

THE SYNTHESIS AND MOLECULAR STRUCTURE OF π -CYCLOPENTADIENYL- π -TETRAPHENYLCYCLOBUTADIENERHODIUM(I)

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SUMMARY

The reaction of π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) and diphenylacetylene gives hexaphenylbenzene as the principal product with a low yield of π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I). The crystal structure of π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) was determined by X-ray diffraction techniques using diffractometer data. The crystals are monoclinic with unit cell dimensions of $a = 13.416$ (3), $b = 19.534$ (6), $c = 13.411$ (2) Å and $\beta = 135.01$ (1)°. The space group is $P2_1/c$ and, with four molecules per unit cell, no molecular symmetry is required ($D_m = 1.40$ g/cm³ and $D_c = 1.411$ g/cm³). The structure was solved by the heavy atom method and refined by least-squares methods to a final R of 0.043 for the 3675 observed reflections used in the analysis. The rhodium atom is coordinated to both the cyclopentadienyl group (Rh-ring distance is 1.868 Å) and the tetraphenylcyclobutadiene group (Rh-ring distance is 1.828 Å). The phenyl groups are twisted relative to the C₄ ring and bent away from the rhodium atom.

INTRODUCTION

The formation of cyclobutadiene derivatives of cobalt has been carried out by several routes: (1) the reaction of dicyclopentadienylcobalt(II), π -cyclopentadienyldicarbonylcobalt(I) or π -cyclopentadienyl- π -1,5-cyclooctadienecobalt(I) with internal acetylenes¹, (2) by the irradiation of π -cyclopentadienyldicarbonylcobalt(I) with α -pyrone², (3) by a multistep synthesis starting with 3,4-dichlorocyclobutene³ and (4) by ligand-transfer reactions⁴. Despite the interest in these very stable cyclobutadienecobalt complexes none of the analogous rhodium compounds has been reported. We have studied the reaction of π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) with diphenylacetylene and found that π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) can be obtained in low yields. The small amount of I, which was obtained in the reaction limited its characterization. Therefore an X-ray crystal structure study was undertaken.

SYNTHESIS AND SPECTRA

The yellow, air-stable, crystalline compound π -cyclopentadienyl- π -tetra-

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phenylcyclobutadienerhodium(I), I, was synthesized by reaction of π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) and excess diphenylacetylene at 180° for 48 hours. The yields were consistently low (ca. 3%) with the major product being hexaphenylbenzene. The use of toluene as a solvent failed to improve the yield and increased the difficulty of isolating I. Longer reaction times increased the production of hexaphenylbenzene without a corresponding increase in the yield of I. Since it was found that diphenylacetylene did not trimerize under the same conditions in the absence of the rhodium compound, it appears that I may be an intermediate in the trimerization process. Similar trimerization has not been observed in the reaction of π -cyclopentadienyl- π -1,5-cyclooctadienecobalt(I) and diphenylacetylene. Apparently the low-lying unoccupied orbitals in the larger rhodium atom may be closer in energy to the filled orbitals thereby facilitating the coordination of a diphenylacetylene molecule. Subsequent rearrangement of the complex could yield a hexaphenylbenzene molecule loosely coordinated to the rhodium atom. The hexaphenylbenzene could then be displaced by diphenylacetylene with ultimate regeneration of I.

An interesting solvent effect on the NMR spectrum of I was observed. In CS₂ the phenyl protons were found as a multiplet at τ 2.9. In C₆D₆ two multiplets were found in the phenyl region at τ 2.4 and 2.9 (relative areas 2/3). Either one or two multiplets for phenyl protons have been found previously in the NMR spectra of other tetraphenylcyclobutadiene metal complexes^{4c}. However, there has apparently been no other instance where both patterns have been exhibited by the same compound as the result of solvent change. In both media the cyclopentadienyl protons [τ 4.99 (CS₂), τ 5.01 (C₆D₆)] appear as a doublet ($J(\text{Rh-H})$ 1.1 Hz). Since the peak separation was identical in spectra measured on Varian A60-A and XL-100 instruments, it undoubtedly results from coupling to Rh¹⁰³. The magnitude of the Rh-H coupling is about the same as those reported for other compounds such as tris-allylrhodium⁵. Similar coupling is not discernible for the precursor, π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I).

