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A NOVEL ORGANORHODIUM COMPLEX: THE STRUCTURE OF THE PRODUCT OF THE REACTION OF $Rh(PPh_3)_2(PPh_2C_6H_4)$ WITH TWO MOLECULES OF DIPHENYLACETYLENE

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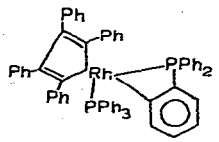
SUMMARY

On the basis of an X-ray structural study it is shown that the product of the reaction of $Rh(PPh_3)_2(PPh_2C_6H_4)$ (Ph = phenyl) with two molecules of diphenylacetylene represents a novel molecular system. The product has the composition $Rh(PPh_3)(PPh_2{-}C_6H_4{-}C_4Ph_4)$ and may be named 5,5,7,8,9,10-hexaphenyl-6-(triphenylphosphine)-5,6-dihydro-5-phospha-6-rhodabenzocyclooctene. The coordination about the Rh atom is distorted square-planar. The P of the PPh_3 group is at one coordination site. The P of the $PPh_2C_6H_4X$ is at a second coordination site. The X group *ortho* to P on the C_6H_4 ring has formal composition C_4Ph_4 and is coordinated to the Rh in a bidentate manner via both a π and a σ bond, thus completing the coordination. The material crystallizes as a 1/1 toluene complex with four formula units in space group C_{2h}^5 $-P2_1/n$ of the monoclinic system in a cell of dimensions $a = 20.262(7)$, $b = 14.535(5)$, $c = 18.476(8)$ Å, $\beta = 91.54(2)^\circ$. The final conventional R factor is 0.049 for the 2019 X-ray data collected by counter methods.

INTRODUCTION

There are several[1-3] organometallic systems in the literature in which there is a postulated tautomerism between a given species and one formed by hydrogen migration from an aromatic ring of a ligand onto the metal with consequent formation of a metal–ring-carbon σ bond. Such a tautomerism seems necessary, for example, to explain the deuterium exchange of the 18 *ortho*-hydrogen atoms in $CoH(N_2)(PPh_3)_3$[4]. None of the above systems has yielded products sufficiently stable for direct structural confirmation of the postulated metal–carbon σ bond. Yet, close metal–hydrogen interactions, for example in $RuCl_2(PPh_3)_3$[5], make such exchange reactions structurally plausible.

Keim[6] has described the formation of $Rh(PPh_3)_2(PPh_2C_6H_4)$ by the action of heat on the complex $Rh(CH_3)(PPh_3)_3$ with evolution of methane. Subsequent reaction of this product with diphenylacetylene[7] yields a diamagnetic species whose postulated structure is



with the Rh atom in a trigonal bipyramidal coordination. Evidence for this formulation is based on NMR, spectroscopic, mass spectral, and elementary analyses. At the time this work was initiated there were no reports in the structural literature of a metal–carbon σ bond between a metal and the aromatic portion of a phosphine ligand*. The present study of Keim's compound was undertaken not only because the evidence was very good for a metal–carbon σ bond but also because the compound contains an interesting ring system. Although this structural study did not reveal the presence of a metal–(phenyl)-carbon σ bond it did reveal a totally unexpected and new molecular system.

EXPERIMENTAL

Preparation and preliminary X-ray examination

Crystals were prepared by Dr. W. Keim by refluxing a toluene suspension of $Rh(PPh_3)_2(PPh_2C_6H_4)$ and diphenylacetylene. Upon cooling the solution, dark-red crystals were obtained. The preparation and spectral data have been discussed previously[7]. However, the product as confirmed by our study is different from that originally proposed. On the basis of precession and oscillation photographs we established that the crystals belong to the monoclinic system. The cell dimensions obtained with Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) at 21.3° from the refinement of the setting angles of 14 reflections centered on a four-circle diffractometer[9] are $a = 20.262(7)$, $b = 14.535(5)$, $c = 18.476(8)$ Å, $\beta = 91.54(2)°$. A density of 1.31 g/cm^3 calculated for four formula units of $Rh(PPh_3)(PPh_2\text{–}C_6H_4\text{–}C_4Ph_4)\cdot C_7H_8$ per unit cell agrees with that of 1.29 g/cm^3 measured by flotation in aqueous zinc chloride. Precession photographs of the $hk0$, $hk1$, $0kl$, and $1kl$ nets show systematic absences $h0l$ for $h+l$ odd and $0k0$ for k odd that are characteristic of the space group C_{2h}^5–$P2_1/n$.

