NMR STUDY OF THE PHOTOCHEMICAL REACTION OF $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ WITH P, As, Sb, S AND N DONOR LIGANDS
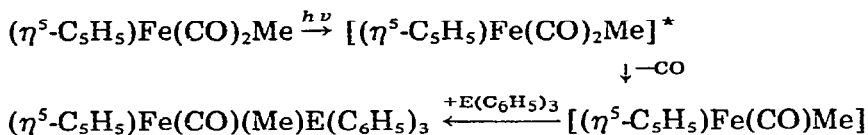
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Summary

The photochemical reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with $E(C_6H_5)_3$ (E = P, As, Sb) has been studied quantitatively in situ by NMR spectroscopy and the rate of reaction, as monitored by $\eta^5\text{-}C_5H_5$ and Me resonances, determined as a function of ligand, ligand concentration, solvent, wavelength and likely competing reactions. The product at temperatures above 27°C was found to be $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)E(C_6H_5)_3$ in all cases and rate plots showed that the rate-determining step did not involve the ligand $E(C_6H_5)_3$ and also that an acetyl complex was not involved as an intermediate. The photoreaction may be considered as:

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]^*$

$\downarrow -CO$

$(\eta^5\text{-}C_5H_5)Fe(CO)(Me)E(C_6H_5)_3 \xleftarrow{+E(C_6H_5)_3} [(\eta^5\text{-}C_5H_5)Fe(CO)Me]$

Qualitative NMR studies showed that C_5H_5N, $(C_2H_5)_2S$, and *o*-phenylenebis(dimethylarsine) gave products of the type $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)L$ in photochemical reactions.

Introduction
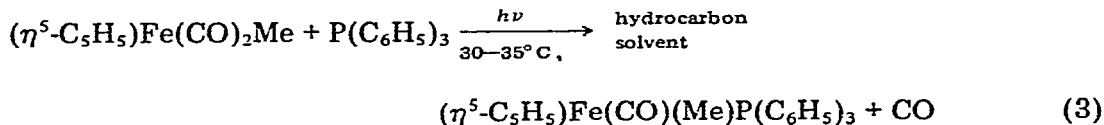
Thermal reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = alkyl, aryl) with ligands (L) have been extensively studied in recent years [1]. At lower temperatures a carbonyl insertion product is formed (eq. 1) which, at higher temperatures and especially in polar solvents, decarbonylates (eq. 2).

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R + L \xrightarrow[\text{MeCN}]{60°C} (\eta^5\text{-}C_5H_5)Fe(CO)(COR)L \qquad (1)$$

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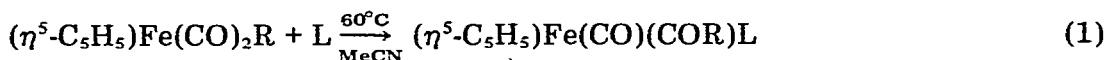
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$$(\eta^5\text{-}C_5H_5)Fe(CO)(COR)L \xrightarrow[\text{MeCN}]{80-85\,^\circ C} (\eta^5\text{-}C_5H_5)Fe(CO)(R)L + CO \qquad (2)$$

The photochemical reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with $P(C_6H_5)_3$ has been found to yield the alkyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)P(C_6H_5)_3$ directly (eq. 3) with no intermediate formation of an acetyl [2].

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + P(C_6H_5)_3 \xrightarrow[30-35^\circ C,]{h\nu} \begin{array}{l}\text{hydrocarbon}\\\text{solvent}\end{array}$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(Me)P(C_6H_5)_3 + CO \qquad (3)$$

However at elevated temperatures an acetyl is formed in the photochemical reaction [3] but this is thought [2] to occur via a competing thermal process (eq. 4).

