

THE STRUCTURE OF (DIBENZYLIDENEACETONE)(PENTAMETHYLCYCLOPENTADIENYL)RHODIUM(I)

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(Received January 2nd, 1974)

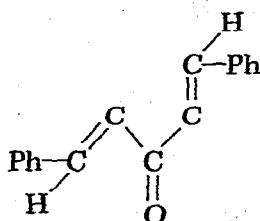
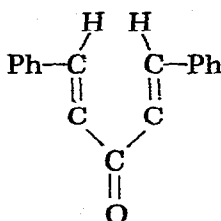
Summary

The structure of (dibenzylideneacetone)(pentamethylcyclopentadienyl)rhodium(I), $\text{Rh}(\text{C}_5\text{Me}_5)(\text{dba})$, ($\text{dba} = \text{PhCH}=\text{CHCOCH}=\text{CHPh}$, $\text{Ph} = \text{C}_6\text{H}_5$, $\text{Me} = \text{CH}_3$), has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R index on F of 0.035 based on 2100 observations above background. The material crystallizes in the monoclinic space group $C_{2h}^5-P2_1/a$, with four molecules in a cell of dimensions $a=14.348(12)$, $b=14.063(13)$, $c=11.393(10)$ Å, $\beta=104.42(3)^\circ$. The observed and calculated densities are 1.35(3) and 1.41 g/cm³. The compound is monomeric. The Rh atom is bonded to the C_5Me_5 ring on one side and to the dba molecule through the two olefinic double bonds on the other. The C_5 and Me_5 portions of the C_5Me_5 ring are planar, but not coplanar as the Me groups are bent away from the Rh atom by 0.10 Å relative to the C_5 plane. The dba molecule is in the *s-cis,s-cis* conformation with the two double bonds in a plane which is parallel to the planes of the C_5Me_5 ring. The rest of the dba molecule is nonplanar with the CO group pointing away from Rh. The olefinic double bonds have lengthened on coordination to 1.411(9) Å. The H atoms on the terminal C atoms of the dba molecule are in very close contact, the refined H...H distance being 1.83(9) Å. It is suggested that the strain imposed on the coordinated dba molecule by this interaction might contribute to its ease of dissociation from the complex in solution and hence account for the catalytic properties of the complex.

Introduction

There is considerable chemical and structural interest in transition metal complexes of dibenzylideneacetone (dba). Takahashi et al. [1] initially prepared complexes of the type $\text{Pd}(\text{dba})_2$. Moseley and Maitlis [2] subsequently prepared $\text{Pt}(\text{dba})_2$ and $\text{Pt}(\text{dba})_3$. Both groups subsequently showed [3,4] that these zero-valent Pd and Pt complexes catalyze various cyclotrimerization reactions of alkynes and also show promise as hydrogenation catalysts.

Since the dba molecule contains a carbonyl group in addition to the two olefinic bonds it is potentially capable of complexing to transition metals in several ways. Moseley and Maitlis [2] concluded from spectral studies that in $M(\text{dba})_2$ complexes the bonding is through the carbonyl groups, rather than through the olefinic double bonds. The two principal conformers of dba are I and II. Scaled models of the symmetric conformer II show it to contain a very short H...H interaction if a planar structure is assumed. Hence the coordination through the two olefinic double bonds might seem unlikely. Yet the geometry of conformer I is such that only one of the double bonds could coordinate to a given metal, with the other double bond dangling. Thus the suggestion of Moseley and Maitlis for coordination through the CO group cannot be dismissed.

(I) *s-cis,s-trans*(II) *s-cis,s-cis*

Recently the complex $\text{Pd}_2(\text{dba})_3$ has been prepared [5] and the structure of both the CHCl_3 [5] and CH_2Cl_2 [6] solvates have been determined. These structural studies demonstrate the ability of the dba ligand to coordinate to two different metal atoms through the olefinic double bonds. The structure of the CHCl_3 solvate consists of the bridging of two Pd atoms by three dba molecules with the two olefinic double bonds of a given dba molecule bonded to the separate Pd atoms to yield trigonal coordination about each Pd atom. Each of the dba molecules has conformation I. Although the structure refined well, the resultant variations in presumably equivalent bond distances suggest the effects of excessive thermal motion. Surprisingly the average C=C bond length is 1.2 Å. In the CH_2Cl_2 solvate [6] the coordination about the Pd atoms is the same, but one of the dba molecules more nearly approaches conformation II. Pierpont and Mazza [7] have also determined the structure of $\text{Pd}(\text{dba})_3$, where trigonal coordination about the Pd atom formed by coordination of a single double bond of each of the three dba molecules is found.