Collection and reduction of intensity data

Intensities were collected with Cu $K\alpha$ radiation from a crystal of tetragonal prismatic habit of approximate dimensions 0.2 mm along b^* (the prism axis) and 0.1 mm diameter. Diffractometer data were collected on a Picker four-circle instrument in a manner previously described[9,10]. A unique data set collected out to $2\theta(\text{Cu } K\alpha) = 77°$ yielded 2994 independent reflections of which 2019 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$, and these are described as being above background. Beyond $2\theta = 77°$ there were relatively few reflections satisfying the above condition. The intensities of four standard reflections were measured periodically; no crystal decomposition was discerned. The data were collected by the θ–2θ scan technique at a scan rate of 1°/minute from $-0.50°$ from $K\alpha_1$ maximum to $+0.50°$ from $K\alpha_2$ maximum. Station-

* Recently, Mason and Towl[8] have provided evidence for a Rh^{III}–C σ bond as part of a five-membered chelate ring system formed by an o-tolylphosphino ligand.

ary-crystal, stationary-counter background counts were taken for 20 sec at each end of the 2θ scan range. The diffracted beams were filtered through 1.0 mm Ni foil. The counter was placed at 31 cm from the crystal and was preceded by an aperture of 3.5 mm by 3.5 mm. The pulse height analyzer was adjusted to receive approximately 90% of the diffracted radiation. The takeoff angle was 1.5°. The diffracted beams were attenuated by Cu foil when necessary to prevent coincidence losses. The data were processed in the manner described previously[9,10] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0.03 for p was used in the estimation of standard deviations.

Solution of the structure

An unsharpened, three dimensional Patterson function* was prepared from the 2019 data which were above background. It was interpreted to give the coordinates of the rhodium and both phosphorus atoms. The remaining non-hydrogen atoms were readily located by the usual combination of Fourier and least-squares methods. In the least-squares calculations the function minimized was $\Sigma(w\cdot\Delta^2)$, where $\Delta = |F_o|-|F_c|$, with $|F_o|$ and $|F_c|$ the observed and calculated structure amplitudes, and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for all non-hydrogen atoms were taken from the usual tabulation[12], while those for H were taken from the calculations of Stewart *et al.*[13]. The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for the rhodium and phosphorus atoms were taken from the calculations of Cromer[14] and were included in F_c[15]. An absorption correction was made. The faces of the data crystal were measured and identified by optical means. Four of the crystal faces belonged to the forms {100} and {101}. The other faces were indexed as $(\bar{1}10)$, $(\bar{1}\bar{1}0)$, $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, and (010). A calculated linear absorption coefficient of 34.4 cm^{-1} led to transmission factors which varied between 0.60 and 0.81. The trial structure was refined by a least-squares procedure in which the phenyl rings were constrained to D_{6h} symmetry and treated as rigid groups[16] (C–C 1.390 Å) with individual isotropic thermal parameters. This initial isotropic refinement, based on 2019 independent reflections obeying the condition $F_o^2 > 3\sigma(F_o^2)$, converged to values of R_1 and R_2 of 0.084 and 0.102 respectively, where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = \{\Sigma[w\cdot(|F_o|-|F_c|)^2]/\Sigma(w\cdot F_o^2)\}^{\frac{1}{2}}$. A difference Fourier synthesis revealed the presence of toluene in the ratio of one toluene molecule to one formula unit of the rhodium complex. The hydrogen atoms of the toluene methyl group were observed in a difference Fourier synthesis and their positions as well as the positions of all 54 phenyl hydrogen atoms were idealized on the assumption that C–H = 0.98 Å. The contributions from these idealized hydrogen atoms were added in a fixed manner to subsequent structure factor calculations. Two cycles of least-squares refinement which allowed for anisotropic thermal vibration of 13 non-group atoms together with rigid group refinement of nine phenyl rings and the solvent molecule (methyl-carbon–phenyl-carbon distance 1.520 Å) with individual isotropic thermal parameters on the carbon atoms led to values of $R_1 = R_2 = 0.048$. However, this refinement yielded non-positive definite temperature factors for two of the anisotropically vibrating carbon atoms. A subsequent cycle in which the rhodium and phosphorus atoms were allowed anisotropic

* In addition to various local programs for the CDC 6400, local variations of the programs in ref. 11 were used in this study. NUCLS, the least-squares program, in its non-group form, resembles the Busing–Levy ORFLS program.