$$(\eta^5\text{-}C_5H_5)Fe(CO)(Me)P(C_6H_5)_3 + CO \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3 \qquad (4)$$
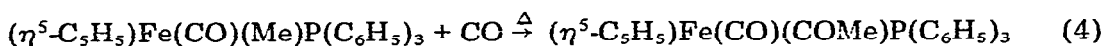
Many transition metal compounds react with a wide range of L, e.g. phosphites, phosphines, arsines, stibines, organic sulphides, organic amines, iodide and CO, to yield the acyl complex as in eq. 1. Other compounds, notably $(\eta^5\text{-}C_5H_5)Mo(CO)_3R$ [4] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ [5] display a marked selectivity towards L and phosphines, which are good nucleophiles, are the only generally successful ligand. We demonstrated recently that $As(C_6H_5)_3$ could react with $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ under carefully controlled temperature conditions [6] and with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ under mild photolysis [7] to yield $M(COCH_3)As(C_6H_5)_3$ complexes, contrary to previous reports. In the Fe case the result was surprising because an alkyl complex was expected cf. eq. 3. We report here a detailed in situ NMR study of the photochemical reaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and ligands $E(C_6H_5)_3$ (E = P, As, Sb) and an investigation of the reactions with organic sulphides and organic amines.

Results

The effects of wavelength of irradiation, intensity of light, solvent, ligand and ligand concentration on the rate of the photochemical reactions of $(\eta^5\text{-}C_5H_5)Fe$-

TABLE 1

NMR DATA (τ Scale, ppm) FOR $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)L$ COMPLEXES

L	$\eta^5\text{-}C_5H_5$ (Solvent CD_3CN)	Me	$\eta^5\text{-}C_5H_5$ (Solvent C_6H_5CN)	Me	$\eta^5\text{-}C_5H_5$ (Solvent C_6H_6)	Me
CO	5.17	9.88	5.36	9.83	5.90	9.65
$P(C_6H_5)_3$	5.75	10.10 [a]	5.80	10.02 [a]	5.82	9.65 [a]
$As(C_6H_5)_3$	5.64	10.15	5.66	9.92	5.77	9.59
$Sb(C_6H_5)_3$	5.48	10.19	5.51	9.94	5.67	9.62
$S(C_2H_5)_3$	5.64	[b]	—	—	—	—
C_5H_5N	5.63	9.73	—	—	—	—
Diars [c]	5.76	10.18				

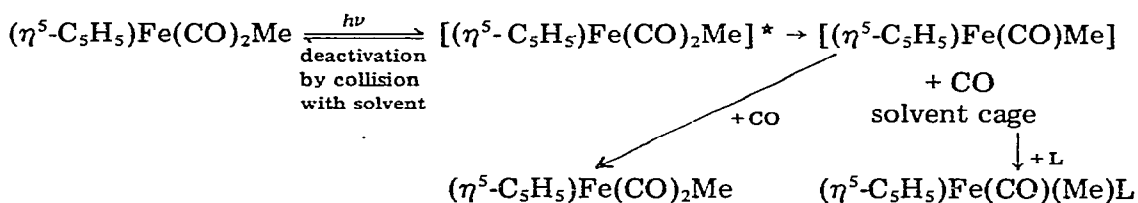[a] Doublet, J(PH) 6 Hz. [b] Partial reaction, signal obscured. [c] Diars (o-phenylenebis(dimethylarsine)) acting as a monodentate ligand because product showed terminal CO ligand (ν(C≡O) 1900 cm^{-1})

$(CO)_2Me$ with $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ were studied by following the course of each reaction via the NMR signals of the reactants and products. The NMR method was used in preference to the more usual infrared method [4,8] because the terminal CO-stretching bands of the compounds concerned were found to overlap, which precluded a detailed study. NMR gave a much clearer picture of exactly which compounds were being formed (Table 1) and integration of signals, particularly for the $(\eta^5\text{-}C_5H_5)$ resonances was used as a measure of the concentration of reactants and products during the reactions. A similar NMR method was used to study the decarbonylation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2$-$(COMe)L$ (L = tertiary phosphine) complexes [9]. The factors affecting the rate of reaction were evaluated from plots of $\ln[a/(a-x)]$ versus time, where a = concentration of starting complex (usually $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$) at $t = 0$ and $(a-x)$ = concentration of that complex at some later time t, and also $\ln x$ versus time, where x = concentration of product when only one product was formed.

