

## INVESTIGATION OF CYCLOPENTADIENYL COMPLEXES OF IRON WITH TRIPHENYLPHOSPHITE LIGANDS

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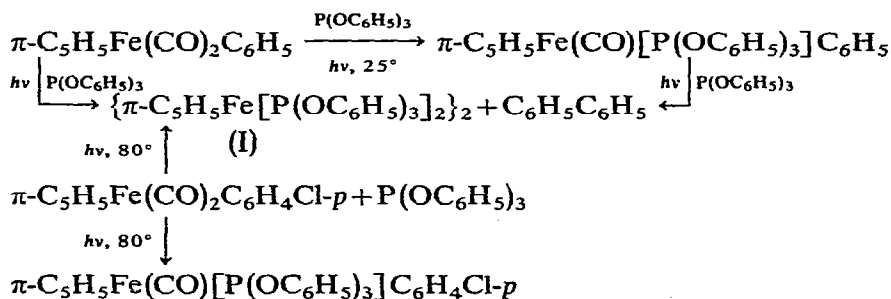
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Our further investigation<sup>1</sup> of the ligand effect of the stability of the carbon-transition metal  $\sigma$ -bond has shown that the interaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> by irradiation of the reaction mixture with UV light and strong heating, is accompanied by an exchange of both carbonyl ligands<sup>2</sup>.

This exchange was found to proceed stepwise.

Under milder conditions it was possible to isolate  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>-C<sub>6</sub>H<sub>5</sub> which in turn reacted with P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> by exchanging the second CO-group. The product must be the  $\sigma$ -phenyl derivative,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, which was found to be unstable (for reasons discussed below); it could be stabilised by the removal of the phenyl radical to form diphenyl. The only reaction product isolated under drastic conditions was { $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]}<sub>2</sub> (I), a crystalline orange substance, unusually stable to temperature and air oxygen since the benzene solution of the dimer did not decompose on boiling in air. The same product was formed under similar conditions when  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p* was made to interact with P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p* was, however, also obtained, even under drastic conditions. The reaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R-*p* (with R = H, Cl) and P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> may be described by the following scheme:



Compound (I) was diamagnetic as shown both by the direct determination of the magnetic susceptibility at the boiling point of liquid nitrogen, and by the NMR spectrum. The latter, taken on JNM-100 at a working frequency of 100 MHz in CCl<sub>4</sub> and C<sub>6</sub>D<sub>12</sub> solutions (using hexamethyldisiloxane as inner standard) revealed a sharp singlet  $\delta$  4.12 ppm, characteristic of the  $\pi$ -C<sub>5</sub>H<sub>5</sub> ring protons, and a multiplet of aromatic protons at 6.7–7.2 ppm with an integral intensity ratio, 1 : 6.

The IR spectrum of { $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]}<sub>2</sub> was very complex (see Table 1) but revealed a clear triplet at 1200 cm<sup>-1</sup> (1180 int, 1200 int, 1225 int) characteris-

tic of the molecule of the coordinated  $P(OC_6H_5)_3$ .<sup>3</sup> Again, in the region of stretching vibrations there were no C-H bonds below  $3000\text{ cm}^{-1}$ .

Also, the spectrum showed no bands characteristic of the stretching vibration of carbonyl ligands.

