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ON THE CYCLODIMERIZATION OF ACETYLENES TO CYCLOBUTADIENE PROBLEM: THE SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF (η^5-CYCLOPENTADIENYL)-(η^4-1,2-DIPHENYLCYCLOBUTA[*l*]PHENANTHRENE)RHODIUM

GEORGE M. REISNER, IVAN BERNAL *,

Chemistry Department, University of Houston, Houston, Texas 77004 (U.S.A.)

MARVIN D. RAUSCH *, SYLVIA A. GARDNER,

Chemistry Department, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

and ABRAHAM CLEARFIELD

Chemistry Department, Texas A&M University, College Station, Texas 77813 (U.S.A.)

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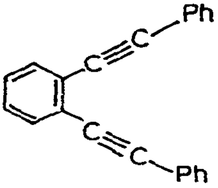
Summary

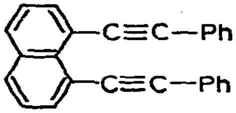
A reaction between 2,2′-bis(phenylethynyl)biphenyl and η^5-cyclopentadienylcarbonylrhodium has been found to produce several organometallic products, including (η^5-cyclopentadienyl)(η^4-1,2-diphenylcyclobuta[*l*]phenanthrene)rhodium has been determined by single-crystal X-ray diffraction using data acquired by a computer-controlled diffractometer. The substance crystallizes in the triclinic system, space group $P\bar{1}$, with cell constant of a 10.023(1), b 11.146(3), c 22.314(4) Å, α 101.26(2), β 97.53(1) and γ 96.55(1)°. The observed and calculated densities (for two molecules in the asymmetric unit) are 1.45(1) and 1.446 g/cm^3, respectively. The structure was solved by Patterson, Fourier and least-squares refinement techniques. Final discrepancy indices are $R(F)$ = 3.6% and $R_w(F)$ = 4.2%. The (η^5-C_5H_5)Rh fragments have normal distances and angles, the Cp rings being planar as expected. The cyclobutadiene rings are also planar (largest deviations from planarity being 0.003 Å) and parallel to the Cp rings. The most important change, as a result of the constraints of the fused cyclobuta[*l*]phenanthrene system, is the trapezoidal shape of the (η^4-C_4) ring. The effects of fusion and of strain, caused by the crowding of two hydrogen atoms at the open side of phenanthrene, on the cyclobuta[*l*]-phenanthrene system are discussed.

Introduction

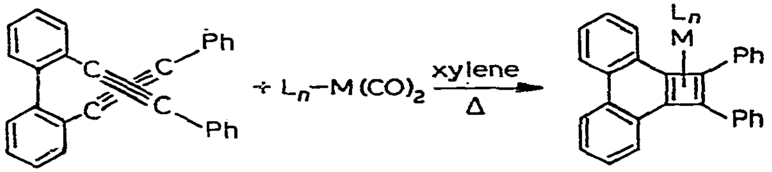
As pointed out earlier [1], the study of reactions of diacetylenes (diynes) and metal carbonyls is a relatively young field. Thus, reactions of the acyclic diacetylenes 1,2-bis(phenylethynyl)benzene (I) with either $Fe(CO)_5$ or (η^5-C_5H_5)$M(CO)_2$ (M = Co, Rh) produce intermolecularly-derived cyclobutadieneiron ferrole [2,3], bis(cyclobutadiene)dicobalt [4,5] or cyclobutadienecyclopentadienonedirhodium [4] derivatives, respectively, whereas analogous reactions of 1,8-bis(phenylethynyl)napthalene (II) with these reagents lead to intramolecularly derived cyclopentadienonemetal products [4—7]. In contrast to reactions of I and II, the related diacetylene-2,2'-bis(phenylethynyl)biphenyl (III) undergoes preferential intramolecular cyclodimerization with Group VIII metal carbonyls such as $Fe(CO)_5$ and (η^5-C_5H_5)$M(CO)_2$ (M = Co, Rh) to produce η^4-1,2-diphenylcyclobuta[1]phenanthrenemetal complexes (IV).



(I)



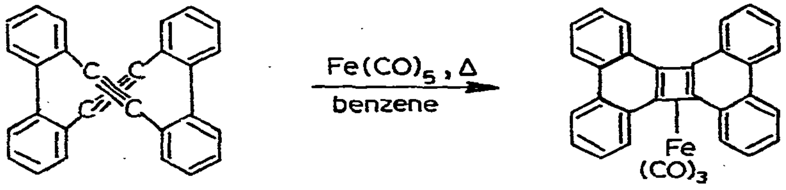
(II)



(III)

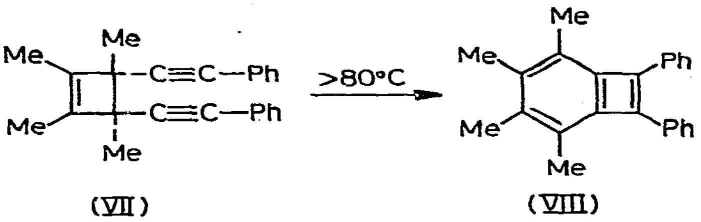
(IVa) $L_nM = (\eta^5-C_5H_5)Co$
(IVb) $L_nM = (\eta^5-C_5H_5)Rh$
(IVc) $L_nM = (CO)_3Fe$

Related studies by Staab et al. [8] have shown that the crossed diacetylene (V) will internally cyclodimerize to form the tricarbonyliron derivative (VI) upon reaction with $Fe(CO)_5$. The X-ray structure of (VI) has been examined, although the details have not yet been published [9,10]. However, Irngartinger [11] has reported the structure of the parent compound (V) to contain a pair of acetylene units whose C—C(acetylene) vectors make an angle of 52.6°.



(V) (VI)

The acetylenic groups in I and II would be expected to be essentially coplanar. If metal-promoted intramolecular cyclodimerization to form η^4-cyclobutadienemetal complexes were to occur, it would involve a sterically demanding process in which both members of the diacetylene pair would be forced to stay planar during the reaction, constrained by the rigid aromatic rings to which they are attached. However, this is not the case for molecules III or V. In this regard, Straub [11] has recently reported that the thermal cyclodimerization of diacetylene (VII) produces the benzocyclobutadiene derivative (VIII). In diacetylene (VII), the acetylenic linkages occupy a *trans*-geometry



and thus share characteristics similar to those of III and V.

In order to unequivocally establish the structures of the products derived from diacetylene III and metal carbonyls, and to better understand the factors leading to their formation, a single crystal X-ray diffraction investigation of the rhodium analog IVb has been undertaken.

Experimental

All synthetic operations were conducted under a nitrogen atmosphere using Schlenk tube techniques. Hexane, benzene and xylene were purified by distillation from calcium chloride under nitrogen. Ethyl ether was pre-dried over sodium wire and then distilled from sodium benzophenone. 2,2'-Bis(phenylethynyl)biphenyl [12] and η^5-cyclopentadienyldicarbonylrhodium [13] were prepared by known procedures. Alumina for chromatography was deactivated and degassed before use. Microanalyses were performed by Microanalytical Laboratory, University of Massachusetts, Amherst, MA. IR, NMR and mass spectra were performed on P.E. IR-10, Varian A-60 and P.E. RMU-6L instruments, respectively.

Reaction of η^5-cyclopentadienyldicarbonylrhodium and 2,2'-bis(phenylethynyl)biphenyl

2,2'-Bis(phenylethynyl)biphenyl (1.6 g, 4.5 mmol) and η^5-cyclopentadienyldicarbonylrhodium (1.0 g, 4.5 mmol) were mixed with 25 ml of xylene in a reaction vessel that was covered with aluminum foil. The mixture was heated to reflux for 24 h, cooled to room temperature and chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with hexane removed a yellow band which was rechromatographed on a dry-packed alumina column (2 × 30 cm). The product was recrystallized from benzene/hexane to yield 0.50 g (21%) of yellow crystals identified as (η^5-cyclopentadienyl)(η^4-1,2-diphenylcyclobuta[l]phenanthrene)rhodium. (Found: C, 75.55; H, 4.45; Rh, 19.40. $C_{33}H_{23}Rh$ calcd.: C, 75.86; H, 4.45; Rh, 19.70%). The molecular weight was 522 as determined by mass spectrometry (calcd. 522). The following major bands were observed in the IR spectrum (KBr): 1600m, 1500m, 1450m, 950m, 770s, 750s, 700s cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of a doublet (5H, J 1.0 Hz, η^5-C_5H_5) at τ 4.85 ppm and a multiplet (18H, aromatic) from τ 1.7—2.6 ppm.