The mass spectrum included a large parent peak and the expected peaks resulting from loss of Ph₂C₂ and Ph₄C₄, respectively. An unexpected peak at m/e 267 may be ascribed to the triphenylcyclopropenium ion, a fragment not found in the mass spectrum of the corresponding cobalt complex.

Extensive examination of the chemistry of I was precluded by the low yields and by its tendency to undergo decomposition when exposed to compounds other than hydrocarbons. It was not possible to make an unequivocal assignment of a cyclobutadiene complex structure based on spectral and limited chemical evidence alone since no other cyclobutadienerhodium complexes were known. Incorporation of two diphenylacetylene moieties in the coordination sphere of rhodium might conceivably have occurred in any of 3 ways, either as a tetraphenylcyclobutadiene ligand, as independent diphenylacetylene ligands, or as a tetraphenylmetallocyclopentadiene unit. To distinguish among these possibilities an X-ray diffraction study was conducted.

EXPERIMENTAL

General Comments

Spectra were obtained using a Beckmann IR-10 infrared spectrophotometer, Varian A-60A and XL-100 NMR spectrometers, a Perkin-Elmer RMU-6E single-focussing mass spectrometer, and a Cary 15 ultraviolet-visible spectrometer. Elemen-

tal analyses were performed by PCR, Inc.

π -1,5-Cyclooctadienerhodium(I) chloride dimer⁶ and π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I)⁷ were prepared in 94 and 93% yields, respectively, by published methods.

Reaction of diphenylacetylene and π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I)

A glass reaction tube containing diphenylacetylene (3.00 g, 16.8 mmol) and π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) (1.25 g, 4.50 mmol) was sealed inside a 30 ml stainless steel Hoke bomb under nitrogen. After 48 hours at 180° the reaction mixture was cooled and extracted with hexane. A white, insoluble solid (1.67 g, 55%) was identified as hexaphenylbenzene by its mass spectrum. The red hexane solution was chromatographed on Al₂O₃ and provided unreacted π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) (1.04 g, 83%), unreacted diphenylacetylene (0.97 g, 32%), and π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) (6.4 mg, 0.27%). Also present on the column was some orange-brown material which could not be eluted. In other instances the yield of cyclobutadiene complex was as high as 3.3%.

The yellow, crystalline cyclobutadiene complex, m.p. 227–228° (sealed tube), was air-stable in the crystalline state and in hydrocarbon solutions but was rapidly degraded by CCl₄.

Anal. Found: C, 75.75; H, 5.09. C₃₃H₂₅Rh calcd.: C, 75.57; H, 4.80%. IR (KBr): 3060 w, 3030 w, 2930 w, 2870 vw, 1600 m, 1494 m, 1445 m, 1270 w, 1115 w, 1070 w, 1029 w, 871 w, 800 w, 766 m, 749 m, 700 s, 561 m cm⁻¹. UV (isooctane), λ (ϵ): 225 nm (38, 700), 294 nm (31, 700). Mass spectrum, *m/e* (rel. intensity): 524 (100), 358 (34), 356 (48), 346 (64), 279 (25), 267 (50), 178 (42), 168 (61), 167 (28), 150 (26), 105 (20), 71 (24), 69 (26), 57 (71), 56 (38), 55 (36). NMR (CS₂): τ 2.9 (m), τ 4.99 (d), rel. area 4/1; NMR (C₆D₆): τ 2.4 (m), τ 2.9 (m), τ 5.01 (d), rel. area 8/12/5; *J*(Rh–H) 1.1 Hz.

Attempted thermal trimerization of diphenylacetylene.

When pure diphenylacetylene was heated to 180° for 48 hours under nitrogen it was recovered unchanged.

Crystal data and intensity measurement.

Preliminary Weissenberg and precession photographs showed the yellow crystals to be monoclinic. Crystal data. RhC₃₃H₂₅, *M* = 524.26, *a* = 13.416 (3), *b* = 19.534 (6), *c* = 13.411 (2) Å, β = 135.01 (1)°, *U* = 2484.6 (1.1) Å³, *D_m* (by flotation in a carbon tetrachloride/cyclohexane mixture) = 1.40 g/cm³, *Z* = 4, *D_c* = 1.411 g/cm³. Systematic absences, *h*0*l* if *l* = 2*n* + 1 and 0*k*0 if *k* = 2*n* + 1, indicate space group *P*2₁/*c* (C_{2h}⁵).