The compound $\text{Rh}(\text{C}_5\text{Me}_5)(\text{dba})$ has been prepared by Lee and Maitlis [8]. This compound may also be used to carry out cyclotrimerization reactions of alkynes. Lee and Maitlis have shown spectroscopically that in this complex the dba ligand in conformation II is coordinated to the formally Rh^{I} atom through the two double bonds. The present structural study of this complex was undertaken for several reasons: (1) There was the incentive to look for structural clues to its activity in cyclotrimerization reactions; (2) there was the desire to define more accurately the C=C bond lengths in a metal-dba complex; (3) since dba in conformer II appears to be a very crowded molecule there was the desire to determine the shape of the coordinated dba molecule; (4) there is also an interest in the geometry of the coordinated C_5Me_5 ring, since only two structures of complexes containing this ring have been reported [9,10]. Churchill and Ni [10]

have commented on the nonplanarity of the C_5Me_5 ring, with the Me atoms pointing away from the Rh^{III} atom in their complex. This bending away they ascribe to steric crowding. Yet Rees and Coppens [11] have found that the H atoms in $Cr(CO)_3(C_6H_6)$ bend toward the Cr. The steric effects in the present Rh^I complex should be less than in the Rh^{III} complex and so the present structure determination affords the opportunity to contribute to the question of whether nonplanarity in these various metal—ring systems is steric or electronic in origin.

Experimental

Crystal data

Red-orange crystals of $Rh(C_5Me_5)(dba)$ were kindly supplied by Lee and Maitlis and were suitable for use without further recrystallization. $RhC_{27}H_{29}O$: mol. wt. 472.46; monoclinic, $C_{2h}^2-P2_1/a$; $a=14.348(12)$, $b=14.063(13)$, $c=11.393(10)$ Å, $\beta=104.42(3)^\circ$, $V=2226$ Å³; $d_{calc}=1.41$ g/cm³ for $Z=4$; $d_{obs}=1.35(3)$ g/cm³ by flotation in $ZnCl_2$ solution; $\mu(Mo-K_\alpha)=7.68$ cm⁻¹.

Data collection

Data collection was achieved on a Picker FACS-I Diffractometer by methods standard in this laboratory [12]. Abbreviated details of this process are: Crystal selected for data collection was a rhombic needle with girdle faces of the forms $\{001\}$ and $\{02\bar{1}\}$ with irregular end faces approximated by $(\bar{4}01)$ and $(6\bar{2}3)$, the needle axis being $[100]$. Dimensions were 0.47 mm long by 0.20 mm by 0.14 mm wide, crystal volume (calculated) 0.0041 mm³. Test calculations led to minimum and maximum transmission coefficients of 0.92 and 0.96, so no correction for absorption was made. The radiation used was $Mo-K_\alpha$ monochromatized from the (002) face of a graphite crystal. The counter aperture was positioned 32 cm from the crystal and had dimensions 4 mm wide by 5 mm high. Data collection was by the $\theta-2\theta$ technique at a scan rate of 2 deg/min in 2θ . Background counts were taken at each end of the scan range, which was 0.9° below the K_{α_1} peak to 0.7° above the K_{α_2} peak. Counting times for backgrounds were 10, 20, and 40 s for 2θ in the range $2\theta < 33^\circ$, $33^\circ \leq 2\theta < 38^\circ$, and $2\theta \geq 38^\circ$, respectively. Data collection was terminated at $2\theta = 43.7^\circ$ because of the small number of reflections significantly above background past this point. A total of 2987 reflections was scanned, including 163 $0kl$ Friedel

TABLE 1
REFINEMENT OF THE STRUCTURE

Model	R	R_w
1 Isotropic, no H atoms	0.077	0.096
2 Anisotropic for nongroup atoms, isotropic for phenyl C atoms, no H atoms	0.049	0.065
3 As in 2, but with all H atoms added in idealized positions except for omission of the 4 H atoms on the olefinic C atoms of dba	0.039	0.049
4 As in 3 but with the 4 H atoms on the olefinic C atoms of dba refined positionally with fixed B	0.035	0.043

