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ARYLATION OF SODIUM SALTS OF CYCLOPENTADIENYLIRONDICARBONYL HYDRIDE BY ONIUM COMPOUNDS

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An important method for the synthesis of organometallic compounds involves arylation by onium compounds, either through the decomposition of double-onium (primarily diasonium) salts with non-transition metal salts[1] or through direct interaction of onium compounds with the free metals[2-5].

It appeared possible to extend the method to compounds containing a σ-bond of the carbon atom with the atom of the transition metal, as in a number of cases other methods proved to be of little value. For example, the three methods used to prepare π-$C_5H_5Fe(CO)_2$-C_6H_5[6,7] gave low yields of the product.

An investigation of the arylation of π-$C_5H_5Fe(CO)_2Na$ by phenyldiazonium-, diphenyliodonium- and triphenylsulphonium-boron fluorides shows that the first step of interaction, the formation of sodium boron fluoride by exchange of ions, does take place at −50°. The further reaction did not, however, prove to be similar for different salts. Thus, with the phenyldiazonium salt, the only organometallic compound isolated experimentally was the dimer, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, that must have been formed by the coupling of the corresponding radicals. With diphenyliodonium- and triphenylsulphonium-salts, however, the dimer was isolated together with the compound sought, π-$C_5H_5Fe(CO)_2$-C_6H_5. The method under investigation becomes of a preparative value by using triphenylsulphonium as an arylating agent and thus increasing the yield to 45% (Table 1).

TABLE 1

YIELD OF THE PRODUCTS OF THE REACTION OF π-$C_5H_5Fe(CO)_2Na$ WITH ONIUM COMPOUNDS

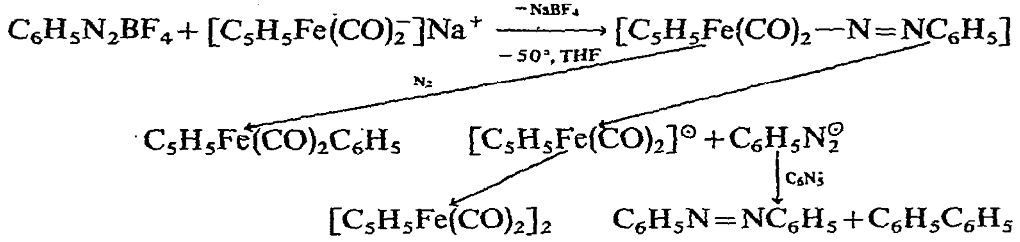
Onium compounds used	$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (%)[a]	$\pi\text{-}C_5H_5Fe(CO)_2C_6H_5$ (%)[a]
$C_6H_5N_2BF_4$	95	traces
$(C_6H_5)_2IBF_4$	65	18
$(C_6H_5)_3SBF_4$	47	40

[a] The percentage is an average of at least two runs. The scatter of data is not greater than ±5% on π-$C_2H_5Fe(CO)_2Na$.

Two competing reactions appear to take place: electrophilic arylation of cyclopentadienylirondicarbonyl anion by the onium-salt cation and the redox process resulting in the formation of two coupled radicals. In fact, diphenyl was observed to be formed in all instances and azobenzene was isolated from the reaction products of the diazonium salt. The yield of $C_5H_5Fe(CO)_2\text{-}C_6H_5$ is lower the higher the yield of $[C_5H_5Fe(CO)_2]_2$ for all onium salts studied.

The sequence of the above processes can therefore be illustrated as follows:

(1)



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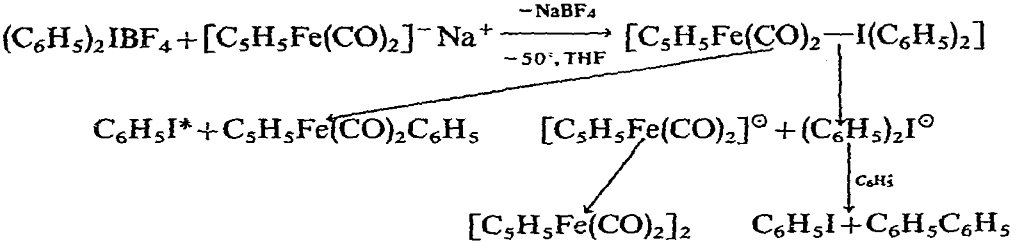

