The Molecular Structure of (η^5-Cyclopentadienyl)bis(ethene)rhodium determined by Gas-phase Electron Diffraction

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The molecular structure of [Rh(η^5-C_5H_5)(C_2H_4)$_2$] has been determined in the gas phase by electron diffraction at 473 K. The molecule has C_{2v} local symmetry for the Rh(C_2H_4)$_2$ fragment and C_{5v} for the Rh(C_5H_5) fragment, with the local rotation axes coincident. The distance from the rhodium atom to the centre of the cyclopentadienyl ring is 190.7(3) pm, and that from the rhodium atom to the centres of the C–C bonds of the ethene ligands is 198.0(3) pm. The C–C bond distances in the cyclopentadienyl ligands refined to 143.2(2) pm, as expected for such five-co-ordinated rings, but the C–C bonds of the ethene ligands [145.7(7) pm] are longer than those previously reported for rhodium–ethene compounds. The angle between the lines linking the midpoints of the C=C bonds of the ethene ligands to the rhodium atom is not uniquely determined by the electron diffraction data, and models with values of 91.2(13) and 111.8(12)° both fit well. The former value is preferred, as it gives a lower *R* factor, and is consistent with corresponding angles reported for bis(ethene) complexes in the crystalline phase. The two ethene ligands are tilted about their C=C axes away from one another by 11.7(18)°.

In 1964 Cramer[1] reported that the ethene ligands of (η^5-cyclopentadienyl)bis(ethene)rhodium undergo internal rotation about the rhodium–ethene bond axis. This discovery, the first of its kind, remains one of the cornerstones of modern organometallic chemistry. Cramer and his colleagues[2,3] made many further investigations of this compound and its derivatives, and indeed, studies of metal–ethene rotation in related compounds continue to attract interest.[4–7] The crystal structure of [Rh(η^5-C_5H_5)(C_2H_4)(C_2F_4)] established that the C=C axes of the two alkenes are parallel to one another and form a plane parallel to the plane of the cyclopentadienyl ring,[8] supporting Cramer's original analysis of the NMR data. More recently, structures have been reported for two η^5-indenyl analogues[5,6] and [Rh([9]aneS$_3$)(C_2H_4)$_2$]$^+$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane),[9] but neither the structure of [Rh(η^5-C_5H_5)(C_2H_4)$_2$] nor that of its iridium analogue has been studied crystallographically. A partial crystal structure is available for [Co(η^5-C_5H_5)(C_2H_4)$_2$].[10]

Comparisons of crystal structures with structures in the gas phase have revealed valuable information on the effect of crystal packing on the softer parameters of molecular geometry.[11] Gas-phase structures of metallocenes, metal alkyls and metal carbonyls provide scope for investigations of the dependence of some aspects of metal–ligand co-ordination on phase,[12,13] but there are no such data on metal–ethene complexes. Following extensive studies of the photochemistry of [Rh(η^5-C_5H_5)(C_2H_4)$_2$],[14–17] we now report its molecular structure determined in the gas phase by electron diffraction. Unfortunately, it has proved impossible to obtain high-quality structural data for the crystalline phase, because of the poor quality of crystals and disorder of the cyclopentadienyl group. Studies at 173 and 300 K revealed the major features of the structure, but the details are insufficiently reliable to be published.

Experimental

The compound [Rh(η^5-C_5H_5)(C_2H_4)$_2$] was synthesised as described previously.[16] Electron-diffraction scattering intensities were recorded photographically on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus,[18] operating at *ca.* 44.5 kV. During the measurements the sample was maintained at 473 K and the nozzle at 493 K. Three plates were exposed at 261 mm, three at 200 mm and two at 95 mm. Data for benzene were also recorded to provide calibration of the camera distances and electron wavelength (Table 1). The ranges of the data sets, weighting points used in setting up the off-diagonal weight matrices, scale factors and correlation parameters are also listed in Table 1. Optical density data were obtained using a Joyce-Loebl MDM6 microdensitometer[19] at the SERC Daresbury Laboratory. The scanning program[19] and programs used subsequently for data reduction[19] and least-squares refinements[20] are those described earlier. The scattering factors used were those calculated by Fink and co-workers.[21]