TABLE 2
FINAL PARAMETERS FOR Rh[C₅(CH₃)₅] (PHC=CHCOCH=CHP)^a

Atom	x	y	z	β_{11} or B(A ²)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.48366(3) ^b	0.19534(3)	-0.30902(4)	0.00335(3)	0.00464(3)	0.00661(4)	0.00001(2)	0.00122(2)	-0.00095(3)
O	0.61517(34)	-0.00792(32)	-0.33908(41)	0.00891(37)	0.00530(31)	0.01285(54)	0.00177(26)	0.00126(35)	-0.00138(32)
C(1)	0.60450(40)	0.07902(47)	-0.38313(55)	0.00402(36)	0.00569(44)	0.01023(69)	0.00088(32)	0.00102(39)	-0.00112(45)
C(2)	0.55239(43)	0.13462(45)	-0.43888(55)	0.00437(39)	0.00572(43)	0.00815(63)	0.00037(31)	0.00214(39)	-0.00167(41)
C(3)	0.55640(43)	0.23345(45)	-0.45530(55)	0.00406(36)	0.00553(42)	0.00964(66)	-0.00022(30)	0.00315(39)	-0.00146(41)
C(4)	0.61655(42)	0.12784(47)	-0.21761(56)	0.00348(35)	0.00617(46)	0.00904(66)	0.00062(31)	-0.00017(38)	-0.00059(42)
C(5)	0.63094(42)	0.22645(46)	-0.19520(55)	0.00368(35)	0.00594(44)	0.00800(61)	0.00046(29)	0.00064(36)	-0.00107(39)
C(6)	0.34851(40)	0.28083(46)	-0.33781(57)	0.00352(33)	0.00705(49)	0.00971(67)	0.00147(31)	0.00256(38)	-0.00136(45)
C(7)	0.38298(39)	0.26400(45)	-0.21299(55)	0.00355(34)	0.00623(42)	0.00896(65)	0.00037(29)	0.00199(37)	-0.00237(42)
C(8)	0.39445(42)	0.16225(47)	-0.19362(56)	0.00427(38)	0.00712(46)	0.00849(63)	0.00048(32)	0.00235(39)	0.00082(44)
C(9)	0.34831(44)	0.11814(47)	-0.30523(63)	0.00436(38)	0.00636(45)	0.01144(75)	-0.00118(33)	0.00321(43)	-0.00234(49)
C(10)	0.32880(39)	0.18926(54)	-0.39526(64)	0.00322(33)	0.00908(53)	0.00813(59)	-0.00009(37)	0.00136(35)	-0.00208(53)
C(11)	0.32834(54)	0.37426(58)	-0.39598(80)	0.00663(51)	0.01011(65)	0.02060(111)	0.00351(46)	0.00613(62)	0.00591(70)
C(12)	0.40490(52)	0.33748(56)	-0.11408(71)	0.00681(50)	0.00960(59)	0.01539(90)	0.00026(42)	0.00390(54)	-0.00637(59)
C(13)	0.41115(57)	0.11384(63)	-0.07212(71)	0.00789(54)	0.01269(73)	0.01317(86)	0.00102(50)	0.00397(55)	0.00460(66)
C(14)	0.33384(62)	0.01313(50)	-0.32783(93)	0.00938(56)	0.00803(60)	0.02831(150)	-0.00331(50)	0.00773(81)	-0.00481(76)
C(15)	0.28216(48)	0.17404(69)	-0.52806(60)	0.00428(40)	0.01964(93)	0.00828(66)	0.00006(51)	0.00071(40)	-0.00459(66)
C(2)H	0.515(5)	0.094(5)	-0.504(6)	5.0					
C(3)H	0.614(5)	0.270(5)	-0.411(7)	5.0					
C(4)H	0.616(5)	0.084(5)	-0.150(6)	5.0					
C(5)H	0.661(5)	0.262(6)	-0.247(7)	5.0					
Group	x_c^c	y_c^c	z_c^c	δ	ϵ	η			
Ring 1	0.45784(19)	0.33141(20)	-0.67373(25)	2.7604(27)	2.7717(24)	2.2214(29)			
Ring 2	0.65712(20)	0.31564(22)	0.03809(27)	3.0046(35)	-2.6384(26)	-1.4973(34)			

^aThe form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^bNumbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. ^cThe group variables have been defined previously [18].

TABLE 3
DERIVED PARAMETERS FOR THE GROUP CARBON ATOMS^a

Atom	x	y	z	B(Å ²)
R(1)C(1)	0.5034(3)	0.2827(3)	-0.5688(3)	3.7(1)
R(1)C(2)	0.5107(3)	0.3812(3)	-0.5736(3)	4.8(1)
R(1)C(3)	0.4651(3)	0.4299(2)	-0.6785(4)	5.6(1)
R(1)C(4)	0.4122(3)	0.3802(3)	-0.7787(3)	6.0(2)
R(1)C(5)	0.4050(3)	0.2816(3)	-0.7739(3)	5.7(2)
R(1)C(6)	0.4506(3)	0.2329(2)	-0.6689(4)	4.7(1)
R(2)C(1)	0.6433(3)	0.2695(3)	-0.0730(3)	4.1(1)
R(2)C(2)	0.6606(4)	0.3669(3)	-0.0652(3)	5.6(2)
R(2)C(3)	0.6744(4)	0.4131(2)	0.0459(4)	6.8(2)
R(2)C(4)	0.6710(4)	0.3618(4)	0.1492(3)	7.1(2)
R(2)C(5)	0.6537(4)	0.2644(3)	0.1414(3)	7.0(2)
R(2)C(6)	0.6398(3)	0.2182(2)	0.0303(4)	5.4(2)

^a Ring 1 is attached to C(3) at R(1)C(1); ring 2 is attached to C(5) at R(2)C(1).

pairs. Six standards were monitored every 75 reflections and these showed no variations greater than expected on the basis of Poisson statistics. The data were processed in the usual manner [12], using a p of 0.03, to yield 2100 unique reflections obeying the condition $F_o^2 > 3\sigma(F_o^2)$. Only these reflections were used in subsequent calculations.