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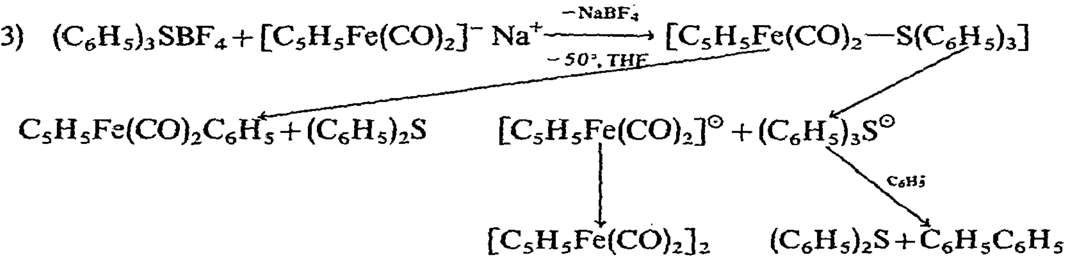

The yield of $\pi\text{-}C_5H_5Fe(CO)_2\text{-}C_6H_5$ must, in particular, depend on the reducibility of the cation from the onium salt into a radical:

$$(C_6H_5)_nEl^+ + e \rightleftarrows (C_6H_5)_nEl \qquad (El = N, I \text{ or } S)$$

The reducibility can be estimated quantitatively from the polarographic half-wave potentials of the onium salts taken under similar conditions, for it is reported in the literature that the first wave potential of phenyldiazonium and diphenyliodonium salts corresponds, as expected, to the reduction of the cation into the radical[8,9]. The polarographic results obtained with onium salts substantiate the suggestion regarding the interdependence between the yield of $\pi\text{-}C_5H_5Fe(CO)_2\text{-}C_6H_5$ and the values of first half-wave potentials of onium salts**.

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* Note that iodobenzene does not react markedly with $\pi\text{-}C_5H_5Fe(CO)_2Na$ under our conditions.

** The authors are indebted to L. J. Denisovich for polarographic measurements.

TABLE 2

POLAROGRAPHIC REDUCTION OF SALTS [a]

Salts	I		II		III		IV	
	i_d (μA)	$E_{\frac{1}{2}}$ (V)	i_d (μA)	$E_{\frac{1}{2}}$ (V)	i_d (μA)	$E_{\frac{1}{2}}$ (V)	i_d (μA)	$E_{\frac{1}{2}}$ (V)
$C_6H_5N_2BF_4$ [b]	0.65	+0.06	2.18	−0.1	2.40	−0.76	5.45	−1.17
$(C_6H_5)_2IBF_4$	0.58	−0.07	2.18	−0.2	2.47	−1.19	6.06	−1.645
$(C_6H_5)_3SBF_4$	2.33	−1.34						

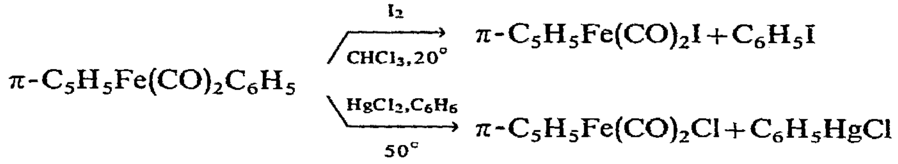
[a] The base electrolyte used was 0.1 N K_2SO_4 in water, pH = 6.7.

[b] The concn. of all onium salts was $2 \cdot 10^{-3}$ M/l.

Table 2 lists the values of the half-wave potentials ($E_{\frac{1}{2}}$) of the compounds investigated and the respective values of the electric current (i_d).