TABLE 1

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B (Å^2)
Rh	−0.01009(5)[a]	0.22037(7)	0.27795(5)	
P(1)	0.0874(2)	0.2421(2)	0.2214(2)	
P(2)	−0.0044(2)	0.3481(2)	0.3524(2)	
C(1)	0.0917(6)	0.1474(8)	0.1590(6)	3.0(3)
C(2)	0.0351(6)	0.0952(9)	0.1493(6)	3.1(3)
C(3)	0.0332(6)	0.0246(8)	0.0968(6)	3.4(3)
C(4)	0.0864(6)	0.0063(8)	0.0561(6)	4.1(3)
C(5)	0.1438(6)	0.0568(9)	0.0663(6)	4.3(3)
C(6)	0.1477(6)	0.1271(9)	0.1162(7)	4.4(3)
C(7)	−0.0232(5)	0.1098(8)	0.1985(6)	3.0(3)
C(8)	−0.0234(5)	0.0704(7)	0.2685(6)	2.7(3)
C(9)	−0.0864(5)	0.0793(8)	0.3093(6)	2.7(3)
C(10)	−0.0970(5)	0.1675(8)	0.3219(6)	2.7(3)

ANISOTROPIC THERMAL PARAMETERS

Atom	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.00131(3)	0.00367(7)	0.00176(4)	−0.00019(5)	0.00022(3)	−0.00037(6)
P(1)	0.0018(1)	0.0046(3)	0.0026(2)	0.0000(1)	0.0003(1)	−0.0004(2)
P(2)	0.0020(1)	0.0045(3)	0.0025(2)	−0.0001(2)	0.0002(1)	−0.0004(2)

RIGID GROUP PARAMETERS

Group[c]	x_c[d]	y_c	z_c	δ	ε	η
A[d]	0.1015(3)	0.4159(4)	0.1124(3)	−1.740(6)	3.034(6)	0.675(5)
B	0.2226(3)	0.2271(4)	0.3167(3)	2.986(7)	−3.098(6)	−0.592(4)
C	0.1193(3)	0.4905(4)	0.3506(3)	−2.360(14)	−2.089(5)	0.115(13)
D	0.4999(2)	0.2263(4)	0.0161(3)	2.344(5)	−2.837(6)	−1.823(5)
E	−0.1227(2)	0.4937(4)	0.3267(3)	2.577(9)	2.368(5)	−3.360(7)
F	−0.1389(3)	0.1401(4)	0.1038(6)	−0.389(6)	2.875(5)	0.680(5)
G	0.0800(3)	−0.0328(4)	0.3428(3)	0.588(10)	−2.110(6)	−1.899(9)
H	−0.3396(2)	0.4134(4)	0.1565(2)	0.164(6)	3.009(5)	−0.736(4)
I	−0.2065(3)	0.2499(3)	0.3949(3)	1.271(10)	2.090(6)	−1.759(9)
T	0.5255(3)	0.2154(4)	0.3766(3)	2.584(15)	1.912(6)	3.036(15)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2h\cdot k\cdot\beta_{12}+2h\cdot l\cdot\beta_{13}+2k\cdot l\cdot\beta_{23})$. These parameters lead to the following rms amplitudes of vibration (A) for Rh, P(1), and P(2): 0.158(2), 0.171(2), 0.206(2): 0.188(7), 0.207(6), 0.229(7): 0.196(7), 0.203(7), 0.228(6). [c] Groups A–E are phenyl rings attached to the two phosphorus atoms [A and B to P(1), C, D, E to P(2)], groups F–I are phenyl rings attached to carbons (7)–(10) respectively, and group T is the toluene molecule of crystallization. [d] x_c, y_c, and z_c are the fractional coordinates of the ring center; δ, ε, and η (in radians) have been defined in ref. 16.

vibration while the non-group carbon atoms were restricted to isotropic motion with the phenyl rings and solvent molecules included as above resulted in values of $R_1 = R_2 = 0.049$ for 189 variables. There was no discernible change in the positions of the non-group carbon atoms in going from anisotropic to isotropic refinement. Hence,

these R values are taken as the final ones and the final parameters are given in Table 1. Also included in Table 1 are the standard deviations of these parameters as estimated from the inverse matrix. The derived positions for the ring carbon atoms as well as the idealized positions of the hydrogen atoms are given in Table 2. An analysis of $\Sigma[w\cdot(|F_o|-|F_c|)^2]$ as a function of scattering angle, $|F_o|$, and Miller indices reveals no unexpected trends and provides no evidence for extinction effects. Thus the relative weighting scheme used appears to be a reasonable one. The error in an observation of unit weight is 1.69. The final values of the structure amplitudes are tabulated as $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinement*. The maximum density on a final difference Fourier synthesis is 0.37 electron/Å^3, approximately 12% of the height of a carbon atom in this structure.

