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THESIS

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by

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IRON CARBONYL COMPLEXES OF SCHIFF
BASES AND AZO COMPOUNDS

SUMMARY

Schiff bases of aromatic aldehydes and ketones react with diiron enneacarbonyl at room temperature giving complexes with the molecular formula (base) $Fe_2(CO)_6$. Azines and hydrazones afford analogous complexes. Schiff bases give low yields of the same complexes when irradiated with iron pentacarbonyl, whereas azines do not react under these conditions. Azobenzene reacts with iron pentacarbonyl when irradiated to give a metal carbonyl complex corresponding to the formula '(azobenzene)$Fe_2(CO)_6$', which in fact is a derivative of ortho-semidine; in addition to this type, substituted azobenzenes also give products of the type (azobenzene)$_2$Fe$(CO)_2$. Reaction of azotoluene with diiron enneacarbonyl at room temperature give yet another type of complex in extremely low yield. The mass spectral and chemical degradation and probable structures of these complexes are discussed.

Diphenyldiazomethane reacts with iron pentacarbonyl when irradiated giving two different types of complexes; its reactio with triiron dodecacarbonyl gives predominantly one of these. 4,4'-Ditolyldiazomethane affords similar complexes, but phenyldiazomethane and phenylbenzoyldiazomethane give only unstable products in low yields. The most notable feature of this work is that diphenylketene, an irradiation product of

phenylbenzoyldiazomethane reacts smoothly with iron pentacarbonyl when irradiated to give complex in fairly high yield. Based on analytical, mass spectral and chemical degradation work, possible structures are proposed for these complexes. Diphenyldiazomethane does not react to give any complexes when irradiated with nickel tetracarbonyl, methylcyclopentadienylmanganese tricarbonyl and chromium hexacarbonyl.

Tetramethyl-2-tetrazene reacts with iron pentacarbonyl when irradiated giving a complex in low yield; its reaction with diiron enneacarbonyl at room temperature gives an unstable liquid complex. Diazofluorine affords two complexes in very low yields, on treatment with diiron enneacarbonyl and a differe complex when irradiated with iron pentacarbonyl; the latter compound shows both bridging and terminal metal carbonyl absorptions in the infrared spectrum. Diazocyclopentadiene gives an unstable liquid complex when irradiated with iron pentacarbonyl. No complexes are formed from ethyl azodicarboxylate and iron pentacarbonyl or diiron enneacarbonyl. In view of the instability and low yields of these complexes, it has not been possible to carry out any chemical work on them. Attempts to form complexes from fluorene, fluorenone or tetraphenylethylene and iron pentacarbonyl by irradiation are not successful.

Some reactions between the complex obtained from acetylen and the iron tetracarbonyl anion and the following reagents are carried out in order to study the chemistry of this rather interesting compound. Its reaction with dichlorophenylphosphine does not give any phosphole. When irradiated, it yields an unstable complex. In order to see whether it is possible to replace one or more carbonyl groups by diphenylcarbene it is irradiated with diphenyldiazomethane. No such reaction occurs; instead two nitrogen containing complexes are obtained. Its reaction with phenylacetylene gives a metal complex in very low yield. Although the study of these compounds is incomplete some data are presented on them.

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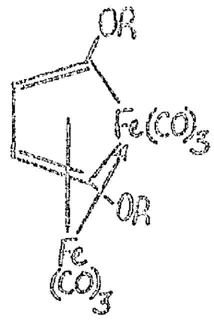
INTRODUCTION

COMPLEXES FROM ACETYLENE AND IRON CARBONYLS

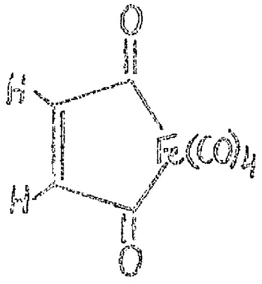
Reppe and Vetter[1] reported in 1953 that the reaction of acetylene with iron pentacarbonyl in aqueous alcohol under pressure produced, in addition to ethyl acrylate and hydroquinone, a stable organoiron compound $FeC_{11}H_7O_6$ (I). The latter was decomposed readily by hot water or dilute acids, giving hydroquinone and a new complex $FeC_7H_4O_3$ (II) which, in turn, could be oxidised to $FeC_8H_4O_4$ (III). Another complex $Fe_2C_{10}H_4O_8$ (IV; R = H) was obtaine from the reaction of acetylene with an aqueous alkaline solution of iron carbonyl hydride. No structures were postulated for these complexes.

The reaction of acetylene with an alkaline solution of iron carbonyl hydride to give complex (IV; R = H) was studied by several groups.[2,3,4] It was shown[2,3] that the reactive species was $[HFe(CO)_4]^-$. The complex contains two acidic hydroxyl groups which can be benzoylated, methylated[3] or acetylated[4], and a chain of four carbon atoms.[4] Several structures were proposed for this complex,[2,3,4,5] but the problem was not solved until x-ray data became available for the analogous complex obtained from 2-butyne[6,] Based on this, the complex $Fe_2C_{10}H_4O_8$ (IV; R = H) is represented as below:



(IV)

The complex (IV; R = H) can be oxidised with ferric chloride to (V) which undergoes a normal Diels-Alder reaction with cyclopentadiene to give (VI), thus showing that the ethylenic linkage in (V) is not bonded to the metal[8]. The complex (IV; R = CH_3) reacts with sulphur dioxide under irradiation to give (VII; R = CH_3)[9].



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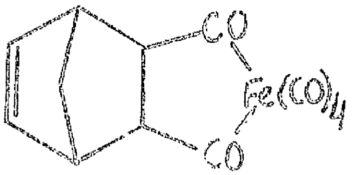

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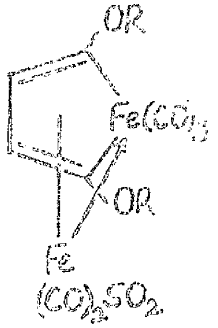
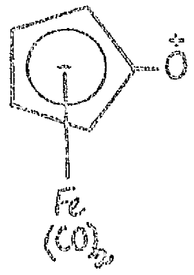


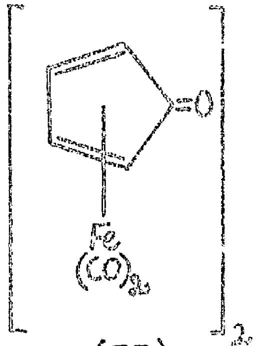
(VII)

The mechanism of formation of the complex (IV; R = H) is obscure; it has been suggested[10] that $Fe_2(CO)_8^{2-}$ rather than $HFe(CO)_4^-$ is the reactive species.

The complexes $FeC_{11}H_7O_5$ (I), $FeC_7H_4O_5$ (II) and $FeC_8H_4O_4$ (III) first reported by Reppe and Vetter[1] were investigated again by Wilkinson[11] and Hübel[12] and their co-workers. The complex $FeC_8H_4O_4$ (III) was shown to be cyclopentadienoneiron tricarbonyl by both groups of workers.[11,12] The complex $FeC_7H_4O_3$ (II) was formulated as cyclopentadienoneiron dicarbonyl (IIa) by Wilkinson and co-workers[11] on the basis of its n.m.r. spectrum, but has been shown to be a dimer, $2FeC_7H_4O_3$ (II), by Hübel and co-workers.[12] Molecular weight determinations vary in different solvents,[11,12,13] Both complexes (II and III) on treatment with triphenylphosphine give (VIII); also (II) and (III) can be interconverted[13] by carbonylation and oxidation respectively.



(IIa)



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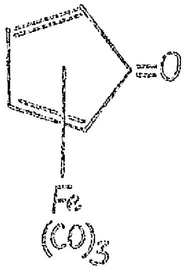

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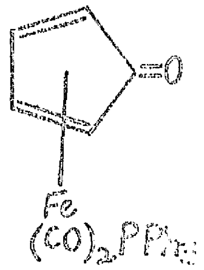
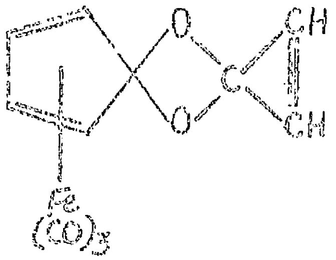
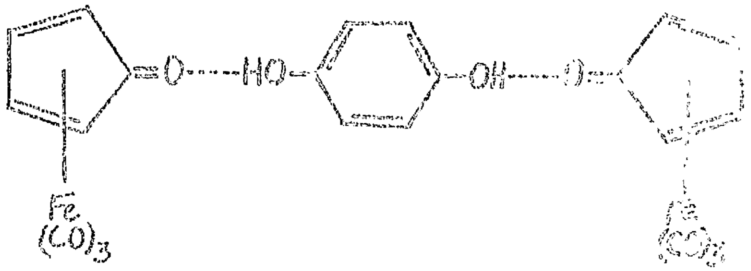


(VIII)

The complex $FeC_{11}H_7O_5$ (I) has been shown to be identical with a 2:1 adduct of cyclopentadienoneiron tricarbonyl with hydroquinone,[12,13] and the structure (Ia) suggested by Wilkinson *et al.*[11] on the basis of its n.m.r spectrum can be safely rejected



(Ia)



(I)

The reaction of acetylene with triiron dodecacarbonyl or diiron enneacarbonyl gives more complicated products than with iron pentacarbonyl.[14,15] Twelve complexes are reported to have been formed. In addition to the three complexes reported by Reppe and Vetter,[1] the following products are obtained.

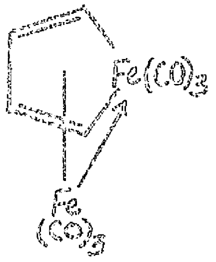
(a) Complex (IX), also formed from thiophene and iron carbonyls.[16]

(b) Two isomeric complexes of the formula $(C_2H_2)_3Fe_2(CO)_6$, one of which was originally given the structure (Xa)[17], but has since been shown to be (X)[15,18] and the other originally formulated as (XIa)[15] but now known to be (XI).[18]

(c) Troponeiron tricarbonyl (XII), identical with the product obtained from tropone and triiron dodecacarbonyl.

(d) The complex (V) obtained in a different reaction by Whiting *et al.*[8]

(e) The complexes of molecular formulas $(C_2H_2)_3Fe_2(CO)_6$, $(C_2H_2)_2Fe_3(CO)_8$, $(C_2H_2)_3Fe_2(CO)_7$ and $(C_2H_2)_4Fe(CO)_3$ to which structures have not been assigned.



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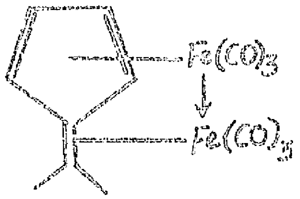
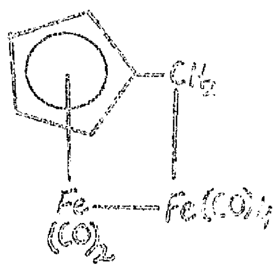
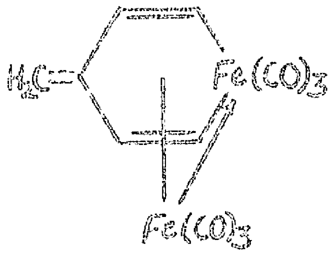


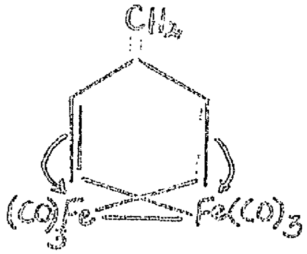
(Xa)



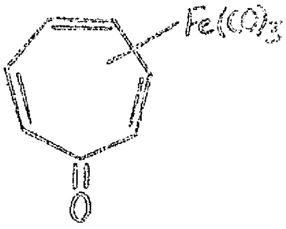
(X)



(XIa)

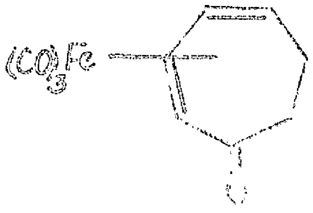


(XI)



(XII)

Hübel and co-workers[19] have further studied the complex (XII). It has been shown to form adducts with hydroquinone like the cyclopentadienone complex, but unlike the latter, it gives normal ketone derivatives. Catalytic reduction with hydrogen and platinum gives a mixture of 2,4-cycloheptadienone- and 3,5-cycloheptadienoneiron tricarbonyl complexes (XIII) and (XIV).



