The Gas-Phase Structure of $P_5Fe(C_5Me_5)$ from Electron Diffraction

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The molecular structure of $P_5Fe(C_5Me_5)$ at about 200 °C has been determined by gas electron diffraction (GED). The GED data are consistent with a molecular model of C_{5v} symmetry with both the P_5 and C_5Me_5 rings η^5 bonded to the iron atom. The rings are in a staggered conformation. The most important geometrical parameters are r_a(P-P) = 211.7(4) pm with root-mean-square amplitude of vibration, l(P-P), of 6.0(8) pm, r_a(Fe-P) = 237.7(5) pm with l(Fe-P) = 9.7(6) pm, and r_a(Fe-C) = 213.5(11) pm with l(Fe-C) = 10.1(26) pm.

The P_5^- ring is an interesting new ligand with many properties that are similar to those of the cyclopentadienyl ring, $C_5H_5^-$. P_5^- shows a narrow singlet in the ^{31}P NMR spectrum, which is consistent with a structure where all phosphorus-phosphorus bonds are equal, as is the case for the carbon-carbon bonds of the cyclopentadienyl ring.[1] A number of triple-deckers and sandwich compounds have recently been synthesized in which the P_5 ring is η^5 bonded to one or two metal atoms. The ferrocene-like compound (cyclopentaphosphorus) (pentamethylcyclopentadienyl)iron, $P_5Fe(C_5Me_5)$, has also been prepared.[2] Because of the thermal stability (to at least 270 °C), the relatively high volatility, and presumably high symmetry of this compound, it is suitable for an investigation by the electron diffraction method. We therefore decided to perform an electron diffraction study of the compound in order to determine its molecular structure in the gas phase.

Experimental

The sample of $P_5Fe(C_5Me_5)$ used for electron diffraction was prepared as described by Scherer *et al.*[2] Gas electron diffraction (GED) patterns of the compound were recorded on a Balzers Eldiograph KD-G2[3] with an accelerating potential of 42 kV. The electron wavelength was calibrated against diffraction patterns of benzene [r_a(C-C) = 139.75 pm], with an estimated uncertainty of 0.1 %. In order to keep the temperature at a minimum, and thus minimize the thermal decomposition, we used a torus-shaped nozzle,[4] which permits the diffraction pattern to be recorded with a vapor pressure of approximately 1 mmHg. The nozzle and reservoir temperature was 204(7) °C. Exposures were made with nozzle-to-plate distances of 498.43 and 248.10 mm. The photographic plates were subjected to photometry and the optical densities processed by standard procedures.[5] Five plates were used from the long camera distance experiment, with s ranging from 15.0 to 150.0 nm^{-1} with Δs=1.25 nm^{-1}, and seven plates from the short camera distance, with s ranging from 40.0 to 260.0 nm^{-1} with Δs=2.5 nm^{-1}. The backgrounds were computer drawn by a least-squares fit of the sum of a polynomial and a theoretical molecular intensity curve to the experimental levelled intensity curve. The degree of the polynomial was 8 for both sets. Least-squares refinements of the structural parameters were performed on an average curve from each camera distance. Complex atomic scattering factors, $f(s)$, were calculated from an analytical representation of the atomic Hartree-Fock-Slater potentials for C,[6] and from a bonded potential for H.[7] Tabulated scattering factors were used for P and Fe.[8] The molecular intensities were modified by multiplication by $\frac{s}{|f_P||f_{Fe}|}$.

Structure refinements

The molecular model is shown in Fig. 1. The P_5 ring was assumed to be of D_{5h} symmetry, and the C_5Me_5 ring of C_{5v}

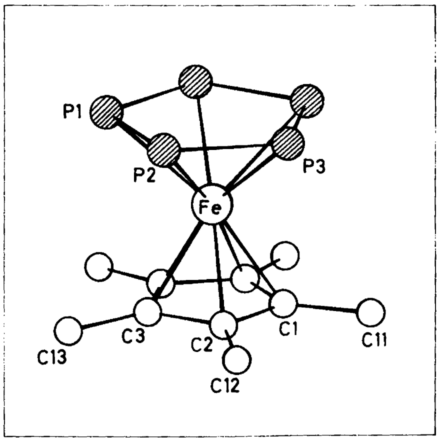

Fig. 1. The molecular structure of $P_5Fe(C_5Me_5)$ in the gas phase. The numbering of the atoms is shown. The hydrogen atoms are omitted for clarity.

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Table 1. The correlation matrix (×100) for $P_5Fe(C_5Me_5)$.