The unit cell dimensions and intensity data were measured on a computer-controlled Syntex *P* $\bar{1}$ diffractometer using a graphite monochromator with Mo-K α radiation (λ = 0.71069 Å). A θ –2 θ scan at a variable rate (1 to 24°/min depending on the peak intensity) was used to measure all the independent reflections up to a 2 θ limit of 50°. The background was measured at a point 1° to each side of the α_1 and α_2 peaks for a time equal to one-quarter of the total scan time. The intensity, *I*, is equal to { [total scan counts – (background count/background to scan ratio)] · scan rate } with a standard deviation $\sigma(I)$ equal to [total scan counts + (background count/background to scan ratio)²]^½. The 3675 reflections which had *I* ≥ 1.2 $\sigma(I)$ were considered observed and used in the analysis. These data were then reduced to a set of structure amplitudes

on an arbitrary scale by the application of Lorentz-polarization assuming the monochromator was a 50% mosaic and 50% perfect crystal.

STRUCTURE DETERMINATION AND REFINEMENT

The position of the rhodium atom was determined from a sharpened three-dimensional Patterson function. A Fourier synthesis phased only on the rhodium atom revealed the positions of all the cyclobutadiene and phenyl carbon atoms. A second Fourier synthesis phased on the rhodium atom and the 28 located carbon

TABLE 1

ATOMIC PARAMETERS ($\times 10^{-4}$) OF THE NON-HYDROGEN ATOMS IN π -CYCLOPENTADIENYL- π -TETRAPHENYLCYCLOBUTADIENERRHODIUM(I)