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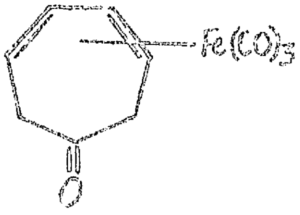


(XIV)

Several good reviews have appeared dealing with the complexes from acetylene and substituted acetylenes with iron carbonyls.[20,21,22,23]

PHOTOCHEMICAL REACTIONS ON METAL CARBONYLS AND THEIR DERIVATIVES.

Introduction

Most photochemical reactions carried out on metal carbonyls and their derivatives are substitution reactions. Some reactions involving rearrangements are also known and they are separately mentioned under miscellaneous reactions. The reaction of a metal carbonyl $M(CO)_x$ or its derivative $RM(CO)_x$ (M = metal; R = ligand) with an electron donor D can either lead to the substitution of carbonyl group by the donor D or the metal carbonyl undergoes disproportionation to form substituted metal carbonylates,[24,26] i.e.,

$$RM(CO)_x + D \longrightarrow RM(CO)_{x-1}D + CO$$

or

$$3Mn_2(CO)_{10} + 12D \longrightarrow 2[MnD_6][Mn(CO)_5]_2 + 10CO$$

The carbonyls of group VI metals undergo substitution with n-electron donors, while those of group VII and VIII metals undergo disproportionation with donors incapable of back donation. Even in the latter case, substitution occurs as the tendency of the donor to participate in back donation increases. The photochemical substitution reactions of metal carbonyls with n- and π-electron donors are discussed here.

Method of Preparation

The general method of preparation consists of irradiating a solution of the metal carbonyl and the donor in a suitable solve under a current of nitrogen. The course of the reaction can be followed by quantitative determination of carbon monoxide evolved. The choice of the solvent is important both to the yield and purity of the product. Pure product can be often obtained directly if it is sparingly soluble in the solvent and is precipitated out during irradiation, e.g. in the preparation of $C_5H_5Mn(CO)[(CH_3)_2SO]_2$[26] in diethyl ether. Generally speaking, th solubility of the products appears to be in the order monosubstituted > disubstituted > trisubstituted.[27] The disubstitution product, if formed directly, can be converted to the monosubstituted product by passing carbon monoxide into the solution of the disubstituted product, i.e.,

$$M(CO)_4D_2 \quad + \quad (CO)solv. \longrightarrow M(CO)_5D \quad + \quad D$$

With photochemically unstable donors, such as p-phenylenediamine, the best method is donor exchange, e.g.,

$$Cr(CO)_6 \quad + THF \xrightarrow{hv} Cr(CO)_5THF \xrightarrow{D} Cr(CO)_5D$$

Advantages of Photochemical over Thermal Substitution Reactions.

(i) In a photochemical reaction, the unstable intermediate acceptor $[RM(CO)_{x-1}]$ is produced at or below room temperature, on account of the high energy supplied by irradiation. This enables the isolation of relatively unstable products or the product not obtainable thermally. Thus, cyclopentadienylmanganese tricarbonyl does not react with triphenylphosphine even at 200°, but gives both mono- and disubstituted products photolytically.[28,29]

(ii) Thermal reactions usually do not permit the specific preparation of mono- and disubstitution products, whereas this seems to be possible by photochemical procedures. For example, butadieneiron tricarbonyl and triphenylphosphine react thermally to give iron dicarbonyl tris-triphenylphosphine[30] or butadieneiron dicarbonyl triphenylphosphine.[31] It has been possible to obtain both butadieneiron dicarbonyl triphenylphosphine and butadieneiron carbonyl bis-triphenylphosphine by photolytic methods.[32] Tungsten hexacarbonyl reacts with acetonitrile thermally to give tri-substituted compound,[33] whereas mono- and disubstituted products are obtained photolytically.[34] Sheline <u>et al.</u>[35] have reported the formation of mono-, di- and trisubstituted products in this photolytic reaction.

(iii) Thermal and photolytic reactions may yield quite different type of products. Triphenylphosphine and triethylphosphine react thermally with dimanganese decacarbonyl to give paramagnetic monomers, $Mn(CO)_4PR_3$ (R = Ph or Et).[36] With photochemical techniques diamagnetic dimers $[Mn(CO)_4PR_3]_2$

(R = Ph or Et) are formed.[29,37]

(iv) Attempts to exchange CO ligands with ^{14}CO in metal carbonyls at room temperature and at higher temperature were not successful.[38] The metal carbonyls on irradiation split off carbon monoxide and this adds on again in a dark reaction in the absence of donor. This observation led to a photochemical method of preparation of ^{14}CO-labelled metal carbonyls and their derivatives.[39,40]

If an arene metal tricarbonyl $ArM(CO)_3$ is dissolved in an aromatic solvent Ar^* which is labelled with ^{14}C and irradiated, exchange of the ligand Ar is photochemically induced according to the equation.

(XV)

This would suggest that not only M-CO bonds are broken but Ar-M bonds are also broken photolytically.[41,42]

The Nature of Photochemical Substitution.

The photochemical substitution proceeds by an S_N1 mechanism, whereas thermal substitution may proceed by an S_N1 or S_N2

mechanism.

If a solution of metal carbonyl or its derivative $RM(CO)_x$ is irradiated, one molecule of carbon monoxide is split off from the excited molecule $[RM(CO)_x]^*$ with the formation of an electron acceptor $[RM(CO)_{x-1}]$. The best studied carbonyls in this respect are $M(CO)_6$ $[M = Cr, Mo, W]$, and the existence of $M(CO)_5$ as an electron acceptor has been demonstrated chemically[43] as well as spectroscopically.[38,44,45,46] The infrared spectrum in the metal carbonyl region is characteristic of a square pyramid of five carbonyl groups about the metal atom.[47] The half-life of this unstable acceptor is of the order of a few minutes; it has been shown to be two minutes for $W(CO)_5$ at room temperature.[45] The substitution product is then formed by the addition of an n- or π-electron donor into the vacant orbital of the acceptor.

Reaction Mechanism and Quantum Yield.

Most of the work concerning these aspects has been done in metal hexacarbonyls, and is due to Strohmeier and co-workers.[43,48,49,5 The quantum yield Φ of the primary photochemical reaction was found in all cases to be 1.0 for time $t = 0$ at wavelength $\lambda = 3660$ and 4360 Å. and to be independent of the central metal atom and the don D. The quantum yield decreases with the increasing time of irradiation on account of the absorption of light by secondary products formed. Several dark reactions also occur simultaneously at various rates. The secondary reactions depend on the central atom, on the nature of metal carbonyl, and on the donor D. The following scheme is given for metal hexacarbonyls:

Primary photochemical reaction:

$$M(CO)_6 + h\nu \longrightarrow [M(CO)_6]^* \longrightarrow [M(CO)_5] + CO$$

Secondary Reactions:

$$[M(CO)_5] + D \longrightarrow M(CO)_5D$$

$$[M(CO)_5] + (CO)\text{solv.} \longrightarrow M(CO)_6$$

$$M(CO)_5D + (CO)\text{solv.} \longrightarrow M(CO)_6 + D$$

In the case of substitution products of metal carbonyl derivatives, the mechanism has been worked out for complexes $M(CO)_5D$.

Primary photochemical reaction:

$$\begin{tikzcd} & & {[M(CO)_4D] + CO \quad (a)} \\ M(CO)_5D \arrow[r, "h\nu"] & {[M(CO)_5D]^*} \arrow[ur] \arrow[dr] & \\ & & {[M(CO)_5] + D \quad (b)} \end{tikzcd}$$

Secondary reactions:

$$[M(CO)_4D] + D \longrightarrow M(CO)_4D_2$$

$$[M(CO)_4D] + (CO)\text{solv.} \longrightarrow M(CO)_5D$$

$$M(CO)_4D_2 + (CO)\text{solv.} \longrightarrow M(CO)_5D + D$$

Since reaction (b) does not take part in the formation of disubstitution product $M(CO)_4D_2$, the quantum yield for the preparation of disubstitution products of metal carbonyl derivativ cannot be unity, even at time $t = 0$. It was found to be 0.05 - 0.3, depending on the system examined.[49,50]

Polynuclear Compounds with Bifunctional Donors.

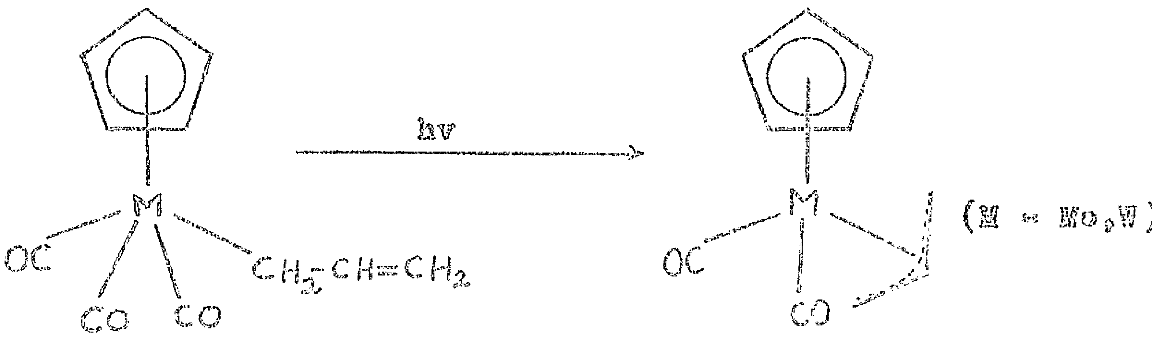
Several polynuclear substitution products have been obtained,[29,52] by the use of bifunctional donors of the type D-A-D, where D is an atom from group V or VI of the periodic table, or a residue containing double or triple bonds. The donors act as bridge ligands.

$$2RM(CO)_x + D\text{-}A\text{-}D \longrightarrow RM(CO)_{x-1}\,D\text{-}A\text{-}D(CO)_{x-1}\,MR + 2CO$$

Miscellaneous Photochemical Reactions.

Several isolated instances of photochemical reactions have been reported, for which there is no evidence as yet that they occur in other systems. The following examples are given.