	σ_{ls}	h_1	h_2	r_1	r_2	r_3	r_4	$\angle_1$	$\angle_2$	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8
h_1	0.24	100	20	−44	**59**	−9	−7	−45	−14	20	**59**	**−57**	−1	−6	−46	−12	−22
h_2	0.45		100	−27	20	−16	**−78**	**−64**	−36	2	−33	35	**53**	9	39	−17	−26
r_1(C1-C2)	0.24			100	**−72**	25	8	31	14	−10	0	0	0	14	22	−12	−6
r_2(C1-C11)	0.31				100	−5	−8	**−55**	−20	22	17	−6	19	13	−18	3	−9
r_3(C-H)	0.33					100	7	3	−15	0	6	−3	0	9	0	−5	9
r_4(P1-P2)	0.13						100	**52**	4	−3	36	−42	**−72**	−23	**−52**	32	22
$\angle_1C_5$,C1-C11	0.38							100	30	−13	4	−16	**−52**	−7	−20	27	38
$\angle_2$CCH	0.64								100	−4	−2	0	−20	−13	11	−21	18
l_1(C-H)	0.43									100	8	−7	5	6	−8	−2	−5
l_2(P1-P2)	0.25										100	**−88**	−32	−15	**−62**	−2	−10
l_3(Fe-C)	0.85											100	47	25	**83**	6	12
l_4(Fe···C(Me))	0.54												100	44	51	−18	−9
l_5(Fe-P)	0.19													100	26	−11	1
l_6(P1···P3)	0.20														100	−5	4
l_7(P···C(Cp))	0.45															100	32
l_8(P···C(Me))	0.51																100

symmetry. The two rings are fixed in a *staggered* conformation and the CCH_3 fragments were assumed to have local C_{3v} symmetry with two hydrogen atoms pointing towards and one hydrogen atom pointing away from the iron atom. The overall molecular symmetry is then C_{5v}. With these assumptions the model can be described by eight independent geometrical parameters: the heights from the Fe atom to the center of the P_5 and C_5Me_5 rings, h_1 and h_2, respectively, the C1-C2, C1-C11, C-H and P1-P2 bond distances, the angle between the C_5 ring plane and the C-C(Me) bond, $\angle C_5$, C-C(Me) and $\angle$CCH. In addition, eight root-mean-square amplitudes of vibration (l values) were refined as independent parameters. The non-refined l values were fixed at values obtained in a previous electron diffraction study of $Fe(C_5Me_5)_2$.[9]

Attempts were also made to fit a model where the P_5 and C_5Me_5 rings were fixed in an *eclipsed* conformation. These refinements led to significantly poorer fit of the theoretical molecular intensity curve to the experimental ones, with a total R value[10] of 9.7, compared to 3.9 obtained for the *staggered* molecular model. The difference between the experimental radial distribution curve and the theoretical one obtained with an *eclipsed* molecular model is shown as curve **b** in Fig. 3.

In all least-squares refinements where all the independent parameters and the eight l values were varied, the distance from the iron atom to the ring carbons, r(Fe-C), converged to a value that was longer than the P-P bond distance, r(P-P). The order of these two distances is re-

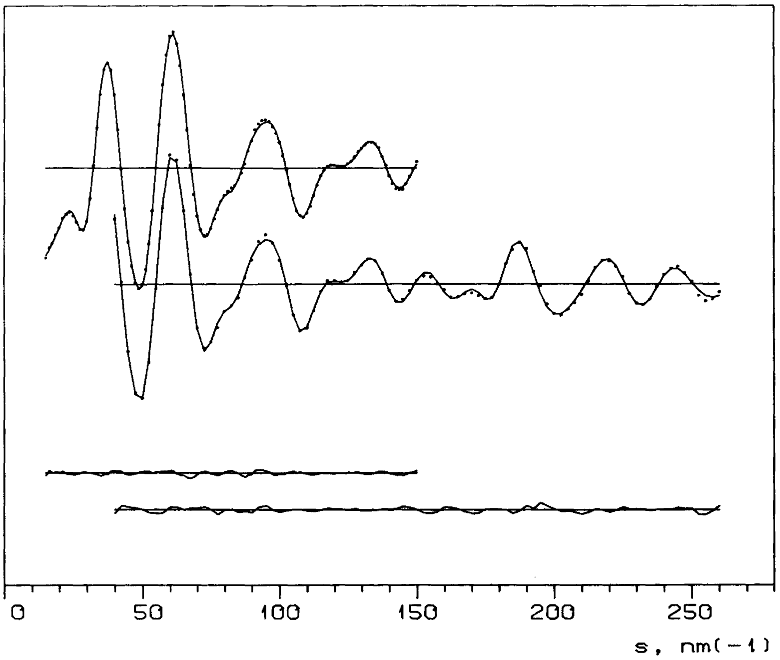

Fig. 2. The experimental (points) and theoretical (full line) molecular intensity curves for $P_5Fe(C_5Me_5)$ for the long (top) and short camera distance. In the lower part of the figure the difference between the experimental and theoretical intensity curves obtained for the best molecular model is drawn.