Continued elution of the original column with 1/1 benzene/hexane and evaporation to dryness yielded 1.0 g of a red solid. The IR spectrum (KBr) contained the following major bands: 1840m, 1600m, 1485m, 1450m, 1175m, 1105m, 1070m, 1000s, 815vs, 775s, 760vs, 730vs, 710vs, 680vs cm^{-1}. The NMR spectrum consisted of a singlet at τ 5.48 ppm (5H, η^5-C_5H_5), a singlet at τ 4.83 ppm (5H, η^5-C_5H_5) and a multiplet (18H, aromatic) from τ 2.3—3.3 ppm. Attempts to obtain reliable, reproducible elemental analytical and mass spectral data for this product have thus far been unsatisfactory.

Further elution of the column with 1/3 ether/benzene produced a dark blue band. This was collected and the product recrystallized from benzene/hexane to yield 60 mg of a deep blue solid (Found: C, 71.64; H, 3.64; Rh, 16.2%). The IR spectrum (KBr) contained major bands at 1700s, 1260m, 1100—1000vs, 790vs, 755—720w and 690m cm^{-1}. The NMR spectrum ($CDCl_3$) contained several broad peaks in the cyclopentadienyl region from τ 4.6—4.9 and from 5.6—5.9 ppm, as well as strong absorption in the aromatic region from τ 2.3—3.5 ppm.

Final elution of the column with ether brought down a black band. The product was identified as $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_3$ by comparison of its NMR, IR and mass spectra with a known sample [14].

Crystallographic studies

A crystal of irregular shape was ground to a sphere, mounted on a goniometer head and placed on an ENRAF-NONIUS CAD-4 computer controlled diffractometer. A summary of the crystallographical important parameters for data collection and data processing is given in Table 1. The procedures employed to obtain the cell and X-ray data were similar to those described in detail previously [15].

Solution and refinement

Data decoding was accomplished using a locally written program (Houston). Lorentz and polarization factors were applied to convert the intensities to structure factor amplitudes, $|F_0|$. No absorption correction was necessary due to the spherical shape of the crystal and to the low value of the absorption coefficient (μ = 7.2 cm^{-1}). Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{\text{Tot}} + 2\Sigma I_{\text{BG}}$. Standard deviations in the structure amplitudes, $\sigma(F_0)$, were estimated as $\sigma(F_0) = \sigma(I)/2Lp|F_0|$. All data processing and calculations were carried out using the X-Ray '72 System of programs [16].

A three dimensional Patterson map was computed and the initial positions of the two Rh atoms were determined. All of the remaining nonhydrogen atoms were found using successive difference Fourier maps. Hydrogen atoms were added at theoretically calculated positions (C—H = 0.95 Å) after conversion to anisotropic thermal parameters. Final anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogens yielded the following val-

TABLE 1

CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION

Empirical formula	$C_{33}H_{23}Rh$
Molecular weight	522.45 g mol^{-1}
Cell constants	a 10.023(1) Å b 11.146(3) Å c 22.314(4) Å α 101.26(2)° β 97.53(1)° γ 96.55(1)°
Unit cell volume	V 2398.7 Å^3
Space group	$P\overline{1}$
Number of molecules in asymmetric unit	2
Density	ρ(calc.) 1.446 g cm^{-3} ρ(meas.) 1.45 g cm^{-3}
Absorption coefficient (Mo-K_α)	7.2 cm^{-1}
Radiation used for data collection	Mo-K_α (λ 0.71069 Å)
Crystal shape	Sphere, 0.55 mm diameter
Scanning range for 2θ	$4.00° < 2\theta < 52.0°$
Standards for intensity control (every 30 reflections)	$[3, \overline{3}, 9; 1, 2, 11$ and $3, 2, \overline{13}]$
Scan wifth for each reflection	$\Delta\theta$ $(0.90 + 0.35 \tan\theta)°$
Maximum scan time	10 minutes
Minimum number of counts above background for each reflection	3000
Scan technique	θ—2θ
Total number of reflections collected [a]	8818
Number of contributing reflections in the last least-squares [b]	8081
Number of variables	797
Weighting scheme	$w = 1/\sigma^2(F_0)$
Final $R(F)$ [c]	0.036
Final $R_w(F)$ [d]	0.042

[a] A total of 8818 reflections were collected of which 6949 having $I > 3\sigma(I)$ were classified as "observed" with the remaining 1869 being termed "less-thans". [b] 6949 "observed" and 1132 "less-thans", for which $|F_c| > |F_0|$. [c] $R(F) = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [d] $R_w(F) = [\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2]^{1/2}$.

ues for the agreement factors: $R(F) = 0.036$ and $R_w(F) = 0.040$. The function minimized during all the least-squares refinements was $\Sigma w(|F_0| - |F_c|)^2$, where w, the weighting factors, were $[\sigma(F_0)]^{-2}$. The atomic scattering curves of Cromer and Mann [17] were used for the nonhydrogen atoms; the curve of Stewart et al. [18] was used for the hydrogen atoms. Corrections for the real part of the anomalous scattering for Rh were also applied [19]. The estimated standard deviations were computed from the inverse matrix of the final least-squares cycle.

Final positional and thermal parameters are presented in Tables 2—4. Bond lengths and angles are given in Tables 5 and 6. The equations of the least-squares planes through selected groups of atoms are given in Table 7. The stereo drawings were obtained by using Johnson's ORTEP2 [20]. A table of

TABLE 2

FINAL POSITIONAL PARAMETERS OF THE NON-HYDROGEN ATOMS [a, b]

Atom	x	y	z	Atom	x	y	z
Rh	0.34246(4)	0.24624(4)	0.14379(2)	C(17)	−0.0901(6)	0.4422(7)	0.1890(3)
	0.29287(4)	0.25243(4)	−0.38557(2)		0.7980(6)	0.4304(6)	−0.3166(3)
C(1)	0.4389(7)	0.3543(7)	0.2371(3)	C(18)	−0.0996(6)	0.2158(7)	0.2397(3)
	0.2281(9)	0.3739(8)	−0.3060(3)		0.7131(7)	0.2904(7)	−0.2260(3)
C(2)	0.4867(8)	0.4146(7)	0.1926(4)	C(19)	−0.1097(7)	0.1069(8)	0.2610(3)
	0.2571(8)	0.4450(6)	−0.3475(4)		0.6795(8)	0.2188(8)	−0.1842(3)
C(4)	0.5583(7)	0.3345(9)	0.1572(3)	C(20)	−0.0419(7)	0.0113(7)	0.2370(3)
	0.1692(9)	0.3993(7)	−0.4032(4)		0.5728(8)	0.1206(7)	−0.2015(3)
C(4)	0.5544(7)	0.2248(8)	0.1789(4)	C(21)	0.0401(6)	0.0252(6)	0.1917(3)
	0.0815(7)	0.2955(7)	−0.3963(4)		0.4963(6)	0.0968(6)	−0.2604(3)
C(5)	0.4815(7)	0.2381(7)	0.2297(4)	C(22)	0.2335(5)	−0.0273(5)	0.0543(2)
	0.1197(9)	0.2804(8)	−0.3342(4)		0.2610(5)	−0.0456(5)	−0.4149(2)
C(6)	0.2142(5)	0.1007(5)	0.0790(2)	C(23)	0.3568(5)	−0.0592(5)	0.0388(3)
	0.3455(5)	0.0741(4)	−0.4104(2)		0.1208(6)	−0.0644(5)	−0.4328(3)
C(7)	0.2250(5)	0.2149(5)	0.0541(2)	C(24)	0.3667(7)	−0.1799(6)	0.0104(3)
	0.3812(5)	0.1496(4)	−0.4557(2)		0.0449(7)	−0.1806(7)	−0.4366(3)
C(8)	0.1465(5)	0.2698(5)	0.1020(2)	C(25)	0.2541(7)	−0.2708(6)	−0.0016(3)
	0.4900(5)	0.2256(4)	−0.4076(2)		0.1108(8)	−0.2759(6)	−0.4223(4)
C(9)	0.1353(5)	0.1581(5)	0.1256(2)	C(26)	0.1316(7)	−0.2408(5)	0.0149(3)
	0.4541(5)	0.1523(4)	−0.3638(2)		0.2494(8)	−0.2575(6)	−0.4041(4)
C(10)	0.0522(5)	0.1358(5)	0.1718(2)	C(27)	0.1205(6)	−0.1201(5)	0.0418(3)
	0.5287(5)	0.1705(5)	−0.3020(2)		0.3257(6)	−0.1424(5)	−0.3994(3)
C(11)	−0.0194(5)	0.2333(6)	0.1937(2)	C(28)	0.2690(5)	0.2455(5)	−0.0014(2)
	0.6404(6)	0.2676(5)	−0.2866(2)		0.3420(5)	0.1356(5)	−0.5226(2)
C(12)	−0.0126(5)	0.3486(5)	0.1689(2)	C(29)	0.3249(6)	0.3646(6)	−0.0034(3)
	0.6820(6)	0.3400(5)	−0.3322(2)		0.3572(6)	0.2390(6)	−0.5496(3)
C(13)	0.0709(5)	0.3692(5)	0.1236(2)	C(30)	0.3679(7)	0.3902(6)	−0.0569(3)
	0.6106(5)	0.3178(5)	−0.3928(3)		0.3139(7)	0.2250(7)	−0.6141(3)
C(14)	0.0690(6)	0.4760(5)	0.0988(3)	C(31)	0.3568(7)	0.2967(7)	−0.1092(3)
	0.6596(6)	0.3801(6)	−0.4364(3)		0.2663(7)	0.1081(7)	−0.6505(3)
C(15)	−0.0115(6)	0.5645(6)	0.1190(3)	C(32)	0.2993(7)	0.1758(7)	−0.1080(3)
	0.7757(7)	0.4661(7)	−0.4207(3)		0.2555(7)	0.0056(7)	−0.6237(3)
C(16)	−0.0905(7)	0.5467(7)	0.1645(3)	C(33)	0.2553(6)	0.1512(6)	−0.0544(2)
	0.8438(7)	0.4929(6)	−0.3588(4)		0.2940(6)	0.0182(6)	−0.5600(3)