(i) Conversion of a σ-bonded to a π-bonded complex.[56-58,59]



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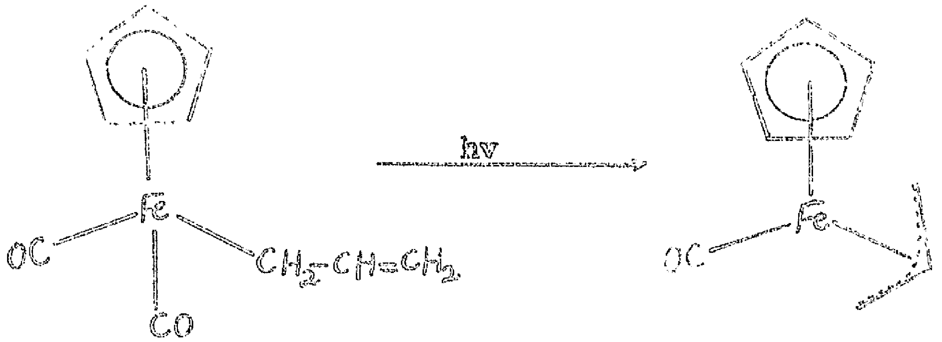

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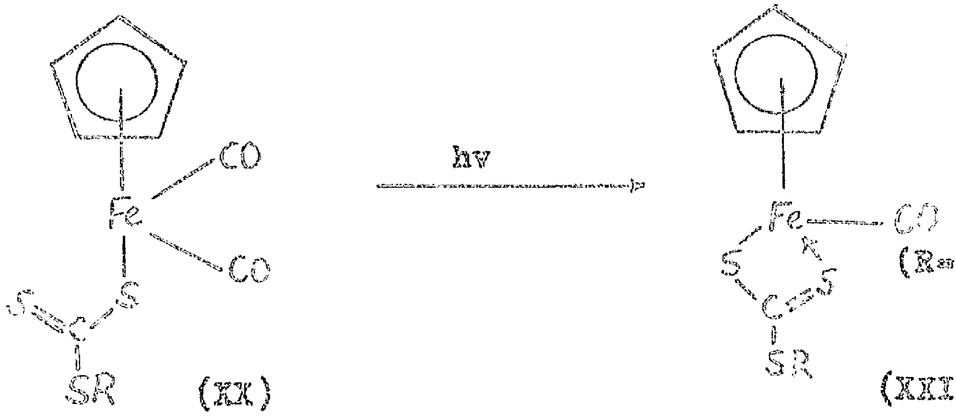
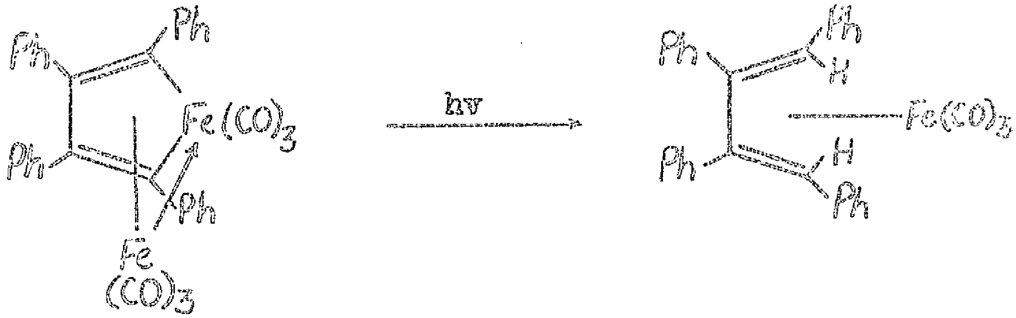


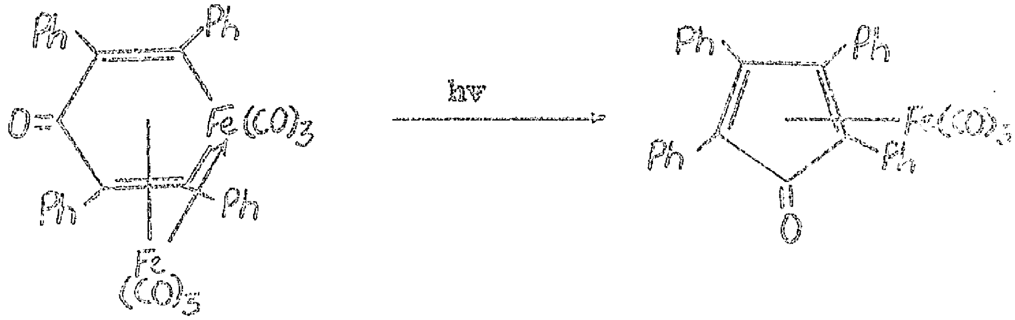
(XX) (XXI)

(R=Ph, Et or Me

(ii) Conversion of the complex (XXII) into tetraphenylbutadieneiron tricarbonyl (XXIII) and of the complex (XXIV) now thought to be of the type (XI) into tetraphenylcyclobutadienoneiron tricarbonyl (XXV).[25,60]



(XXII) (XXIII)



(XXIV) (XXV)

(iii) Disproportionation of metal carbonyls[61]

$$Fe(CO)_5 + Me_2SO \xrightarrow{h\nu} [Fe(Me_2SO)_6][Fe_4(CO)_{13}]$$

(XXVI)

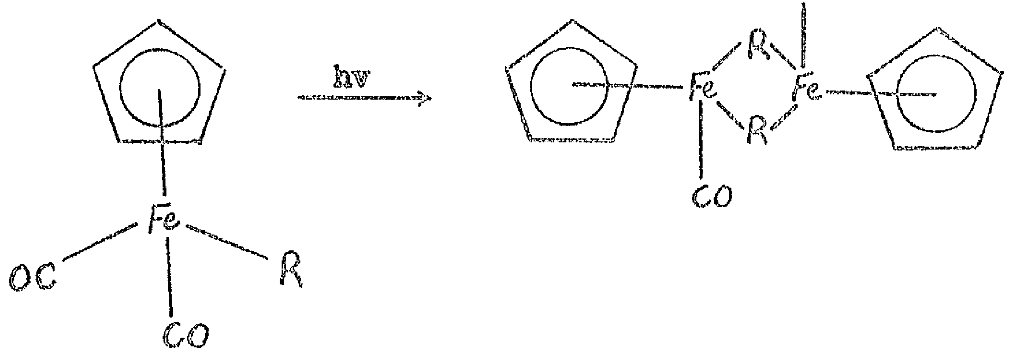
$$Fe(CO)_5 + Ph_3PO \xrightarrow{h\nu} [Fe(Ph_3PO)_2][Fe_2(CO)_8]$$

(XXVII)

$$Fe(CO)_5 + Ph_3AsO \xrightarrow{h\nu} [Fe(Ph_3AsO)_3][Fe_2(CO)_8]$$

(XXVIII)

(iv) Dimerisation of a mononuclear complex to a binuclear complex by the loss of carbon monoxide.[59,62,104]



[R=SPh; As(CF$_3$)$_2$

(XXIX)

(XXX)

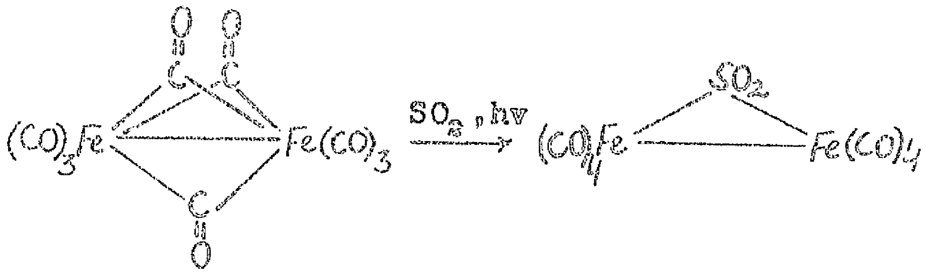
(v) Decarbonylation of acyl derivatives of cyclopentadienyl metal carbonyls into the corresponding alkyl derivatives.[63]

$$RCOFe(CO)_2C_5H_5 \xrightarrow{h\nu} RFe(CO)_2C_5H_5 \ (R=CF_3, C_2F_5, C_3F_7, CH_3, C_6H_5 \text{ and } CH_2=CH)$$

(XXXI)

(XXXII)

(vi) Reaction of sulphur dioxide with diiron enneacarbonyl gives the complex (XXXIII).[9]



(XXXIII)

Strohmeier[64] has recently reviewed the substitution reactions on metal carbonyls and their derivatives under photolytic conditions and has given an exhaustive list of the compounds described in the literature up to the end of 1963.

REACTIONS OF IRON CARBONYLS WITH NITROGEN BASES

The reaction of an alkali salt of hydroxylamine-o-sulphonic acid with aqueous alkaline tetracarbonyliron solution at 0° gives the product $Fe(CO)_4NH_3$,[66] which from benzene solution at room temperature in 5 min. gives $[Fe(NH_3)_6][Fe_3(CO)_{11}]$.[66] The reaction of $Fe(CO)_4^{2-}$ with hydroxylamine gives $[Fe(CO)_3NH]_2$.[66] Treatment of iron pentacarbonyl with liquid ammonia gives $[NH_2]_2[Fe(CO)_4]$.[67,68] Diiron enneacarbonyl and triiron dodecacarbonyl with liquid ammonia give $[NH_2]_2[Fe_2(CO)_8]$ and $[Fe(NH_3)_6][Fe_2(CO)_8]$ respectively. The formation of $[Fe(NH_3)_6][Fe_3(CO)_{11}]$ is suggested as an intermediate in the formation of $[Fe(NH_3)_6][Fe_2(CO)$ Treatment of iron pentacarbonyl with aqueous ammonia in the presence of pyridine[69] or hydroxylamine[70] also gives $[Fe(NH_3)_6][Fe_2(CO)_8]$.

Treatment of triiron dodecacarbonyl with ethylenediamine at 40° gives $[Fe(en)_3][Fe_3(CO)_{11}]$, which reacts further with ethylenediamine at 90° to give $[Fe(en)_3][Fe_2(CO)_8]$. The latter compound reacts further with ethylenediamine at 145° to give $[Fe(en)_3][Fe(CO)_4]$.[71] The cation in $[Fe(en)_3][Fe_2(CO)_8]$ undergoes ligand exchange with ammonia yielding $[Fe(NH_3)_6][Fe_2(CO)_8]$ (en = ethylenediamine).[71]

Pyridine reacts with iron pentacarbonyl when irradiated, and with triiron dodecacarbonyl at room temperature to give

$[Fe(py)_6][Fe_4(CO)_{13}]$[72]. The latter compound on treatment with ammonia and o-phenanthroline gives $[Fe(NH_3)_6][Fe_4(CO)_{13}]$ and $[Fe(o\text{-phenanthroline})_3][Fe_4(CO)_{13}]$[72] respectively. Acidificatio of the $[Fe_4(CO)_{13}]^{2-}$ salt with hydrochloric acid gives the hydride $H_2Fe_4(CO)_{13}$ as a brown-black pyrophoric solid which gives a deep red ether solution.[72]

Iron pentacarbonyl and o-phenanthroline react when briefly heated in acetone at 65° with the formation of a blue unstable compound $Fe(CO)_5(O\text{-phen})$.[73] Treatment of iron pentacarbonyl or triiron dodecacarbonyl with o-phenanthroline in acetone, benzene, or pyridine for somewhat longer time gives $[Fe(O\text{-phen})_3][Fe_2(CO)_8]$ and in pyridine $[Fe(O\text{-phen})_3][Fe_4(CO)_{13}]$ is also formed.[73] (o-phen = o-phenanthroline).

Treatment of iron pentacarbonyl with piperidine and pyrrolidine at low temperatures gives $Fe(CO)_5$ (piperidine)$_2$ and $Fe(CO)_5$ (pyrrolidine)$_2$ respectively.[74] If the reaction between iron pentacarbonyl and piperidine is carried out in benzene at 85 or if N-formylpiperidine is heated with iron pentacarbonyl at 95° the product is $[Fe(N\text{-formylpiperidine})_6][Fe_4(CO)_{13}]$.[74] Pyrrolidine gives $[Fe(pyrrolidine)_6][Fe_4(CO)_{13}]$ when irradiated in benzene at 85° with iron pentacarbonyl. Morpholine and iron pentacarbonyl give $[Fe(N\text{-formylmorpholine})_6][Fe(CO)_4]$ or $[Fe(morpholine)_6][Fe_4(CO)_{13}]$ depending on the reaction conditions. N-formylmorpholine and iron pentacarbonyl when refluxed in benzene give $[Fe(N\text{-formylmorpholine})_6][Fe_4(CO)_{13}]$. Dimethyl- and diethylformamide similarly give $[Fe\ (HCO.R)_6][Fe_4(CO)_{13}]$ ($R = NMe_2$ or NEt_2). 2,4-Lutidine and 1,2-di(2-pyridyl)ethylene give $[Fe(2,4\text{-lutidine})_6][Fe_4(CO)_{13}]$ and $[Fe(1,2\text{-di}(2\text{-pyridyl})\text{ethylene})_3][Fe_4(CO)_{13}]$[74] respectively.

4-Picoline and iron pentacarbonyl when heated to 80° give $[Fe(4\text{-picoline})_4][Fe_2(CO)_8]$. 2-Picoline and iron pentacarbonyl when irradiated at 80° give $[Fe(2\text{-picoline})_2][Fe_2(CO)_8]$. The latter compound is also formed, though slowly, by the use of triiron dodecacarbonyl.[75] 2-Picolylamine and iron pentacarbonyl when irradiated at reflux temperature give $[Fe(2\text{-picolylamine})_2][Fe_2(CO)_8]$. Using suitable conditions of reactions, 2-amino pyridine, bis(diethyltriamine) and benzidine give respectively $[Fe(2\text{-aminopyridine})_{2-3}][Fe_2(CO)_8]$, $[Fe(bis(diethyltriamine)_2][Fe_2(CO)_8]$ and $[Fe(benzidine)][Fe(CO)_4]$ respectively.[75]

A number of other N-bases have been treated with iron carbonyls[76] and the products obtained are listed below.