Table 2. Geometrical parameters and root-mean-square amplitudes of vibration (*l*-values) for $P_5Fe(C_5Me_5)$. The molecule has C_{5v} symmetry with the rings in a staggered conformation. In the right column the results from an X-ray study of $P_5Fe(C_5Me_4Et)$ are shown. The numbers in parentheses are $3\sigma_{ls}$.

	r_a/pm	l/pm	r(XR)[c]/pm
P_5Fe-fragment:			
h_1[a]	155.1(7)	–	152.6
r(Fe-P)	237.7(5)	9.7(6)	234.5
r(P1-P2)	211.7(4)	6.0(8)	210
r(P1···P3)	342	8.2(6)	–
$Fe(C_5Me_5)$-fragment:			
h_2[a]	175.0(14)	–	170.7
r(Fe-C)	213.5(11)	10.1(26)	208.9
r(C1-C2)	143.8(7)	4.8[b]	141.5
r(C1-C11)	150.9(10)	5.3[b]	149.7
r(C-H)	109.7(10)	7.1(13)	108[f]
r(C1···C3)	233	5.5[b]	–
r(C1···C12)	262	7.2[b]	–
r(C1···C13)	379	7.2[b]	–
r(C11···C12)	321	13.6[b]	–
r(C11···C13)	519	9.7[b]	–
$\angle C_5$,C1-C11	1.3(12)°	–	–
$\angle$CCH	111(2)°	–	–
Inter-ring distances:			
r(P1···C1)	448	10.6(14)[d]	–
r(P1···C2)	412	17.6(14)[d]	–
r(P1···C3)	347	24.6(14)[d]	–
r(P1···C11)	563	18.6(16)[e]	–
r(P1···C12)	499	25.6(16)[e]	–
r(P1···C13)	373	32.6(16)[e]	–
R(50 cm)/%	3.2		
R(25 cm)/%	6.5		
R(total)/%	3.9		

[a]The height from the ring center to the metal atom. [b]Fixed values, taken from Ref. 9. [c]Values taken from an X-ray study of $P_5Fe(C_5Me_4Et)$, Ref. 11. [d,e]*l* values with the same index had the same shift throughout the least-squares refinements. [f]Fixed value.

versed in $P_5Fe(C_5Me_4Et)$ at 20°C in the solid state. The reversed order of these two distances may seem to be a consequence of errors in the electron diffraction investigation due to high correlation between the P-P and Fe-C bond distances (the latter represented by h_2 in the correlation matrix) and their l values, as seen in Table 1. Since electron diffraction only gives a one-dimensional representation of all the interatomic distances in the molecule, the r(P-P) and r(Fe-C) bond distances may be interchanged during the refinements and a false minimum in the least-squares analysis may be obtained instead of the chemically meaningful one. In order to check whether there is such a double-well least-square surface, we have performed a number of additional refinements as described below.

A number of refinements were performed where l(Fe-C) was kept fixed at the value of 6.6(2) pm found in $Fe(C_5Me_5)_2$, while the r(P-P) were fixed at the values 213, 214 and 215 pm, respectively. When r(P-P) was kept at 213 pm, only a modest increase of 0.5% in the R(total) factor was obtained. When increasing r(P-P) to 214 pm and higher, the fit became increasingly worse and some vibrational amplitudes refined to intolerable values. We also tried to keep the distance from the iron atom to the center of the C_5Me_5 ring, h_2, fixed at the value 170.7 pm obtained for $P_5Fe(C_5Me_4Et)$ in the solid state,[11] at the same time keeping l(Fe-C) at 6.6 pm. When doing this, the value of r(P-P) converged to 213.2(3) pm, but the R(total) factor obtained was 0.6% larger than when all parameters were refined. When redrawing the backgrounds and then refining all the independent parameters, we always ended up with the parameters presented in Table 2. We feel therefore that we can exclude the possibility that there are two distinct least-squares minima, and conclude that there is only one flat global minimum due to high correlation among certain parameters which is reflected in the large standard deviations of these parameters. The geometrical parameters and l values obtained for the best model are shown in Table 2, together with the parameters for $P_5Fe(C_5Me_4Et)$ in the solid state for comparison. The estimated errors in parentheses are $3\sigma_{ls}$, in order to compensate for errors introduced by the assumptions and the systematic errors.