DISCUSSION

The structure consists of discrete monomeric molecules of the rhodium complex interspersed with molecules of toluene. There are no unusual intermolecular contacts.

A drawing of the coordination sphere about the rhodium atom, together with selected bond lengths and the numbering scheme, is presented in Fig. 1. The compound may be named 5,5,7,8,9,10-hexaphenyl-6-(triphenylphosphine)-5,6-dihydro-5-phospha-6-rhodabenzocyclooctene. A stereoscopic drawing of the complete molecule is shown in Fig. 2. This complex differs from that postulated by Keim[7] because of the presence of a C(2)–C(7) bond and the absence of a Rh–C(2) bond. The entire molecule appears to be without precedent. Thus while a structure is known in which there is a

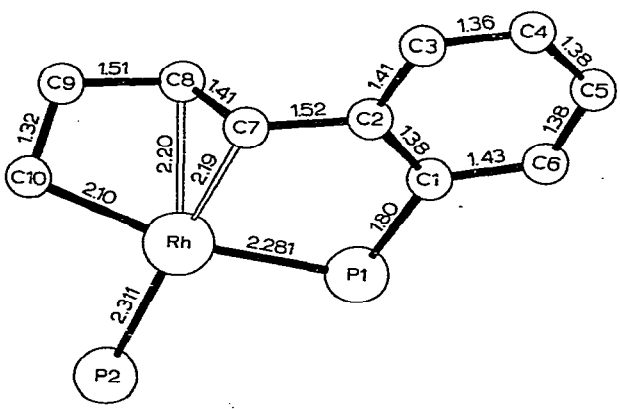


Fig. 1. The inner coordination sphere about the Rh atom, showing important bond distances and the numbering scheme. Note that the addition of nine phenyl rings completes the molecule. Thus C(7), C(8), C(9), and C(10) each have an attached phenyl ring, P(1) has two attached phenyl rings, and P(2) has three attached phenyl rings.