TABLE I

THE FREQUENCIES OF THE IR SPECTRA OF CYCLOPENTADIENYL IRON COMPLEXES WITH TRIPHENYLPHOSPHITE LIGANDS

No.	Formula of the compounds	Frequencies in IR spectra ( $\text{cm}^{-1}$ ) <sup>a</sup>
1.	$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(\text{OC}_6\text{H}_5)_3\text{C}_6\text{H}_5^b$	690 m <sup>c</sup> , 697 m, 720 sh, 730 int, 762 int, 835 m, 845 m, 897 int, 905 sh, 920 int, 925 int, 1010 m, 1030 m, 1075 w, 1167 int, 1195 int, 1230 w, 1290 w, 1310 w, 1490 int, 1565 int, 1595 int, 1935 int.
2.	$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(\text{OC}_6\text{H}_5)_3\text{C}_6\text{F}_5$	670 int, 685 w, 698 int, 710 int, 720 int, 735 int, 755 int, 775 w, 790 w, 815 int, 855 int, 880 int, 898 int, 910 sh, 935 int, 965 w, 990 m, 1007 m, 1020 m, 1032 m, 1052 m, 1140 int, 1170 int, 1200 int, 1245 w, 1270 w, 1290 w, 1325 m, 1360 int, 1430 int, 1450 int, 1525 w, 1570 int, 1940 int, 1910 sh, 3000-3156 m quadruplet.
3.	$\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$	697 int, 710 int, 722 int, 735 int, 765 int, 800 int, 830 m, 860 int, 880 int, 890-935 int, 970 w, 985 w, 1000 m, 1010 m, 1020 int, 1032 int, 1078 m, 1105 m, 1120 w, 1180 int, 1200 int, 1225 int, 1295 m, 1315 w, 1340 w, 1385 m, 1437 int, 1450 int, 1462 int, 1500 int, 1560 w, 1600 int, 1950 w, 2375 w, 2870 w, 2935 w, 2975 w, 3033 m, 3045 m, 3068 m.
4.	$\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$	670 int, 688 int, 702 int, 720 int, 735 int, 757 int, 800 m, 860 int, 912 int, 985 m, 1010 m, 1085 m, 1152 int, 1180 int, 1210 int, 1265 w, 1407 m, 1450 m, 1480 int, 1580 int, 1920 m, 2350 w, 2990 w, 3010 m, 3025 m, 3053 m, 3110 w.
5.	$\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I (II)}$	690 int, 708 int, 725 int, 760 int, 770 sh, 820 m, 837 w, 855 sh, 880 int, 900 int, 915 int, 940 int, 998 w, 1007 m, 1025 m, 1070 m, 1160 int, 1190 int, 1205 int, 1220 sh, 1290 w, 1380 int, 1470 int, 1490 sh, 1592 int, 1947 w, 3023 w, 3040 w, 3060 m, 3070 m, 3090 w, 3120 w.
6.	$\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I (III)}$	690 int, 710 int, 728 int, 760 int, 772 int, 818 m, 832 w, 843 m, 880 int, 895 int, 915 int, 940 int, 1008 m, 1025 m, 1040 w, 1070 m, 1122 m, 1160 int, 1190 int, 1205 int, 1225 int, 1262 m, 1290 w, 1380 int, 1462 int, 1490 int, 1592 int, 1940 w, 3025 w, 3040 w, 3060 m, 3070 m, 3090 w, 2020 w.

<sup>a</sup> All the spectra taken were of solid compounds in vaseline on a KUR 10 apparatus (NaCl and Li F prisms).

<sup>b</sup> Only the NaCl prism. <sup>c</sup> int = intensive; m = medium intensity; w = weak intensity; sh = shoulder.

The mass-spectrum of (I), taken at  $200^\circ$  and at an energy of ionising electrons of 40 eV (the samples were introduced directly into the ion source) revealed a group of peaks in the region corresponding to the m/e of the fragment  $\{\text{C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}^+$  ( $m = 741$ ), as well as peaks with m/e 431  $[\text{C}_5\text{H}_5\text{FeP}(\text{OC}_6\text{H}_5)_3]^+$ , 310  $[\text{P}(\text{OC}_6\text{H}_5)_3]^+$ , 217  $[\text{P}(\text{OC}_6\text{H}_5)_2]^+$ , 121  $[\text{C}_5\text{H}_5\text{Fe}]^+$ , 94  $[\text{C}_6\text{H}_5\text{OH}]^+$ , 77  $[\text{C}_6\text{H}_5]^+$ , 66  $[\text{C}_5\text{H}_6]^+$  and 65  $[\text{C}_5\text{H}_5]^+$ .