Discussion

Linear plots (e.g. Fig. 1) of $\ln(a/(a-x))$ versus time (slope expressed as a rate constant, Table 2) were obtained in all three solvents for all excess ligand concentrations even down to quite small excess, e.g. $Sb(C_6H_5)_3/(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ of 1.31/1 in C_6H_5CN. This implied that the rate-determining step in the photoreaction did not involve the ligand L (eq. 4). The rate constant (Table 2) was found to be dependent on the substituting ligand and on ligand concentration with ligands in the order of decreasing nucleophilicity, $P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3$. This result is similar to that observed for the thermal insertion reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with ligands [8]. For the photochemical reaction to proceed to the alkyl via the acetyl, the photochemical decarbonylation of $(\eta^5\text{-}C_5H_5)$-$Fe(CO)(COMe)E(C_6H_5)_3$ must be fast but this is not the case for E = P. The observation may be explained by Scheme 1. An alternative to nucleophilicity to explain

SCHEME 1

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me \underset{\substack{\text{deactivation}\\\text{by collision}\\\text{with solvent}}}{\overset{h\nu}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]^* \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)Me]$$

$$+ CO$$
$$\text{solvent cage}$$

$$+CO$$

$$\downarrow +L$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me \qquad (\eta^5\text{-}C_5H_5)Fe(CO)(Me)L$$

the order P > As > Sb is the rate of diffusion of the ligand which is related to bulkiness, an explanation which finds support from the fact that reactions went slowest in the most viscous solvent C_6H_5CN.

The electronic spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and the likely reaction products for $P(C_6H_5)_3$, $(\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)P$-$(C_6H_5)_3$, all showed intense charge transfer absorptions in the 215—350 nm region with pronounced weaker absorption at 344, 330 and 338 nm, respectively. Photoreactions in the quartz ($\lambda > 200$ nm) and ordinary ($\lambda > 300$ nm) NMR tubes gave the same product $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)E(C_6H_5)_3$ with similar values of k for each ligand (Table 2) which indicates that the photoreactions for both
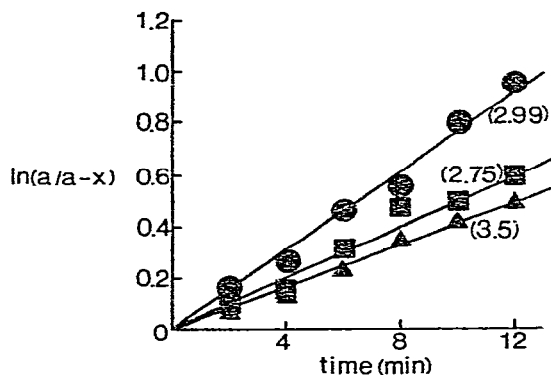
Fig. 1. Plot of $\ln(a/(a-x))$ versus time for the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with L (● = $P(C_6H_5)_3$, ■ = $As(C_6H_5)_3$, ▲ = $Sb(C_6H_5)_3$) in CD_3CN at 30°C. Figures in parentheses refer to the excess ligand concentration, i.e. 2.99 corresponds to 2.99 times the theoretical amount of $P(C_6H_5)_3$ necessary.
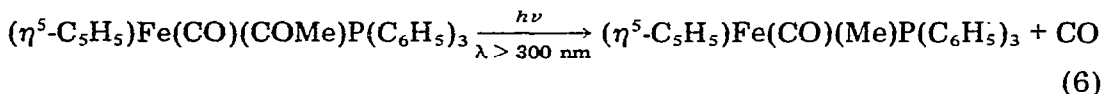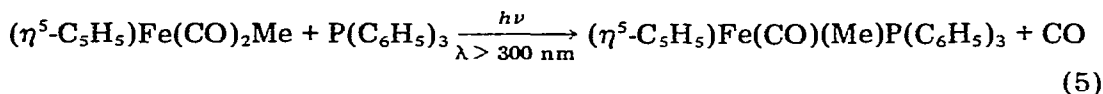
irradiating wavelengths involve the breaking of a metal—terminal CO bond. This is consistent with the study of the photochemical decarbonylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(^{13}COMe)$ where the ^{13}C label was retained entirely in the product [10]. As would be expected, the rate of reaction decreased with decreasing light intensity (increasing distance in Table 2) with no change in the product.