The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	2276 (1)	1719 (1)	2965 (1)	83 (1)	21 (1)	77 (1)	1 (1)	118 (1)	3 (1)
C(1)	1780 (4)	2560 (2)	1697 (4)	84 (4)	21 (1)	90 (5)	8 (4)	131 (8)	10 (4)
C(2)	1288 (4)	1917 (2)	896 (4)	83 (4)	22 (1)	77 (4)	10 (3)	114 (8)	10 (3)
C(3)	2757 (4)	1705 (2)	1772 (4)	94 (4)	21 (1)	81 (4)	12 (4)	133 (8)	14 (4)
C(4)	3245 (4)	2350 (2)	2579 (4)	87 (4)	20 (1)	81 (4)	5 (4)	125 (8)	10 (4)
C(5)	2346 (6)	1864 (3)	4654 (6)	181 (8)	45 (2)	130 (7)	0 (6)	262 (13)	3 (6)
C(6)	1081 (6)	1521 (4)	3496 (6)	146 (7)	68 (3)	148 (7)	- 6 (7)	241 (14)	29 (7)
C(7)	1437 (8)	884 (4)	3315 (7)	274 (12)	48 (2)	178 (9)	- 92 (9)	362 (19)	-16 (7)
C(8)	2895 (8)	836 (3)	4360 (7)	299 (13)	36 (2)	197 (9)	42 (8)	412 (20)	61 (7)
C(9)	3470 (6)	1432 (3)	5175 (5)	146 (7)	50 (2)	100 (6)	12 (6)	183 (12)	37 (6)
C(A1)	1114 (4)	3202 (2)	1527 (4)	101 (5)	23 (1)	96 (5)	18 (4)	144 (9)	10 (4)
C(A2)	- 94 (6)	3203 (3)	1270 (7)	148 (7)	39 (2)	198 (9)	51 (6)	274 (14)	44 (7)
C(A3)	- 706 (8)	3845 (4)	1097 (8)	217 (10)	52 (3)	232 (11)	101 (8)	373 (19)	65 (8)
C(A4)	- 128 (8)	4445 (3)	1182 (7)	258 (11)	37 (2)	199 (10)	94 (8)	357 (19)	50 (7)
C(A5)	1070 (7)	4442 (3)	1442 (6)	207 (9)	29 (2)	150 (8)	50 (6)	249 (15)	29 (6)
C(A6)	1687 (5)	3819 (2)	1609 (5)	121 (6)	24 (1)	106 (6)	16 (5)	143 (10)	10(4)
C(B1)	- 103 (4)	1647 (2)	- 387 (4)	84 (4)	24 (1)	83 (4)	16 (4)	118 (8)	15(4)
C(B2)	- 432 (5)	955 (3)	- 494 (5)	110 (6)	24 (1)	107 (6)	- 1 (5)	104 (10)	- 6 (4)
C(B3)	-1757 (5)	699 (3)	-1707 (6)	104 (6)	35 (2)	119 (6)	- 8 (5)	108 (11)	-10 (5)
C(B4)	-2734 (5)	1136 (3)	-2822 (5)	97 (6)	41 (2)	103 (6)	2 (5)	122 (10)	- 7 (5)
C(B5)	-2422 (5)	1818 (3)	-2722 (5)	106 (6)	42 (2)	99 (6)	23 (5)	114 (10)	28 (5)
C(B6)	-1119 (5)	2079 (3)	-1523 (5)	106 (6)	34 (2)	96 (5)	18 (5)	132 (10)	34 (5)
C(C1)	3453 (4)	1153 (2)	1709 (4)	97 (5)	22 (1)	89 (5)	15 (4)	140 (9)	15 (4)
C(C2)	4786 (5)	928 (3)	2915 (5)	116 (6)	29 (1)	108 (6)	38 (5)	149 (10)	28 (5)
C(C3)	5440 (6)	402 (3)	2833 (6)	134 (7)	30 (2)	144 (7)	43 (5)	184 (12)	27 (5)
C(C4)	4762 (6)	100 (3)	1554 (6)	153 (7)	31 (2)	174 (8)	33 (6)	235 (14)	8 (6)
C(C5)	3441 (6)	338 (3)	332 (6)	156 (7)	33 (2)	148 (7)	22 (6)	212 (13)	-15 (6)
C(C6)	2782 (5)	861 (3)	408 (5)	119 (6)	28 (1)	105 (6)	9 (5)	152 (10)	- 8 (5)
C(D1)	4579 (4)	2728 (2)	3632 (4)	83 (5)	21 (1)	98 (5)	9 (4)	118 (8)	15 (4)
C(D2)	4800 (5)	3141 (2)	4622 (5)	96 (5)	23 (1)	111 (6)	2 (4)	115 (9)	- 9 (4)
C(D3)	6008 (6)	3531 (3)	5580 (6)	121 (7)	27 (2)	159 (8)	3 (5)	121 (13)	-14 (6)
C(D4)	7015 (6)	3510 (3)	5539 (8)	112 (7)	31 (2)	214 (10)	7 (6)	140 (14)	32 (7)
C(D5)	6822 (5)	3105 (3)	4562 (7)	103 (6)	36 (2)	187 (9)	7 (5)	178 (13)	46 (6)
C(D6)	5608 (5)	2697 (3)	3612 (6)	106 (6)	33 (2)	158 (7)	15 (5)	192 (11)	41 (5)

TABLE 2

ATOMIC PARAMETERS OF THE CYCLOPENTADIENYL HYDROGEN ATOMS

The positional parameters are $\times 10^3$.

Atom	Bonded to	Dist. (Å)	x	y	z
H(5)	C(5)	1.06	270	233	524
H(6)	C(6)	0.98	10	166	295
H(7)	C(7)	1.07	61	56	248
H(8)	C(8)	0.95	338	46	440
H(9)	C(9)	0.97	449	144	592

atoms revealed the other five carbon atoms. Three full-matrix least-squares cycles with isotropic thermal parameters reduced R , $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, to 0.074. An additional six least-squares cycles with anisotropic thermal parameters using a block approximation to the full matrix reduced R to 0.043. The largest shift in a positional parameter was approximately $\frac{1}{3}$ of the corresponding e.s.d. and for the thermal parameters, $\frac{2}{3}$ of an e.s.d. (for β_{12} of C(A3)). However, the majority of the shifts were much smaller so that the refinement was terminated. A difference Fourier synthesis revealed the positions of the cyclopentadienyl hydrogen atoms; no attempt was made to locate the phenyl hydrogen atoms. The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1. The final cyclopentadienyl hydrogen parameters are given in Table 2 together with the corresponding C-H distances*.