The molecular peak of  $\{\text{C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  was above the region recorded by a mass-spectrometer MCH-1303. The spectrum showed that phosphite ligands were split off from the complex before the cyclopentadienyl ligand, just as

was shown to be the case for the CO-groups in  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_x^4$ . It is of interest that the mass-spectrum revealed a clear peak with  $m/e$  39 assigned to the cyclopropenyl cation  $[\text{C}_3\text{H}_3]^+4$  resulting from the cyclopentadienyl ligand by the action of electron impact.

This evidence, together with the results of the analysis indicate one  $\pi\text{-C}_5\text{H}_5$  ligand and two  $\text{P}(\text{OC}_6\text{H}_5)_3$  groups per iron atom in (I), and diamagnetism requires that the compound be dimeric.

The conclusion about dimerism is, however, not in accord with the monomeric molecular weight, determined cryoscopically and ebullioscopically in benzene (670 and 720, respectively; 741, theory).

It should be noted that both in this and the following cases the former method gives a much higher error than usual. The molecular weight data cannot, as yet, be accounted for and it is hoped that the X-ray analysis now being carried out by Struchkov *et al.* will lead to a definite conclusion. Owing to the strong steric hindrances caused by triphenylphosphite ligands it is hardly likely that the compound under investigation has a Fe-Fe bond similar to that in  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ . The shape and intensity of the NMR spectral signals of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  in  $\text{C}_6\text{D}_{12}$  in a sealed ampoule is, however, not markedly affected up to  $140^\circ$ .

The dimeric cyclopentadienyl-bis(triphenylphosphite)iron although so stable to oxygen is, however, decomposed by hydrochloric acid and excess iodine at room temperature, and also when heated in the presence of carbon tetrachloride. It was possible to carry out the iodine reaction using an equimolecular amount of iodine at low temperature; two products were isolated. Despite the close  $R_F$  values obtained by adsorption over alumina the compounds may be quantitatively separated because of the considerable difference in colour. The analysis for C, H, Fe, I and P, and the cryoscopic molecular weight determinations in benzene (725 and 757, respectively; 867, theory) indicate that the two compounds are isomeric iodides,  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II and III).

As isomerism of monomeric complexes of transition metals with cyclopentadienyl ligands is unknown it can only be assumed that we are dealing with geometrical isomers with each iron atom bound to one cyclopentadienyl ligand, two triphenyl phosphite ligands, and iodine. Both compounds are reduced polarographically in dimethylformamide on a dropping mercury electrode to give one wave with  $E_{1/2} = 1.33$  V and 1.31 V, respectively (relative to a saturated calomel electrode in a 0.1 N solution of  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ ).

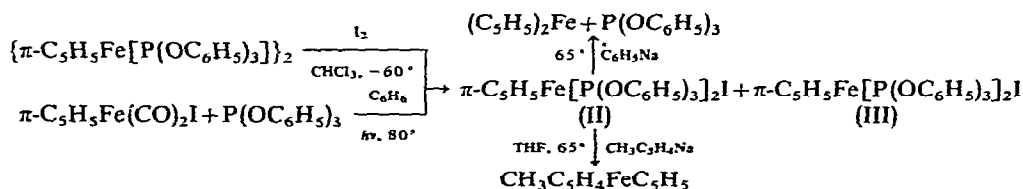
Since isomer (II) was obtained by independent synthesis from  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$  by irradiating the reaction mixture with UV light, the close similarity of the polarographic data substantiates the presence of the Fe-I bond in the two compounds. This bond is the first to be reduced. The IR spectra of (II) and (III) are also very similar in the region  $700\text{--}3500\text{ cm}^{-1}$  and differ very little from those of  $\{\text{C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$ .

However, (III) is not converted to (II) by irradiating the boiling benzene solution with UV light.

