-H(1)	107 (6)	C(1)-C(2)-H(2')	104 (6)
C(2)-C(1)-H(1')	127 (6)	C(1)-C(2)-H(2)	126 (6)
H(1)-C(1)-H(1')	120 (8)	H(2)-C(2)-H(2')	119 (8)
H(1)-C(1)-C(2)-H(2)			13
H(1)-C(1)-C(2)-H(2')			129
H(2)-C(2)-C(1)-H(1')			168
H(2)-C(2)-C(1)-H(1)			26

^a The estimated standard deviations are in parentheses.

average of the others (1.421 Å). A similar situation was found by Ibers¹⁴ in the complex (dibenzylideneacetone)(pentamethylcyclopentadienyl)rhodium(I) where also two sets of Rh-C(Me_5Cp) distances (2.235 and 2.204 Å) were determined; however, in the latter complex the effect seems to be smaller as indicated also by the fact that no significant differences are seen among the C-C(Cp) distances. The present results are consistent with a ring structure characterized by some localization of electron charge on one of the five C-C bonds and indicate that of the two localized forms¹⁵ A and B the largest



contribution comes from A. This was also shown to be the case in $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$,³ while Day et al.¹⁵ found that form B gives a significant contribution in three η^5 -cyclopentadienyl metal derivatives.

The carbon atoms of the five CH_3 groups are significantly out of the average plane (for the equation of this plane see Table VI) of the Cp ring on the side of the plane which is further from the metal atom.

The ethylene C-C bond distance (1.408 Å) is larger than the corresponding distances in the Zeise's salt and in the uncoordinated molecule, while the average Rh-C(C_2H_4) distance (2.093 (9) Å) is very significantly shorter than the corresponding average distance in $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$ ³ (2.167 (5) Å). As reported in the Experimental Section the ethylene hydrogen atoms were clearly located in a Fourier difference map (Figure 2) and their positions were refined by least squares.

All the bond distances and angles and the torsion angles relevant to the description of the ethylene conformation are given in Table VIII.

Clearly (see also Figure 2) the ligand geometry of ethylene strongly deviates from the one of the free molecule and is characterized by both a bending back—away from the metal—of the hydrogen atoms and a torsion of the CH_2 groups about the C-C bond axis. Since no inter- or intramolecular distance involving the ethylene hydrogens is shorter than the sum of the van der Waals radii, these conformation distortions can be attributed essentially to electronic factors.

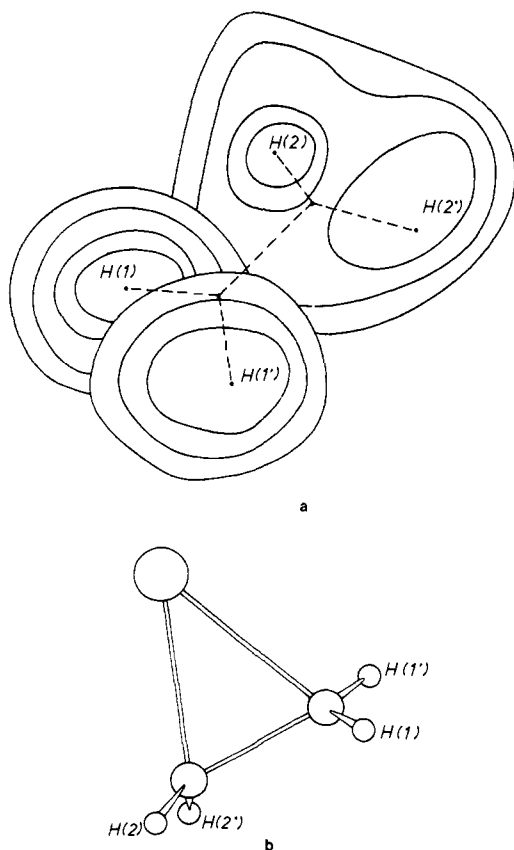


Figure 2. (a) Ethylene hydrogens, as shown by the Fourier difference map calculated at the R -value level of 0.037. Contours are drawn at intervals of 0.1 e. Dots represent least-squares refined ethylene atomic positions. (b) Perspective drawing of the distorted ethylenic ligand and of its coordination bond to rhodium.

One-half (20°) of the difference of the torsion angles $H(1)-C(1)-C(2)-H(2')$ and $H(2)-C(2)-C(1)-H(1')$, which correspond to the dihedral angles γ and γ' defined by Ittel and Ibers,¹⁶ is a measure of the twist of the CH_2 groups relative to each other about the C-C bond axis in the olefinic ligand and constitutes a clear trend toward the staggered geometry characteristic of the first excited state of the free molecule.¹⁷

The bending back can be described by the angle β defined¹⁶ as the angle between the C-C bond axis and the normal to the CH_2 plane. In the present case for the $H(1)-C(1)-H(1')$ group the β value is 71° , not far from the average value (69.1°) found in $(\eta^5-C_5H_5)Rh(C_2F_4)(C_2H_4)$,³ while for $H(2)-C(2)-H(2')$ this value is 61° , much closer to the value (54.8°) computed³

for an idealized tetrahedral geometry of the carbon atoms. We are not able to offer an easy explanation for this apparent dissymmetry in the coordinated ethylene conformation.

Both features, the relative twist of the CH_2 groups and their bending back, together with the very short average $Rh-C(C_2H_4)$ distance and the long C-C bond, are in agreement with a relatively strong π component in the metal-olefin bond and with the proposition put forward by McWeeny et al.,¹⁸ that charge distributions and geometries of unsaturated ligands tend to be identical with those of the corresponding isolated molecules in their first excited triplet states.

The observations leading to the above conclusions about the weight of the π component in the metal-olefin bond, as compared with the case of $(C_5H_5)Rh(C_2F_4)(C_2H_4)$, constitute direct experimental evidence of the effect of ligand substitution on the ground state properties of rhodium-ethylene complexes and show the usefulness of systematic diffraction studies of comparable accuracy and precision on classes of isostructural complex molecules containing different ligands as well as different metals in various oxidation states.

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Supplementary Material Available: A listing of the observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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