The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$, where

$$w^{\frac{1}{2}} = |F_o|/4F_M, \text{ if } |F_o| < 4F_M$$

$$w^{\frac{1}{2}} = 1, \text{ if } 4F_M \leq |F_o| \leq 6F_M$$

$$w^{\frac{1}{2}} = 6F_M/|F_o|, \text{ if } |F_o| > 6F_M$$

The value F_M , the mean minimum observable F_o , was 20.0 in this case. The scattering factors were taken from the usual source⁸. The Rh atom was corrected for the real part of the anomalous dispersion factor. All calculations were carried out on an IBM-360/65 computer with programs written or modified by one of us (G.J.P.).

RESULTS AND DISCUSSION

A view of the π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) molecule is given in Fig. 1 together with the atomic numbering. The cyclopentadienyl ligand is planar within experimental error (Table 3) with a rhodium to cyclopentadienyl ring plane distance of 1.868 Å. This compares favorably with the corresponding distance reported for other such complexes which ranges from 1.86 Å to 1.91 Å⁹⁻¹⁷. The Rh-C distances (see Table 4) involving the five-membered ring vary from 2.202 (10) to 2.229

* The Table of structure factors has been deposited as NAPS Document No. 00000, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

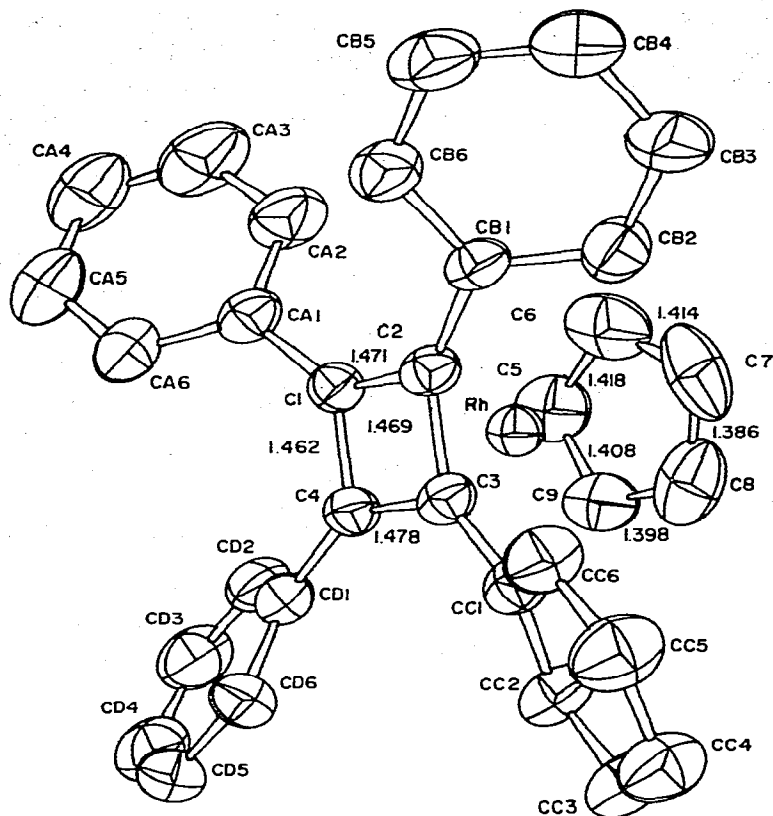


Fig. 1. A view of the molecule drawn by the ORTEP computer program. The enclosed areas are the 50% probability thermal ellipsoids.

(7) Å with a mean value of 2.214 (4) Å. It is interesting to note that the two longest of these distances (Rh-C(8), Rh-C(9)) are to the two carbon atoms which nearly eclipse the C(3) and C(4) atoms of the other ligand, while the shortest (Rh-C(6)) is to the carbon atom nearly staggered with the other ligand. Although this variation in Rh-C distances may be too small to be significant, the pattern is the same as that observed in three similar complexes^{10,17}. The difference in Rh-C bond lengths indicates that the ring planes are not parallel but intersect at an angle calculated to be 2.4°. Also, in the present compound and in the other three complexes, the difference in Rh-C distances is mirrored in the C-C distances, *i.e.*, the carbon atoms which are more loosely bonded to rhodium are more tightly bonded to each other. In the other complexes, particularly (π -cyclopentadienyl)(π -ethylene)(π -tetrafluoroethylene)rhodium¹⁷, this difference is quite pronounced; in the present compound the difference is less pronounced, but the pattern is similar. The mean Rh-C distance, *vide supra*, falls well within the range (2.19–2.26 Å) of corresponding mean values reported for other (π -cyclopentadienyl)rhodium complexes^{10–17}. The internal angles (see Table 5) in the five-membered ring vary from 107.0 (7)° to 109.7 (8)° with a mean of 108.0 (3)°, the expected value.