Solution and refinement of the structure

Definitions of the agreement indices, R and R_w , sources of atomic scattering factors, listings of computer programs, and details of the rigid-group refinement are identical with those given previously [13]. The structure was solved by direct methods, using symbolic addition. It was refined by full-matrix least-squares methods. Table 1 details the course of the refinement. The final agreement index on F is 0.035 based on 2100 observations and 190 variables. The error in an observation of unit weight is 1.56 e^- . The highest peak on the final difference

TABLE 4
IDEALIZED PARAMETERS FOR HYDROGEN ATOMS^a

Ring H	x	y	z	B(Å ²)	Methyl H ^b	x	y	z
R(1)C(2)H	0.548	0.417	-0.502	5.8	C(11)H(1)	0.356	0.428	-0.338
R(1)C(3)H	0.470	0.501	-0.682	6.3	C(11)H(2)	0.361	0.381	-0.467
R(1)C(4)H	0.380	0.415	-0.855	7.0	C(11)H(3)	0.258	0.386	-0.430
R(1)C(5)H	0.367	0.246	-0.846	6.7	C(12)H(1)	0.350	0.345	-0.076
R(1)C(6)H	0.445	0.162	-0.666	5.7	C(12)H(2)	0.464	0.319	-0.049
R(2)C(2)H	0.664	0.404	-0.139	6.7	C(12)H(3)	0.418	0.402	-0.147
R(2)C(3)H	0.687	0.483	0.052	7.8	C(13)H(1)	0.353	0.079	-0.056
R(2)C(4)H	0.680	0.395	0.229	8.1	C(13)H(2)	0.463	0.065	-0.068
R(2)C(5)H	0.650	0.228	0.216	8.1	C(13)H(3)	0.434	0.160	-0.003
R(2)C(6)H	0.627	0.148	0.025	6.2	C(14)H(1)	0.268	-0.008	-0.330
					C(14)H(2)	0.348	-0.006	-0.409
					C(14)H(3)	0.381	-0.026	-0.263
					C(15)H(1)	0.210	0.175	-0.543
					C(15)H(2)	0.301	0.226	-0.578
					C(15)H(3)	0.302	0.111	-0.558

^a A C-H distance of 1.0 Å was assumed. The C₆H₅ rings were assumed to be planar with C-C-H angles of 120°. ^b Tetrahedral geometry was assumed about the central C atom. B was taken as 8.0 Å².

TABLE 5
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (in Å)

Atom	Min.	Intermed.	Max.
Rh	0.1797(8)	0.1889(8)	0.228(8)
O	0.208(7)	0.272(6)	0.329(6)
C(1)	0.188(9)	0.228(9)	0.273(8)
C(2)	0.180(9)	0.218(9)	0.260(9)
C(3)	0.171(9)	0.220(8)	0.266(8)
C(4)	0.174(10)	0.236(9)	0.268(8)
C(5)	0.186(9)	0.213(9)	0.260(8)
C(6)	0.163(10)	0.231(9)	0.284(9)
C(7)	0.167(9)	0.209(9)	0.280(8)
C(8)	0.191(9)	0.227(8)	0.272(9)
C(9)	0.186(10)	0.220(9)	0.297(9)
C(10)	0.176(9)	0.211(9)	0.311(9)
C(11)	0.206(10)	0.263(10)	0.411(10)
C(12)	0.189(10)	0.266(9)	0.382(10)
C(13)	0.236(10)	0.276(10)	0.384(11)
C(14)	0.230(11)	0.295(11)	0.439(11)
C(15)	0.196(9)	0.220(9)	0.454(11)

Fourier map is $0.59(7) e^{-/\text{Å}^3}$, about 15% of the height of a typical C atom in previous Fourier maps. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, scattering angles, and Miller indices showed no unusual trends. Structure factor calculations for the 758 reflections omitted from the refinement because they obeyed the condition $F_o^2 < 3\sigma(F_o^2)$ showed none for which $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$. Consequently these reflections are omitted from the listing of structure amplitudes*. The final parameters for the structure are given in Table 2; Table 3 gives the coordinates for the C atoms of the phenyl groups that may be derived from the data of Table 2. Table 4 presents the idealized positions for those hydrogen atoms that were not refined. Table 5 lists the root-mean-square amplitudes of vibration for those atoms refined anisotropically.