Both compounds react on heating with cyclopentadienylsodium or its derivatives. The  $\sigma$ -cyclopentadienyl derivatives thus formed are also unstable and undergo rearrangement to ferrocene or its derivatives. Thus (III) and  $\text{CH}_3\text{C}_5\text{H}_5$  give, in small yield, methylferrocene identified by a comparison of its IR spectrum

with that of an authentic sample. The spectrum of methylferrocene, in particular the absorption bands at 1000 and 1100  $\text{cm}^{-1}$ , substantiate the presence of an unsubstituted  $\text{C}_5\text{H}_5$ -ring in isomer (III).

The Series of the process under study may be pictured as follows:



The investigation of the NMR spectra of the isomers (on a JNM-100 apparatus with a working frequency of 100 MHz) in  $\text{CDCl}_3$  showed that they were very different in the signal region of cyclopentadienyl protons. Thus the spectrum of (II) revealed, besides a multiplet of aromatic protons of phenyl nuclei in the region 6.6–7.2 ppm, also a sharp singlet with  $\delta$  3.72 ppm, whereas the spectrum of (III) involved two symmetric doublets with centres at 3.92 and 4.27 ppm.

A special study of the spectrum of (III) on an apparatus with a working frequency of 60 MHz showed that the quadruplet did not result from the spitting of the singlet into two different atoms of  $^{31}\text{P}$ . The  $\pi$ - $\sigma$ -rearrangement for the  $\text{C}_5\text{H}_5$  ring in (III) has also been ruled out, for the square planar complex of iron must have two unpaired electrons<sup>6</sup>.

It can only be supposed that steric hindrances caused by bulky  $\text{P}(\text{OC}_6\text{H}_5)_3$ -groups in isomer (III) must have led to the disturbance of the  $\text{C}_{5v}$  symmetry of the fragment  $\text{C}_5\text{H}_5\text{Fe}$ . It is hoped that the X-ray analysis of the isomers now in progress will enable the type of isomerism to be elucidated.

We found that  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  was readily reduced by Na/Hg to  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ .

The reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) and Na/Hg at room temperature in tetrahydrofuran, however yielded  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$  (IV) as the sole product. The structure of the resulting hydride was proved by IR and NMR spectra. Thus, the NMR spectrum of (IV) revealed the multiplet assigned to phenyl protons together with a singlet,  $\delta$  3.86 ppm, characteristic of the protons of the  $\text{C}_5\text{H}_5$  ring, and a triplet,  $\delta$  14.05 ppm, corresponding to the signal of the hydride<sup>7</sup>, split into two phosphorus atoms with  $J(^{31}\text{P}\text{-H}) = 82$  cps. The IR spectrum of the hydride revealed a distinct absorption band at 1920  $\text{cm}^{-1}$  assignable to the stretching vibrations of the Fe–H bond. The IR spectra of (I), (II) and (III) also showed a weak band in this region.

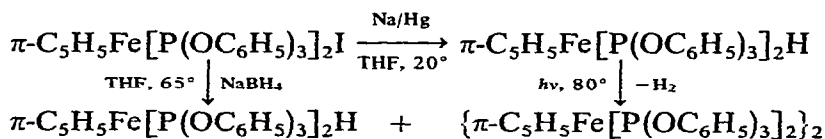
Only when irradiated with UV light under severe conditions was the hydride converted to (I), molecular hydrogen being evolved, whereas  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$  was converted to  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  at 0°<sup>8</sup>.

Compound (I) gave no distinct wave on polarographic reduction under conditions similar to those leading to the reduction of (II) and (III).  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  revealed only one wave with  $E_{\frac{1}{2}} = 1.53$  V. Attempt to make (I) react with Na/Hg resulted only in its decomposition.

