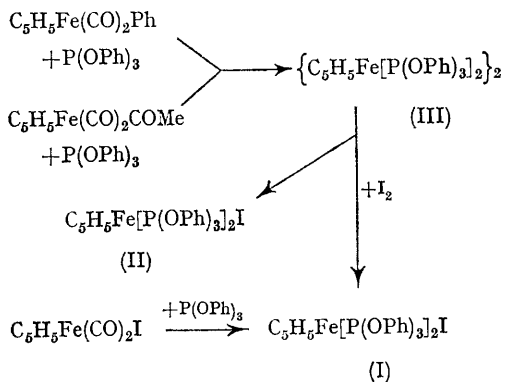


Crystal Structure of Two "Isomers" of π -Cyclopentadienylbis(triphenyl phosphite)iron Iodide, $C_5H_5Fe[P(OC_6H_5)_3]_2I$

By V. G. ANDRIANOV,* (the late) YU. A. CHAPOVSKII, V. A. SEMION, and YU. T. STRUCHKOV
(Institute of Organo-element Compounds, Academy of Sciences of the U.S.S.R., Moscow)

PREVIOUSLY one of us, with co-workers,¹ obtained two mutually non-interconvertible isomers (I) and (II) of π -cyclopentadienylbis(triphenyl phosphite)-iron iodide by the following sequence of reactions:



Isomer (I) is a reddish-violet compound which decomposes at temperatures $>130^\circ$ (according to

revised data it has m.p. $155\text{--}162^\circ$ without decomposition).[†] Isomer (II) is a dark violet solid with m.p. $172\text{--}174^\circ$ (according to a new determination it melts at $180\text{--}190^\circ$ without decomposition). The two isomers have similar i.r. spectra in the region $700\text{--}3500\text{ cm.}^{-1}$ but their 1H n.m.r. spectra in the region of the cyclopentadienyl proton signals are quite different. The 1H n.m.r. spectrum of (I) has a sharp singlet with $\delta = 3.72$ p.p.m.; in the spectrum of (II) two symmetrical doublets centred at $\delta = 3.92$ and 4.27 p.p.m. were found. On this basis it was supposed that in isomer (II) the proper C_{5v} symmetry of the π - C_5H_5Fe fragment was distorted. We report here the results of a detailed X-ray study of (I) and (II).

Crystal data:—Isomer (I): monoclinic. Space group $P2_1/a$, $a = 19.72$, $b = 18.18$, $c = 10.99$ Å, $\beta = 102.9^\circ$, $U = 3842$ Å³, $D_m = 1.45$, $D_c = 1.51$ g.cm.⁻³ for $Z = 4$, $M = 868.5$. Isomer (II): orthorhombic. Space group $Pbca$, $a = 20.43$, $b = 27.15$, $c = 13.73$ Å, $V = 7616$ Å³, $D_m = 1.43$, $D_c = 1.52$ g.cm.⁻³ for $Z = 8$, $M = 868.5$.

[†] All melting points were redetermined before X-ray study.

Intensities of *ca.* 3500 independent reflections for isomer (I) and of *ca.* 1200 independent reflections for isomer (II) were estimated visually, disregarding absorption correction (equi-inclination Weissenberg goniometer, unfiltered copper radiation). The two structures were solved by the standard heavy-atom technique and refined by the isotropic full-matrix least-squares method. At the present stage of refinement (which is being pursued further) the discrepancy indices are 0.16₂ for (I) (with the mean overall temperature factor $B = 4.2 \text{ \AA}^2$) and 0.13₉ for (II) ($B = 3.7 \text{ \AA}^2$).

The geometry of the molecules is represented in Figures 1 and 2, which show average values of

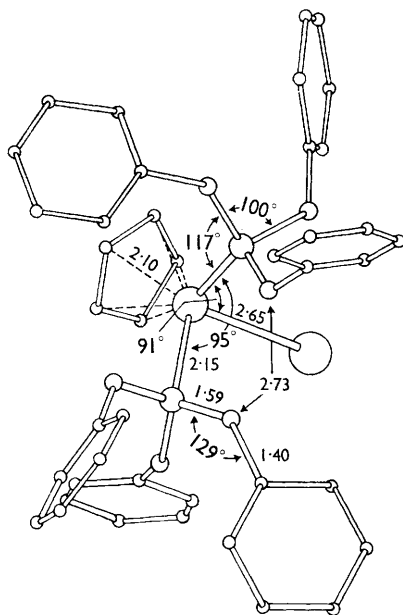


FIGURE 1. Molecular structure of "isomer" I.

structurally equivalent spatial parameters. In both molecules the iron atom has a "piano-stool" co-ordination typical for semi-sandwich π -complexes. The phosphorus atom co-ordination is distorted tetrahedral. In isomer (I), steric hindrance between bulky triphenyl phosphite ligands results in the P-Fe-P bond angle increasing to 95° as compared with P-Fe-I bond angles (91°). In the $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ molecule² C-Mn-C bond angles are $92 \pm 2^\circ$, and this value may be taken as typical for non-overcrowded π -complexes with piano-stool configuration. Phenyl and cyclopentadienyl rings are planar with the usual C-C

interatomic distances 1.40 ± 0.03 and $1.43 \pm 0.03 \text{ \AA}$ respectively.