Results

For the purposes of the structure refinements it was necessary to make several assumptions about the molecular model, which were subsequently justified by the quality of the fit of theoretical and experimental data. The Rh(C_5H_5) fragment was assumed to have C_{5v} symmetry, and the Rh(C_2H_4)$_2$ fragment to have C_{2v} symmetry. The position of the Rh(C_2H_4)$_2$ fragment relative to the cyclopentadienyl ring was chosen so that the local C_{2v} and C_5 axes coincided and the overall symmetry of the molecule was C_s. All C–H bonds were assumed to be of equal length and all the C–C–H angles of the ethene ligands were also taken to be equal. If the centre of the C_5 ring is labelled J, and the centres of the ethene C–C bonds as K and K′, the molecular structure could be described by 10 independent parameters, p_1–p_{10}, as listed in Table 2. These parameters include one angle defining the out-of-plane distortion of the cyclopentadienyl hydrogen atoms, labelled C_5,C–H in Table 2, one angle labelled C_2,C–H in Table 2, defining the distortion of the ethene hydrogen atoms out of the ligand planes, maintaining C_{2v} local symmetry for each ligand and an angle called τ, representing tilting of the ethene ligands symmetrically about their C=C axes, so that the C_{2v} symmetry of the Rh(C_2H_4)$_2$ fragment was maintained. The angles C_5,C–H and C_2,C–H, representing distortions of hydrogen atoms, were defined to be positive when the hydrogen

Table 1 Camera heights, electron wavelengths, weighting functions, correlation parameters and scale factors for the electron diffraction data *

Data set	Camera height/mm	Electron wavelength/pm	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor
			nm^{-1}						
1	260.85	5.671	2	20	40	140	164	0.4601	0.429(4)
2	199.83	5.672	4	40	60	192	224	0.3632	0.425(6)
3	94.58	5.673	4	140	150	300	320	−0.3306	0.700(20)

* In principle the correlation parameters and scale factors are different for the two models presented in this paper. The differences are, however, very small, and only the data for model 1 have been given.

Table 2 Structural parameters[a] for $[Rh(C_5H_5)(C_2H_4)_2]$ in the gas phase

	Model 1		Model 2	
	r_a	u	r_a	u
$Rh(C_5H_5)$ fragment				
p_1 r(Rh–J)[b]	190.7(3)	—	190.9(4)	—
r(Rh–C)[c]	226.3(2)	6.8(3)	226.5(3)	7.1(3)
p_2 r(C–C)	143.2(2)	4.5(2)	143.4(2)	4.6(2)
p_3 r(C–H)	107.7(4)	7.7[d]	107.6(4)	7.7[d]
r(Rh · · · H)[c]	299.0(3)	11.6(26)	299.2(3)	9.7(17)
p_4 Angle C_5,C–H[e]	−0.5[d]	—	−0.5[d]	—
$Rh(C_2H_4)_2$ fragment				
p_5 r(Rh–K)[f]	198.0(3)	—	198.6(3)	—
r(Rh–C)[c]	210.9(2)	6.1(3)	211.4(3)	6.2(3)
p_6 r(C–C)	145.7(7)	5.4[g]	145.0(7)	5.5[g]
r(C–H)[c]	107.7[h]	7.7[d]	107.6[h]	7.7[d]
r(Rh · · · H)[c]	259.3(42)	14.8[i]	271.4(13)	12.4[i]
	285.3(29)	14.8[i]	271.4(13)	12.4[i]
p_7 K–Rh–K′[f]	91.2(13)	—	111.8(12)	—
p_8 Angle C_2,C–H[e]	−16.7(26)	—	−15.0(11)	—
α[c,j]	52.9(68)	—	48.3(31)	—
p_9 Tilt, τ[e]	11.7(18)	—	0.0[d]	—
Rh–C–C[c]	69.8(2)	—	69.9(2)	—
p_{10} C–C–H	120.0[d]	—	120.0[d]	—
Interligand distances				
r[C(ethene) · · · C(ethene)]				
short	279	16[d]	329	16[d]
long	315	11[d]	359	11[d]
r[C(ring) · · · C(ethene)]				
short	334–379	18.4(19)	308–360	22.6(38)
long	394–433	15.6(14)	385–427	12.4(12)
R factor[k]				
R_1	0.054		0.060	
R_2	0.051		0.048	
R_3	0.132		0.144	