[a] First entry is for Molecule 1, second entry for Molecule 2 in this and succeeding tables. [b] Numbers in parentheses are the estimated standard deviations in the least significant digits in this and succeeding tables.

observed and calculated structure factors is available as supplementary material *.

Results and discussion

The reaction between diacetylene III and η^5-cyclopentadienyldicarbonylrhodium in refluxing xylene produced four organometallic products. One of these was the η^4-cyclobutadienerhodium complex (IVb), which was fully char-

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* A table of structure factors has been deposited as NAPS Document No. 03511 (28 pages). Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured citing the document number, and remitting $ 7.00 for photocopies of $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the U.S. and Canada add postage of $ 3.00 for photocopy and $ 1.00 for microfiche.

TABLE 3

FINAL POSITIONAL AND THERMAL (× 10^3) PARAMETERS OF THE HYDROGEN ATOMS

Atom	x	y	z	U_{iso}
H(1)	0.385(9)	0.405(8)	0.282(4)	145(34)
	0.295(13)	0.392(12)	−0.261(6)	241(58)
H(2)	0.470(10)	0.510(9)	0.191(5)	177(42)
	0.347(11)	0.529(10)	−0.335(5)	182(43)
H(3)	0.602(9)	0.354(8)	0.120(4)	144(35)
	0.168(10)	0.429(9)	−0.452(5)	172(41)
H(4)	0.592(8)	0.160(7)	0.165(3)	103(26)
	0.005(10)	0.238(9)	−0.426(5)	165(40)
H(5)	0.459(7)	0.166(7)	0.252(3)	98(25)
	0.070(9)	0.211(8)	−0.314(4)	132(32)
H(14)	0.131(6)	0.487(6)	0.061(3)	71(19)
	0.609(5)	0.357(5)	−0.482(2)	51(16)
H(15)	−0.013(7)	0.645(7)	0.098(3)	104(26)
	0.804(8)	0.513(7)	−0.455(4)	115(28)
H(16)	−0.150(7)	0.613(6)	0.180(3)	85(22)
	0.934(8)	0.560(8)	−0.339(4)	126(31)
H(17)	−0.151(6)	0.428(6)	0.225(3)	74(20)
	0.855(6)	0.447(5)	−0.273(4)	64(18)
H(18)	−0.157(7)	0.292(7)	0.257(3)	96(42)
	0.793(8)	0.369(7)	−0.209(4)	116(29)
H(19)	−0.170(7)	0.094(6)	0.298(4)	82(21)
	0.742(8)	0.230(7)	−0.144(3)	112(28)
H(20)	−0.045(6)	−0.063(6)	0.259(3)	73(20)
	0.554(7)	0.058(6)	−0.171(3)	84(22)
H(21)	0.099(6)	−0.047(5)	0.176(3)	69(19)
	0.408(6)	0.023(5)	−0.277(3)	69(19)
H(23)	0.439(6)	0.007(6)	0.045(3)	77(20)
	0.067(7)	0.009(6)	−0.449(3)	95(24)
H(24)	0.466(7)	−0.198(6)	−0.003(3)	95(24)
	−0.066(10)	−0.192(9)	−0.466(4)	160(38)
H(25)	0.266(6)	−0.361(5)	−0.016(3)	65(18)
	0.060(7)	−0.371(17)	−0.431(3)	103(26)
H(26)	0.043(7)	−0.310(6)	0.002(3)	86(22)
	0.308(11)	−0.326(10)	−0.380(5)	187(44)
H(27)	0.026(6)	−0.094(6)	0.051(3)	80(21)
	0.433(7)	−0.124(6)	−0.384(3)	92(24)
H(29)	0.331(6)	0.438(5)	0.035(3)	59(17)
	0.380(6)	0.332(5)	−0.518(3)	68(19)
H(30)	0.410(7)	0.487(6)	−0.058(3)	87(22)
	0.320(7)	0.306(6)	−0.639(3)	94(24)
H(31)	0.392(8)	0.316(7)	−0.152(3)	110(27)
	0.240(8)	0.108(9)	−0.690(4)	121(30)
H(32)	0.290(7)	0.100(6)	−0.151(3)	93(24)
	0.211(7)	−0.086(7)	−0.659(3)	102(25)
H(33)	0.210(6)	0.060(6)	−0.047(3)	71(20)
	0.296(7)	−0.062(6)	−0.534(3)	80(21)

acterized by elemental analysis, spectral properties and by single crystal X-ray diffraction analysis, as is described below. A second major reaction product was a red solid, which is not yet fully identified, but which is believed to be a binuclear rhodiacyclic derivative [5]. Two minor products proved to be the known [14] rhodium cluster complex $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_3$ as well as a yet unidentified deep blue complex.

(Continued on p. 246)