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TABLE 2

DERIVED PARAMETERS FOR RING ATOMS AND IDEALIZED HYDROGEN ATOM POSITIONS

Ring atom	Carbon				Hydrogen[a]		
	x	y	z	B (Å²)	x	y	z
A1[b]	0.0970(5)[c]	0.3412(5)	0.1591(4)	3.8(3)			
A2	0.0410(4)	0.3924(7)	0.1410(4)	4.4(3)	−0.002[d]	0.377	0.162
A3	0.0454(4)	0.4671(6)	0.0944(5)	5.0(4)	0.006	0.504	0.082
A4	0.1060(6)	0.4906(5)	0.0658(4)	7.1(4)	0.109	0.544	0.033
A5	0.1620(4)	0.4393(7)	0.0838(5)	6.7(4)	0.204	0.455	0.063
A6	0.1575(4)	0.3647(6)	0.1305(5)	5.5(4)	0.197	0.328	0.143
B1	0.1661(3)	0.2371(8)	0.2731(4)	3.4(3)			
B2	0.2036(5)	0.3138(5)	0.2924(5)	4.9(4)	0.191	0.375	0.275
B3	0.2601(4)	0.3038(7)	0.3360(5)	5.9(4)	0.287	0.359	0.350
B4	0.2792(3)	0.2170(9)	0.3603(4)	6.9(4)	0.319	0.211	0.392
B5	0.2417(5)	0.1403(6)	0.3411(5)	8.3(5)	0.256	0.080	0.359
B6	0.1852(5)	0.1503(6)	0.2975(5)	6.4(4)	0.160	0.096	0.284
C1	0.0661(4)	0.4304(5)	0.3533(5)	3.6(3)			
C2	0.0720(4)	0.4895(7)	0.2947(4)	4.6(4)	0.039	0.489	0.255
C3	0.1252(5)	0.5497(6)	0.2920(4)	6.1(4)	0.131	0.591	0.250
C4	0.1725(4)	0.5507(6)	0.3479(6)	6.2(4)	0.211	0.592	0.346
C5	0.1667(4)	0.4915(7)	0.4065(4)	6.1(4)	0.200	0.493	0.446
C6	0.1135(5)	0.4313(6)	0.4092(4)	4.9(4)	0.109	0.391	0.451
D1	0.4976(4)	0.1898(6)	−0.0534(3)	3.1(3)			
D2	0.5393(4)	0.2632(6)	−0.0370(4)	4.4(3)	0.567	0.289	−0.075
D3	0.5416(4)	0.2997(5)	0.0325(6)	5.2(4)	0.573	0.352	0.043
D4	0.5022(5)	0.2628(6)	0.0857(3)	4.6(3)	0.506	0.290	0.135
D5	0.4605(4)	0.1893(6)	0.0692(4)	4.8(4)	0.433	0.166	0.107
D6	0.4582(4)	0.1528(4)	−0.0003(5)	4.4(3)	0.428	0.103	−0.011
E1	−0.0716(3)	0.4316(6)	0.3398(5)	2.9(3)			
E2	−0.0744(4)	0.5127(7)	0.3794(4)	4.3(3)	−0.042	0.527	0.416
E3	−0.1254(5)	0.5749(5)	0.3663(4)	5.3(4)	−0.129	0.632	0.394
E4	−0.1737(3)	0.5559(6)	0.3135(5)	4.2(3)	−0.211	0.599	0.304
E5	−0.1709(4)	0.4748(7)	0.2739(4)	5.1(4)	−0.206	0.462	0.236
E6	−0.1199(5)	0.4126(5)	0.2871(4)	3.9(3)	−0.118	0.357	0.258
F1	−0.0852(3)	0.1266(7)	0.1510(4)	2.4(3)			
F2	−0.1338(5)	0.0594(4)	0.1439(4)	4.1(3)	−0.131	0.002	0.171
F3	−0.1875(4)	0.0729(6)	0.0967(5)	4.5(3)	−0.223	0.026	0.091
F4	−0.1926(3)	0.1536(7)	0.0565(4)	4.7(3)	−0.232	0.164	0.023
F5	−0.1440(5)	0.2208(5)	0.0636(4)	6.0(4)	−0.149	0.278	0.035
F6	−0.0903(4)	0.2073(5)	0.1109(5)	4.7(3)	−0.057	0.254	0.115
G1	0.0307(3)	0.0147(5)	0.3048(5)	3.4(3)			
G2	0.0723(5)	−0.0444(6)	0.2683(3)	4.6(3)	0.067	−0.052	0.216
G3	0.1216(4)	−0.0920(5)	0.3064(5)	5.7(4)	0.152	−0.133	0.281
G4	0.1293(4)	−0.0803(6)	0.3808(5)	5.2(4)	0.165	−0.114	0.408
G5	0.0877(5)	−0.0212(6)	0.4172(3)	5.4(4)	0.094	−0.014	0.470
G6	0.0384(4)	0.0264(5)	0.3792(5)	4.8(4)	0.010	0.067	0.406
H1	−0.3748(4)	0.4929(5)	0.1719(5)	3.1(3)			
H2	−0.3236(4)	0.4960(5)	0.1234(4)	4.4(3)	−0.312	0.553	0.099
H3	−0.2884(3)	0.4166(8)	0.1080(4)	5.3(4)	−0.252	0.417	0.073
H4	−0.3044(4)	0.3340(5)	0.1412(5)	5.0(4)	−0.280	0.276	0.130
H5	−0.3556(5)	0.3308(5)	0.1897(4)	4.7(3)	−0.366	0.272	0.214
H6	−0.3908(3)	0.4103(7)	0.2051(3)	4.0(3)	−0.426	0.408	0.240
I1	−0.1543(4)	0.2088(5)	0.3598(5)	3.1(3)			
I2	−0.1522(3)	0.2172(6)	0.4348(5)	4.1(3)	−0.115	0.195	0.464

TABLE 2 (*cont'd*)

Ring atom	Carbon				Hydrogen[a]		
	x	*y*	*z*	*B* (Å^2)	*x*	*y*	*z*
I3	−0.2043(5)	0.2584(6)	0.4699(3)	5.0(4)	−0.204	0.267	0.523
I4	−0.2586(4)	0.2911(5)	0.4300(5)	5.7(4)	−0.296	0.322	0.454
I5	−0.2607(4)	0.2826(6)	0.3551(5)	6.1(4)	−0.299	0.306	0.326
I6	−0.2086(5)	0.2415(6)	0.3199(3)	4.8(4)	−0.210	0.235	0.267
T1	0.5798(3)	0.1570(5)	0.3809(4)	6.8(4)			
T2	0.5632(4)	0.2097(6)	0.4405(4)	9.0(5)	0.590	0.205	0.485
T3	0.5088(5)	0.2680(6)	0.4362(5)	9.0(5)	0.497	0.304	0.478
T4	0.4712(4)	0.2738(6)	0.3724(6)	8.8(5)	0.433	0.314	0.368
T5	0.4878(4)	0.2211(7)	0.3128(4)	8.4(4)	0.462	0.224	0.267
T6	0.5421(4)	0.1627(6)	0.3170(4)	7.8(4)	0.555	0.125	0.275
T7[e]	0.6392(5)	0.0932(7)	0.3855(8)	13.4(6)	0.628 0.653 0.676	0.036 0.076 0.123	0.412 0.337 0.411