TABLE 3

LEAST-SQUARE PLANES

The deviations from the plane ($\text{\AA} \times 10^3$) are given for the specified atom

Atoms	Planes ^a		Atoms	Planes	
	1	2		1	2
C(1)	2*	3662	H(5)		-16
C(2)	- 2*	3667	H(6)		-91
C(3)	2*	3731	H(7)		13
C(4)	- 2*	3718	H(8)		61
C(5)	-3679	- 2*	H(9)		13
C(6)	-3649	- 3*	C(A1)	196	
C(7)	-3678	6*	C(B1)	136	
C(8)	-3744	- 7*	C(C1)	191	
C(9)	-3728	6*	C(D1)	183	
			Rh	-1828	1868

Parameters for the planes ($\times 10^4$)

	1	2
<i>l</i>	6300	6615
<i>m</i>	4404	4234
<i>n</i>	-6397	-6190
<i>p</i>	16611	-20258

^a Equation of the plane in the form: Deviation (\AA) = $lX + mY + nZ - p$, where XYZ are the orthogonal coordinates (in \AA) relative to a, b, c^* and p is the distance of the plane from the origin. The atoms used to define the plane are noted by an asterisk following the deviation. The dihedral angle between planes 1 and 2 is 2.4° .

TABLE 4

BOND LENGTHS (\AA)

Rh-C(1) 2.104 (4)	C(8)-C(9) 1.398 (9)	C(B4)-C(B5) 1.374 (9)
Rh-C(2) 2.098 (4)	C(9)-C(5) 1.408 (11)	C(B5)-C(B6) 1.388 (8)
Rh-C(3) 2.106 (6)	C(1)-C(A1) 1.461 (7)	C(B6)-C(B1) 1.397 (6)
Rh-C(4) 2.104 (6)	C(2)-C(B1) 1.476 (6)	C(C1)-C(C2) 1.384 (8)
Rh-C(5) 2.218 (8)	C(3)-C(C1) 1.467 (8)	C(C2)-C(C3) 1.406 (10)
Rh-C(6) 2.202 (10)	C(4)-C(D1) 1.473 (7)	C(C3)-C(C4) 1.381 (8)
Rh-C(7) 2.214 (10)	C(A1)-C(A2) 1.398 (12)	C(C4)-C(C5) 1.391 (10)
Rh-C(8) 2.229 (7)	C(A2)-C(A3) 1.425 (11)	C(C5)-C(C6) 1.401 (10)
Rh-C(9) 2.225 (5)	C(A3)-C(A4) 1.366 (12)	C(C6)-C(C1) 1.400 (6)
C(1)-C(2) 1.471 (6)	C(A4)-C(A5) 1.382 (16)	C(D1)-C(D2) 1.393 (7)
C(2)-C(3) 1.469 (8)	C(A5)-C(A6) 1.399 (9)	C(D2)-C(D3) 1.383 (9)
C(3)-C(4) 1.479 (6)	C(A6)-C(A1) 1.391 (8)	C(D3)-C(D4) 1.391 (15)
C(4)-C(1) 1.463 (8)	C(B1)-C(B2) 1.398 (7)	C(D4)-C(D5) 1.390 (11)
C(5)-C(6) 1.419 (10)	C(B2)-C(B3) 1.402 (8)	C(D5)-C(D6) 1.405 (10)
C(6)-C(7) 1.414 (12)	C(B3)-C(B4) 1.382 (8)	C(D6)-C(D1) 1.402 (11)
C(7)-C(8) 1.386 (14)		

TABLE 5

BOND ANGLES (°)