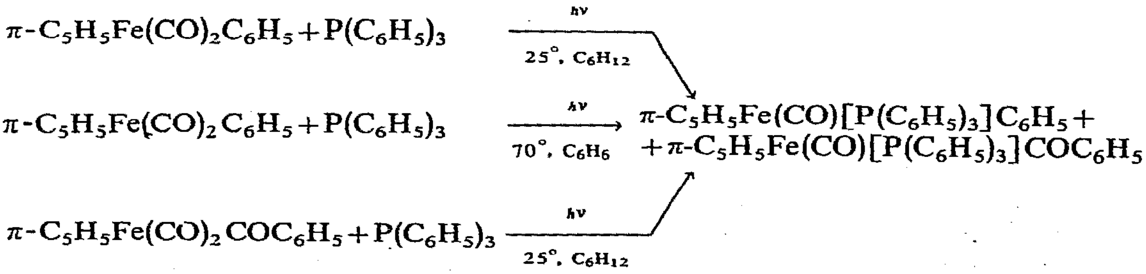
The polarographic evidence indicates that $C_6H_5N_2BF_4$ and $(C_6H_5)_2IBF_4$ are readily reduced. The difference between the first half-wave potential of $(C_6H_5)_2$-IBF_4 and that of $(C_6H_5)_3SBF_4$ is large compared to that between $C_6H_5N_2BF_4$ and $(C_6H_5)_2IBF_4$, but even special measurements at different concentrations failed to detect any wave of more positive potentials for $(C_6H_5)_3SBF_4$.

σ-Phenyl-π-cyclopentadienylirondicarbonyl readily enters into the reactions typical of transition metal–σ-aryl complexes. It is cleaved by iodine at room temperature and arylates $HgCl_2$ to give phenylmercurychloride.



$$\pi\text{-}C_5H_5Fe(CO)_2C_6H_5 \begin{cases} \xrightarrow[CHCl_3,20^\circ]{I_2} \pi\text{-}C_5H_5Fe(CO)_2I + C_6H_5I \\ \xrightarrow[50^\circ]{HgCl_2,C_6H_6} \pi\text{-}C_5H_5Fe(CO)_2Cl + C_6H_5HgCl \end{cases}$$

On exposure to UV-irradiation at 20°, π-$C_5H_5Fe(CO)_2C_6H_5$ readily exchanges one of its CO-groups for triphenylphosphine[11]. When the reaction mixture is heated to 70°, the exchange is accompanied by a rearrangement that results in the formation of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ the structure of which was confirmed by an independent synthesis from $P(C_6H_5)_3$ and π-$C_5H_5Fe(CO)_2COC_6H_5$. The triphenylphosphine compounds obtained in different ways have the same melting points and IR-spectra*.



$$\pi\text{-}C_5H_5Fe(CO)_2C_6H_5 + P(C_6H_5)_3 \xrightarrow[25^\circ,\ C_6H_{12}]{h\nu} \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$$

$$\pi\text{-}C_5H_5Fe(CO)_2C_6H_5 + P(C_6H_5)_3 \xrightarrow[70^\circ,\ C_6H_6]{h\nu} \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5 + \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$$

$$\pi\text{-}C_5H_5Fe(CO)_2COC_6H_5 + P(C_6H_5)_3 \xrightarrow[25^\circ,\ C_6H_{12}]{h\nu} \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$$

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* The authors are indebted to B. V. Lokshin for his study of the spectra and discussion of the results obtained.

An intrusion of the CO-group into a metal–carbon bond, accompanying the direct ligand exchange, has been thoroughly investigated for the case of manganese-σ-alkyl complexes[12].

π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ is a red crystalline substance, air-stable in the solid form and for a long time in solution. The IR-spectrum of the compound in benzene shows an absorption band at 1928 cm^{-1} which corresponds to the valence vibration of a $C{\equiv}O$-group and is markedly shifted from that of π-$C_5H_5Fe(CO)_2$-C_6H_5. Although the mass and the geometry of a molecule is affected when it exchanges its carbonyl ligand for a triphenylphosphine group, the shift may be chiefly attributed to electronic effects, the absorption band of $C{\equiv}O$ being very characteristic in respect to form and situation.