The Fe-C(cyclopentadienyl) distances are consistent, the average value being $2.10 \pm 0.03 \text{ \AA}$, somewhat elongated as compared with the ferrocene molecule (2.045 \AA).³ However, this elongation is usual for semi-sandwich π -complexes and found, for instance, in $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{SnPh}_3$ (2.095 \AA)⁴ and similar molecules. The Fe-I bond distance, 2.65 \AA , is little longer than the sum of Fe octahedral and I single-bond covalent radii (*ca.* 2.59 \AA)⁵ but distinctly shorter than that found in $(\pi\text{-allyl})\text{Fe}(\text{CO})_3\text{I}$ (2.75 \AA).⁶ The mean Fe-P bond distance, $2.15 \pm 0.02 \text{ \AA}$, is significantly

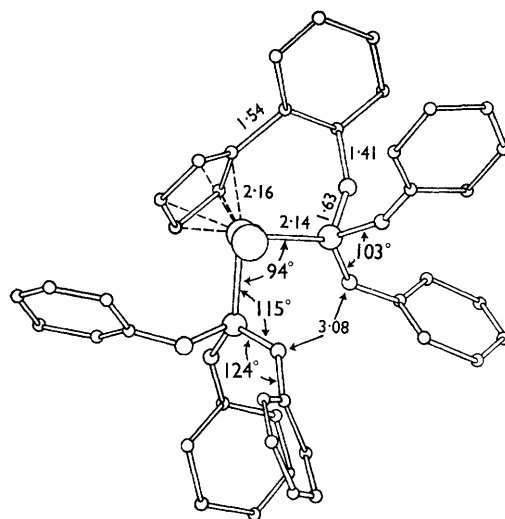


FIGURE 2. Molecular structure of "isomer" II.

shorter than that found in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\sigma\text{-Ph})\text{-PPh}_3$ (2.24 \AA),⁷ *i.e.*, this bond is shorter than the sum of Fe octahedral and P tetrahedral radii (*ca.* 2.40 \AA). This contraction reflects back-donation $d_\pi(\text{Fe}) \rightarrow d_\pi(\text{P})$. The P-O ($1.59 \pm 0.02 \text{ \AA}$) and C-O ($1.40 \pm 0.03 \text{ \AA}$) bond lengths coincide with usual values in the limits of experimental errors; in triphenyl phosphate,⁸ for instance, these distances are 1.57 and 1.41 \AA respectively. A significant difference of bond angles at phosphorus atoms (Fe-P-O 117° and O-P-O 100°) is due to various spatial requirements of their substituents.

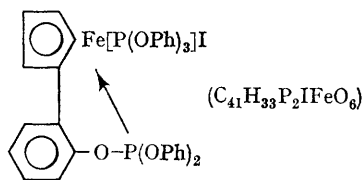
It seemed natural to suppose that a serious intramolecular overcrowding due to the large volume and "inconvenient" configuration of triphenyl phosphite ligands could result in the

existence of several rotamers divided by sufficiently high energy barriers. Co-ordination isomerism of the compounds investigated is impossible (in this respect a "piano stool" is equivalent to a tetrahedron).

The present *X*-ray study shows, however, that (II) is not an isomer of (I) but has a different structure. The molecule of (II) is found to have the usual C-C covalent bond (1.54 ± 0.03 Å) between one of triphenyl phosphite ligand phenyl rings and the cyclopentadienyl ring. Hence the appearance of two symmetrical doublets in the ^1H n.m.r. spectrum is easily explained by the non-equivalence of the cyclopentadienyl ring protons.



"isomer" I



"isomer" II

The failure of all attempts to effect the interconversion (I) \rightleftharpoons (II) by heating in various solvents and by melting with subsequent cooling under various conditions is now fully understandable.

Other geometrical features of (II) are equally consistent with the presence of the covalent bond C(cyclopentadienyl)-C(phenyl). The mean Fe-C(cyclopentadienyl) interatomic distance (2.16 Å) is elongated by 0.06 Å as compared with (I), *i.e.* interaction of the iron atom with the cyclopentadienyl ligand is weakened due to C-C bond formation. Also the shortest O...O distance between triphenyl phosphite ligands is distinctly greater than that found in "isomer" (I) (3.08 and 2.73 Å, respectively). This feature reflects some decrease of steric hindrance between these ligands at the iron atom of (II) due to the aforementioned bond formation, which causes a reorientation of ligands and a displacement of one of them towards the cyclopentadienyl ring.

Other bond lengths in (II) coincide with those found in (I) within the limits of experimental errors: Fe-I 2.65; Fe-P 2.14; P-O 1.63; C-O 1.41 Å. The phenyl and cyclopentadienyl rings are also planar with the same C-C bond length as in (I).

At present we are investigating the crystal structure of a "dimeric" complex $\{[\pi\text{-C}_5\text{H}_5\text{Fe-P}(\text{OPh})_3]_2\}_2$ ⁹ to decide whether units of (I) and (II) pre-exist in its molecule.

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