Base	Iron Carbonyl	Product
C_5H_4NCHO 2-Pyridal	$Fe(CO)_5$	$[Fe(C_5H_4NCHO)_3][Fe_2(CO)_8]$
$C_5H_4NCH{=}NCH_3$ 2-Pyridal-methylimine	$Fe(CO)_5$	$[Fe(C_5H_4NCH{=}NCH_3)_3][Fe_2(CO)_8]$
$C_5H_4NCH{=}NCH_3$ 2-Pyridal-methylimine	$Fe_3(CO)_{12}$	$[Fe(C_5H_4NCH{=}NCH_3)_3][Fe_2(CO)_8]$
$C_5H_4NCH{=}NC_2H_5$ 2-Pyridal-ethylimine	$Fe(CO)_5$	$[Fe(C_5H_4NCH{=}NC_2H_5)_3][Fe_2(CO)_8]$
$C_5H_4NCH{=}NC_6H_5$ 2-Pyridal-anil	$Fe(CO)_5$	$[C_5H_4NCH{=}NC_6H_5][2Fe(CO)_5]$
$C_5H_4NCH{=}NC_6H_5$ 2-Pyridal-anil	$Fe_3(CO)_{12}$	$[Fe(C_5H_4NCH{=}NC_6H_5)_3][Fe_3(CO)_{11}]$
$C_5H_4NCH{=}NC_6H_4CH_3-p$ 2-Pyridal-p-tolylimine	$Fe_3(CO)_{12}$	$[Fe(C_5H_4NCH{=}NC_6H_4CH_3-p)_3][Fe_3(CO)_{11}]$
$o-C_6H_4(NH_2)_2$ O-Phenylenediamine	$Fe(CO)_5$	$[Fe(C_6H_4(NH_2)_2)_3][Fe_3(CO)_{11}]$
$(C_5H_4N)_2$ 2,2'-Bipyridyl	$Fe(CO)_5$	$[Fe((C_5H_4N)_2)_3][Fe_3(CO)_{11}]$
C_9H_7N Isoquinoline	$Fe(CO)_5$	$[Fe(C_9H_7N)_6][Fe_4(CO)_{13}]$
C_4H_7ON Pyrrolidone	$Fe(CO)_5$	$[Fe(C_4H_7ON)_6][Fe_4(CO)_{13}]$
$C_4H_6ONCH_3$ N-Methylpyrrolidone	$Fe(CO)_5$	$[Fe(C_4H_6ONCH_3)_4][Fe_4(CO)_{13}]$

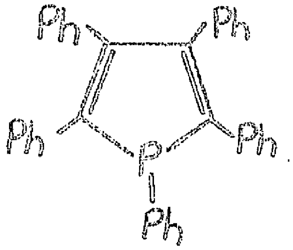
DISCUSSION

REACTIONS ON THE COMPLEX FROM ACETYLENE AND IRON TETRACARBONYL ANION

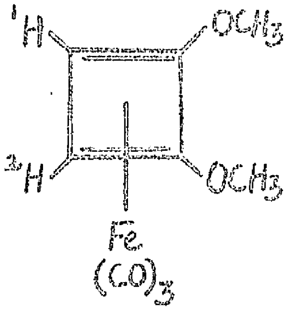
This work was started with a view to studying the chemistry of the complex (IV, R = H) obtained from acetylene and iron tetracarbonyl anion, first reported by Reppe and Vetter.[1] It was intended to carry out several types of reactions on this complex (IV; R = CH_3). Some of these involved the replacement of one or more carbonyl groups by other ligands or of the ring iron atom by hetero-atoms to obtain 2,5-disubstituted heterocyclic compounds; other reactions involved attempting to replace one or both methoxy groups by treatment with nucleophilic reagents. Also, it was decided to study the behaviour of this compound when irradiated in solution.

The reaction of the complex (IV, R = CH_3) with dichlorophenylphosphine was carried out with a hope to obtaining 2,5-dimethoxy-1-phenylphosphole. Heating the two reactants at reflux in petroleum ether (b.p. 100-120°) for 4 hr., or in diglyme at 160-180° for 1 hr., or without solvent at 130-140° for 1 hr. did not furnish any such compound. Hübel *et al.* had reported[23,77] the formation of 1,2,3,4,5-pentaphenylphosphole (XXXIV) by reacting the complex (XXII) with dichlorophenylphosphine at 140°.

Hübel *et al.*[23,60] described the formation of tetracylone and tetraphenylbutadiene iron tricarbonyl (XXIII) by irradiation of the benzene solution of the complex (XXII). No such product appeared to be formed by irradiation of benzene or ether solution of the complex (IV; R = CH_3), but its solution in methyl alcohol gave an unstable light pink coloured product, which showed metal carbonyl absorption in the infrared spectrum. Molecular weight determination gave the formula $C_9H_8FeO_5$. This compound could possibly have the structure (XXXV) assigned to it on the basis of an n.m.r. spectrum (carbon tetrachloride). It shows only two peaks, that at $5.08\,\tau$ (singlet, relative intensity 1.6, protons 1 and 2), and $6.13\,\tau$ (singlet, relative intensity 6, methoxy protons). The complex (IV, R = CH_3)



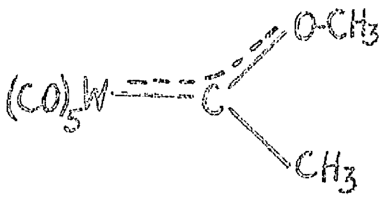
(XXXIV)



(XXXV)

reacted with phenylacetylene when heated to reflux in petroleum ether (b.p. 100-120°) to give 1,2,4-triphenylbenzene and only traces of a metal carbonyl containing compound showing two infrared active absorptions in that region. No conclusions could be drawn concerning this product.

In a further study of the complex (IV, R = CH_3), it was decided to see whether it would be possible to replace one or more carbonyl groups in the complex by a carbene. When this work was started, no examples of the replacement of a carbonyl group in a metal carbonyl compound by a carbene had been described. Later, Fischer *et al*[78] reported the first carbene complex for which the structure (XXXVI) has been suggested. In the present work, diphenyldiazomethane and the complex



(XXXVI)

(IV, R = CH_3) were irradiated in benzene, hoping that diphenylcarbene, generated under irradiation, would replace one or more carbonyl groups. Two nitrogen containing metal carbonyl complexes could be isolated, both showing metal carbonyl absorption in the infrared spectrum. One of these, with m.p. 157°, did not give a good n.m.r. spectrum though this spectrum indicated the presence of phenyl and methoxy protons. The n.m.r. spectrum (carbon tetrachloride) of the other compound, with m.p. 148°, had peaks at 2.7 τ (doublet, relative intensity 10, aromatic protons), 4.41 and 4.80 τ (singlets, relative intensities 0.6 and 0.8 respectively, olefinic protons), 6.17

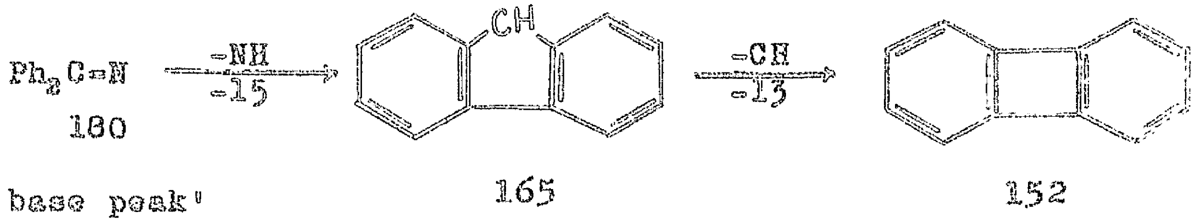
and 6.37τ (singlets, relative intensities 2.8 and 3.0 respectively, methoxy protons). Based on this, it would be tempting to assume that the original complex (IV, R = CH_3) has not undergone any fundamental change and that some nitrogen containing ligand derived from diphenyldiazomethane could have replaced one carbonyl group. It would thus appear that it might not be possible to replace a carbonyl group by a carbene under these conditions. To carry out further study at this stage on these two complexes obtained from the complex (IV, R = CH_3) was not thought very desirable, for two main reasons. One was that it could be more profitable to study the reaction of iron pentacarbonyl with diphenyldiazomethane, and if complexes were formed, they would probably be much simpler; secondly, it was difficult to obtain the complex (IV, R = CH_3) in reasonable yields.

REACTIONS OF DIAZOALKANES AND AZINES WITH IRON CARBONYLS

The decomposition of diazoalkanes by nickel carbonyl has been described by Schrauzer *et al.*[79] The products obtained suggest the presence of carbenes as intermediates. In the presence of excess nickel carbonyl, ketenes were formed. It was suggested[79] that carbonylation of carbenes occurs *via* nickel-carbene complexes. Diazonium salts also react readily with nickel carbonyl and the main products are carboxylic acids.[80,81] Intermediate formation of nickel carbonyl complexes was assumed. Iron pentacarbonyl and dicobalt octacarbonyl behaved similarly, but chromium hexacarbonyl and molybdenum hexacarbonyl were hardly effective.[80] It thus seemed that no metal carbonyl containing intermediates had actually been isolated. In view of the reaction of diphenyldiazomethane with the complex (IV, R = CH_3),[9] which had yielded two stable metal carbonyl containing compounds, it was desirable to carry out the reactions of some of the diazoalkanes with the iron carbonyls under similar conditions.

Diphenyldiazomethane and iron pentacarbonyl on irradiation in benzene did in fact afford two stable nitrogen containing metal carbonyl compounds, in addition to benzophenone azine. In order to exclude the possibility of any of these complexes being the complex of benzophenone azine, it was irradiated with iron pentacarbonyl. No such complex was isolated from this reaction. One of the complexes obtained from diphenyldiazomethane was black and the other was orange coloured. The black complex, on decomposition with lithium aluminium hydride, gave benzophenone azine and a colourless liquid which was not identified. These results seemed to indicate that benzophenone azine was one of the ligands in this complex. In view of the failure to get a complex from iron pentacarbonyl and benzophenone azine, and the isolation of the latter from the decomposition of the black complex obtained from iron pentacarbonyl and diphenyldiazomethane, it was decided to treat benzophenone azine with diiron enneacarbonyl. It was in fact possible to isolate a stable complex from benzophenone azine and diiron enneacarbonyl by refluxing them in benzene. This will be discussed later. However, this was not identical with either of the two complexes obtained from diphenyldiazomethane. The black complex referred to above did not give a good n.m.r. spectrum, but this spectrum nevertheless indicated that only phenyl protons were present. It was too involatile to obtain a mass spectrum. It was not possible to assign any structure based on analysis and the information given above. The orange complex referred to above was not degraded, although the analogous compound obtained from di-(p-tolyl) diazomethane was, and is described later. The n.m.r. spectrum (hexafluorobenzene) of the orange complex had peaks at 2.45 τ (multiplet, relative intensity 20, aromatic protons), 3.36 τ (singlet, relative intensity 0.9, proton 1 or 2) and 4.14 τ (singlet, relative intensity 0.6, proton 1 or 2) [XXXVII, R = Ph, requires the ratio 20:1:1]. The mass measurement of the orange complex gave its molecular weight as 670 and molecular formula as $C_{32}H_{22}Fe_2N_4O_6$. There was a successive loss of six carbonyl groups (a similar phenomena has been observed by other workers[22,23]) and then a large peak at 502, which corresponded to $C_{26}H_{22}Fe_2N_4$. The base peak at 180 corresponded to $Ph_2C{=}N$. The majority of the remaining fragments were derived from this and one hydrogen i.e. 181. Below 181, peaks were the same as they occur in the decomposition of benzophenone azine. Thus, the positive ions corresponding to the following mass numbers m/e) and formulae were identifiable.