The study of the photoreaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ (eq. 5) versus decarbonylation of $(\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3$ (eq. 6) showed that reaction proceeded considerably faster than decarbonylation and furthermore that decarbonylation was unaffected by the presence of excess $P(C_6H_5)_3$.

TABLE 2

RATE CONSTANT DATA [a] FOR THE REACTION $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + L$

L	Excess [L] [b]	Solvent	Distance [c] (cm)	Wavelength (nm)	Temperature [d] (°C)	$k \times 10^4$ (sec^{-1})
$P(C_6H_5)_3$	2.99	CD_3CN	3	>300	27	12.6
$As(C_6H_5)_3$	2.76	CD_3CN	3	>300	27	8.2
$Sb(C_6H_5)_3$	3.50	CD_3CN	3	>300	27	6.8
$P(C_6H_5)_3$	6.15	C_6H_5CN	3	>300	27	9.6
$As(C_6H_5)_3$	6.50	C_6H_5CN	3	>300	27	8.3
$Sb(C_6H_5)_3$	6.50	C_6H_5CN	3	>300	27	7.4
$P(C_6H_5)_3$	7.98	C_6H_6	3	>300	30	11.8
$As(C_6H_5)_3$	7.35	C_6H_6	3	>300	30	9.8
$Sb(C_6H_5)_3$	8.20	C_6H_6	3	>300	30	6.1
$P(C_6H_5)_3$	2.23	CD_3CN	3	>200	27	12.5
$As(C_6H_5)_3$	1.66	CD_3CN	3	>200	27	9.1
$Sb(C_6H_5)_3$	1.64	CD_3CN	3	>200	27	5.9
$As(C_6H_5)_3$	standard solution	CD_3CN	3	>300	27	3.8
$As(C_6H_5)_3$	standard solution	CD_3CN	6	>300	27	2.3
$As(C_6H_5)_3$	standard solution	CD_3CN	8.8	>300	27	1.3

[a] Slope of $\ln(a/(a-x))$ versus time plots expressed as $k \times 10^4$ sec^{-1}. [b] The number of times the theoretical number of moles of L which were used. [c] Distance of the NMR tubes from the lamp. [d] Ambient laboratory temperature.

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + P(C_6H_5)_3 \xrightarrow[\lambda > 300 \text{ nm}]{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(Me)P(C_6H_5)_3 + CO$$

$$(5)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3 \xrightarrow[\lambda > 300 \text{ nm}]{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(Me)P(C_6H_5)_3 + CO$$

$$(6)$$

The effect of temperature was not studied in detail. It is worth noting that the reactions with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ which resulted in the formation of significant amounts of acetyl were carried out at 20°C (winter ambient temperature) [7] whereas the present work at 30°C (summer ambient temperature) gave mainly the alkyl compound with very little acetyl. It would appear that the extra energy available in photolysis reactions at higher temperatures is sufficient to eject the labilised CO from the solvent cage. At lower temperature, CO remaining in the solvent cage [11] might promote the secondary formation of the acetyl especially if high dilutions were used.

The possible reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with other ligands was investigated by irradiating solutions in CD_3CN in ordinary NMR tubes. A photoreaction occurred for C_5H_5N, $(C_2H_5)_2S$ and o-phenylenebis(dimethylarsine) (Table 1), although the reactions with C_5H_5N and $(C_2H_5)_2S$ were very far from complete. It is interesting to note that the bidentate arsenic ligand did not replace both terminal CO groups but acted as a monodentate ligand as shown by infrared spectroscopy.

Conclusion

The major and in many cases the only product in the photoreaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and ligand L at temperatures at or above 27°C is the substitution product $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)L$ with no involvement of an acetyl complex as an intermediate. Acetyls can be formed under conditions of lower temperature, low excess ligand concentration and with dilute solutions probably via a competing photochemical process rather than a competing thermal process, as has been suggested by other workers [2,3].