Description of the structure and discussion

The overall crystal structure consists of the packing of monomeric molecules. Figure 1 presents a stereoview of the contents of the unit cell. The shortest H...H intermolecular contacts are greater than 2.45 Å. The shortest intermolecular contacts are between O and C(15)H(3) (2.37 Å) and between O and C(2)H [2.51(7) Å].

Figure 2 displays the molecular structure and the labeling scheme. Selected distances and angles are presented in Table 6. The labeling for the phenyl carbon atoms attaches R(n)C(1) to the dba inner framework and then numbers the C atoms consecutively around the ring. The overall molecular structure is that deduced by Lee and Maitlis [8]. It consists of a Rh atom essentially symmetri-

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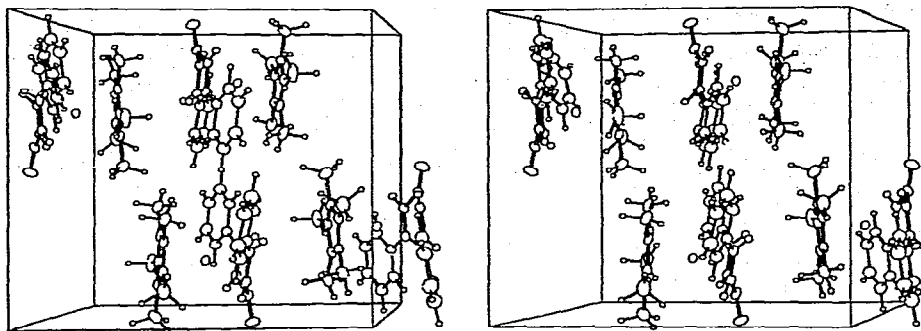


Fig. 1. A stereoview of the contents of the unit cell of $\text{Rh}(\text{C}_5\text{Me}_5)(\text{dba})$. The thermal ellipsoids are drawn at their 20% probability levels, except for the hydrogen atoms which have been drawn artificially small for the sake of clarity. The x axis goes from left to right, the y from bottom to top, and the z axis comes out of the paper.

cally placed with respect to the C_5 ring of the C_5Me_5 group and coordinated to the two double bonds, $\text{C}(2)\text{—C}(3)$ and $\text{C}(4)\text{—C}(5)$, of the dba molecule. Table 7 presents information on selected, weighted least-squares planes through the molecule. The planar portion of the dba molecule (Plane 1) containing the two double bonds is essentially parallel (dihedral angle, 2.69°) to the plane (No.4) through the 10 C atoms of the C_5Me_5 group.

The Rh—C (of C_5Me_5) distances range from 2.196(6) to 2.237(6) Å and average 2.222(18) Å, where the standard deviation of a single observation of 0.018 Å is obtained on the assumption that the distances averaged are from the same population. The fact that the standard deviation estimated in this way is three times that estimated from the inverse matrix indicates that either all of

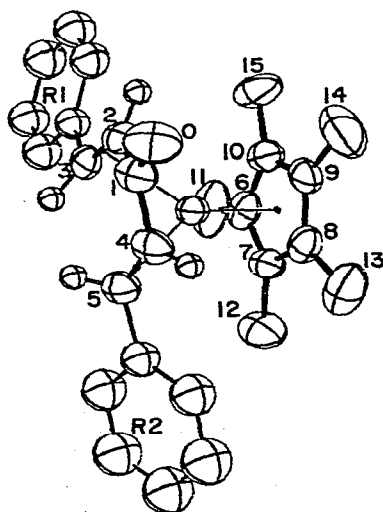


Fig. 2. A drawing of the $\text{Rh}(\text{C}_5\text{Me}_5)(\text{dba})$ molecule, showing the numbering scheme as well as the thermal ellipsoids at their 50% probability levels. The olefinic hydrogen atoms have been drawn artificially small. Other hydrogen atoms have been omitted for the sake of clarity.

TABLE 6 SELECTED DISTANCES (Å) AND ANGLES (deg.)