The theoretical molecular intensity curve calculated for the best model with experimental points and difference curves between the experimental and theoretical curves are

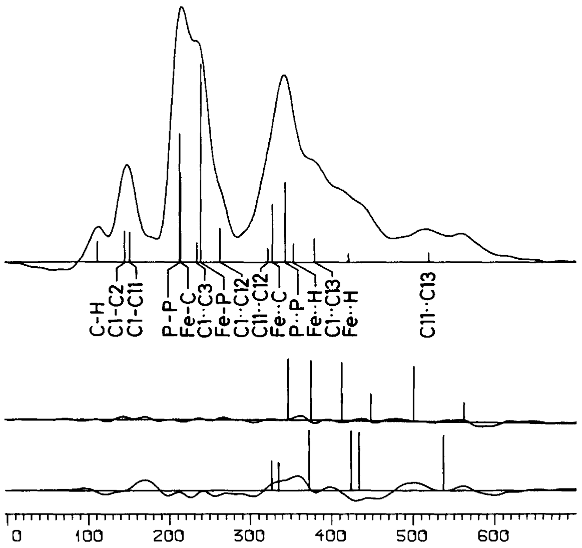

Fig. 3. The experimental radial distribution (RD) curve for $P_5Fe(C_5Me_5)$. The most important distances are shown with bars with heights approximately equal to the weight of the corresponding distance. (**a**) The difference between the experimental and theoretical RD curves for the model with the P_5 and C_5Me_5 rings fixed in a *staggered* conformation, and (**b**) fixed in an *eclipsed* conformation. The inter-ring P···C distances for the two conformers are shown as bars. The artificial damping constant, *k*, is $2 \cdot 10^{-5}$ nm^2.

shown in Fig. 2. In Fig. 3, the experimental radial distribution curve (RD curve) is shown together with the difference between the experimental and theoretical RD curves obtained for the best model with the P_5 and C_5Me_5 rings fixed in the *staggered* conformation, denoted **a**, and in the *eclipsed* conformation, denoted **b**.

Results and discussion

As is seen in Table 2, the gas-phase structure of $P_5Fe(C_5Me_5)$ is very similar to the structure obtained for $P_5Fe(C_5Me_4Et)$ in the solid state, but there are small differences. Both compounds have ferrocene-like structures in which the P_5 and C_5Me_5 rings are η^5-bonded to the iron atom, and in both compounds the two rings have a *staggered* conformation. A *staggered* conformation of the rings has also been found for $Fe(C_5Me_5)_2$ in both the gas phase[9] and in the solid state,[12] while an *eclipsed* conformation has been found to be energetically favourable for $Fe(C_5H_5)(C_5Me_5)$ in the solid[13] and for $Fe(C_5H_5)_2$ in the gas phase.[14] The *eclipsed* conformation has also been observed for the latter compound at 90K in the solid.[15]

The conformational trend of $Fe(C_5H_5)_2$, $Fe(C_5Me_5)_2$ and $P_5Fe(C_5Me_5)$ in the gas phase can be understood by considering the increased inter-ring repulsions when methyl groups are introduced on the cyclopentadienyl ring: $Fe(C_5H_5)_2$ has *eclipsed* conformation of the cyclopentadienyl rings, which has been calculated to be the energetically favourable conformation by *ab initio* calculations.[16] The rings of $Fe(C_5Me_5)_2$ are forced in to the *staggered* conformation by the inter-ring Me···Me repulsions; the shortest inter-ring Me···Me contact is 388 pm, somewhat shorter than twice the van der Waals radius for the methyl group of about 200 pm.[17] In $P_5Fe(C_5Me_5)$, the shortest inter-ring P···C(Me) contact would have been about 333 pm if the conformation had been *eclipsed,* but on going to a *staggered* conformation it increases to 347 pm. The van der Waals radius of P and the methyl group are 190 and 200 pm, respectively.