Phosphine phosphorus 3*d*-orbitals are generally accepted to account for the formation of the strong dative (d_π–d_π) bonding between a transition metal and phosphine; the antibonding molecular orbitals of carbon monoxide are taken as accounting for the formation of the similar CO–transition metal bonding, and so we may say that, in our case, the greater basicity of $P(C_6H_5)_3$ as compared with that of CO is essential[13]. Therefore the exchange of the carbonyl ligand for the triphenylphosphine molecule increases the electron density on the metal atom. Subsequent charge delocalization causes the shift of the CO absorption bond, but stabilizes the bonding between the metal and the aryl-ring carbon. This results in thermal and oxidative stabilization of the complex, as in the case of a strong electron-withdrawing substituent introduced into the ring.

Further, the synthesis of the series π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* was attempted directly from $[\pi\text{-}C_5H_5Fe(CO_2)]_2$, without isolation of the intermediates. It was found, however, that UV-irradiation of the reaction mixture leads not only to π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* but also to π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$[14]. Likewise, π-$C_5H_5Fe(CO)_2I$ when UV-irradiated at 20°, exchanges its CO-ligand for the triphenylphosphine molecule unlike π-$C_5H_5Fe(CO)_2Cl$ which reacts with $P(C_6H_5)_3$ to give $[\pi\text{-}C_5H_5Fe(CO)_2P(C_6H_5)_3]^+Cl^-$ only at higher temperatures[15]. The IR-spectrum of the iodide irradiation product is identical with that of the π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$ described above.

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 \xrightarrow[\text{THF}]{\text{Na/Hg}} \pi\text{-}C_5H_5Fe(CO)_2Na \xrightarrow[-60\,^\circ,\ \text{THF}]{(p\text{-}RC_6H_4)_2II}$$

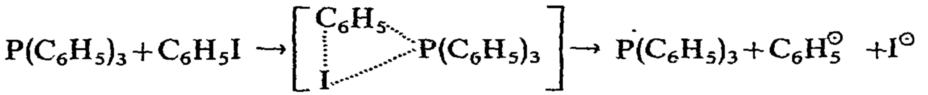
$$\rightarrow \pi\text{-}C_5H_5Fe(CO)_2C_6H_4\text{-}R\text{-}p + [\pi\text{-}C_5H_5Fe(CO)_2]_2 + p\text{-}RC_6H_4I \xrightarrow[h\nu,\ 20\,^\circ]{P(C_6H_5)_3}$$

$$\rightarrow \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R\text{-}p \;+\; \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]I$$

$$\pi\text{-}C_5H_5Fe(CO)_2I + P(C_6H_5)_3 \xrightarrow[h\nu,\ 20^\circ]{\qquad\qquad} \uparrow$$

We have shown that $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, π-$C_5H_5Fe(CO)_2C_6H_5$ and π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4R$-*p* do not react with iodobenzene when UV-irradiated and that $[C_5H_5Fe(CO)_2]_2$ does not react with triphenylphosphine under the same conditions, therefore we supposed that the formation of the iodide is caused by a triphenylphosphine–iodobenzene interaction. Actually, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ reacts with the irradiated mixture of iodobenzene and triphenylphosphine forming

π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$. An irradiated iodobenzene is known to react slowly with triphenylphosphine giving $(C_6H_5)_4PI^{16}$. It might be supposed that an UV-irradiated tetraphenylphosphonium iodide decomposes (as does $(C_6H_5)_2II^{17}$) to give $P(C_6H_5)_3$, $C_6H_5^{\odot}$ and $I^{\odot}$. However, we have shown $(C_6H_5)_4PI$ to be stable under our conditions. Hence, π-$C_5H_5Fe(CO)_2I$ is formed from $[\pi$-$C_5H_5Fe(CO)_2]_2$ and converted to π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$ *via* formation of the triphenylphosphine–iodobenzene active complex followed by its radical decomposition. Indeed, biphenyl was bound among the products of the reaction carried out in benzene.



$$P(C_6H_5)_3+C_6H_5I \rightarrow \left[\begin{matrix} C_6H_5 \\ I \end{matrix} \!\!> P(C_6H_5)_3\right] \rightarrow P(C_6H_5)_3+C_6H_5^{\odot}+I^{\odot}$$

$$C_6H_5^{\odot}+C_6H_6 \rightarrow C_6H_5C_6H_5$$

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2+2I^{\odot} \rightarrow 2\ \pi\text{-}C_5H_5Fe(CO)_2I$$

$$\pi\text{-}C_5H_5Fe(CO)_2I+P(C_6H_5)_3 \rightarrow \pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]I$$

Probably π-$C_5H_5Fe(CO)_2C_6H_5$ as well as $[\pi$-$C_5H_5Fe(CO)_2]_2$ may react with the mixture of iodobenzene and triphenylphosphine forming π-$C_5H_5Fe(CO)$-$[P(C_6H_5)_3]I$.