[a] All hydrogen atoms have $B = 5.5$ Å^2. [b] Ring atoms are numbered sequentially with carbon atoms A1 and B1 attached to P(1); C1, D1, and E1 attached to P(2) and F1 through I1 attached to C(7) through C(10) respectively. Atom T1 through T7 are those of the toluene molecule. [c] The estimated standard deviations are derived from those of the group parameters. [d] Hydrogen atom A2 is attached to carbon A2, hydrogen A3 to carbon A3, etc. [e] Carbon atom T7 is the methyl carbon of the toluene molecule and the three hydrogen atom positions are those of the methyl hydrogens.

five-membered chelate ring formed by a Rh and an *o*-tolylphosphino ligand[8] [equivalent to the absence of C(8), C(9), and C(10) and with C(7)=methylene] we can find no examples where the *ortho* substituent on the benzene rings acts as a bidentate ligand. In addition the Rh–C(7)–C(8)–C(9)–C(10) ring system appears to be novel. The Rh–C(10) bond length of 2.10 Å is typical of a metal–carbon σ bond. The Rh–C(7), Rh–C(8), and C(7)–C(8) bond lengths are typical[17] of a π bond between Rh and C(7)–C(8). If one accepts the σ and π bonding of the C(7)–C(8)–C(9)–C(10) moiety, then 3 electrons are contributed to the metal. These, together with the 4 electrons from the two P atoms, lead to a 52 electron system typical for a Rh^{I} d^8 square-planar system. The distorted square-planar coordination about the rhodium atom is illustrated in Fig. 2, where the π-bond between Rh and the C(7)–C(8) system is shown. The novel σ and π bonding of the C(7)–C(8)–C(9)–C(10) system may be thought of as inter-

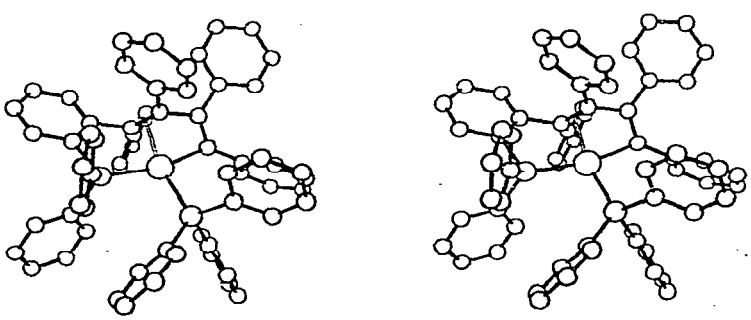

Fig. 2. A stereoscopic view of the molecule. The atom radii in this drawing are arbitrary. The light bond is intended to represent the metal–olefin bonding.

mediate between that of a butadiene ligand, $CH_2{=}CH{-}CH{=}CH_2$, whose coordination to the metal involves two π bonds, and that of the dianion of butadiene, $^{-}CH{=}CH{-}CH{=}CH^{-}$, which would utilize two σ bonds.