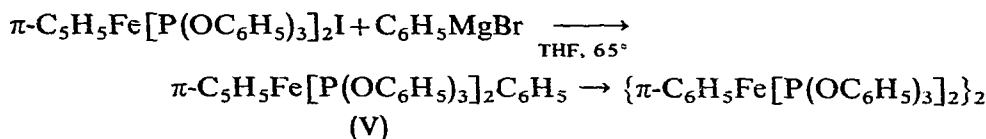
The reduction of (II) by  $\text{NaBH}_4$  produced a mixture of the hydride (IV) and the dimer (I). The composition of the mixture, recrystallised from heptane, was

determined by the relative intensity of signals with  $\delta$  3.86 ppm, and 4.12 ppm from the  $C_5H_5$  ring protons in compounds (IV) and (I), respectively. It was shown by thin-layer chromatography that the isomer (III) reacted with  $NaBH_4$  and  $Na/Hg$  similarly to (II). It was, however, impossible to isolate the reaction products quantitatively because under these conditions (III) was essentially decomposed.

The reduction of (II) by  $NaBH_4$  and  $Na/Hg$  may be represented by the following scheme:



The reaction of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$  (II) and  $C_6H_5MgBr$  yielded only the dimer (I) in low yield thus proving the instability of the intermediate,  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2C_6H_5$ .



The reason for the instability of (V) has not yet been conclusively proved. On one hand, the successive substitution of the CO-groups by the greater electron donor capacity molecules of tertiary phosphites should conceivably lead to increased electron density on the metal atom which would be delocalised along its bonds with other ligands. The absence in compound (II) of CO-groups that are to a great extent capable of being delocalised, appears to lead to the weakening of the metal bonds with other ligands, primarily with the  $\sigma$ -bonded aryl radical. On the other hand, although  $\pi-C_5H_5Fe(CO)_2I$  readily exchanges both its CO-groups for  $P(OC_6H_5)_3$ , to form  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$ , we have found that  $\pi-C_5H_5Fe(CO)_2C_6F_5$  exchanges only one carbonyl ligand under the same conditions. This fact might be accounted for by steric hindrances, for the  $\sigma$ -bonded I- and  $C_6H_5$ -groups should, according to our data<sup>9</sup>, exert practically similar electron effects on the  $C_5H_5Fe(CO)_2$  radical.

## EXPERIMENTAL

### The reaction of $\pi-C_5H_5Fe(CO)_2C_6H_5$ and $P(OC_6H_5)_3$

(a) An equimolecular mixture of  $\pi-C_5H_5Fe(CO)_2C_6H_5$  (1.1 g, 0.043 mole) and  $P(OC_6H_5)_3$  (1.33 g, 0.043 mole) in cyclohexane (50 mole) was irradiated by UV light using a PRK-4 mercury lamp for 2 h at  $30^\circ$ . Chromatography of the reaction mixture on an alumina column resulted in 0.66 g of the starting material  $\pi-C_5H_5Fe(CO)_2C_6H_5$  (elution with a mixture of benzene and petroleum ether 1 : 9) and 0.65 g (73%) of a yellow crystalline substance (elution with a mixture of benzene and petroleum ether, 2 : 8), m.p.  $144.5-145.5^\circ$  after crystallisation from heptane. It was characterised as  $\pi-C_5H_5Fe(CO)P(OC_6H_5)_3C_6H_5$  from the analysis and IR spectrum. (Found: C, 67.01, 66.78; H, 4.79, 4.94; Fe, 10.93, 10.90; P, 6.09, 6.02.  $C_{30}H_{25}FeO_4P$  calcd.: C, 67.17; H, 4.70; Fe, 10.43; P, 5.78%)

(b) A boiling mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{C}_6\text{H}_5)$  (0.9 g, 0.035 mole) and  $\text{P}(\text{OC}_6\text{H}_5)_3$  (3.1 g, 0.01 mole) in absolute benzene (50 ml) was irradiated with UV light for 9 h using a PRK-2 lamp.

Chromatography of the reaction mixture on an alumina column yield 1.7 g (68%), of an orange crystalline substance (elution with a mixture of benzene and petroleum ether, 2:8), m.p. 132–133, after crystallisation from heptane. This was  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  according to the analysis and physico-chemical data. (Found: C, 66.47; H, 4.89, 4.79; Fe, 8.22, 8.29; P, 8.43, 8.21.  $\text{C}_{41}\text{H}_{35}\text{FeO}_6\text{P}_2$  calcd: C, 66.36; H, 4.69; Fe, 7.42; P, 8.23%.)