The distances from the iron atom to the C_5Me_5 ring centroid, h_2, are significantly longer in $P_5Fe(C_5Me_5)$ and $P_5Fe(C_5Me_4Et)$ than the iron–ring centroid distances found for $Fe(C_5H_5)_2$ and $Fe(C_5Me_5)_2$ in the gas phase of 165 and 166.2(2) pm, respectively.[9,14] This stretching of the iron–ring centroid distance may be a consequence of increased inter-ring steric repulsions in the two former compounds as compared to the latter, but may also have its origin in electronic differences between the C_5Me_5 and P_5 ligands. Cf. the *trans* effect observed for pentamethylcyclopentadienyl-rhenium and -tungsten compounds in cases where the metal coordinates to one or more oxo ligands;[18] for these compounds, the metal-carbon bonds *trans* to each oxo ligand are stretched more than 10 pm.

The long h_2 observed in the cyclopentaphosphorus-iron compounds indicate a somewhat weaker bond between the iron atom and the cyclopentadienyl ring in these compounds than in ferrocene and decamethylferrocene. We should for this reason also expect l(Fe-C) for $P_5Fe(C_5Me_5)$ to be somewhat larger than the values found for the two latter compounds, viz. 6.2(1) and 6.6(2), respectively.[9,14] Indeed, our l(Fe-C) of 10.1(26) is of the right order of magnitude, but because of its incertainty no strict conclusions should be drawn from this value.

It is tempting to compare the structural features of the P_5 ring with those of the cyclopentadienyl ring: The normal C-C bond distance in the cyclopentadienyl ring is approximately 143 pm, which is close to the mean of a normal C-C single bond length and a normal C=C double-bond length if we take C-C bond distance in ethane of 153.2(2) pm[19] to be representative for the former, and the C=C bond distance in ethylene of 133.6(1) pm[20] to be representative of the latter. If we consider the P-P bond distance of 221.8(4) pm[21] in gaseous P_2H_4 to be a normal P-P single-bond length, and the P=P double-bond distance of 200.9 pm[22] found in solid $P_2[C(SiMe_3)_3]_2$ to be a normal P=P double-bond length, the P-P bond distance of 211.7(4) pm in $P_5Fe(C_5Me_5)$ is exactly the mean of the two former. The difference between the normal P-P single-bond length and the P=P double-bond length of about 21 pm is equal within the estimated errors to the difference between the bond lengths for the carbon analogues. Our P-P bond distance of 211.7(4) pm in $P_5Fe(C_5Me_5)$ is similar to the P-P bond distance found in solid $(C_6H_5)_2P_2[Cr(CO)_5]_3$ of 212.5 pm, in which the RP=PR fragment is η^2-bonded to a chromium atom.[23]

The l(P-P) value of 6.0(8) pm is in the expected range when compared with previously found P-P single-bond *l*-values of 7.8(9) pm in $P_2(CH_3)_4$,[24] and 4.4(6) pm in P_2H_4. Once again drawing a parallel to the cyclopentadienyl ring, a normal C-C *l* value in a C_5H_5 or C_5Me_5 fragment is approximately 4.6 pm, which is of the same magnitude or somewhat smaller than a normal C-C single-bond *l* value of about 5.0 pm (the value found in ethane).

There are some differences in the solid-state structure of $P_5Fe(C_5Me_4Et)$ at 20 °C and in the structure of $P_5Fe(C_5Me_5)$ in the gas phase at about 200 °C. Both h_1 and h_2 are somewhat longer in the gas phase. This may be a consequence of intermolecular forces in the crystals of $P_5Fe(C_5Me_4Et)$ that may have compressed the Fe-P_5 and FeC_5Me_4Et bonds. The shorter distances in the solid state may also be a consequence of anharmonicity of the metal-ring vibrations and therefore an effect of the large temperature difference in the two structural investigations.

The difference of about 2 pm between the P-P bond distance found in this electron diffraction study and the mean P-P bond distance from the X-ray study of $P_5Fe(C_5Me_4Et)$ is as expected from well known systematic differences in the C-C bond distances for the C_5H_5 and C_5Me_5 analogues observed when comparing results obtained with the two methods. This systematic difference is at least partly a consequence of restricting the thermal motion of the ring carbon atoms to ellipsoidic motion during the X-ray structure analysis. The libration motion of the ring causes the ring carbons to have a more curved motion that is poorly described by ellipsoids. This effect also leads systematically to shorter metal-carbon (and metal-phosphorus) bond distances for sandwich compounds in the solid state than those found in the gas phase. h_1 and h_2 are not affected by this error to the same degree, so these distances should be used when comparisons are made between X-ray and electron diffraction results for this kind of compounds.

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