Rh—C(1)	2.448(6)		C(2)—Rh—C(4)	69.8(2)
Rh—C(2)	2.149(6)	} 2.151(6) ^a	Rh—C(1)—O	140.2(5)
Rh—C(4)	2.152(6)		Rh—C(1)—C(2)	60.5(3)
Rh—C(3)	2.241(6)	} 2.236(8)	Rh—C(1)—C(4)	60.8(3)
Rh—C(5)	2.230(6)		O—C(1)—C(2)	121.6(6)
Rh—C(2)H	2.76(7)	} 2.76(7)	O—C(1)—C(4)	121.8(6)
Rh—C(4)H	2.76(7)		C(2)—C(1)—C(4)	114.2(5)
Rh—C(3)H	2.65(7)	} 2.65(8)	C(3)—C(2)—C(1)	127.2(6)
Rh—C(5)H	2.65(8)		C(5)—C(4)—C(1)	127.2(6)
Rh—O	3.489(5)		C(2)H—C(2)—C(3)	120.5(4.2)
Rh—C(6)	2.235(6)	} 2.222(18)	C(4)H—C(4)—C(5)	120.0(4.3)
Rh—C(7)	2.237(6)		C(2)H—C(2)—C(1)	112.2(4.2)
Rh—C(8)	2.211(6)	} 2.222(18)	C(4)H—C(4)—C(1)	112.7(4.3)
Rh—C(9)	2.232(6)		C(2)—C(3)—C(3)H	120.3(4.2)
Rh—C(10)	2.196(6)	} 3.341(26)	C(4)—C(5)—C(5)H	118.1(4.8)
Rh—C(11)	3.348(7)		C(3)H—C(3)—R(1)C(1)	111.9(4.2)
Rh—C(12)	3.384(7)	} 3.341(26)	C(5)H—C(5)—R(2)C(1)	113.4(4.5)
Rh—C(13)	3.328(8)		C(2)—C(3)—R(1)C(1)	122.9(5)
Rh—C(14)	3.317(8)	} 2.362(10)	C(4)—C(5)—R(2)C(1)	123.0(5)
Rh—C(15)	3.329(7)		C(3)—R(1)C(1)—R(1)C(2)	117.9(3)
O—C(1)	1.236(7)	} 2.362(10)	C(3)—R(1)C(1)—R(1)C(6)	122.1(4)
O—C(2)	2.369(8)		C(5)—R(2)C(1)—R(2)C(2)	116.0(4)
O—C(4)	2.355(8)	} 2.51(7)	C(5)—R(2)C(1)—R(2)C(6)	124.0(4)
O—C(2)H	2.51(7)		C(10)—C(6)—C(7)	106.8(5)
O—C(4)H	2.51(7)	} 1.465(13)	C(6)—C(7)—C(8)	108.1(5)
C(1)—C(2)	1.474(8)		C(7)—C(8)—C(9)	108.5(6)
C(1)—C(4)	1.456(8)	} 2.06(7)	C(8)—C(9)—C(10)	107.4(6)
C(1)—C(2)H	2.06(7)		C(9)—C(10)—C(6)	109.1(5)
C(1)—C(4)H	2.05(7)	} 2.83(8)	C(10)—C(6)—C(11)	125.9(6)
C(1)—C(5)H	2.81(8)		C(7)—C(6)—C(11)	127.2(7)
C(1)—C(3)H	2.85(7)	} 2.576(9)	C(6)—C(7)—C(12)	126.8(6)
C(1)—C(3)	2.579(9)		C(8)—C(7)—C(12)	124.9(6)
C(1)—C(5)	2.572(9)	} 1.411(9)	C(7)—C(8)—C(13)	125.9(6)
C(2)—C(3)	1.406(8)		C(9)—C(8)—C(13)	125.4(7)
C(4)—C(5)	1.416(9)	} 0.98(7)	C(8)—C(9)—C(14)	126.6(7)
C(2)—C(2)H	0.98(7)		C(10)—C(9)—C(14)	126.0(7)
C(4)—C(4)H	0.98(7)	} 0.98(7)	C(9)—C(10)—C(15)	125.6(7)
C(3)—C(3)H	1.00(7)		C(6)—C(10)—C(15)	124.8(7)
C(5)—C(5)H	0.96(8)		C(5)—C(4)—C(1)—O	162.5(6) ^b
C(3)—R(1)C(1)	1.496(10)	} 1.492(10)	O—C(1)—C(2)—C(3)	-161.7(6)
C(5)—R(2)C(1)	1.488(10)			
C(3)—C(4)	3.020(9)	} 3.018(9)		
C(2)—C(5)	3.015(9)			
C(5)H—C(3)H	1.83(9)			
O...C(15)H(3)	2.37			
O...C(2)H	2.51(7)			
C(3)—C(5)	2.891(9)	} 1.418(18)		
C(6)—C(7)	1.404(8)			
C(7)—C(8)	1.433(9)	} 1.502(12)		
C(8)—C(9)	1.409(8)			
C(9)—C(10)	1.402(9)	} 1.502(12)		
C(10)—C(6)	1.440(9)			
C(6)—C(11)	1.482(9)			
C(7)—C(12)	1.503(9)			
C(8)—C(13)	1.511(9)			
C(9)—C(14)	1.503(10)			
C(10)—C(15)	1.509(9)			

^aIf given, the value in parentheses following the mean value is the standard deviation of a single observation, based on the larger of that estimated from the agreement among the averaged values or that estimated from the average standard deviation of a single observation. ^bThe sign of the conformation or torsion angle of atoms I—J—K—L is positive if when looking from J to K a clockwise motion of atom I would superimpose it on atom L.