TABLE 4

THERMAL PARAMETERS (X 10^3) [a] OF THE NON-HYDROGEN ATOMS

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	34.6(2)	43.5(2)	39.2(2)	2.3(2)	5.3(2)	6.2(2)
	43.9(2)	35.1(2)	39.9(2)	8.9(2)	8.0(2)	7.6(2)
C(1)	61(4)	94(5)	59(4)	4(4)	—10(3)	—11(4)
	105(6)	95(6)	58(4)	50(5)	12(4)	—10(4)
C(2)	78(5)	57(4)	91(5)	—13(4)	—27(4)	8(4)
	94(6)	52(4)	101(6)	27(4)	14(5)	—3(4)
C(3)	43(4)	129(8)	67(4)	—30(4)	—5(3)	26(5)
	103(6)	72(5)	95(5)	54(4)	30(5)	34(4)
C(4)	39(4)	90(6)	100(6)	17(4)	—16(4)	—10(5)
	50(4)	74(5)	114(6)	31(4)	4(4)	—6(4)
C(5)	63(4)	89(5)	66(4)	—4(4)	—14(3)	31(4)
	88(6)	93(6)	110(6)	46(5)	65(5)	41(5)
C(6)	33(3)	45(3)	44(3)	3(2)	5(2)	7(2)
	38(3)	33(2)	50(3)	9(2)	5(2)	11(2)
C(7)	30(3)	43(3)	54(3)	5(2)	6(2)	6(2)
	41(3)	36(2)	34(2)	7(2)	4(2)	5(2)
C(8)	27(3)	51(3)	43(3)	8(2)	4(2)	11(2)
	41(3)	35(2)	41(3)	6(2)	9(2)	4(2)
C(9)	32(3)	50(3)	40(3)	2(2)	6(2)	8(2)
	39(3)	37(3)	44(3)	9(2)	8(2)	10(2)
C(10)	35(3)	61(3)	39(3)	—4(2)	7(2)	5(2)
	46(3)	41(3)	41(3)	13(2)	5(2)	6(2)
C(11)	34(3)	74(4)	35(3)	1(3)	6(2)	5(2)
	48(4)	47(3)	47(3)	10(2)	2(2)	4(2)
C(12)	30(3)	65(4)	41(3)	7(2)	4(2)	—2(2)
	45(3)	42(3)	45(3)	5(2)	2(2)	5(2)
C(13)	31(3)	51(3)	41(3)	4(2)	1(2)	—2(2)
	40(3)	37(3)	58(3)	4(2)	10(2)	11(2)
C(14)	46(3)	51(3)	52(3)	10(3)	5(3)	2(3)
	56(4)	58(4)	50(3)	—3(3)	7(3)	14(3)
C(15)	54(4)	60(4)	65(4)	19(3)	2(3)	1(3)
	58(4)	68(4)	83(5)	—7(3)	14(4)	28(4)
C(16)	57(4)	78(5)	64(4)	29(3)	6(3)	—1(3)
	54(4)	59(4)	89(5)	—8(3)	9(4)	11(4)
C(17)	43(4)	79(4)	53(3)	17(3)	12(3)	1(3)
	47(4)	57(4)	69(4)	—3(3)	—1(3)	7(3)
C(18)	46(4)	92(5)	55(4)	2(3)	16(3)	7(3)
	66(4)	72(4)	55(4)	2(3)	—4(3)	4(3)
C(19)	56(5)	109(6)	63(4)	—6(4)	25(3)	20(4)
	77(5)	100(6)	46(3)	11(4)	—8(3)	14(4)
C(20)	66(5)	93(5)	52(4)	—13(4)	8(3)	27(4)
	82(5)	82(5)	42(3)	21(4)	5(3)	25(3)
C(21)	52(4)	70(4)	53(3)	—6(3)	11(3)	16(3)
	60(4)	60(4)	50(3)	12(3)	8(3)	18(3)
C(22)	38(3)	46(3)	36(2)	4(2)	3(2)	6(2)
	41(3)	37(3)	43(3)	5(2)	8(2)	8(2)
C(23)	38(3)	50(3)	62(3)	5(2)	10(3)	6(3)
	46(4)	52(3)	64(4)	1(3)	0(3)	10(3)
C(24)	58(4)	59(4)	68(4)	19(3)	13(3)	6(3)
	54(4)	66(4)	78(4)	—11(3)	9(3)	10(3)
C(25)	81(5)	46(3)	55(3)	14(3)	4(3)	3(3)
	75(5)	51(4)	98(5)	—9(3)	32(4)	16(4)
C(26)	60(4)	48(3)	54(3)	—4(3)	2(3)	6(3)
	80(5)	46(4)	105(6)	8(3)	25(4)	28(4)
C(27)	41(3)	51(3)	54(3)	—1(2)	4(2)	6(3)
	55(4)	41(3)	78(4)	12(3)	17(3)	20(3)
C(28)	34(3)	55(3)	31(2)	10(2)	6(2)	8(2)
	37(3)	50(3)	39(3)	11(2)	7(2)	7(2)

TABLE 4 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	57(4)	55(3)	51(3)	13(3)	16(3)	17(3)
	52(4)	63(4)	47(3)	14(3)	11(3)	19(3)
C(30)	70(5)	73(4)	67(4)	22(3)	25(3)	33(3)
	58(4)	97(5)	64(4)	22(4)	12(3)	32(4)
C(31)	67(5)	94(5)	69(4)	28(4)	28(3)	40(4)
	62(4)	125(7)	41(3)	24(4)	5(3)	16(4)
C(32)	57(4)	88(5)	47(3)	18(4)	12(3)	10(3)
	56(4)	91(5)	55(4)	11(4)	6(3)	−18(3)
C(33)	41(3)	66(4)	43(3)	10(3)	9(2)	6(3)
	50(4)	58(4)	50(3)	12(3)	8(3)	−6(3)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$.

TABLE 5

BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Rh—C(1)	2.225(6)	2.229(8)	C(24)—C(25)	1.388(9)	1.380(11)
Rh—C(2)	2.229(7)	2.236(7)	C(25)—C(26)	1.385(10)	1.376(11)
Rh—C(3)	2.229(7)	2.227(8)	C(26)—C(27)	1.385(8)	1.395(9)
Rh—C(4)	2.222(7)	2.218(7)	C(27)—C(22)	1.403(7)	1.397(8)
Rh—C(5)	2.240(7)	2.221(9)	C(28)—C(29)	1.392(8)	1.401(9)
Rh—C(6)	2.119(4)	2.103(5)	C(29)—C(30)	1.391(10)	1.412(9)
Rh—C(7)	2.128(5)	2.108(5)	C(30)—C(31)	1.394(9)	1.388(10)
Rh—C(8)	2.128(5)	2.137(5)	C(31)—C(32)	1.401(11)	1.389(12)
Rh—C(9)	2.145(5)	2.124(5)	C(32)—C(33)	1.391(9)	1.399(9)
C(1)—C(2)	1.407(12)	1.368(12)	C(33)—C(28)	1.401(7)	1.402(7)
C(2)—C(3)	1.399(12)	1.395(11)	C(6)—C(22)	1.470(7)	1.474(7)
C(3)—C(4)	1.399(14)	1.417(11)	C(7)—C(28)	1.455(8)	1.465(7)
C(4)—C(5)	1.420(11)	1.436(13)	C(1)—H(1)	1.26(9)	1.10(12)
C(5)—C(1)	1.395(12)	1.403(11)	C(2)—H(2)	1.10(11)	1.18(10)
C(6)—C(7)	1.484(8)	1.490(8)	C(3)—H(3)	1.03(10)	1.20(11)
C(7)—C(8)	1.487(8)	1.478(6)	C(4)—H(4)	0.87(8)	1.01(9)
C(8)—C(9)	1.442(8)	1.447(8)	C(5)—H(5)	1.05(8)	1.08(9)
C(9)—C(6)	1.479(7)	1.469(6)	C(14)—H(14)	1.12(7)	1.05(7)
C(8)—C(13)	1.454(8)	1.451(7)	C(15)—H(15)	1.10(8)	1.07(9)
C(9)—C(10)	1.447(8)	1.445(7)	C(16)—H(16)	1.03(7)	1.09(7)
C(11)—C(12)	1.494(9)	1.490(8)	H(17)—H(17)	1.10(7)	1.04(6)
C(12)—C(13)	1.428(8)	1.406(9)	C(18)—H(18)	1.12(8)	1.09(7)
C(13)—C(14)	1.408(9)	1.406(7)	C(19)—H(19)	1.10(7)	1.00(7)
C(14)—C(15)	1.388(9)	1.380(9)	C(20)—H(20)	1.05(7)	1.08(7)
C(15)—C(16)	1.397(10)	1.416(10)	C(21)—H(21)	1.08(6)	1.10(5)
C(16)—C(17)	1.380(11)	1.373(11)	C(23)—H(23)	1.01(6)	1.12(8)
C(17)—C(12)	1.410(9)	1.406(8)	C(24)—H(24)	1.10(8)	1.19(9)
C(10)—C(11)	1.414(9)	1.421(7)	C(25)—H(25)	1.02(6)	1.09(7)
C(11)—C(18)	1.413(9)	1.411(8)	C(26)—H(26)	1.08(6)	1.19(12)
C(18)—C(19)	1.385(12)	1.389(11)	C(27)—H(27)	1.05(7)	1.07(7)
C(19)—C(20)	1.386(12)	1.396(10)	C(29)—H(29)	1.05(5)	1.12(5)
C(20)—C(21)	1.403(10)	1.392(8)	C(30)—H(30)	1.11(7)	1.15(8)
C(21)—C(10)	1.388(9)	1.399(9)	C(31)—H(31)	1.11(8)	0.88(8)
C(22)—C(23)	1.392(8)	1.389(8)	C(32)—H(32)	1.13(6)	1.16(7)
C(23)—C(24)	1.391(9)	1.406(9)	C(33)—H(33)	1.11(6)	1.16(7)
			H(17)—H(18)	1.80(10)	1.94(11)