*The reaction of  $\pi\text{-C}_5\text{H}_6\text{Fe}(\text{CO})[\text{P}(\text{OC}_6\text{H}_5)_3]\text{C}_6\text{H}_5$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$*

A boiling mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{OC}_6\text{H}_5)_3]\text{C}_6\text{H}_5$  (1.15 g, 0.002 mole) and  $\text{P}(\text{OC}_6\text{H}_5)_3$  (0.9 g, 0.003 mole) in absolute benzene (50 ml) was irradiated with UV light for 14 h using a PRK-4 lamp.

Chromatography of the reaction mixture on an alumina column gave 1.1 g (73%), of an orange crystalline substance the m.p. and IR spectrum of which were similar to those of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  described above.

*Synthesis of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{Cl-p}$*

To a solution of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  (0.085 mole) in absolute tetrahydrofuran (50 ml) cooled to  $-50^\circ$  was added dry ( $p\text{-ClC}_6\text{H}_4$ )<sub>2</sub>(II) (4.2 g, 0.009 mole) during 20 min. The reaction mixture was stirred for 30 min at  $-50^\circ$  and 30 min at room temperature. The solvent was then removed and the residue chromatographed on an alumina column to give 0.64 g (28%) of a chromatographically pure (elution with a mixture of benzene and petroleum ether, 1:9) yellow crystalline substance, m.p.  $89.5\text{--}91^\circ$ , after crystallisation from hexane at  $0^\circ$ . The product was characterised as  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{Cl-p}$ , from the analysis and IR spectrum. (Found: C, 55.20, 55.27; H, 3.43, 3.46; Cl, 12.36, 12.10; Fe, 18.47, 18.77.  $\text{C}_{13}\text{H}_9\text{ClFeO}_2$  calcd.: C, 54.07; H, 3.14; Cl, 12.30; Fe, 19.34%.)

*The reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{Cl-p}$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$*

A boiling mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{Cl-p}$  (0.7 g, 0.0024 mole) and  $\text{P}(\text{OC}_6\text{H}_5)_3$  (2.1 g, 0.007 mole) in absolute benzene (50 ml) was irradiated for 15 h using a PRK-4 lamp. Chromatography of the reaction mixture on a column (elution with a mixture of benzene and petroleum ether, 2:8) resulted in two products: (1) 0.2 g (14%), of a yellow crystalline substance, m.p.  $90.5\text{--}91.5^\circ$  after crystallization from heptane. The product was found to be  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(\text{OC}_6\text{H}_5)_3\text{C}_6\text{H}_4\text{Cl-p}$ , according to the analysis and IR spectrum. (Found: C, 64.08, 63.84; H, 4.40, 4.50; Cl, 6.39, 6.33.  $\text{C}_{30}\text{H}_{24}\text{ClFeO}_4\text{P}$  calcd.: C, 64.23; H, 4.32; Cl, 6.34%.)

(2) 0.75 g (43%), of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$ , identical with the compound described above in m.p. and IR spectrum.

*The reaction of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  and  $\text{I}_2$*

To a solution of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  (0.5 g, 0.007 mole) in absolute chloroform (20 ml) was added during 30 min a solution of iodine (0.09 g, 0.007 mole) in absolute chloroform (15 ml), at  $-60^\circ$ . The reaction mixture was then stirred for 30 min at  $-60^\circ$ , and for 1 h at room temperature. The solvent was removed and the

residue chromatographed on an alumina column to give 90 mg of the starting material and two reaction products. The final separation was effected by repeated chromatography (elution with a mixture of benzene and petroleum ether, 7:3). Crystallisation from heptane of the first product gave 0.1 g, of a black crystalline substance, decomposing at 130°. (Found: C, 55.86, 56.08; H, 4.30, 4.27; I, 14.39, 14.41; Fe, 6.13, 6.23; P, 6.25, 6.47.  $C_{41}H_{35}FeIO_6P_2$  calcd.: C, 56.74; H, 4.07; I, 14.52; Fe, 6.45; P, 7.15%.)