C(1)-C(2)-C(3) 90.1 (4)	C(2)-C(3)-C(C1) 135.1 (5)
C(2)-C(3)-C(4) 89.7 (4)	C(4)-C(3)-C(C1) 134.3 (5)
C(3)-C(4)-C(1) 90.0 (4)	C(3)-C(C1)-C(C2) 121.0 (5)
C(4)-C(1)-C(2) 90.2 (4)	C(3)-C(C1)-C(C6) 119.8 (5)
C(2)-C(1)-C(A1) 135.2 (5)	C(C2)-C(C1)-C(C6) 119.2 (5)
C(4)-C(1)-C(A1) 133.6 (5)	C(C1)-C(C2)-C(C3) 120.2 (6)
C(1)-C(A1)-C(A6) 119.2 (5)	C(C2)-C(C3)-C(C4) 120.7 (7)
C(1)-C(A1)-C(A2) 120.9 (6)	C(C3)-C(C4)-C(C5) 119.5 (7)
C(A2)-C(A1)-C(A6) 119.8 (6)	C(C4)-C(C5)-C(C6) 120.1 (7)
C(A1)-C(A2)-C(A3) 118.5 (7)	C(C5)-C(C6)-C(C1) 120.4 (6)
C(A2)-C(A3)-C(A4) 120.8 (8)	C(3)-C(4)-C(D1) 137.5 (5)
C(A3)-C(A4)-C(A5) 120.5 (8)	C(1)-C(4)-C(D1) 131.5 (5)
C(A4)-C(A5)-C(A6) 119.8 (7)	C(4)-C(D1)-C(D2) 119.9 (5)
C(A5)-C(A6)-C(A1) 120.6 (6)	C(4)-C(D1)-C(D6) 120.4 (5)
C(1)-C(2)-C(B1) 134.4 (5)	C(D2)-C(D1)-C(D6) 119.6 (5)
C(3)-C(2)-C(B1) 135.0 (5)	C(D1)-C(D2)-C(D3) 121.6 (6)
C(2)-C(B1)-C(B2) 120.8 (5)	C(D2)-C(D3)-C(D4) 118.7 (7)
C(2)-C(B1)-C(B6) 120.7 (5)	C(D3)-C(D4)-C(D5) 121.0 (7)
C(B2)-C(B1)-C(B6) 118.6 (5)	C(D4)-C(D5)-C(D6) 120.1 (7)
C(B1)-C(B2)-C(B3) 120.9 (6)	C(D5)-C(D6)-C(D1) 119.0 (6)
C(B2)-C(B3)-C(B4) 119.2 (6)	C(5)-C(6)-C(7) 108.4 (7)
C(B3)-C(B4)-C(B5) 120.2 (6)	C(6)-C(7)-C(8) 107.0 (8)
C(B4)-C(B5)-C(B6) 121.1 (6)	C(7)-C(8)-C(9) 109.7 (8)
C(B5)-C(B6)-C(B1) 119.9 (6)	C(8)-C(9)-C(5) 107.8 (7)
	C(9)-C(5)-C(6) 107.0 (7)

Two of the cyclopentadienyl hydrogen atoms are apparently displaced toward the metal atom from the ring plane and the other three away from the metal atom. Since the hydrogen atom positions were not refined, it is probable that the displacements from the plane are not significant.

The mean C-C distance in the cyclobutadiene ring is 1.470 (4) Å, not significantly different from the corresponding mean distances in tetraphenylcyclobutadiene complexes of iron (1.459 (7) Å)¹⁸ and molybdenum (1.461 (13) Å)¹⁹, but somewhat longer than the corresponding mean distance reported for a tetramethylcyclobutadiene complex of nickel (1.431 (24) Å)²⁰. While this difference is interesting to note, it is difficult to ascribe a cause with the few data available. The phenyl groups are bent away from the metal atom at a mean angle of 7.1°, and are twisted about their bonds to the four-membered ring at angles of 42.8°, 42.8°, 32.2°, and 39.3° (rings A, B, C, and D, respectively). The C ring which is twisted by 32.2° is adjacent to the C(8)-C(9) bond of the cyclopentadienyl group. Therefore this smaller angle of twist may be the result of an intramolecular steric effect.

The four-membered ring is planar within experimental error. The Rh atom is equidistant from all four carbon atoms, av. Rh-C distance of 2.103 Å, with a metal atom to the ring plane distance of 1.828 Å. The main point of interest with regard to the cyclobutadiene ligand is the establishment of the fact that is a true cyclobutadiene and not an isomer.

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