TABLE 6

ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(2)—C(1)—C(5)	108.6(7)	109.0(7)	C(12)—C(13)—C(14)	120.5(5)	120.1(5)
C(1)—C(2)—C(3)	107.7(7)	109.2(7)	C(13)—C(14)—C(15)	120.7(6)	121.4(6)
C(2)—C(3)—C(4)	108.5(8)	108.1(8)	C(14)—C(15)—C(16)	119.2(7)	118.4(7)
C(3)—C(4)—C(5)	107.7(7)	106.4(6)	C(15)—C(16)—C(17)	120.8(7)	120.3(6)
C(4)—C(5)—C(1)	107.5(7)	107.2(8)	C(16)—C(17)—C(12)	121.9(6)	122.0(6)
C(7)—C(6)—C(9)	90.1(4)	89.2(4)	C(10)—C(11)—C(18)	116.8(6)	116.6(6)
C(6)—C(7)—C(8)	88.3(4)	89.1(4)	C(11)—C(18)—C(19)	121.3(7)	121.5(6)
C(7)—C(8)—C(9)	91.4(4)	90.6(4)	C(18)—C(19)—C(20)	120.5(7)	120.6(6)
C(8)—C(9)—C(6)	90.2(4)	91.1(4)	C(19)—C(20)—C(21)	120.1(8)	119.8(7)
C(9)—C(6)—C(22)	133.9(5)	134.6(5)	C(20)—C(21)—C(10)	119.0(0)	119.5(5)
C(7)—C(6)—C(22)	133.2(5)	134.6(4)	C(21)—C(10)—C(11)	122.2(6)	121.9(5)
C(8)—C(7)—C(28)	136.7(5)	136.0(5)	C(6)—C(22)—C(23)	122.9(5)	122.6(5)
C(8)—C(7)—C(28)	133.9(5)	133.9(4)	C(6)—C(22)—C(27)	118.5(3)	117.9(5)
C(7)—C(8)—C(13)	146.8(5)	147.6(5)	C(7)—C(28)—C(29)	122.3(4)	120.5(4)
C(6)—C(9)—C(10)	144.9(5)	145.6(5)	C(7)—C(28)—C(33)	118.6(5)	120.0(5)
C(9)—C(8)—C(13)	120.7(5)	121.0(4)	C(23)—C(22)—C(27)	118.5(5)	119.4(5)
C(8)—C(9)—C(10)	124.2(5)	123.1(4)	C(22)—C(23)—C(24)	120.6(5)	120.4(6)
C(9)—C(10)—C(11)	115.2(5)	115.1(5)	C(23)—C(24)—C(25)	120.3(6)	119.5(6)
C(10)—C(11)—C(12)	121.7(5)	122.5(5)	C(24)—C(25)—C(26)	119.6(6)	120.4(5)
C(11)—C(12)—C(13)	122.2(5)	121.6(5)	C(25)—C(26)—C(27)	120.3(5)	120.7(7)
C(8)—C(13)—C(12)	115.9(5)	116.7(5)	C(26)—C(27)—C(22)	120.7(6)	119.6(6)
C(9)—C(10)—C(21)	122.5(5)	122.9(5)	C(29)—C(28)—C(33)	119.1(5)	119.5(5)
C(8)—C(13)—C(14)	123.4(5)	123.1(5)	C(28)—C(29)—C(30)	120.9(5)	120.3(5)
C(18)—C(11)—C(12)	121.5(6)	121.2(5)	C(29)—C(30)—C(31)	120.0(6)	119.5(7)
C(11)—C(12)—C(17)	121.0(5)	120.7(5)	C(30)—C(31)—C(32)	119.6(6)	120.3(6)
C(13)—C(12)—C(17)	116.8(6)	117.7(5)	C(31)—C(32)—C(33)	120.0(6)	120.6(6)
			C(32)—C(33)—C(28)	120.4(6)	119.7(6)

Description of the structure of IVb

A view of one of the two independent molecules (molecule 1) and the numbering system used for both are given in Fig. 1. The two molecules have similar geometries which can be seen from the molecular dimensions (Tables 5 and 6) and the packing diagram (Fig. 3). An important structural feature of the molecule is the existence of a (η^4-C_4)Rh species, in contrast to the rhodiacyclic structure determined by Müller et al. [21] for a similarly derived complex.

The cyclopentadienyl ligands are planar, with rhodium to (η^5-Cp) ring plane distances of 1.882 and 1.878 Å for the two molecules. These values are in agreement with a recent observation by Hermann et al. [22]. In comparing (η^5-Cp)Rh distances for various complexes, it was found [22] that there are two distinct metal-ring centroid ranges; one, associated with compounds of the class (η^5-Cp)RhL (L = unsaturated hydrocarbon) has the metal situated at about 1.87 Å from the center of the cyclopentadienyl ring; the other has values close to 1.91 Å. The (η^5-Cp)Rh(η^4-C_4) fragment of (η^5-cyclopentadienyl)-(η^4-1,2-diphenylcyclobuta[*l*]phenanthrene)rhodium (A) is similar to that described by Cash et al. [23] for the (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)rhodium (B). The rhodium—Cp(ring centroid) distances for molecule A compare well with the value of 1.868 Å observed for B. The Rh—C distances involving the five-membered ring vary from 2.222(7) to 2.240(7) Å and from 2.218(7) to 2.236(7) Å. The C—C distances in the five-membered ring

TABLE 7a

LEAST SQUARES PLANES (in Orthogonal Å Space) AND DEVIATIONS OF ATOMS FROM THESE PLANES (in Å)

(a) Plane based on C(1), C(2), C(3), C(4), and C(5)

$$0.7306x + 0.3852y + 0.5637x = 6.3454$$

$$-0.7764x + 0.6000y + 0.1927z = -1.1476$$

C(1)	−0.0052	−0.0019	C(2)	0.0002	0.0011
C(3)	0.0048	0.0002	C(4)	−0.0079	−0.0013
C(5)	0.0081	0.0019	Rh	−1.8822	−1.8784

(b) Plane based on C(6), C(7), C(8), and C(9)

$$0.7390x + 0.3545y + 0.5729z = 2.5699$$

$$-0.7700x + 0.6154y + 0.1654z = -4.5530$$

C(6)	0.0031	−0.0020	C(7)	−0.0031	0.0020
C(8)	0.0032	−0.0021	C(9)	−0.0032	0.0021
C(22)	−0.3113	−0.1924	C(28)	−0.2137	−0.2449
Rh(1)	1.8578	1.8444			

(c) Plane based on C(8), C(9), C(10), C(11), C(12), C(13), C(14), C(15), C(16), C(17), C(18), C(19), C(20), and C(21)

$$0.6324x + 0.4277y + 0.6459z = 2.7780$$

$$0.7093x - 0.6833y - 0.1733z = 4.2012$$

C(8)	0.0388	−0.0883	C(9)	0.0055	−0.0242
C(10)	0.0013	−0.0029	C(11)	0.0445	−0.0645
C(12)	0.0431	−0.0700	C(13)	0.0570	−0.0446
C(14)	−0.0181	0.0689	C(15)	−0.0742	0.1246
C(16)	−0.0504	0.0317	C(17)	0.0173	−0.0509
C(18)	0.0678	−0.0861	C(19)	0.0187	−0.0072
C(20)	−0.0701	−0.1112	C(21)	−0.0811	0.1024
Rh	1.7466	−1.8315			

(d) Plane based on C(22), C(23), C(24), C(25), C(26), and C(27)

$$0.1536x - 0.2027y + 0.3671z = 1.6293$$

$$-0.2936x + 0.2772y + 0.9148z = -0.5664$$

C(22)	−0.0047	−0.0100	C(23)	0.0107	0.0028
C(24)	−0.0057	0.0039	C(25)	−0.0054	−0.0034
C(26)	0.0114	−0.0040	C(27)	−0.0063	0.0106