The physico-chemical data and the chemical behaviour of the products showed them to be isomers of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$ , (II) (17%) and (III) (28%).

One of the reaction products of  $\{\pi-C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$  and  $Br_2$  under conditions similar to those of the reaction with  $I_2$  is a black crystalline substance, m.p. 117–118° with decomposition after crystallisation from a mixture of heptane and methylene chloride. The product has been characterised as  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2Br$ , from the analysis. (Found: C, 59.87, 59.99; H, 4.75, 4.56; Br, 10.20, 9.85.  $C_{41}H_{35}BrFeO_6P_4$  calcd.: C, 59.92; H, 4.30; Br, 9.73%.)

#### *The reaction of $\pi-C_5H_5Fe(CO)_2I$ and $P(OC_6H_5)_3$*

A boiling mixture of  $\pi-C_5H_5Fe(CO)_2I$  (16.27 g, 0.053 mole) and  $P(OC_6H_5)_3$  (49.29 g, 0.16 mole) in absolute benzene (100 ml) was irradiated with UV light for 10 h using a PRK-2 lamp. The solvent was removed and the residue repeatedly chromatographed on an alumina column. This resulted in a complete separation of the product from the starting substance (elution with a mixture of benzene and petroleum ether, 7:3) to give 16.7 g (36%) of a black crystalline substance decomposing at 130°, with analysis and IR data corresponding to those of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$  (II) described above. Found: C, 56.90, 56.92; H, 4.52, 4.40%.)

#### *The reaction of $\{\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$ (II) and $C_5H_5Na$*

To a solution of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$  (II) (2.1 g, 0.024 mole) in absolute tetrahydrofuran (20 ml) was added a solution of  $C_5H_5Na$  in 10 ml of tetrahydrofuran obtained from 0.14 g, (0.006 mole) of Na and 0.66 g (0.01 mole) of  $C_5H_6$ . The reaction mixture was stirred for 1 h at room temperature and for 1 h with boiling. The solution was then cooled and the solvent removed and the residue chromatographed on an alumina column to yield 0.3 g (65%) of ferrocene. Thin-layer chromatography has shown that the reaction mixture contains triphenylphosphite.

#### *The reaction of $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$ (III) and $CH_3C_5H_4Na$*

To a solution of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$  (III) (2.4 g, 0.0028 mole) in absolute tetrahydrofuran (20 ml) was added a solution of  $CH_3C_5H_4Na$  in 10 ml of tetrahydrofuran obtained from 1.2 g, (0.015 mole) of  $CH_3C_5H_5$  and 0.14 g (0.006 mole) of Na. The reaction mixture was boiled for 5 h and the solvent removed. Repeated chromatography of the residue on an alumina column yielded the starting compound together with a small amount of chromatographically pure crystalline methylferrocene identified by comparing its IR spectrum with that of an authentic sample.

#### *The reaction of $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$ (II) and sodium amalgam*

A solution of  $\pi-C_5H_5Fe[P(OC_6H_5)_3]_2I$  (II) (2.1 g, 0.0024 mole) in absolute

tetrahydrofuran (20 ml) was stirred with sodium amalgam, obtained from 70 mg (0.003 mole) of Na and 0.5 ml of Hg, for 12 h at room temperature. The solvent was removed and the residue chromatographed on an alumina column to give 0.3 g of the starting compound together with 0.4 g (23 %) of a yellowish crystalline substance (elution with a mixture of benzene and petroleum ether, 2:8), m.p. 121–122 after crystallisation from heptane. The product was found to be  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_3\}_2\text{H}$ , according to the IR and NMR spectra. (Found: C, 66.54, 66.80; H, 4.82, 4.92.  $\text{C}_{41}\text{H}_{36}\text{FeO}_6\text{P}_2$  calcd.: C, 66.36; H, 4.89%.)