Uncertainties, in parentheses, are estimated standard deviations obtained in the least-squares refinements.
[a] Distances and u values in pm, angles in °. [b] J is the centre of the C_5 ring. [c] Dependent parameter. [d] Fixed value. [e] For definition, see text. [f] K and K′ are the centres of the ethene C=C bonds. [g] Tied to u(C–C) in the C_5 ring. [h] Assumed equal to the C–H bond distance in the C_5 ring. [i] Tied to u(Rh · · · H) in the C_5H_5 group. [j] Angle between perpendiculars to the two CH_2 planes of an ethene ligand. [k] The subscripts indicate the data set number in Table 1.

atoms were bent towards the rhodium atom, and τ was defined to be positive when the two ethene ligands were tilted away from one another.

The data were fitted well by two structures, differing primarily in the angles between the Rh–C=C (midpoint) vectors (K–Rh–K′ in Table 2). This does not imply that both these structures are physically plausible, but arises because the change in this angle is associated with interchange of the ring–ethene and ethene–ethene non-bonded C · · · C distances. Both models were refined fully, and the results are listed in Table 2. Model 1, in which the angle K–Rh–K′ is 91°, is preferred, first because it gave a slightly better R factor than model 2, for which the angle K–Rh–K′ is 112°. The overall R factors were 0.0732 and 0.0785 respectively, and the R factor ratio test[22] indicated that model 1 gives a better fit to the data at the 75% confidence level. Secondly, the smaller angle between the ethene ligands is consistent with results for many other bis(ethene) complexes, for which the corresponding angles are usually in the range 93–97°. The angle in $[Rh(C_5H_5)(C_2H_4)_2]$ in the crystalline phase has been determined to be 95.0(6)°.[23]

Owing to the low scattering power of hydrogen atoms, not all of the parameters describing their positions could be refined simultaneously, and for this reason some were kept fixed during the refinements. Variation of the tilt angle, τ, caused little change in the R factor, so it was initially fixed at 0.0, since there was no reason to expect the ethene ligands to be tilted, and angle C_5,C–H was fixed at −0.5°, which is the mean out-of-plane deviation observed in a neutron diffraction study of $[\{Rh(C_5H_5)(CO)\}_2(\mu\text{-}CH_2)]$.[24] In addition, the C–C–H angle was kept fixed at 120°. However, under these conditions, the non-bonded H · · · H interactions between the ethene ligands in model 1 were as short as 200 pm, substantially less than twice the van der Waals radius for hydrogen. At this stage in the refinement the tilt angle was allowed to vary, refining to

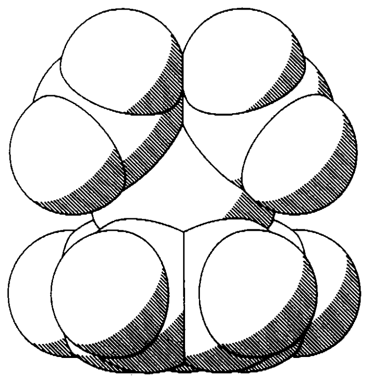

Fig. 1 Projection of the structure of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$, with hydrogen and carbon atoms having van der Waals radii of 1.2 and 1.5 Å respectively