(e) Plane based on C(28), C(29), C(31), C(32), and C(33)

$$0.9080x - 0.2049y + 0.3654z = 1.3941$$

$$0.9858x - 0.1258y - 0.1115z = 5.8541$$

C(28)	0.0065	0.0019	C(29)	0.0001	−0.0058
C(30)	−0.0073	0.0038	C(31)	0.0077	0.0021
C(32)	−0.0010	−0.0061	C(33)	0.0061	0.0040

(f) Plane based on C(8), C(9), C(10), C(11), C(12) and C(13)

$$0.6393x + 0.4111y + 0.6499z = 2.7741$$

$$0.7174x - 0.6781y + 0.1843z = 4.3261$$

C(8)	0.0065	0.0319	C(9)	−0.0040	−0.0070
C(10)	−0.0064	−0.0208	C(11)	0.0140	0.0230
C(12)	−0.0113	0.0028	C(13)	0.0012	−0.0299
C(14)	−0.0970	−0.1692	C(15)	−0.1748	−0.2411
C(16)	−0.1498	−0.1410	C(17)	−0.0597	−0.0350
C(18)	0.0384	0.0510	C(19)	0.0116	−0.0037
C(20)	−0.0553	−0.1036	C(21)	−0.0663	−0.1016

(g) Plane based on C(14), C(15), C(16) and C(17)

$$0.6195x + 0.4751y + 0.6249z = 2.9831$$

$$0.6935x - 0.7139y - 0.1076z = 3.3286$$

C(14)	0.0011	0.0061	C(15)	−0.0021	−0.0119
C(16)	0.0022	0.0121	C(17)	−0.0011	−0.0062
C(12)	−0.0308	−0.0252	C(13)	0.0036	−0.0177

(h) Plane based on C(18), C(19), C(20) and C(21)

$$0.6623x + 0.3782y + 0.6467z = 2.6784$$

$$0.7547x - 0.6244y - 0.2013z = 4.7924$$

C(18)	0.0030	−0.0047	C(19)	0.0060	0.0095
C(20)	−0.0059	−0.0094	C(21)	0.0029	0.0047
C(10)	0.0267	0.0161	C(11)	−0.0092	−0.0234

TABLE 7b

ANGLES BETWEEN PLANES

Plane 1	Plane 2	Angle	
		Molecule 1	Molecule 2
(a)	(b)	1.90	1.86
(b)	(c)	8.52	5.21
(b)	(d)	53.44	56.21
(b)	(e)	36.95	36.44
(f)	(g)	4.10	5.23
(f)	(h)	2.30	3.58
(g)	(h)	6.19	8.26

vary from 1.395(12) to 1.420(11) Å and from 1.368(12) to 1.436(13) Å. These values fall within the range of corresponding distances reported for other (π-cyclopentadienyl)rhodium complexes [22—25]. Although the variation in the Rh—C distances may be too small to be significant, it seems to be mirrored in the C—C bonds i.e., the carbon atoms which are more loosely bonded to rhodium are more tightly bonded to each other. The same pattern was observed by Cash et al. [23] in B and by others [26,27]. The internal angles of the five-

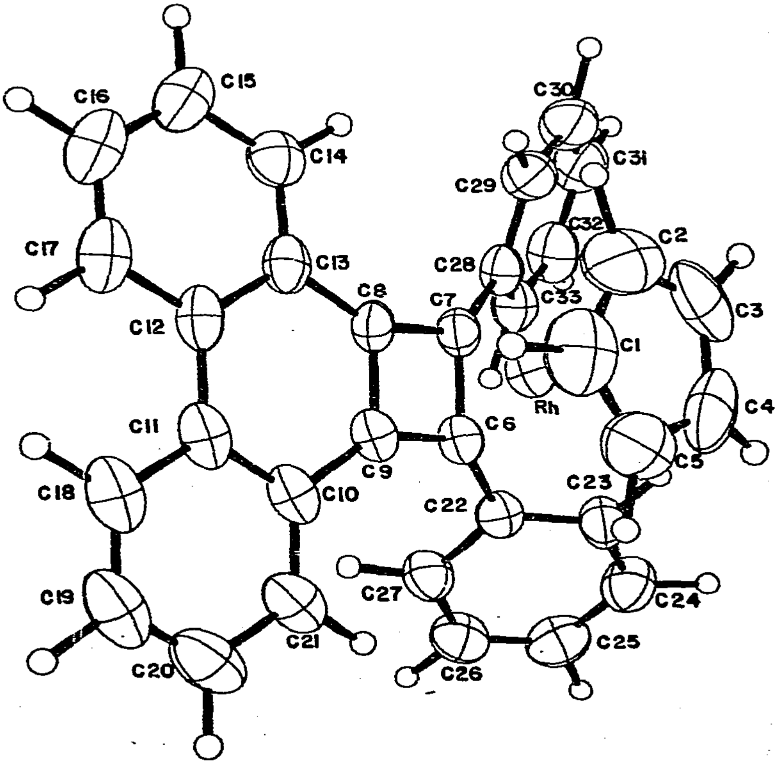

Fig. 1. A general view of the first of the two independent molecules showing the numbering system used in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms.

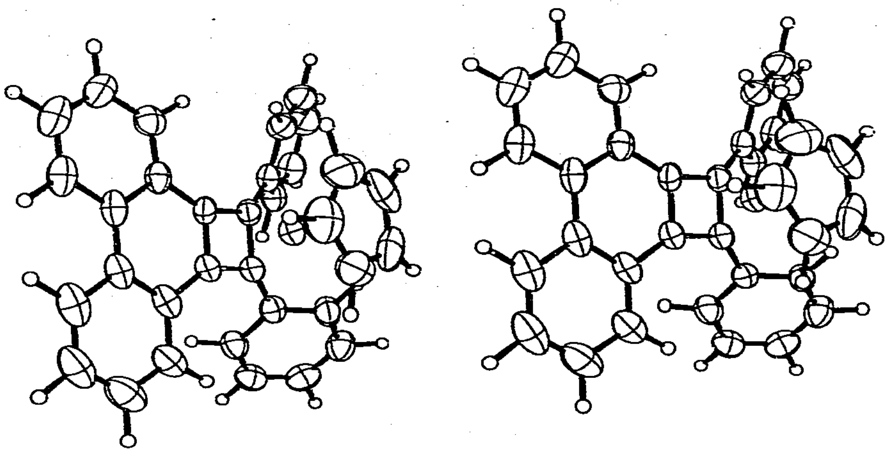

Fig. 2. A stereo pair of the molecule.