EXPERIMENTAL

I. Reaction of π-$C_5H_5Fe(CO)_2Na$ with onium compounds.

1. In all runs, the sodium salt of cyclopentadienylirondicarbonyl hydride was obtained after an hour's stirring at room temperature of 50 ml of a solution of 1.77 g (0.01 mole) of $[C_5H_5Fe(CO)_2]_2$ in abs. tetrahydrofuran with a two-fold excess of 1% sodium amalgam (2.5 ml of Hg, 0.5 g of Na)[6] under a sweep of purified argon.

2. The dry salt of phenyldiazoniumboron fluoride (1.9 g, 0.01 mole) was added during 30 min to a solution of $C_5H_5Fe(CO)_2Na$ (0.009 mole, 45 ml), cooled to −50°, in abs. tetrahydrofuran. The mixture was then stirred for 30 min at −20°. Different runs resulted in the evolution of 1500–2000 ml of nitrogen mixed with 1.5–5% of carbon monoxide.

After removal of tetrahydrofuran *in vacuo*, the residue was carefully extracted with hexane and the solution chromatographed on an alumina column (hexane : benzene, 9 : 1). The data obtained from thin-layer chromatography (compared with authentic samples) indicated that the mixture obtained consisted of diphenyl, azobenzene (10% yield) and traces of π-$C_5H_5Fe(CO)_2$-C_6H_5 that are not readily separated by chromatography from the azobenzene. The dimer, $[C_5H_5Fe(CO)_2]_2$, eluted from the column by a hexane–benzene (1 : 1) mizture was combined with the residue from the hexane extraction of the reaction mixture. The final product had m.p. 189–190° (aqueous pyridine), the mixed melting point with an authentic sample showed no depression (literature[12], m.p. 192°). Yield in different runs: 1.45 – 1.6 g (90–100%)

3. The dry salt of diphenyliodoniumboron fluoride was added during 30 min to a solution of $C_5H_5Fe(CO)_2Na$ (0.0085 mole, 42 ml), cooled to −50°, in abs. tetrahydrofuran. The mixture was stirred for 30 min at −50° and for another 30 min at 20°. After treatment similar to that described for phenyldiazoniumboron fluoride,

the products (iodobenzene, diphenyl and π-$C_5H_5Fe(CO)_2C_6H_5$), were isolated and characterised by comparison with authentic samples (eluation with a 9 : 1 mixture of hexane–benzene).

Chromatographically pure, non-recrystallised π-$C_5H_5Fe(CO)_2C_6H_5$ was obtained in a 0.4 g yield (18%) m.p. 34° (hexane, −70°) (literature[7], 35–36°). (Found: C, 62.04, 61.74; H, 4.30, 4.14; Fe, 21.92, 21.82. $C_{13}H_{10}FeO_2$ calcd.: C, 61.45; H, 3.94; Fe, 22.01%.) A dimer, $[\pi$-$C_5H_5Fe(CO)_2]_2$, was also isolated. Yield in different runs: 0.9–1.05 g (60–70%).

4. The reaction of $C_5H_5Fe(CO)_2Na$ with triphenylsulfoniumboron fluoride was studied under similar conditions and with the same molar quantities as in the reaction with diphenyliodoniumboron fluoride. The yield of π-$C_5H_5Fe(CO)_2C_6H_5$ in different runs was 0.75–0.96 g of the chromatographically pure, non-recrystallised compound (35–45%); the yield of $[\pi$-$C_5H_5Fe(CO)_2]_2$ was 0.6–0.85 g (40–56%).

II. Polarographic measurements were carried out on a polarograph PA-2 using a mercury drop electrode, with the following capillary tube characteristics: $m = 1.53$ mg/sec, $t = 0.35$ sec, h (mercury column) = 50 cm. All measurements were conducted under the same conditions in aqueous medium at 25°.