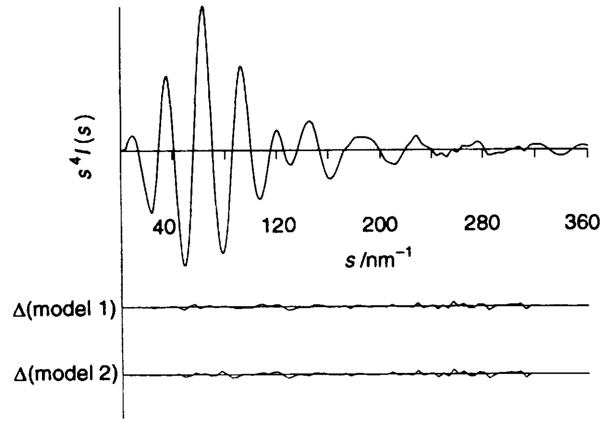

Fig. 2 The combined experimental molecular scattering intensity curve for $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$. In the lower part of the Figure the difference curves (experimental – theoretical) for models 1 and 2 are shown

Table 3 Least-squares correlation matrices (× 100) for analysis of gas-phase electron diffraction data,* model 1

	p_2	p_5	p_6	p_8	u_2	u_4	k_2	k_3
p_1	−58	—	—	—	—	—	—	—
p_2		67	−81	—	—	—	—	—
p_5			−70	—	—	—	—	—
p_7				64	−60	—	—	—
p_8					−75	—	—	—
u_1					—	61	—	—
u_3						—	—	72
k_1							59	—

* Only elements > 50% have been included: p_n is the nth parameter in Table 2, u_1 is $u[Rh–C(C_5H_5)]$, u_2 is $u(Rh \cdots H)$, u_3 is $u(C–C)$, u_4 is u[Rh–C(ethene)] and u_5 is the u value for the short r[C(ring) ··· C(ethene)]; k_n is the scale factor of data set numbered n in Table 1.

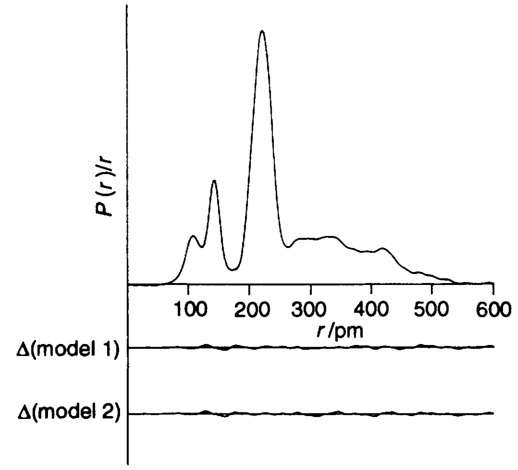

Fig. 3 The experimental radial distribution curve, $P(r)/r$, for $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$. In the lower part of the Figure the differences between the experimental and theoretical curves for models 1 and 2 are shown. Before Fourier inversion the data were multiplied by $s{\cdot}\exp(-0.000\,02s^2)/(Z_C - f_C)(Z_{Rh} - f_{Rh})$

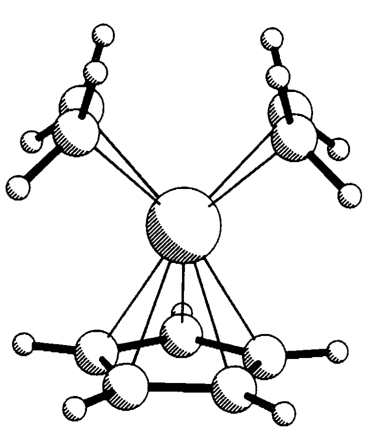

Fig. 4 Structure of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$ as determined in the gas-phase electron diffraction study (model 1)

11.7(18)°, with the two ethene ligands tilted away from one another. Fig. 1 shows a projection of the molecule, with atoms having van der Waals radii, and shows that the interaction between the ethene ligands is small with this tilt angle, as expected. The shortest H ··· H distance between the ligands is 231 pm.

The remaining seven structural parameters could be refined, together with six root mean squares (r.m.s.) amplitudes of vibration (u values). The refined values are listed, with standard deviations, in Table 2 and the least-squares correlation matrix for model 1 is presented in Table 3. Non-refined intra-ligand u values were taken from previous analyses of analogous compounds while fixed inter-ligand values were based on experience with similar compounds. Fig. 2 shows the combined experimental molecular scattering intensity curve with difference curves (experimental – theoretical) obtained for the two models, and in Fig. 3 the experimental radial distribution curve and difference curves are shown. Fig. 4 is a perspective view of the molecule.