$$\underset{670}{C_{32}H_{22}Fe_2N_4O_6} \xrightarrow[168]{-6CO} \underset{502}{C_{26}H_{22}Fe_2N_4} \xrightarrow{\text{various fragments}}$$



The various fragments mentioned above are derived from fragment 180 + 1H i.e. 181

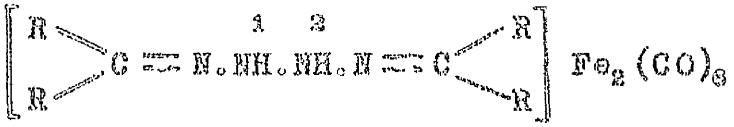
237 = 181 + Fe

293 = 181 + 2Fe

418 = 2 x 181 + Fe

(XXXVII)

From n.m.r. spectrum and mass spectrum it seems that the orange complex could be (XXXVIII. R = Ph). The analysis, however,



$$\left[\begin{matrix}R\\R\end{matrix}>C=N.\overset{1}{NH}.\overset{2}{NH}.N=C<\begin{matrix}R\\R\end{matrix}\right]Fe_2(CO)_8$$

(XXXVIII)

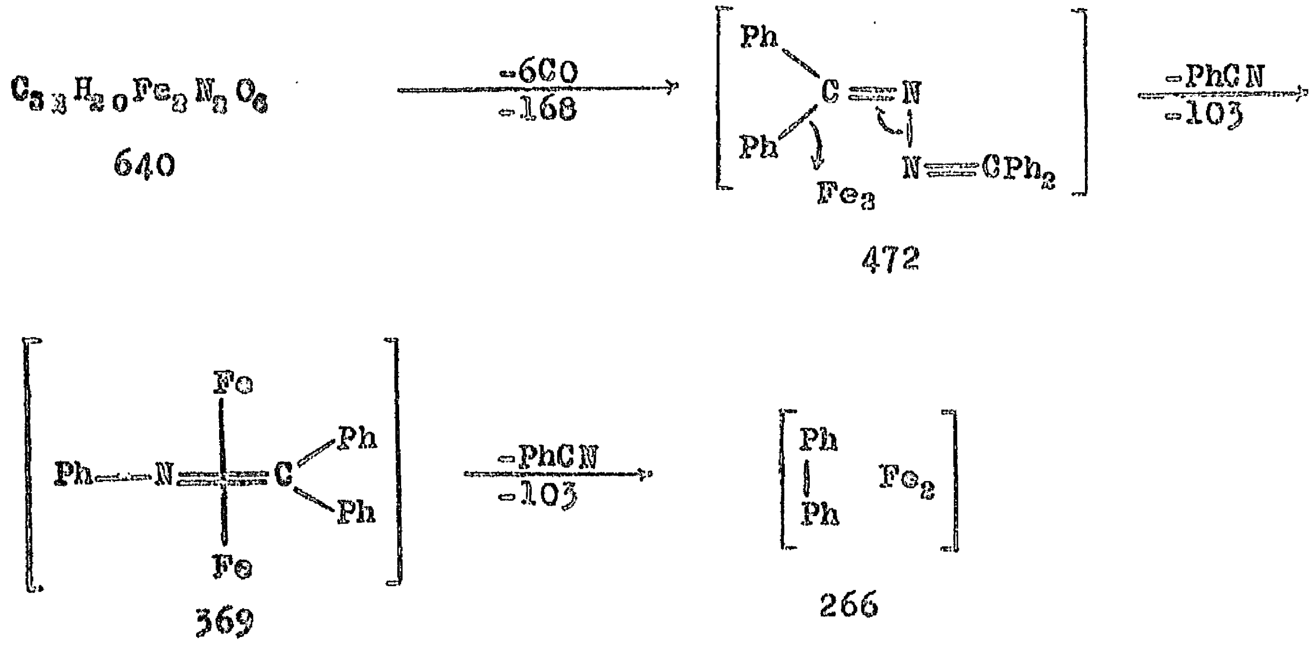
did not fit in with this formulation.

Di-(p-tolyl)diazomethane and iron pentacarbonyl when irradiated in benzene gave analogous complexes, one black and the other orange. Of many organic compounds formed in this reaction, only 4,4'-dimethylbenzophenone azine was identified. The orange complex was decomposed with lithium aluminium hydride to give a light yellow solid, m.p. 121-122°; it showed the presence of NH and CO groups in the infrared spectrum. This compound has not yet been identified. The n.m.r. spectrum (carbon tetrachloride) of the orange complex showed peaks at 3τ (multiplet, relative intensity 16.8, aromatic protons), 4.4τ (broad, relative intensity 0.7, proton 1 or 2), 5.48 τ (broad, relative intensity 1.0, proton 1 or 2) and at 7.7 τ (broad, multiplet, relative intensity 12; methyl protons). Thus, this complex could be (XXXVIII; R = $p\text{-}CH_3C_6H_4\text{-}$) . The analysis did not fit in with this formulation.

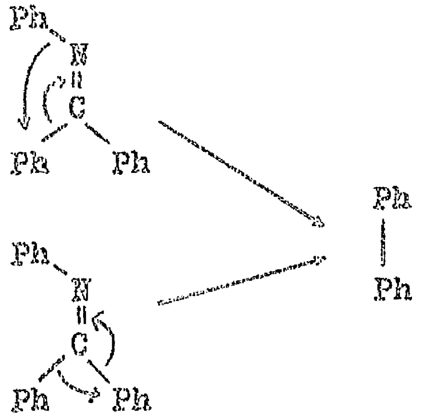
Phenyldiazomethane and iron pentacarbonyl on irradiation in benzene gave only an unstable liquid complex that showed only two infrared active absorptions in the metal carbonyl region. In order to study the behaviour of diazo compounds of this type containing some functional group, phenylbenzoyldiazomethane was irradiated with iron pentacarbonyl. No metal carbonyl complex was isolated. Reaction of this diazo compound with diiron enneacarbonyl also did not give any complex, but with triiron dodecacarbonyl a trace of an unstable complex was obtained. The only organic compound isolated in the pure form in these reactions was identified as bis-benzilketazine.

Attempts to form the complexes from diphenyldiazomethane and chromium hexacarbonyl, nickel tetracarbonyl or methylcyclopentadienylmanganese tricarbonyl under irradiation were not successful.

It has already been mentioned, in connection with the reaction of diphenyldiazomethane and iron pentacarbonyl, that benzophenone azine furnished a stable orange coloured complex on reaction with diiron enneacarbonyl. This compound analysed as (benzophenone azine) $Fe_2(CO)_6$. The mass measurement of this complex gave its molecular weight as 640 and molecular formula as $C_{32}H_{20}Fe_2N_2O_6$. The cracking pattern confirmed the presence of two iron atoms and six carbonyl groups. Thus, the positive ions corresponding to the following mass numbers (m/e) and formulae were identifiable.

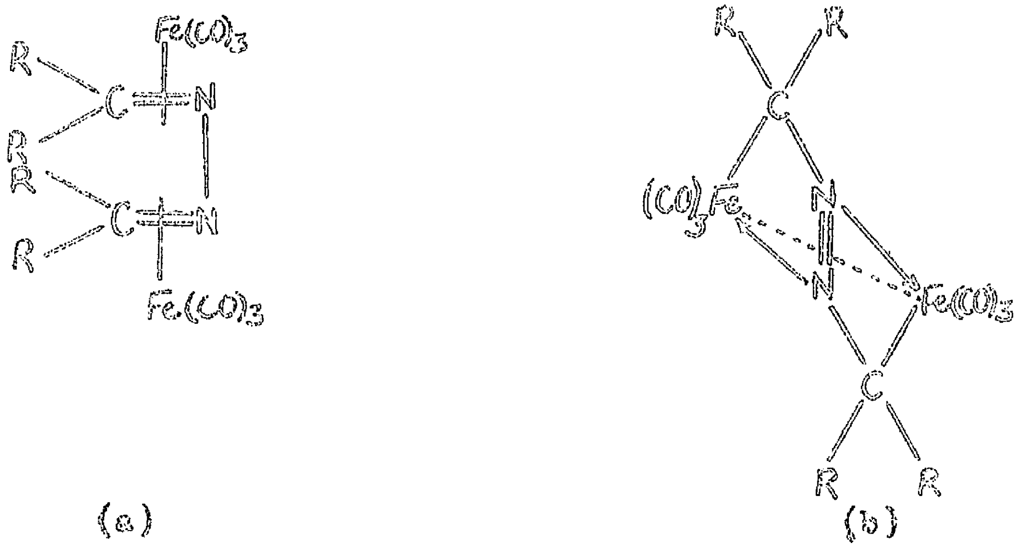


The second loss of 'PhCN' could be either as benzonitrile or phenyl isocyanide. Thus:



(XXXIX)

The cracking pattern thus seems to be consistent with the formulation (benzophenone azine) $Fe_2(CO)_6$. The detailed bonding of a diiron hexacarbonyl residue to benzophenone azine could occur in various ways, but one might give two alternative possible structures (XL; R = Ph). In the structure (XLa, R = Ph) it is assumed that four electrons of the ligand



(XL)

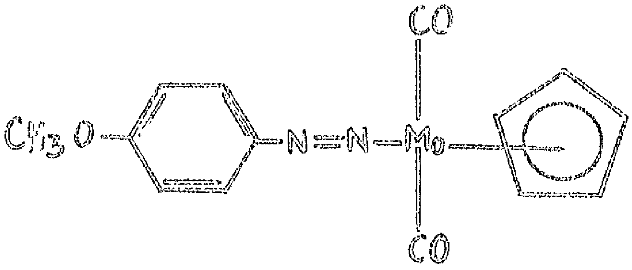
are donated to both iron tricarbonyl residues and in structure (XLb, R = Ph) an iron-iron bond is envisaged.

4,4'-Dimethylbenzophenone azine and diiron enneacarbonyl gave an analogous complex (XL, R =(p-$CH_3C_6H_4$-) accompanied by

4,4'-dimethylbenzophenone. The n.m.r. spectrum (carbon tetrachloride) of this complex showed peaks at 2.93 τ (singlet, relative intensity 3.9, aromatic protons) and 7.63 τ (singlet, relative intensity 3, methyl protons). In contrast, the n.m.r. spectrum (carbon tetrachloride) of 4,4'-dimethylbenzophenone azine showed a multiplet in the region of aromatic protons and a doublet for methyl protons. This is unexpected and probably is due to the presence of stereoisomeric forms.

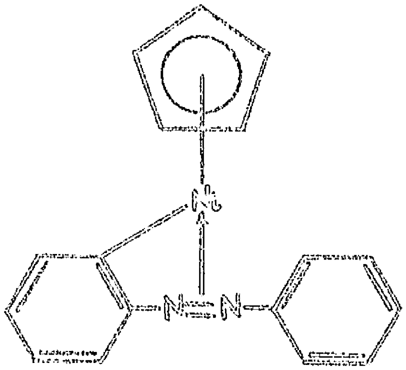
REACTIONS OF AZOBENZENE AND SUBSTITUTED AZOBENZENES WITH IRON CARBONYLS

It was of interest at this stage to try to find out whether it would be possible to form iron carbonyl complexes with azo compounds different in type from diphenyldiazomethane, e.g. with azobenzene. When this work was started no transition metal carbonyl complexes containing azobenzene or substituted azobenzenes had been reported. King *et al.*[84] have reported the formation of the complex (XLI) from p-anisyldiazonium tetrafluoroborate and cyclopentadienylmolybdenum tricarbonyl sodium.