Reaction of π-$C_5H_5Fe(CO)_2C_6H_5$ with $HgCl_2$

A mixture of 0.75 g (0.003 mole) of π-$C_5H_5Fe(CO)_2C_6H_5$ and 0.81 g (0.003 mole) of $HgCl_2$ was heated in 30 ml of abs. benzene at 45–50° for 1.5 h. The solution was observed to become red. After cooling to +5°, the reaction mixture was concentrated *in vacuo* and the organic layer separated from the crystals precipitated during the reaction. The benzene was evaporated and the residue washed with hexane to give 0.48 g (74%) of crude π-$C_5H_5Fe(CO)_2Cl$ which, after recrystallization from hexane–ether (1 : 1), melted at 86–87° (literature[19], m.p. 84–87°).

The crystalline residue formed during the reaction was carefully washed with dilute HCl and water, and dried. After recrystallization from benzene, 0.57 g (61%) of C_6H_5HgCl was recovered, m.p. 249–250°; the mixture with an authentic sample melted without depression.

Reaction of π-$C_5H_5Fe(CO)_2C_6H_5$ with $P(C_6H_5)_3$

(a) A mixture of 1.009 g (0.004 mole) of π-$C_5H_5Fe(CO)_2C_6H_5$ and 1.36 g (0.005 mole) of $P(C_6H_5)_3$ dissolved in 50 ml of cyclohexane was UV-irradiated for 16 h at 30°. Chromatography of the reaction mixture on an alumina column gave:

(i) A mixture of the initial compounds (hexane : benzene = 9 : 1).

(ii) A red crystalline compound (hexane : benzene = 8 : 2) which was identified as π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ by analysis and IR-spectroscopy. (Found: C, 74.19, 73.75; H, 5.35, 5.22; Fe, 10.39, 10.25; P, 6.02, 6.15. $C_{30}H_{25}FeOP$ calcd.: C, 73.77; H, 5.12; Fe, 11.47; P, 6.35%). 0.9 g (46%) of the compound was obtained, m.p. 166–166.5° (decomp.) after recrystallization from heptane.

(b) A mixture of 1.27 g (0.005 mole) of π-$C_5H_5Fe(CO)_2C_6H_5$ and 2.61 g (0.01 mole) of $P(C_6H_5)_3$ dissolved in 50 ml of abs. benzene was irradiated for 8 h at 70°. Chromatography of the solution on alumina gave a difficulty separable mixture of the starting materials together with 0.7 g (28%) of a red crystalline substance, m.p. 166–166.5°, identical with π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ described above. A second product of the reaction was eluted with hexane–benzene mixture (2:8) it was an orange crystalline substance, m.p. 164° (decomp.) after recrystallization from heptane–benzene mixture (2:1). This substance was identified as π-$C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ by analysis and IR-spectroscopy. (Found: C, 72.45, 72.38; H, 5.04, 5.03; Fe, 9.49, 9.97; P, 5.68, 5.29. $C_{31}H_{25}FeO_2P$ calcd.: C, 72.09; H, 4.84; Fe, 10.85; P, 6.02%). The yield was 14% of theoretical.

All the irradiations were carried out in a quartz flask in which the reaction mixture was stirred under an argon sweep; the irradiation spurce was a PRK-4 lamp.

Reaction of π-$C_5H_5Fe(CO)_2COC_6H_5$ with $P(C_6H_5)_3$

1.5 g (0.0053 mole) of π-$C_5H_5Fe(CO)_2COC_6H_5$ and 2 g (0.0076 mole) of $P(C_6H_5)_3$ were irradiated in 70 ml of cyclohexane for 16 h at 30°. A brownish-yellow substance that precipitated from the orange solution during the reaction was filtered and washed with cyclohexane. After chromatography of the filtrate on alumina, 1.47 g (0.0056 mole) of $P(C_6H_5)_3$, 0.32 g of π-$C_5H_5Fe(CO)_2COC_6H_5$ and 0.14 g of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ (an orange crystalline substance, m.p. 164° the IR-spectrum of which was identical with that described above) were obtained. In addition, 0.91 g of the pure compound was recovered from the precipitate. The total yield of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]COC_6H_5$ was theoretical with respect to the amount of $P(C_6H_5)$ reacted.