TABLE 7
BEST WEIGHTED LEAST-SQUARES PLANES

Plane no.	$Ax + By + Cz = D$ (monoclinic coordinates)			
	A	B	C	D
1	14.193	-1.199	-4.122	9.491
2	14.242	-0.730	-4.025	6.123
3	14.249	-0.523	-4.040	6.075
4	14.247	-0.552	-4.045	6.134

Atom	Deviations (Å) from plane no. ^a			
	1	2	3	4
C(2)	-0.003(6)			
C(3)	0.003(6)			
C(4)	0.004(6)			
C(5)	-0.003(6)			
O	0.647			
C(1)	0.367			
C(2)H	-0.22			
C(4)H	-0.23			
C(3)H	0.59			
C(5)H	0.60			
Rh	-1.587	1.867	1.964	1.899
C(6)		-0.005(6)	0.109	0.043(6)
C(7)		-0.004(5)	0.105	0.039(5)
C(8)		0.013(6)	0.100	0.037(6)
C(9)		-0.016(6)	0.064	0.002(6)
C(10)		0.013(6)	0.109	0.045(6)
C(11)		-0.114	0.020(7)	-0.048(7)
C(12)		-0.143	-0.021(7)	-0.090(7)
C(13)		-0.060	0.016(8)	-0.047(8)
C(14)		-0.058	0.000(8)	-0.059(8)
C(15)		-0.106	-0.012(7)	-0.074(7)

Dihedral angles between planes		
Plane no.	Plane no.	Angle (deg.)
2	1	2.00
3	1	2.81
4	1	2.69
3	2	0.85
4	2	0.73
4	3	0.12

^aThe atoms used in the calculation of a given plane equation are those for which estimated standard deviations are given for the deviations from the plane.

the standard deviations from the inverse matrix are underestimated or that there are possibly some significant variations among the Rh—C distances. We favor the latter explanation, both because some distances (e.g. C—Me) do appear to be equivalent on this criterion and because the bulky C₅Me₅ ring might be expected to deviate slightly from a symmetric position with respect to the Rh atom as a result of minimization of lattice energy. In the two other structures containing the C₅Me₅ ring similar deviations of M—C distances are observed:

TABLE 8
COMPARISON OF THE C_5Me_5 GEOMETRY IN THREE METAL COMPLEXES (in Å)

Quantity	$(C_5Me_5)Fe(CO)_2SO_2CH_2CH=CH(C_6H_5)^a$	$[(C_5Me_5)RhCl]_2HCl^b$	$(C_5Me_5)Rh(dba)^c$
C—C range	1.382—1.460(10)	1.403—1.440(8)	1.404—1.440(9)
C—C average	1.431(30) ^d	1.425(14)	1.418(18)
C—Me range	1.492—1.530(11)	1.479—1.503(11)	1.482—1.511(9)
C—Me average	1.509(16)	1.492(9)	1.502(12)

^a Ref. 9. ^b Ref. 10. ^c This work. ^d This is the standard deviation of a single observation calculated on the assumption that the five distances averaged are from the same population.

2.109(6) to 2.178(6) Å in $[(C_5Me_5)RhCl]_2HCl$ [10] and 2.090(8) to 2.137(8) Å in $(C_5Me_5)Fe(CO)_2SO_2CH_2CH=CH(C_6H_5)$ [9]. In the present Rh^I structure the Rh—center (of the Me_5C_5 ring) distance is 1.899 Å, about 0.12 Å longer than that found in the Rh^{III} complex [10]. This difference undoubtedly reflects the increased radius of Rh^I compared with Rh^{III} .

The geometry of the C_5Me_5 ring is compared with that found in the other two structures in Table 8. The conclusion that there are significant differences within the C_5 ring would be tenuous from a single structure determination: this conclusion seems firmer when based on the three structures detailed in Table 8. While one can fall back on packing forces as an explanation for the variations in M—C distances noted above, this cannot be done for the C—C distances. Moreover, there appears to be no discernible trend in the variations of M—C distances with the corresponding C—C distances. It may be that there are subtle electronic forces responsible for these variations in C—C distances but the effect is small and the number of structures is also small.