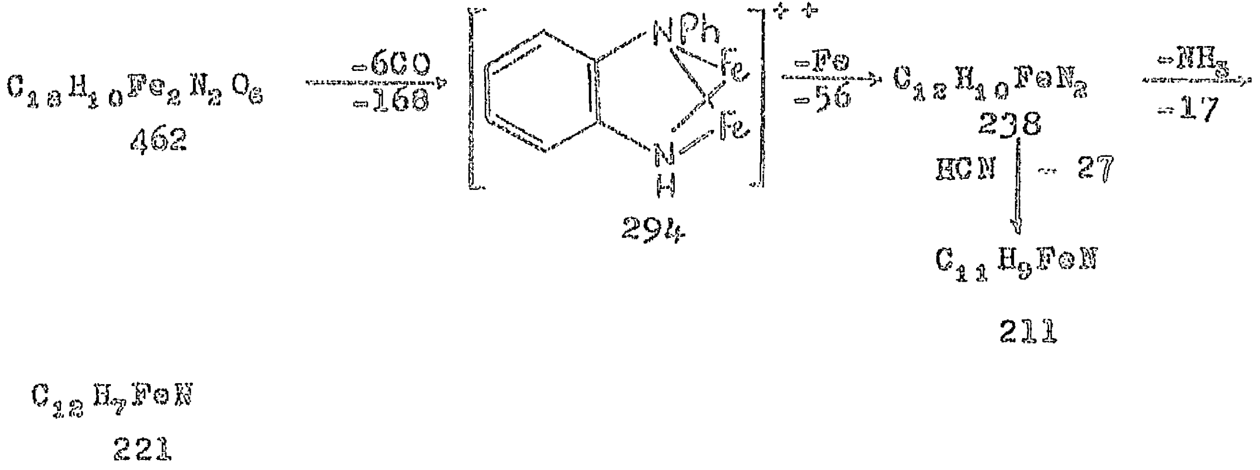
(XLI)

In this connection, azobenzene and iron pentacarbonyl were irradiated in benzene. A red brown nitrogen containing metal carbonyl compound was isolated, which analysed for (azobenzene) $Fe_2(CO)_6$. There were two main objections to this formulation. Firstly, the infrared spectrum of this complex showed absorption at 3362 cm.$^{-1}$ indicating the presence of an NH group in the molecule. Secondly, its degradation with lithium aluminium hydride gave o-aminodiphenylamine and not azobenzene. Dubeck, *et. al.*[85] reported the isolation of azobenzene from the degradation of the compound (XLII) with lithium aluminium hydride, a fact indicating that it should be possible to isolate azobenzene, if present in the complex, by



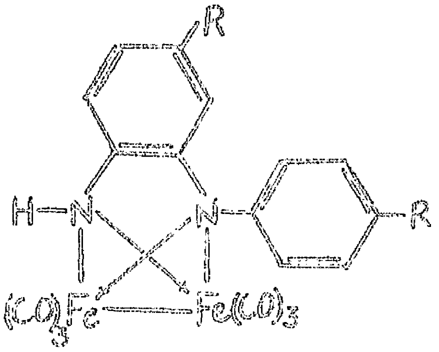
(XLII)

this reaction. It would thus seem that the skeleton of o-aminodiphenylamine is present in the complex. The results of the mass spectrum could be summarised as follows:-



(XLIII)

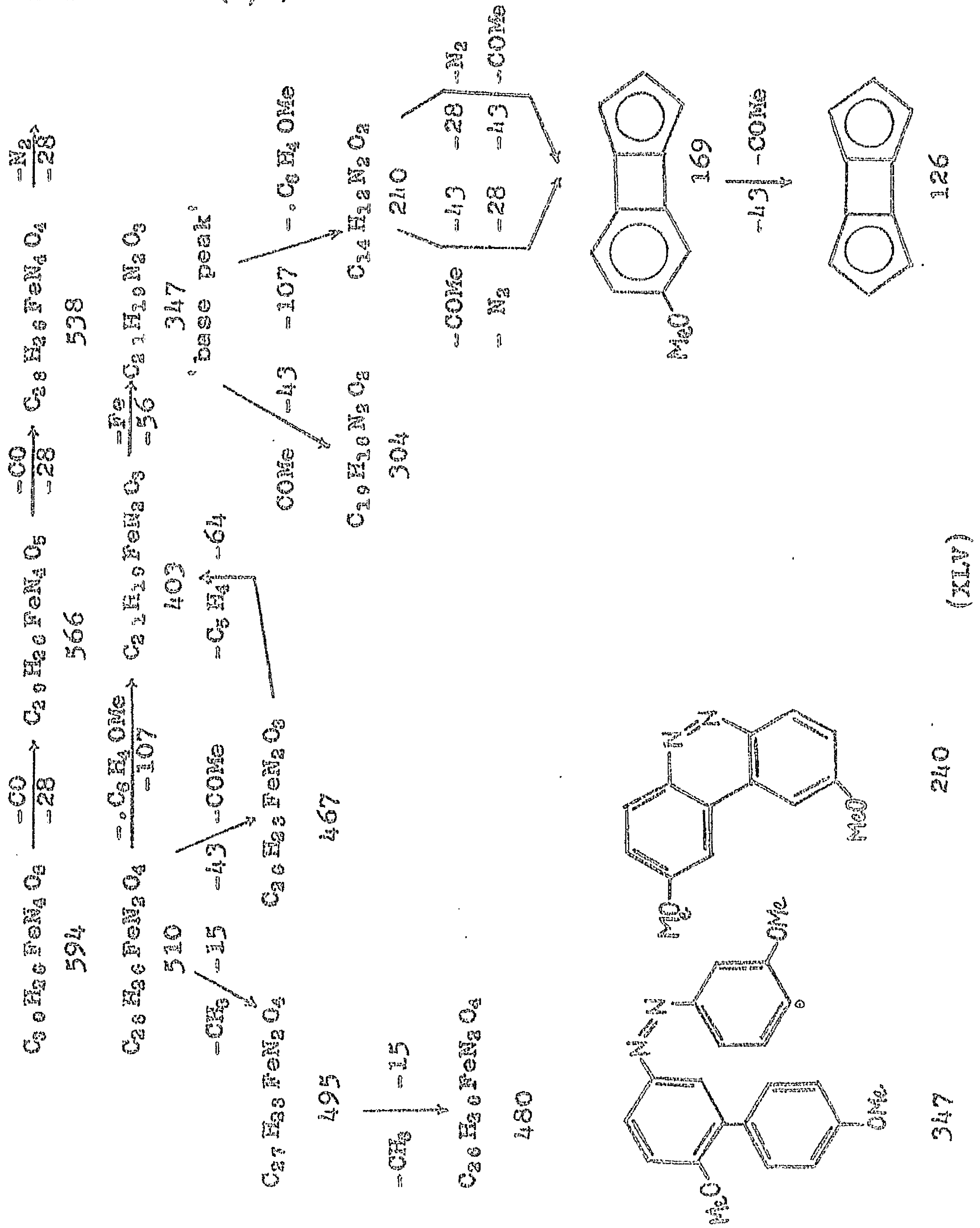
No significant 182 peak corresponded to free azobenzene. The structure of the complex obtained from azobenzene and iron pentacarbonyl could be envisaged as in (XLIV, R = H).



(XLIV)

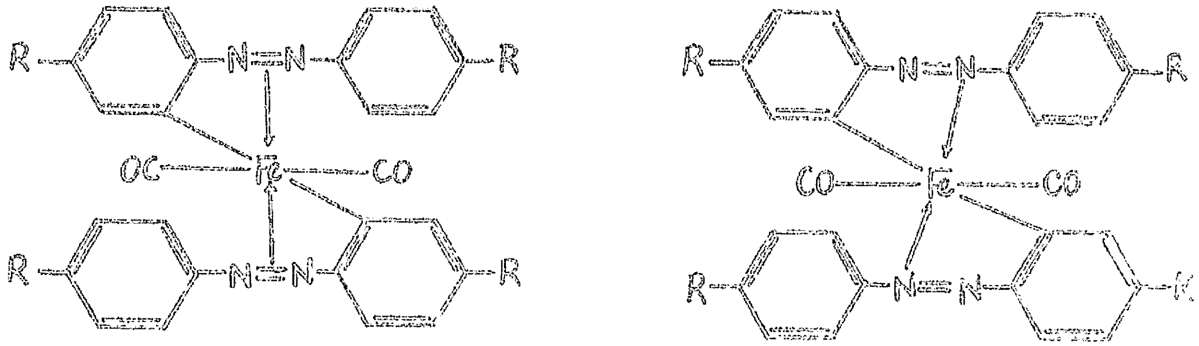
This work was then extended to include 4,4'-disubstituted azobenzenes. 4,4'-Dimethoxyazobenzene on irradiation with iron pentacarbonyl furnished two metal carbonyl compounds. One of them analysed as (dimethoxyazobenzene)$Fe_2(CO)_6$, showed absorption at 3358 cm.$^{-1}$ (NH) in the infrared spectrum, and clearly corresponded to (XLIV, R = OCH_3). The other complex did not show any NH absorption in the infrared spectrum, showed only two metal carbonyl absorptions, and analysed as (dimethoxyazobenzene)$_2$Fe(CO)$_2$. This was mostly in agreement with the results of mass spectrum. The mass measurement of this complex gave its molecular weight as 594 and molecular formula as $C_{30}H_{26}FeN_4O_6$. The molecular weight of dimethoxyazobenzene is 242 which does not occur in the spectrum, but 240 does, probably in the form indicated below.

Isotope ratio measurements showed that one iron was present in the complex. Thus, the positive ions corresponding to the following mass numbers (m/e) and formulae were identifiable.



(XLV)

Based on infrared and mass spectral results, this complex could have the structure (XLVIa or XLVIb, R = OCH_3). It would be necessary to degrade the complex with lithium aluminium



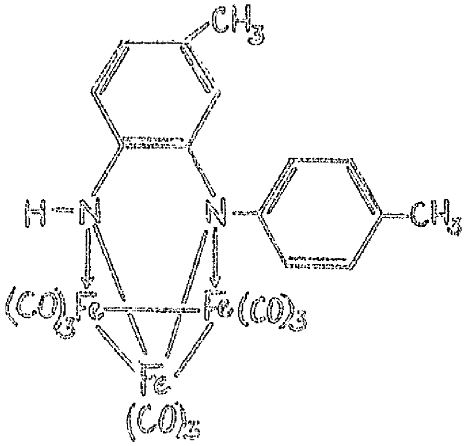
(a) (b)

(XLVI)

deuteride to show the presence of a sigma bond between the iron atom and the aromatic nucleus. The ultraviolet spectra of 4,4'-dimethoxyazobenzene and the complex are so similar as to suggest the structure (XLVIb, R = OCH_3) as more probable, i.e., participation of the lone pair of electrons on a nitrogen atom in bonding to the iron atom seems more likely than the participation of the azo group in delocalised bonding with the iron.

4,4'-Dimethylazobenzene and iron pentacarbonyl on irradiation gave two types of complexes (XLIV, R = CH_3 and XLVI, R = CH_3) analogous to those obtained from 4,4'-dimethoxyazobenzene. Although it was not possible to get elemental analysis for the complex (XLVI, R = CH_3) on account of difficulty in purifying it, its infrared spectrum was closely similar to that of (XLVI, R = OCH_3). Thus, the corresponding structures are proposed for these two complexes.

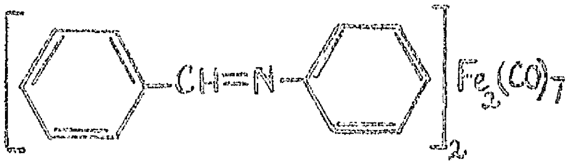
4,4'-Dimethylazobenzene on treatment with diiron enneacarbonyl at room temperature gave yet another type of complex in too poor yields to carry out any chemical studies. Its mass spectrum gave its molecular formula as $C_{23}H_{14}Fe_3N_2O_9$ and molecular weight as 630. This contains three iron atoms and nine carbonyl groups. The cracking pattern suggested that this complex was of the same type as the o-aminodiphenylamine complex with a diiron hexacarbonyl residue (XLIV, R = H). The complex could be (XLVII), and the elemental analysis, though not very good, was pointing towards this. It would be interesting to see whether it would be possible to convert (XLIV, R = CH_3) to (XLVII) by treatment with diiron enneacarbonyl at room temperature.