Synthesis of π-$C_5H_5Fe(CO)P(C_6H_5)_3C_6H_4CH_3$-p

Dry $(p\text{-}CH_3C_6H_4)_2II$ (4 g, 0.0091 mole) was added to a solution of π-$C_5H_5Fe(CO)_2Na$ (0.009 mole) in THF at −60° during 1 h. The reaction mixture was stirred at −60° for 1 h and at 20° for 0.5 h. 2.5 g (0.01 mole) of $P(C_6H_5)_3$ was then added and UV-irradiation carried out for 30 h at 20°. The solvent was removed and the residue dissolved in benzene and chromatographed on alumina. The first yellow band eluted with hexane–benzene mixture (9:1) was found to be an unseparable mixture of $P(C_6H_5)_3$ and π-$C_5H_5Fe(CO)_2C_6H_4CH_3$-p, the R_f of the latter on alumina being similar to that of π-$C_5H_5Fe(CO)_2$-C_6H_5. Evaporation of the second fraction eluted with hexane–benzene mixture (8;2), gave 0.48 g (11%) of a red crystalline substance, m.p. 141.5°–142.5° (decomp.) after recrystallization from heptane. The IR-spectrum and analysis of this substance indicated that it was π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4CH_3$-p. (Found: C, 74.70, 74.79; H, 6.21, 6.16. $C_{31}H_{27}FeOP$ calcd.: C, 74.06; H, 5.42%).

The third compound identified was found to be $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.4 g, 25% in respect to the quantities taken for the reaction). The final compound was eluted with benzene and recrystallized from heptane–benzene mixture (1:1). It was π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$—a dark-green crystalline substance (1.48 g, m.p. 178–179° decomp.). (Found: C, 53.46, 53.66; H, 3.93, 3.94; Fe, 9.36, 9.58; I, 23.46, 23.52; P, 5.70, 5.78. $C_{24}H_{20}FeIOP$ calcd.: C, 53.50; H, 3.73; Fe, 10.40; I, 23.65; P, 5.76%). The yield of the iodide was 29% of theoretical in respect of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ taken for the reaction. Although air-stable in the solid form, the iodide is sensitive to oxidation on heating in solution, thus its purification is somewhat difficult. The compound is insoluble in petroleum ether and water.

Reaction of π-$C_5H_5Fe(CO)_2I$ with $P(C_6H_5)_3$

A mixture of π-$C_5H_5Fe(CO)_2I$ (1 g, 0.0033 mole) with $P(C_6H_5)_3$ (0.95 g, 0.0037 mole) was dissolved in 45 ml of abs. THF and UV-irradiated for 4 h at 20°. The solution was filtered from a small quantity of a white precipitate which was discarded. THF was removed *in vacuo* and the residue was purified by chromatography on alumina. Apart from the starting compounds, 1.2 g (68%) of π-C_5H_5-$Fe(CO)[P(C_6H_5)_3]I$ was obtained, the IR-spectrum of which was identical with that described above.

Reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ *with a mixture of* C_6H_5I *and* $P(C_6H_5)_3$

A mixture of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.54 g, 0.0015 mole) with $P(C_6H_5)_3$ (1.2 g, 0.0046 mole) was dissolved in 30 ml of abs. THF and UV-irradiated for 8 h at 20°. No reaction was observed*. Then C_6H_5I (0.6 g, 0.003 mole) was added to the reaction mixture which was further irradiated for 17 h. THF was removed *in vacuo* and the residue was dissolved in benzene and purified by chromatography on alumina. Apart from $P(C_6H_5)_3$ and C_6H_5I, 0.22 g of unreacted $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ was obtained together with 0.84 g (51%) of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$, the IR-spectrum of the latter being identical with that described above.