In Table 3 important bond lengths, bond angles, and their estimated standard

TABLE 3

DISTANCES AND ANGLES

Bond distances (Å)			Bond angles (deg.)	
Rh–P(1)	2.281(3)		P(1)–Rh–P(2)	97.5(1)
Rh–P(2)	2.311(4)		P(1)–Rh–C(7)	83.5(3)
			P(1)–Rh–C(8)	101.9(3)
Rh–C(7)	2.188(11)		P(2)–Rh–C(10)	95.3(3)
Rh–C(8)	2.203(11)		C(7)–Rh–C(8)	37.6(3)
Rh–C(9)	2.642(11)		Rh–P(1)–C(1)	104.2(4)
Rh–C(10)	2.105(11)		Rh–P(1)–C(A1)	119.9(3)
			Rh–P(1)–C(B1)	120.4(3)
P(1)–C(A1)	1.857(8)		C(1)–P(1)–C(A1)	100.9(4)
P(1)–C(B1)	1.838(8)		C(1)–P(1)–C(B1)	104.3(5)
P(2)–C(C1)	1.863(9)	1.843(17)[a]	C(A1)–P(1)–C(B1)	104.4(5)
P(2)–C(D1)	1.823(7)		Rh–P(2)–C(C1)	123.2(3)
P(2)–C(E1)	1.834(8)		Rh–P(2)–C(D1)	109.1(3)
			Rh–P(2)–C(E1)	115.5(3)
P(1)–C(1)	1.800(12)		C(C1)–P(2)–C(D1)	100.7(4)
			C(C1)–P(2)–C(E1)	98.2(4)
C(1)–C(2)	1.384(13)		C(D1)–P(2)–C(E1)	108.4(4)
C(2)–C(3)	1.411(13)		P(1)–C(1)–C(2)	116.6(10)
C(3)–C(4)	1.358(13)	1.376(24)	P(1)–C(1)–C(6)	124.4(10)
C(4)–C(5)	1.385(14)		C(6)–C(1)–C(2)	118.9(12)
C(5)–C(6)	1.376(14)		C(1)–C(2)–C(3)	119.6(11)
C(6)–C(1)	1.430(14)		C(2)–C(3)–C(4)	121.1(12)
			C(3)–C(4)–C(5)	119.8(12)
C(2)–C(7)	1.524(14)		C(4)–C(5)–C(6)	121.2(12)
			C(5)–C(6)–C(1)	119.4(12)
C(7)–C(8)	1.414(12)		C(1)–C(2)–C(7)	120.0(11)
			C(3)–C(2)–C(7)	120.2(11)
C(8)–C(9)	1.506(13)		C(2)–C(7)–C(8)	120.7(9)
			C(2)–C(7)–Rh	114.8(8)
C(9)–C(10)	1.321(13)		C(2)–C(7)–C(F1)	108.4(9)
			C(8)–C(7)–Rh	71.8(6)
C(7)–C(F1)	1.533(12)		C(8)–C(7)–C(F1)	124.5(9)
C(8)–C(G1)	1.506(12)	1.516(17)	C(F1)–C(7)–Rh	110.5(9)
C(9)–C(H1)	1.527(14)		C(7)–C(8)–C(G1)	127.2(9)
C(10)–C(I1)	1.497(13)		C(7)–C(8)–C(9)	116.5(9)
			C(7)–C(8)–Rh	70.6(6)
			C(G1)–C(8)–Rh	114.3(7)
			C(G1)–C(8)–C(9)	116.1(9)
			C(9)–C(8)–Rh	88.7(7)
			C(8)–C(9)–C(10)	108.4(11)
			C(8)–C(9)–C(H1)	119.5(9)
			C(10)–C(9)–C(H1)	132.1(9)
			C(9)–C(10)–Rh	98.3(8)
			C(9)–C(10)–C(I1)	127.1(9)
			C(I1)–C(10)–Rh	134.5(9)

(continued)

TABLE 3 (*continued*)

Dihedral angles[b] (deg.)		Dihedral angles	(deg.)
C(7)–Rh–C(8) C(8)–Rh–C(10)	63.5(7)	P(1)–Rh–C(7) C(7)–Rh–C(8)	60.7(6)
P(1)–Rh–P(2) C(7)–Rh–C(10)	171.0(3)	P(1)–Rh–P(2) C(7)–Rh–C(8)	119.9(7)

[a] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual deviation or of the standard deviation of a single observation as calculated on the assumption of equivalence. On this basis it appears that the standard deviations of the bond distances may be slightly underestimated. [b] The dihedral angle between two planes is defined as the angle between the normals to these planes.

deviations are presented.