Discussion

Although the metal–ethene bond is fundamental to organometallic chemistry, $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ appears to be the first ethene complex to have its structure determined in the gas phase. Its high thermal stability has enabled us to overcome its low vapour pressure. In the crystalline state, neutron diffraction structures are available for several platinum ethene complexes with square-planar or trigonal-planar co-ordination geometries,[25–27] but information on half-sandwich complexes with ethene ligands is derived from X-ray crystallography.

The basic geometry of $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ conforms to that proposed by Cramer and established crystallographically for related complexes.[5,6,8,9] The C–C bonds of the ethene ligands are parallel to one another, but the preferred bond angle K–Rh–K′, 91.2(13)° in the present structure, compares with *ca.* 96° for related η^5-indenyl complexes, determined crystallographically. This rather smaller angle than usual would lead to close contact between hydrogen atoms of the ethene ligands, were it not that the ligands tilt away from one another, by 11.7(18)°.

The ethene C–C distance of 145.7(7) pm is significantly longer than those in other half-sandwich complexes, which range from 135.8(9) pm for $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_2H_4})(\mathrm{C_2F_4})]$[8] to 138.5(5) pm for one of the ethene ligands of $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_4Me_3}\text{-}1,2,3)(\mathrm{C_2H_4})_2]$.[6] These bond lengths should be considered in relation to the extreme structures which are theoretically possible for metalloalkene complexes. In a very weak complex the metal–carbon distance will be large, the C–C distances will be close to that in unco-ordinated ethene, and the ligand will be planar, *i.e.* the distortion angle, α, defined by Itell and Ibers[28] as the angle between the normals to the $\mathrm{CH_2}$ planes, will be zero. In its most strongly bound form the ligand can be regarded as part of a metallacyclopropane ring, in which the C–C distance will be that of a single bond, the metal–carbon distance will be small, and α will approach 60°. The parameters found in the present study are all consistent with a structure which is not far from the latter limit. The Rh–C(ethene) distance has been compressed to 210.9(2) pm, from 216.7(5) pm in $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_2H_4})(\mathrm{C_2F_4})]$[8] and 213.1(4) pm in $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_9H_4Me_3})(\mathrm{C_2H_4})_2]$,[6] while α for $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_2H_4})_2]$ is 53(7)°, compared to 32° as determined in the neutron diffraction structures of some platinum complexes.[25–27] Structures determined by X-ray diffraction do not usually give reliable values for hydrogen-atom parameters such as α, so there is relatively little information about this distortion in the literature, but there are several other alkene structures with long C–C bond lengths. This distance is 1.445(19) pm in $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_2H_4})(\mathrm{PMe_3})]$,[29] which has short Rh–C(ethene) distances of 208.4(9) and 209.3(14) pm. The longest C–C bond length recorded for a co-ordinated ethene ligand, 147.7(4) pm, is that in $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{C_2H_4})(\mathrm{CHCMe_3})(\mathrm{PMe_3})]$, which has a distortion angle, α, as high as 68°.[30] Finally, the structure of $[\mathrm{Rh}([9]\text{ane}\mathrm{S_3})(\mathrm{C_2H_4})_2]^+$ is particularly revealing.[9] There are two different cations in the crystal, and in one of them the two carbon atoms of one of the ethene ligands are almost *trans* to two of the sulfur atoms of the macrocyclic ligand. The Rh–C distances to these atoms are short, averaging 209 pm, while the distance between them is long, 143(6) pm. In contrast, it is the centre of the other ethene ligand which is *trans* to the third sulfur atom, and this ligand is characterised by long Rh–C (average 221 pm) and short C–C [133(6) pm] bonds.

There is therefore a consistent pattern of parameters for these complexes, and what we report is a structure in which the ethene ligands are strongly co-ordinated, and are therefore greatly distorted from the geometry of the unco-ordinated ligand.

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