*The reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) and  $\text{NaBH}_4$*

A boiling solution of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) (2.1 g, 0.0024 mole) in absolute tetrahydrofuran (40 ml) was stirred with  $\text{NaBH}_4$  (200 mg, 0.005 mole) for 30 min. The solvent was removed and the residue chromatographed on an alumina column (elution with a mixture of benzene and hexane, 2:8) to give 0.5 g (28 %) of a yellow crystalline substance, m.p. 111–113° after crystallisation from heptane. The melting point was constant and did not change after purification. According to the NMR spectrum the product was a mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$  and  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  in the ratio 7:5. (Found: C, 66.57, 66.29; H, 4.91, 4.76%.)

*Dehydrodimerisation of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$*

(a) A boiling mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$  and  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  (1.1 g), obtained from the reaction of the dimer and  $\text{NaBH}_4$  in absolute benzene (50 ml), was irradiated with UV light for 3 h using a PRK-4 lamp.

The reaction mixture was then cooled, filtered through alumina, the solvent removed and the residue crystallised from heptane to give 0.55 g of an orange crystalline substance, m.p. 130.5–131.5°. The NMR spectrum showed that the product was pure  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$ .

(b) A solution of pure  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_3\text{H}$  (0.8 g) in absolute benzene (50 ml) was irradiated by UV light under conditions similar to those used in experiment (a). Similar treatment and three recrystallisations of the product from heptane resulted in the isolation of an orange crystalline substance, m.p. 111–112°. According to the NMR spectrum this was a mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{H}$  and  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  in the ratio 7:5. Gas chromatography showed that molecular hydrogen was present in the gaseous reaction products.

*The reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) and  $\text{C}_6\text{H}_5\text{MgBr}$*

To a solution of  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) (2.33 g, 0.0025 mole) in absolute tetrahydrofuran (50 ml) was added a titrated ethereal solution of  $\text{C}_6\text{H}_5\text{MgBr}$  (4 ml, 0.01 mole). The reaction mixture was stirred with boiling for 4 h and then cooled; the solvent was removed and the residue chromatographed on an alumina column to give 0.7 g, of the starting compound together with a small amount of an orange crystalline substance, m.p. 126–128° after crystallisation from heptane. The product was identified by the NMR spectrum as  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$ . The substance gave no mixed melting point depression.



*The reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{F}_5$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$* 

A boiling mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{F}_5$ <sup>10</sup> (2.9 g, 0.0084 mole) and  $\text{P}(\text{OC}_6\text{H}_5)_3$  (7.8 g, 0.015 mole) in absolute benzene (70 ml) was irradiated with UV light for 3 h using a PRK-2 lamp.

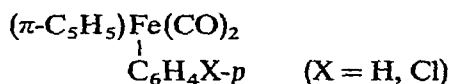
The reaction mixture was cooled and chromatographed on an alumina column to yield 5 g of an orange crystalline substance (elution with a mixture of benzene and petroleum ether, 2 : 8, m.p. 128.5–130° after crystallisation from heptane. The product was characterised as  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{C}_6\text{F}_5$ , from the analysis and IR spectrum. The yield was practically quantitative. (Found: C, 58.02, 58.08; H, 3.32, 3.25; F, 14.86, 14.77; P, 4.48, 4.35.  $\text{C}_{30}\text{H}_{20}\text{F}_5\text{FeO}_4\text{P}$ , calcd.: C, 57.51; H, 3.22; F, 15.17; P, 4.95%.)

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## SUMMARY

1. It is shown, that the interaction of



with  $\text{P}(\text{OC}_6\text{H}_5)_3$  on irradiation of a reaction mixture by UV light is accompanied by an exchange of both carbonyl groups with formation of  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$ .

2.  $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}_2$  interacts with  $\text{I}_2$  at  $-60^\circ$  to give two isomer iodides,  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) and (III).

3.  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{I}$  (II) is reduced by Na/Hg and  $\text{NaBH}_4$  to give a stable hydride,  $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OC}_5\text{H}_5)_3]_2\text{H}$ .

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