The two rhodium–phosphorus bonds differ significantly in length. The longer Rh–P(2) bond [2.311(4) Å] is typical of those found in several complexes containing Rh^{I}–P bonds. The average rhodium–phosphorus distance in the complex $[RhH(CO)(PPh_3)_3]$[16] is 2.322(7) Å, that in *trans*-$[RhCl(CS)(PPh_3)_2]$[18] is 2.336(2) Å, while the mutually *trans*-phosphine ligands in $[RhCl(PPh_3)_2]$ and $[RhCl(C_2F_4)(PPh_3)_2]$ have average Rh–P bond lengths of 2.321 and 2.372 Å respectively[19]. The significantly shorter Rh–P(1) distance of 2.281(3) Å is near the 2.269(4) Å Rh–P distance in the complex $\{RhCl_2(C_6H_5N)_2[P(o\text{-}C_6H_4CH_3)_2(o\text{-}C_6H_4CH_2)]\}$[8]. In this complex the phosphorus and rhodium atoms are part of a five-membered ring that is similar to the one found in the present work. Interestingly, the ring bond lengths and angles, except for the carbon atom attached to rhodium, are similar. Thus, the Rh–P(1)–C(1) angle of 104.2(4)° resembles the corresponding angle of 101.5(6)° while the Rh–C(7)–C(2) angle of 114.8(8)° is similar to that of 113.9(11)°. In both examples there are significant deviations from the tetrahedral values, probably because of the strain present in the five-membered ring. In the present study this ring is almost planar with the maximum displacement of an atom [C(1)] from the weighted least-squares plane being 0.12 Å.

Table 4 gives the equations for several of the weighted least-squares planes in the molecule together with the deviations from planarity. The phenyl ring formed by carbons (1) through (6) has D_{6h} symmetry within the errors of the experiment. The data of Table 4 along with the dihedral angles given in Table 3 provide a quantitative measure of the distortions of the inner coordination about rhodium. Of course, these distortions are best appreciated from Fig. 2. The Rh, P(1), P(2), C(10) system is nearly planar, with a slight deviation of C(10) from the plane. The fourth coordination site, the center of the C(7)–C(8) bond, is 0.32 Å out of this plane. The Rh, P(1), C(1), C(2), C(7) system is almost planar. The Rh, C(7), C(8), C(9), C(10) system is nonplanar; the dihedral angle between the P(1)–Rh–C(7) and C(7)–Rh–C(8) planes is 60.7(6)°.

The Rh–C(10) bond length of 2.105(11) Å does not differ appreciably from the mean value of 2.07 Å for a Rh–C σ bond given in a recent tabulation[20]. The Rh to C(7)–C(8) center distance is also 2.10 Å. The C(7)–C(8) bond distance of 1.414(12) Å is in the range expected for an olefin π bonded to a metal[17].

The rhodium complex, formulated here as a d^8 square planar complex, should undergo oxidative addition. That this was not observed with diphenylacetylene may be due to the steric interference of the phenyl rings surrounding the central metal.

TABLE 4

WEIGHTED LEAST-SQUARES PLANES

Plane equation: $A \cdot x + B \cdot y + C \cdot z - D = 0$, with x, y, z in monoclinic coordinates.

Plane No.	A	B	C	D
1	8.779	−8.920	11.976	1.273
2	9.363	−7.820	12.791	1.741
3	6.315	−9.453	12.640	1.202
4	9.372	−1.703	16.002	3.978
5	9.564	−7.600	12.876	1.819
6	8.528	−8.792	12.276	1.383

DEVIATIONS FROM THE PLANES (Å)

Atom	Plane No.					
	1	2	3	4	5	6
Rh	0.002(1)	−0.004(1)		0.000(1)	−0.011(1)	0.005(1)
P(1)	−0.014(3)	0.016(3)			0.028(3)	−0.048(3)
P(2)		0.003(3)			0.030(3)	
C(1)	0.122(11)		−0.006(11)			0.055(11)
C(2)	−0.026(11)		0.007(11)			−0.088(11)
C(3)			−0.001(11)			−0.128(11)
C(4)			−0.007(11)			−0.013(11)
C(5)			0.008(12)			0.158(12)
C(6)			−0.001(12)			0.186(12)
C(7)	−0.078(11)				−0.319(11)	−0.109(11)
C(8)				−0.020(11)	0.880(11)	
C(9)				0.028(10)		
C(10)		0.158(11)		−0.022(10)		

The structure found here is similar to that postulated by Keim and both are consistent with the spectral results. The two differ only by the presence of the C(2)–C(7) bond and the absence of a Rh–C(2) bond. Assuming that $F_3C{-}C{\equiv}C{-}CF_3$ and diphenylacetylene each react with the parent compound, $Rh(PPh_3)_2(PPh_2C_6H_4)$, in the same manner it is understandable in the light of the actual structure why the ^{19}F NMR spectrum obtained by Keim[7] consisted of a very complex multiplet.

Formation of a similar product upon reaction of the parent compound with norbornadiene[7] does not seem feasible. Hence it is of interest to investigate structurally some of the other compounds produced by Keim[7], as well as the parent complex. Such studies are contemplated.

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