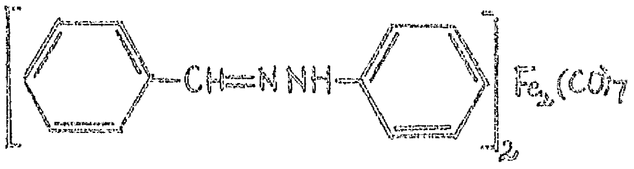
(XLVII)

REACTIONS OF SCHIFF BASES WITH IRON CARBONYLS

It would not be out of place to mention here the reasons which led to the study of the reaction of iron carbonyls with Schiff bases. From preliminary results on the mass spectrum of the orange complex (XXXVIII, R = Ph) from diphenyldiazomethane and iron pentacarbonyl, it was initially suggested that the complex corresponded to either the formulation (XLVIII) or (XLIX), although these were revised later. It was decided to confirm these suggestions by treating N-benzylideneaniline with diiron enneacarbonyl which could give the complex (XLVIII) by the replacement of two carbonyl groups of the enneacarbonyl by two molecules of N-benzylideneaniline. Similarly, benzaldehyde phenylhydrazone could give the complex (XLIX) by treatment with diiron enneacarbonyl. Both N-benzylideneaniline and benzaldehyde phenylhydrazone did in fact react with diiron enneacarbonyl in



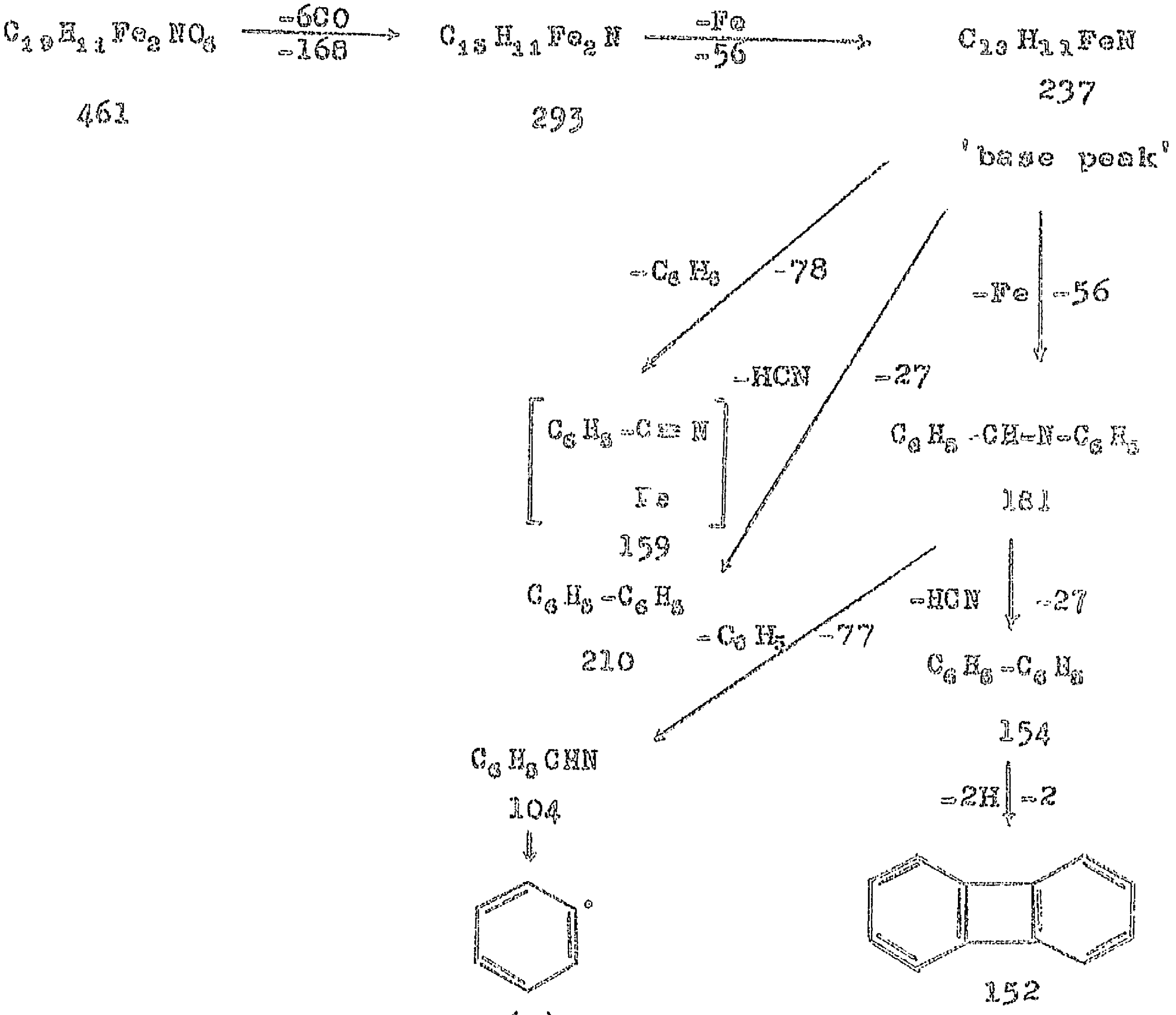
(XLVIII)



(XLIX)

benzene, in the former case at room temperature, and in the latter case on warming. Neither of the two complexes thus isolated corresponded to the orange complex (XXXVIII, R = Ph) obtained from diphenyldiazomethane and iron pentacarbonyl. In each case, the elemental analysis suggested one molecule of ligand joined on to a diiron hexacarbonyl residue. Of three organic byproducts isolated from the reaction of N-benzylideneaniline with diiron enneacarbonyl, two were identified as aniline and benzanilide. The reaction of N-benzylideneaniline with diiron enneacarbonyl was so smooth that it was thought desirable to extend the work on Schiff base complexes and to study their chemistry.

N-Benzylideneaniline and iron pentacarbonyl gave the same complex on irradiation. Reduction of the complex with lithium aluminium hydride gave N-benzylaniline indicative of the fact that N-benzylidene aniline was the ligand in the complex. The complex did not react with anhydrous ferric chloride in benzene, but in ethyl alcohol a white solid was isolated whose identity has not yet been established. The formulation (N-benzylideneaniline)$Fe_2(CO)_6$ for the complex received confirmation from its mass spectrum. The molecular weight was 461 and mass measurement gave a molecular formula as $C_{19}H_{11}Fe_2NO_6$. The positive ions corresponding to the following mass numbers (m/e) and formulae were identifiable.

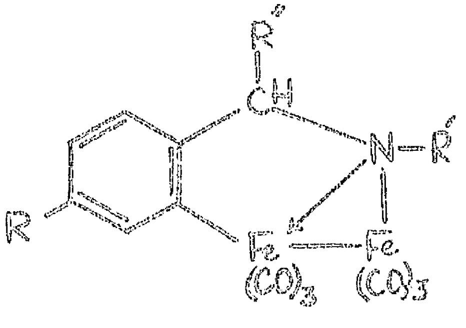


(L)

This work was then extended further to other Schiff bases. N-4-Methylbenzylideneaniline on treatment with diiron ennea-carbonyl at room temperature gave two complexes; both of them seemed to be of the type (Schiff base)$Fe_2(CO)_6$. It would be difficult at this stage to tell what type of isomers they could be. The two organic byproducts isolated were recognised as aniline and p-toluanilide. However, the complex isolated in larger yields was subjected to lithium aluminium hydride reduction and N-4-methylbenzylaniline isolated. This was in keeping with the fact that N-4-methylbenzylideneaniline remained essentially unchanged in the formation of its complex. Likewise, N-4-benzylidene-p-toluidine gave an analogous complex.

Since it was not certain how the diiron hexacarbonyl residue was linked to the Schiff base, and whether or not both phenyl rings were involved with the complex formation, it was decided to use such Schiff bases where one or the other side was aliphatic. Thus, the Schiff base derived from benzaldehyde and methylamine, i.e. N-benzylidenemethylamine, was treated with diiron enneacarbonyl at room temperature in benzene. The reaction went smoothly to give a complex analogous to the ones described earlier. On the other hand, the Schiff base derived from acetone and aniline, i.e. N-isopropylideneaniline, gave only an unstable liquid complex. Acetophenone anil also reacted smoothly with diiron enneacarbonyl to furnish a stable complex of the type described above. This led to the conclusion that, for the formation of a stable complex, the Schiff base must be derived from an aromatic aldehyde or ketone, whereas the amine could be aromatic or aliphatic.

The n.m.r. spectrum (carbon tetrachloride) of the complex obtained from acetophenone anil and diiron enneacarbonyl showed peaks at 2 45 τ (multiplet, relative intensity 8.70, aromatic protons), 5.65 τ (quadruplet, relative intensity 1, methylene proton) and 8.8 τ (doublet, relative intensity 3, methyl protons). This would suggest loss of one phenyl proton (there being one on the carbon atom carrying a methyl group, while there was none in the acetophenone anil) and a probable σ-bond between the phenyl ring and the iron atom. The possibility of π-bonding between the benzene ring and an iron atom can almost certainly be ruled out as the aromatic protons show signals at their normal position. Based on this n.m.r. spectrum and the mass spectrum on the analogous complex obtained from N-benzylideneaniline, the structure (LI; R = H, R' = Ph and R'' = Ph and R'' = CH_3) is proposed for the

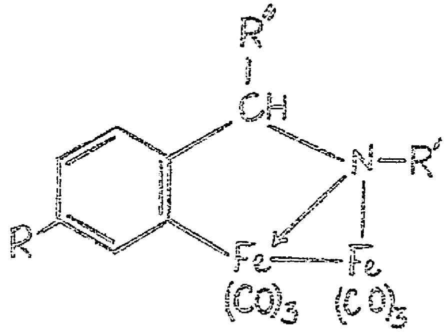


(LI)

acetophenone anil complex, although it leaves one of the two iron atoms short of two electrons. The n.m.r. spectra of other Schiff base complexes are given in the table and they can be explained on the basis of the structure (LI). Hence, analogous structures are proposed for these complexes.

Quite a lot of further experimental evidence would be needed before the suggested structure (LI) for Schiff base complexes can be fully substantiated. For example, in all cases a loss of proton from an ortho position of benzene ring has been assumed. Although this is most likely to be the case, it nevertheless becomes desirable to carry out reaction with the Schiff base derived from an aromatic aldehyde or ketone where the two ortho positions on the benzene ring are blocked. Failure to obtain any complex in this case need not be only on account of non-availability of an ortho position on the benzene ring, but might be because of steric factors. It would be more profitable to carry out lithium aluminium deuteride degradations on some of these complexes and try to determine the position where the deuterium enters. Although this would solve the problem partially, complete x-ray analysis would be necessary to give an unambiguous structure. On the basis of the available evidence, a completely rational structure is difficult to offer; the proposed structure has already been discussed.

N.M.R. Spectra of Iron Carbonyl Complexes of Schiff Bases

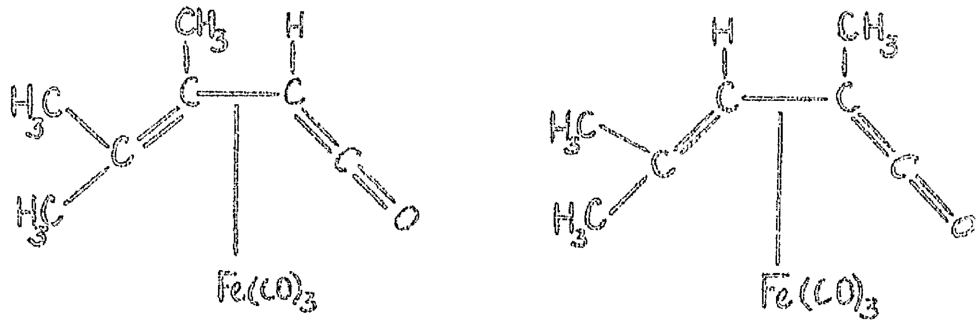


Schiff Base Complex	Value	Relative Intensity	Assignment	
$R'' = R = H$; $R' = Ph$	2.45 (m)	10.4	Aromatic -	- 9
	5.59 (s)	2.0	Methylene-	- 2
$R = CH_3$; $R' = Ph$	2.55 (m)	7.7	Aromatic-	- 8
$R'' = H$	5.68 (s)	2.0	Methylene-	- 2
(minor)	7.55 (s)	3.0	Methyl-	- 3
$R = CH_3$; $R' = Ph$	2.67 (m)	8.1	Aromatic-	- 8
$R'' = H$	5.63 (s)	2.0	Methylene-	- 2
(major)	7.63 (s)	3.0	Methyl-	- 3
$R'' = R = H$;	2.35 (m)	8.0	Aromatic-	- 8
$R' = C_6H_4CH_3-p$	5.60 (s)	1.7	Methylene-	- 2
	7.68 (s)	3.0	Methyl-	- 3
$R'' = R = H$;	2.45 (m)	4.2	Aromatic-	- 4
$R' = CH_3$	5.96 (s)	1.8	Methylene-	- 2
	7.16 (s)	3.0	Methyl-	- 3
$R = H$; $R'' = CH_3$;	2.45 (m)	8.70	Aromatic-	- 9
$R' = Ph$	5.65 (q)	1.0	Methylene-	- 1
	8.8 (d)	3.0	Methyl-	- 3

s = singlet; m = multiplet; d = doublet; q = quadruplet.