Of considerable interest is the nonplanar nature of the C_5Me_5 ring. Whereas the C_5 atoms are coplanar (Plane 2, Table 7) and the Me_5 groups are coplanar (Plane 3, Table 7), it is clear from Table 7 that the Me groups are bent *away* from the Rh atom, the Rh atom being 1.867 Å from the center of the C_5 ring and 1.964 Å from the center of the Me_5 group. This bending back of the Me_5 group has been previously ascribed [10] to steric crowding in the Rh^{III} complex. In view of the longer Rh—center distance in the present Rh^I complex, this explanation does not appear to be valid. Hodgson and Raymond [14] have recently commented on the possible reasons why the methyl groups in $U(C_8H_4(CH_3)_4)_2$ bend *inward* about 0.10 Å toward the U atom. They are able to eliminate both inter- and intramolecular packing effects as an explanation and hence they suggest that the phenomenon has its origin in the electronic structure of the molecule. Similarly, Rees and Coppens [11] have offered some explanations in electronic terms for the fact that the H atoms in $Cr(CO)_3(C_6H_6)$ are displaced from the plane of the benzene ring about 0.03 Å *toward* the Cr atom. Based on these various discussions it may be that in the Rh^I and Rh^{III} (C_5Me_5) complexes the Me groups are bent away from the Rh atoms toward a tetrahedral geometry as a result of small amounts of carbon s character in the Rh—C bonds. It may be that the nonplanarity of these various aromatic rings attached to transition metals is a sensitive indicator of the electronics of

bonding, but the number of accurately documented cases is too small at this point to enable one to comment further.

The coordinated dba molecule has the *s-cis, s-cis* symmetric conformation II, as may be seen in Fig. 2. The least-squares plane through the molecule (Plane 1, Table 7) provides the most convenient description of the bound dba molecule. The two double bonds are parallel to the C_5Me_5 planes. The inner portion of the dba molecule is boat-shaped, with the C(1), O, C(3)H, and C(5)H atoms out of the plane away from the Rh atom. The bond distances within the molecule are normal. The two double bonds are equivalent and average 1.411(9) Å, compared with 1.36(2) and 1.2 Å in the CH_2Cl_2 [6] and $CHCl_3$ [5] solvates of $Pd_2(dba)_3$. In the present instance the double bonds have lengthened considerably over the normal value of 1.34 Å, in agreement with the results on a number of other metal-olefin complexes [15]. Clearly the C=C bonds in $Pd_2(dba)_3 \cdot CHCl_3$ have been foreshortened considerably as a result of the excessive thermal motion. Although the Rh-C(olefin) distances are in the normal range [15], the Rh atom is not symmetrically placed with respect to a given double bond (Table 6).

The C—O bond length of 1.236(7) Å is unexceptional and does not correlate with the polarization of this bond expected on the basis of the low C—O stretching frequency [8].

Of considerable interest is the H...H intramolecular distance between C(3)H and C(5)H. The refined distance is 1.83(9) Å, based on the refined C—H distances of 0.98 Å. Short C—H distances are the rule in X-ray studies [16], and if these C—H distances are lengthened to the normal 1.08 Å by moving the H atoms along the C—H vectors then the H...H interaction is 1.76 Å. It is seen then that, as predicted from molecular models, this H...H interaction is abnormally short. There has been some attempt to lessen this interaction: thus the C(1)—C(4)—C(5) and C(1)—C(2)—C(3) angles have opened up to 127.2(6)°, away from the 120° expected for trigonal C atoms. Nevertheless the dba molecule maintains its parallel double bonds, a condition that is most favorable for maximum overlap with the metal orbitals, at the expense of the severe crowding of the H atoms. Thus the coordinated dba molecule is severely strained. Perhaps the catalytic activity of the complex is caused by this strain; there would presumably be a tendency for the dba molecule to dissociate in solution leaving the reactive, coordinately unsaturated Rh(C_5Me_5) species. It is conceivable that conditions could be found for the elimination of H_2 from dba, rather than for its dissociation. A diphenylcyclopentadienone ring system would then be formed. Transition metal complexes of cyclopentadienone are known [17].

It would be interesting to attempt to prepare complexes analogous to the present one in which a single Me group is substituted for C(3)H. The various possibilities for such a preparative reaction include: (1) Formation of a less stable molecule analogous to the present one but with non-parallel olefinic double bonds; (2) utilization of the two olefinic double bonds in the *s-cis, s-trans* conformation to form an oligomer involving more than a single metal atom; (3) possible attachment of the Me-dba molecule to a single metal through the C=O moiety and one of the olefinic double bonds; (4) elimination of CH_4 to form a cyclopentadienone complex. The possibilities for the dimethyl derivative are equally intriguing.

Acknowledgments

The author is indebted to Dr. H.B. Lee and Prof. P.M. Maitlis for supplying the crystals used in this study. This work was supported by the U.S. National Science Foundation.

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