Experimental

All operations were carried out under an atmosphere of "white spot" grade nitrogen (B.O.C. Ltd). Acetonitrile (A.R.), benzonitrile (A.R.), benzene (A.R.) and deuterioacetonitrile (99% D) were purchased from the Aldrich Chemical Company Limited and used without further purification. Standard literature methods were used to prepare $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ [12], $(\eta^5\text{-}C_5H_5)Fe(CO)-(COMe)PPh_3$ [5] and $(\eta^5\text{-}C_5H_5)Fe(CO)(Me)PPh_3$ [2]. Photolysis reactions used a Philips HPK-125 W medium pressure Hg arc lamp. Infrared spectra were recorded on a Unicam SP 200 spectrometer and were calibrated with a polystyrene reference. Electronic spectra were recorded on a Unicam SP800 spectrometer. NMR spectra were obtained on a Perkin—Elmer R12 spectrometer (probe temperature 35°C). Examples of procedures utilised are given below.

Kinetic studies of the photochemical reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$

(a) Effect of ligand and ligand concentration. The reactions were carried out in ordinary NMR tubes ($\lambda > 300$ nm) placed at a distance of 3 cm from the light source. Solutions were prepared by weighing the complex and the ligand directly into the NMR tube and then adding a known amount of solvent (by syringe) sufficient to dissolve both of the reactants. (This procedure was considered preferential to preparing standard solutions of the reactants and then using varying amounts of these solutions because solutions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ decomposed slowly, giving paramagnetic species, even under a nitrogen atmosphere). Nitrogen was blown into the tube and the tube stoppered. Irradiation was carried out on several solutions simultaneously so as to minimize variations in lamp intensity and ambient laboratory temperature. The effect of ligand on the rate of reaction was observed by preparing three solutions, one containing each ligand and then irradiating the tubes simultaneously. The effect of ligand concentration was similarly observed by preparing three solutions containing the same ligand but different excess ligand concentrations (1.5 to 8 times more than the theoretical amount necessary for one mole of Fe compound reacting with one mole of ligand) and then irradiating the tubes simultaneously. Initial rates of reaction were measured by recording the cyclopentadienyl signals of the reactant and product(s) every two minutes for a total irradiation time of 15 minutes. The cyclopentadienyl signals in all instances were sufficiently far apart to give reasonably accurate integrations (Table 1) whereas the methyl signals were sometimes very close so that accurate integration was impossible. In general the total integral of reactant and product(s) remained constant over the 15 minute period of irradiation.

(b) Effect of solvent. Reactions were carried out in C_6H_6, C_6H_5CN and CH_3CN, varying L and the concentration of L. C_6H_6 and C_6H_5CN did not obscure the cyclopentadienyl and methyl resonances of reactants or product(s). However, integration was sometimes difficult because of the closeness of the solvent resonances to the cyclopentadienyl resonance. CD_3CN was used for obvious reasons in preference to CH_3CN.

(c) Light intensity. For one reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with $As(C_6H_5)_3$ in CD_3CN the effect of intensity was observed by placing the NMR tubes at varying distances from the source.

(d) Wavelength. Ordinary NMR tubes only transmitted light above 300 nm and in order to study the effect of shorter wavelength radiation three quartz NMR tubes were made and reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with the three ligands in CD_3CN were followed as outlined above and also the reaction with $P(C_6H_5)_3$ in C_6H_6.

Relative kinetics of photochemical reactions

The reactions (eqns. 5 and 6 in CD_3CN were compared under as near as possible identical conditions by preparing sets of three tubes, e.g.:

tube 1: 10.9 mg $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ + 42.5 mg $P(C_6H_5)_3$, i.e. 2.86 time the theoretical amount;

tube 2: 9.0 mg $(\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3$ + 14.3 mg $P(C_6H_5)_3$, i.e. corre-

sponds to 3.75 times the amount of $P(C_6H_5)_3$ required if the reaction were to follow Equation (5);

tube 3: 10.1 mg $(\eta^5\text{-}C_5H_5)Fe(CO)(COMe)P(C_6H_5)_3$, and adding 0.5 ml of CD_3CN to each. The tubes were irradiated simultaneously at the same distance from the light source. The NMR tubes were calibrated for their light transmitting properties by observing the reactions of the same standard solution of $(\eta^5\text{-}C_5H_5)Fe\text{-}(CO)_2Me$ and $P(C_6H_5)_3$ in CD_3CN in each tube and the tubes irradiated simultaneously.

Acknowledgement

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