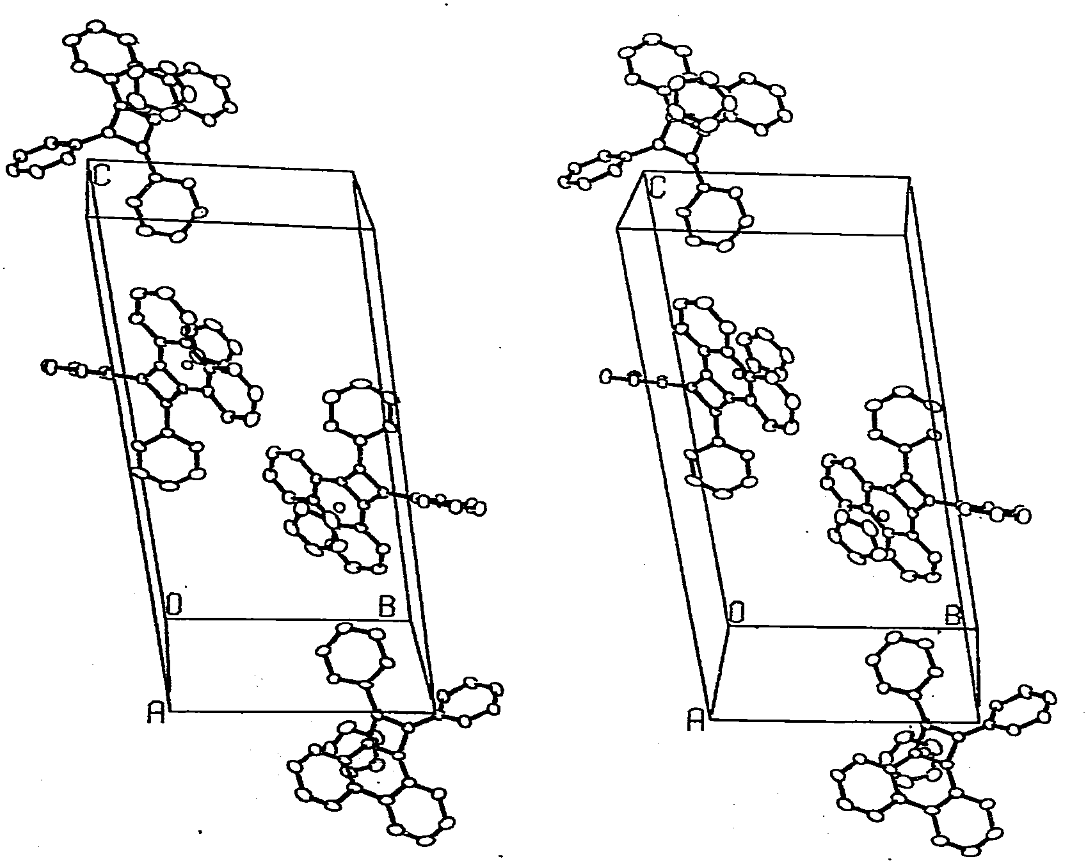

Fig. 3. A packing diagram of the molecule.

TABLE 8

COMPARISON OF THE MOLECULAR PARAMETERS OF THE PHENANTHRENE GROUP WITH LITERATURE VALUES. DISTANCES ARE GIVEN IN A AND ANGLES IN DEGREES

Molecular parameter	Phenanthrene		9,10-Diazaphenanthrene	This study	
	X-ray	Neutron		Molecule 1	Molecule 2
a[a]	1.374(17) [b]	1.398(18) [b]	1.369(6), 1.376(3)	1.388(9), 1.403(10)	1.380(9), 1.392(8)
b	1.386(14)	1.401(16)	1.403(5), 1.397(4)	1.397(10), 1.386(12)	1.416(10), 1.396(11)
c	1.399(15)	1.402(10)	1.376(3), 1.377(3)	1.380(11), 1.385(12)	1.373(11), 1.389(11)
d	1.412(8)	1.406(21)	1.417(4), 1.417(3)	1.410(9), 1.413(9)	1.406(8), 1.411(8)
e	1.416(8)	1.423(8)	1.410(3), 1.412(4)	1.428(8), 1.414(9)	1.406(8), 1.421(7)
f	1.428(9)	1.417(21)	1.416(3), 1.414(3)	1.408(8), 1.388(9)	1.406(7), 1.399(9)
g	1.450(7)	1.455(39)	1.401(4) [c], 1.392(3)	1.454(8), 1.447(8)	1.451(7), 1.445(7)
h	1.341	1.358	1.292(3) [c]	1.442(8)	1.447(8)
i	1.464	1.465	1.436(3)	1.494(9)	1.490(8)
j	2.04		2.23(4)	1.80(10)	1.94(11)
α	123.2(4), 122.3(4)	122.6(6), 122.2(6)	124.5(2), 124.9(2)	121.0(5), 121.5(6)	120.7(5), 121.2(5)
β	118.4(4), 118.9(5)	118.3(5), 119.2(5)	118.9(2), 118.0(2)	116.8(6), 116.8(6)	117.7(6), 116.6(6)
γ	118.7(4), 118.8(4)	119.2(5), 118.5(5)	116.2(2), 117.0(2)	122.2(5), 121.7(5)	121.6(5), 122.2(5)

[a] Nomenclature detailed in Fig. 4. [b] Values are listed in Table 6 [21a]. [c] N—C and N—N bonds, respectively.

membered rings vary from 108.6(7) to 107.5(7)° and from 109.2(7) to 106.4(6)° with a mean value of 108.0°, as expected.

The cyclobutadiene rings are planar (largest deviation from planarity being 0.003 Å) and almost parallel to the cyclopentadienyl ligands, the angles between them being 1.90 and 1.86°, whereas an angle of 2.4° was observed for molecule B. The Rh—(η^4-C_4 ring centroid) distances for molecule A are 1.858 and 1.844 Å and compare favorably with the value of 1.828 Å for molecule B. While the cyclobutadiene ring in B is square (within 2 esd's), the corresponding ring in molecule A is trapezoidal, the C(8)—C(9) bond (1.442(8) and 1.447(8) Å) being shorter by ca. 0.03 Å than the other three C—C bonds (see also the relevant internal angles of the (η^4-C_4) ring). X-Ray and neutron diffraction studies by Kay et al. [28a] have shown that this bond in phenanthrene is nearly an isolated double bond (1.358 Å), in accordance with the theoretical predictions of Coulson and Haigh (1.378 Å) [29]. Thus, the C(8)—C(9) bonds are longer than the value found in phenanthrene and longer than an aromatic bond but shorter than the C—C bonds reported for molecule B (mean 1.470(4) Å). This change in the length of the C(8)—C(9) bond as a result of its being part of two fused ring systems, can be described as a lenghtening of the phenanthrene double bond rather than as a shortening of the cyclobutadiene C—C distance. Fusion of the rings into the cyclobuta[*l*]phenanthrene complex results in a greater perturbation of the π-electron system of the phenanthrene fragment. Thus, the electronic requirements of the complexed cyclobutadiene ring appear to take precedence over those of the phenanthrene fragment. While in molecule B the Rh atom is equidistant from all the four carbon atoms of the cyclobutadiene ring (average 2.103 Å), in molecule A it is slightly closer to carbons 6 and 7 (average 2.123 and 2.103 Å) than to carbons 8 and 9 (average 2.137 and 2.130 Å). The two phenyl substituents are bent from the cyclobutadiene plane and away from the (η^5-Cp)Rh unit. Thus, the C(22) atoms are 0.31 and 0.19 Å out of the plane and the C(28) atoms are 0.21 and 0.24 Å from the (η^4-C_4) ring. For molecule B these values vary between 0.13 and 0.19 Å. The angles between the phenyl and cyclobutadiene rings vary between 56.2 and 36.4° (see Table 7). As a consequence, there is little conjugation between the phenyl rings and the cyclobutadiene as is also indicated by the values of the C(butadiene)—C(phenyl) distances which are close to the value of 1.487(6) Å found by Allmann and Helmer [30] for the C(sp^2)—(sp^2) single bond. The distances and internal angles of the phenyl rings are normal.

The phenanthrene ring is only approximately planar, the largest deviation from the least-squares plane being 0.09 Å for C(18) in the first of the two independent molecules and 0.12 Å for C(15) of the second molecule (see plane c, Table 7). There is a folding at the C(8)—C(9) bond such that the planes of the phenanthrene and cyclobutadiene rings make angles of 8.52 and 5.21°, the folding being away from the (η^5-Cp)Rh fragment. In order to compare the phenanthrene fragment in molecule A with the free molecule and with the related 9,10-diazaphenanthrene [28b], Table 8 was prepared. As in free phenanthrene and for 9,10-diazaphenanthrene, bonds of type a, b and c (see Table 8) are significantly shorter than the other bonds in the benzene rings. As previously stated, a significant lengthening of the nearly double bond in free phenanthrene (type h in Fig. 4) occurs after its being fused into the cyclobuta-

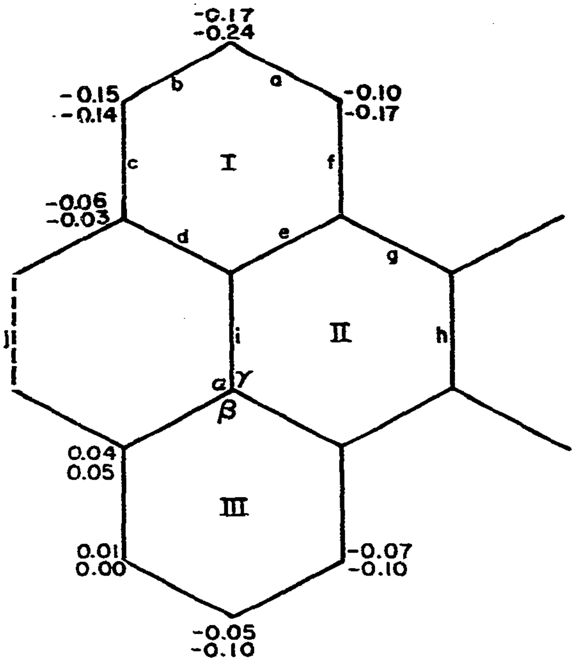

Fig. 4. Distances (in Å) of the carbons from the average plane of ring II. Distance for the second independent molecule are given below those of the first. Definitions of the molecular parameters used in Table 8 are also given.