Synthesis of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_4Cl$-*p*

A solution of π-$C_5H_5Fe(CO)_2Na$ (0.009 mole) in 50 ml of absolute THF was cooled to −60° and $(p\text{-}ClC_6H_4)_2II$ (4.2 g, 0.0088 mole) was added during 1 h. The mixture was stirred for 0.5 h at −60°, and 2 h at 20° and then UV-irradiated for 16 h. No formation of π-$C_5H_5Fe(CO)_2I$ was observed. After the removal of THF, the residue was first treated with 9:1 hexane–benzene mixture and then with benzene alone, and the solution subjected to alumina chromatography. 0.9 g of a compound the R_f and appearance of which was consistent with those of π-$C_5H_5Fe(CO)_2C_6H_5$ was obtained. The compound was dissolved in 50 ml of abs. benzene without further purification. $P(C_6H_5)_3$ (1.2 g, 0.0046 mole) was added to the solution; the latter was UV-irradiated at 20° for 12 h. The solution was then subjected to alumina chromatography to give 1.74 g of a red crystalline substance (eluted by 8:2 hexane–benzene mixture), m.p. 161–162° (decomp.) after crystallization from heptane, together with unreacted starting materials. The red compound was identified as π-$C_5H_5Fe(CO)$-$[P(C_6H_5)_3]C_6H_4Cl$-*p* by IR-spectroscopy and analysis. (Found: C, 68.98, 69.20; H, 4.84, 4.87; Cl, 7.32, 7.61; P, 5.73, 5.92. $C_{30}H_{24}FeOPCl$ calcd.: C, 68.92; H, 4.63; Cl, 6.79; P, 5.92%). The yield of the compound was 87% with respect to π-C_5H_5-$Fe(CO)_2C_6H_4Cl$-*p* and 30% with respect to $[\pi\text{-}C_5H_5Fe(CO)_2]Na$ taken for the first step of the reaction.

Reaction of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_6H_5$ *with* C_6H_5I

The mixture of π-$C_5H_5Fe(CO)P(C_6H_5)_3C_6H_5$ (0.39, 0.0006 mole) with C_6H_5I(0.14 g, 0.00012 mole) was dissolved in 20 ml of abs. THF and UV-irradiated at 20° for 13 h. Only the starting materials were found in the reaction mixture.

graphy on alumina. Apart from the starting compounds, 1.2 g (68%) of π-C_5H_5-

Reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ *with* $(C_6H_5)_4PI$

$(C_6H_5)_4PI$ (0.8 g, 0.0017 mole), m.p. 328° (literature[20], m.p. 333°) was added to

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* The course of all the reactions described in this paper was qualitatively controlled by a thin-layer Al_2O_3 chromatography technique.

a solution of 0.31 g (0.009 mole) of [π-$C_5H_5Fe(CO)_2]_2$ in 40 ml of abs. benzene, and the mixture UV-irradiated at 20° for 40 h. No decomposition of the phosphonium salt was observed, *i.e.*, no iodobenzene or diphenyl was found by thin-layer chromatography.

SUMMARY

1. A new method to synthesise π-$C_5H_5Fe(CO)_2C_6H_5$ by the interaction of π-$C_5H_5Fe(CO)_2Na$ and onium salts has been developed.

2. It has been shown that the formation of π-$C_5H_5Fe(CO)_2C_6H_5$ is accompanied by a competing redox reaction leading to [π-$C_5H_5Fe(CO)_2]_2$. With phenyldiazoniumboron fluoride, the latter process is almost entirely predominant.

3. The photochemical exchange of a carbonyl ligand for a triphenylphosphine molecule is investigated in the case of π-$C_5H_5Fe(CO)_2P(C_6H_5)_3C_6H_5$. At 70° the reaction proceeds, together with formation of the iron-6-benzoyl complex.

4. It is found that [π-$C_5H_5Fe(CO)_2]_2$ undergoes a photochemical reaction with a mixture of $P(C_6H_5)_3$ and C_6H_5I (no reaction is observed with either of the components taken individually) to give π-$C_5H_5Fe(CO)[P(C_6H_5)_3]I$. The reaction is assumed to proceed *via* the formation of an active complex resulting from the interaction of $P(C_6H_5)_3$ with C_6H_5I.

5. π-$C_5H_5Fe(CO)_2I$ is found to exchange its CO-group for $P(C_6H_5)_3$ when UV-irradiated in the presence of the latter.

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