[*l*]phenanthrene ring system of molecule A. This increase seems to be accompanied by a significant, although slighter, increase in bonds of type i (1.465 and 1.436(3) Å in free phenanthrene and 9,10-diazaphenanthrene versus 1.494(9) and 1.490(8) in molecule A. As in free phenanthrene and in 9,10-diazaphenanthrene, the distance between H(17) and H(18) (type j) in molecule A is well below the Van der Waals distance of 2.4 Å and this close approach forces distortion from planarity. Several plane calculations were carried out an attempt to determine the nature of the distortion. Since the positional parameters of the carbon atoms are more accurately known and their thermal parameters are smaller than those of the hydrogen atoms, the planes were fitted to various sets of carbon atoms only. As previously stated the phenanthrene fragment is only approximately planar. Figure 4 shows the displacements of the various carbons from the plane of the six atoms of the central ring (ring II). The central rings are planar (largest deviations from planarity being 0.01 and 0.03 Å). The out of plane distortion is such that C(17) is below ring II, while C(18) is above. Carbons C(12)—C(16) and C(17) form a plane (ring I) and so do carbons C(10), C(11), C(18), C(19), C(20) and C(21) which form ring III (see planes g and h in Table 7). Thus, the distortion from planarity can be best described by the angles between the planes of rings I and II, II and III and I and III which are (1-st molecule/2-nd molecule) 4.10°/5.23°; 2.30°/3.58° and 6.19°/8.26°. The distortion from planarity is greater than in free phenanthrene where the following values for the corresponding angles (X-ray/neutron) were obtained; 1.2°/1.3°; 1.2°/0.7° and 2.4°/2.0°. It has been

noted [21a,b] that as a result of over-crowding, the area occupied by H(17), C(17), C(12), C(11), C(18) and H(18) should open up. In the present case, we note an average of only 121.1° for the *α* type angles (see Table 8) as compared to 122° for phenanthrene and 124.9 for 9,10-diazaphenanthrene. In some other overcrowded molecules such as *ortho*-substituted benzoates [31] similar angles may be as large as 124°. An opening of 127.2(6)° was observed by Ibers [32] for a molecule with a H···H intramolecular distance of 1.83(9) Å. It could be that the lengthening of the C(8)—C(9) bond in molecule A has the net effect of canceling out the angular opening such that the overcrowding is relieved by a greater out of plane distortion and by a slight, but significant lengthening of the C(11)—C(12) bond.

Additional information

A preprint of the paper on the structures of cyclobuta[1,2-*a* · 3,4 · *a*]diphenanthrene)iron tricarbonyl and (cyclohexano[1,2]cyclobuta[3,4-*a*]phenanthrene)iron tricarbonyl was kindly made available to us by Prof. Irngartinger [10]. The geometry of the cyclobuta[*l*]phenanthrene moiety found for these complexes is remarkably similar to that observed by us. Thus, the cyclobutadiene rings have a trapezoid like form, the H···H intramolecular distances at the open side of the phenanthrene are 1.85, 1.96 and 1.99 Å, and this strain causes out of plane distortions characterized by angles of 5.4 and 3.2° between rings of type I and III.

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References

1 M.D. Rausch, S.A. Gardner, E.F. Tokas, I. Bernal, G.M. Reisner and A. Clearfield, J. Chem. Soc. Chem. Commun., (1978) 187 and ref. therein.

2 H.W. Whitlock, Jr., and P.E. Sandvick, J. Amer. Chem. Soc., 88 (1966) 4525.

3 E.F. Epstein and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 502.

4 E.F. Tokas, S.A. Gardner and M.D. Rausch, 166th National Amer. Chem. Soc. Meeting, Atlantic City, New Jersey, September 9—13, 1974; Abstr. Papers INOR 23.

5 M.D. Rausch, A. Clearfield, I. Bernal, E.F. Tokas and S.A. Gardner, unpublished studies.

6 H.A. Staab and J. Ipaktschi, Chem. Ber., 104 (1971) 1170.

7 B. Bossenbrock, D.C. Sanders, H.M. Curry and H. Shechter, J. Amer. Chem. Soc., 88 (1966) 4525.

8 H.A. Staab, E. Wehinger and W. Thorwart, Chem. Ber., 105 (1972) 2290.

9 Quoted only by O. Kennard, D.G. Watson, F.H. Allen and S.M. Weeds in Mol. Struct. Dimensions, 7 (1974—75) 319 as: H. Irngartinger, Eur. Cryst. Meeting, (1974) 372.

10 H. Irntgartinger and H. Rodewalt, private communication to I. Bernal; to be submitted.

11 H. Staub, Angew. Chem. Int. Edit. Engl., 13 (1974) 405.

12 L.P. Klemann, Ph. D. Thesis, University of Massachusetts, 1969.

13 S.A. Gardner, P.S. Andrews and M.D. Rausch, Inorg. Chem., 12 (1973) 2396.

14 O.S. Mills and E.F. Paulus, J. Organometal. Chem., 10 (1967) 331.

15 (a) G.M. Reisner, I. Bernal, H. Brunner and J. Wachter, J. Organometal. Chem., 137 (1977) 329; (b)

G.M. Reisner, I. Bernal, H. Brunner and M. Muschiol, Inorg. Chem., 17 (1978) 783; (c) G.M. Reisner, I. Bernal and G.R. Dobson, J. Organometal. Chem., 157 (1978) 23.
16 J.M. Stewart, G. Kruger, H.L. Ammon, C. Dickinson and S.R. Hall (Eds.), The X-Ray System of Crystallographic Programs, Technical Report No. 192, Computer Science Center, University of Maryland, 1972.
17 D. Cromer and J. Mann, Acta Cryst. A, 24 (1968) 321.
18 R.F. Stewart, E.R. Davison and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
19 International Tables for X-Ray Crystallography Kynoch Press, Birmingham, England, 1967, Vol. III, p. 215.
20 C.K. Johnson, "ORTEP 2", A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration, ORNL-5138, Oak Ridge, Tenn., 1972.
21 E. Müller, E. Langer, H. Jäckle, H. Muhm, W. Hoppe, R. Graziani, A. Gieren and F. Brandl, Z. Naturforsch. B, 26 (1971) 305.
22 W.A. Herrmann, C. Krüger, R. Goddard and I. Bernal, J. Organometal. Chem., 140 (1977) 73, and ref. therein.
23 G.G. Cash, J.F. Helling, M. Mathew and G.J. Palenik, J. Organometal. Chem., 50 (1973) 277, and ref. therein.
24 Trinh-Toan, R.W. Broach, S.A. Gardner, M.D. Rausch and L.F. Dahl, Inorg. Chem., 16 (1977) 279, and ref. therein.
25 M.R. Churchill, S.A. Julius and F.J. Rotela, Inorg. Chem., 16 (1977) 1137.
26 M.G.B. Drew, S.M. Nelson and M. Sloan, J. Organometal. Chem., 39 (1972) C9.
27 L.J. Guggenberger and R. Cramer, J. Amer. Chem. Soc., 94 (1972) 3779.
28 (a) M.I. Kay, Y. Okaya and D.E. Cox, Acta Cryst., B, 27 (1971) 26; (b) H. van der Meer, ibid., 28 (1972) 367.
29 C.A. Coulson and C.W. Haigh, Tetrahedron, 19 (1963) 527.
30 R. Allmann and E. Helmer, Chem. Ber., 101 (1968) 2522.
31 Y. Okaya, Acta Cryst., 22 (1967) 104.
32 J.A. Ibers, J. Organometal. Chem., 73 (1974) 389.