MISCELLANEOUS REACTIONS

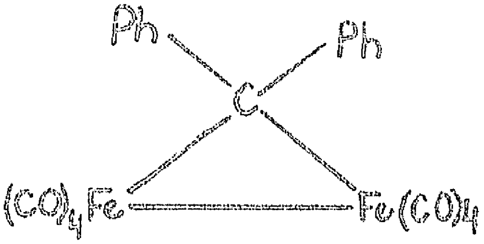
King *et al.*[86] reported that the reactions of triiron dodecacarbonyl and 1,3,3-trimethylcyclopropene gives a complex for which two alternative structures (LIIa, LIIb) were offered. Diphenylketene being the irradiation product of phenylbenzoyldiazomethane, it could have been expected that the irradiation of the latter with iron pentacarbonyl would give a ketene complex It has been mentioned earlier that the reaction of phenylbenzoyldiazomethane with iron carbonyls did not give any complex. Surprisingly, the irradiation of diphenylketene with iron pentacarbonyl gave a stable complex, which, unlike the ketene complex reported by King,[86] did not show any absorption in the ketonic carbonyl region in its infrared spectrum. Its reduction with lithium aluminium hydride gave a colourless liquid; its infrared spectrum was similar to, but not identical with, those of diphenylmethane and 1,1-diphenylethane. The mass spectrum of the complex gave molecular formula as $C_{21}H_{12}Fe_2O_8$ and showed the presence of



(a) (b)

(LII)

two iron atoms and eight carbonyl groups. The n.m.r. spectrum (carbon tetrachloride) showed a peak at 2.78 τ (singlet, phenyl protons), suggesting the presence of protons of only one type. It would thus be difficult to account for the two more protons suggested by the mass spectrum. If these two protons are assumed not to be present then the structure (LIII) for the diphenylketene complex could be possible.



(LIII)

The diazo compounds of the type other than those already described were also treated with either iron pentacarbonyl under irradiation or with diiron enneacarbonyl with a view to forming their complexes. In most cases, the complexes formed were either unstable or formed in very poor yields, insufficient for any further study. Diazocyclopentadiene and iron pentacarbonyl on irradiation in benzene gave an unstable liquid complex which showed both terminal and bridging metal carbonyl absorptions in the infrared spectrum. Diazofluorene, in a similar reaction, gave a solid complex, highly unstable in solution, but stable in the dry condition. This also showed both terminal and bridging metal carbonyl absorptions in the infrared spectrum. The reaction of diazofluorene with diiron enneacarbonyl gave two metal carbonyl compounds; none of these showed bridging carbonyl groups in the infrared spectrum.

Diethyl azodicarboxylate gave only diethyl hydrazine dicarboxylate when irradiated with iron pentacarbonyl or treated with diiron enneacarbonyl. Tetramethyl-2-tetrazene when irradiated with iron pentacarbonyl gave a solid complex and when treated with diiron enneacarbonyl it gave an unstable liquid complex.

Attempts to form complexes from fluorene and fluorenone by irradiation with iron pentacarbonyl were not successful. Tetraphenylethylene did not react when irradiated with iron pentacarbonyl or treated with diiron enneacarbonyl.

EXPERIMENTAL

General Experimental Procedures

Melting Points:- These were determined on a Gallenkamp melting point apparatus and are uncorrected. Melting points of all organometallic compounds were determined in evacuated sealed capillaries.

N.M.R. Spectra:- These were measured on a Perkin-Elmer 40 M/C Spectrometer.

Mass Spectra:- These were determined by Dr. R.I. Reed and Mr. F. Preston on an AEI-MS9 double focussing instrument.

Reagents:-

1. Unless otherwise stated, petroleum ether used was the fraction of b.p. 60-80°.
2. All reactions involving organometallic compounds were carried out under an atmosphere of nitrogen, which had been deoxygenated with Fieser's solution and dried with concentrated sulphuric acid.
3. All reactions were carried out in sodium-dried solvents.
4. Unless otherwise stated, chromatographies were carried out on neutral alumina (activity I). To prepare this, alumina (Spence Grade H) was kept under ethyl acetate for two days, filtered, washed with methyl alcohol and then repeatedly with water. It was then dried in an oven at 160° for not less than 8 hr. Ordinary alumina used refers to alumina (Spence Grade H) exposed for specified number of hours.

5. Molecular weight determinations were carried out cryoscopically in benzene solution.

Irradiation Technique :- The irradiations were carried out in an annular apparatus having a capacity of 650 ml. or 1500 ml. The 500 watt medium pressure mercury arc lamp (Hanovia 509/12) was kept in a water-cooled quartz down tube and this was immersed in an outer glass jacket, containing the reactants in the desired solvent. Nitrogen was passed through the reaction mixture and irradiation carried out until there was some visible change.

Unless otherwise stated, yields of the products obtained were based on unrecovered metal carbonyl.

REACTIONS ON THE COMPLEX FROM ACETYLENE AND IRON TETRACARBONYL ANION

Attempts to prepare 2,5-Dimethoxy-1-phenylphosphole by the reaction of the dimethyl ether of the Complex obtained from Acetylene and Iron Tetracarbonyl Anion with Dichlorophenylphosphine.

(a) The complex[3] (0.5 g., 0.0012 mole) and dichlorophenylphosphine (0.5 g., 0.0027 mole) were refluxed in petroleum ether (b.p. 100-120°; 100 ml.) for 4 hr. The reaction mixture was filtered, the solvent evaporated under reduced pressure and the residue chromatographed on alumina in benzene to give only unchanged complex (0.2 g., 40% recovery).

(b) The complex[3] (0.5 g., 0.0012 mole) and dichlorophenylphosphine (1 g., 0.0055 mole) were stirred in diglyme (40 ml.) at 180-190° for 1 hr. There was vigorous reaction at this temperature and a solid was thrown out. This dark brown solid was insoluble in all organic solvents and did not melt $<$ 280°. The filtrate was evaporated under reduced pressure and the residue left was insoluble in organic solvents.

(c) The complex[3] (0.5 g., 0.0012 mole) and dichlorophenylphosphine (2 g., 0.011 mole) were heated at 130 - 140° for 1 hr. Excess dichlorophenylphosphine was evaporated under reduced pressure. The residue was chromatographed on alumina in benzene to give unchanged complex (0.2 g., 40% recovery).

Irradiation of the dimethyl ether of the Complex obtained from Acetylene and Iron Tetracarbonyl Anion.

(a) The complex[3] (1 g., 0.0025 mole) dissolved in ether (500 ml.) was irradiated for 5 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. Chromatography of the residue in benzene on alumina furnished only unchanged complex (0.67 g., 67% recovery).

(b) The complex (1 g., 0.0025 mole) dissolved in methyl alcohol (500 ml.) was irradiated for 5 hr. The solution was filtered and the solvent evaporated under reduced pressure. The major part of the residue left behind was insoluble in most organic solvents. The benzene soluble portion of the residue was chromatographed on alumina to give:

(1) The unchanged complex (0.39 g., 39% recovery) eluted with benzene.

(2) An almost colourless product (0.085 g.) eluted with chloroform. This could be sublimed at 65-70° at 0.1 mm. to give light pink crystalline product, m.p. 124-6°; it decomposed completely in two days even under a nitrogen atmosphere. (Found: C,42.6; H,3.8; M., 252.1).

$\nu_{\text{max.}}$ ($CHCl_3$) 2045, 1988 and 1980 $cm.^{-1}$ (MC-O)

N.M.R. (CCl_4) 5.08 τ (singlet, relative intensity 1.6) and 6.13 τ (singlet, relative intensity 6).

Reaction of the dimethyl ether of the Complex obtained from Acetylene and Iron Tetracarbonyl Anion with Phenylacetylene.

The complex[3] (2 g., 0.005 mole) and phenylacetylene (4 g., 0.04 mole) were refluxed in petroleum ether (b.p. 100-120°) (120 ml.) for 4 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was dissolved in a minimum amount of a mixture of petroleum ether-benzene (2:1) and chromatographed on alumina to give:

(1) A mixture of products eluted with petroleum ether-benzene (2:1). Rechromatography in petroleum ether on alumina gave unchanged complex (1 g., 50% recovery), phenylacetylene (3 g., 75% recovery) and 1,2,4-triphenylbenzene (0.205 g.).

(2) A mixture of products eluted with chloroform, of which a metal carbonyl compound (9 mg.), m.p. 240 d. could be sublimed out at 150-160° at 0.1 mm. $\nu_{\text{max.}}$ ($CHCl_3$) 2004 and 2057 cm.$^{-1}$ (MC-O). The residue did not show any metal carbonyl absorption in the infrared spectrum and was not studied.

Reaction of the dimethyl ether of the Complex obtained from Acetylene and Iron Tetracarbonyl Anion with Diphenyldiazomethane under irradiation.

Diphenyldiazomethane[87] (4 g., 0.02 mole) and the complex[3] (4 g., 0.01 mole) were irradiated in benzene (400 ml.)

for 5 hr. The reaction mixture was filtered and the solvent distilled under reduced pressure. The residue was chromatographed in petroleum ether on alumina. There were no fewer than ten bands on the column. Thus,

(1) A colourless solid (0.22 g.) was eluted with petroleum ether. Crystallisation from petroleum ether gave crystals, m.p. 103-4°.

(2) An extremely complicated mixture of products (3.8 g.) eluted with petroleum ether. Sublimation upto 100° at 0.02 mm. gave a number of small fractions that were rejected. The residue left behind gave, on crystallisation from petroleum ether, two compounds:

(i) A red crystalline compound (0.3 g.), m.p. 148° (Found: C, 53.4; H, 3.5).

$\nu_{\max.}$ (KCl) a broad band at 1960-2028, 2032 and 2074 $cm.^{-1}$ (MC-O)

N.M.R. (CCl_4) 2.7 τ (doublet, relative intensity 10, aromatic protons), 4.41 and 4.80 τ (singlets, relative intensities 0.6 and 0.8 respectively, olefinic protons), 6.17 and 6.37 τ (singlets, relative intensities 2.8 and 3.0 respectively, methoxy protons).

(ii) Deep brown needles (0.196 g.), m.p. 157° (Found: C, 53.2; H, 3.6).

$\nu_{\max.}$ (KCl) 1923, 1949, 2000 and 2150 $cm.^{-1}$ (MC-O)

REACTIONS OF DIAZOALKANES AND AZINES WITH IRON CARBONYLS

Reaction of Diphenyldiazomethane and Iron Pentacarbonyl under irradiation.

Diphenyldiazomethane[87] (13 g., 0.067 mole) and iron pentacarbonyl (13.4 g., 0.067 mole) were irradiated in benzene (1300 ml.) for 8 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue, dissolved in the minimum volume of benzene and diluted with an equivalent volume of petroleum ether, was chromatographed on alumina (4 hr. deactivated). The following products were obtained.

(1) A mixture of products (3.5 g.) eluted with petroleum ether. Three types of crystals could be seen - white, orange, and black. Rechromatography gave a mixture of orange and black products. They were separated by repeated crystallisation from benzene-ethyl alcohol which separated black product (0.88 g.), m.p. 170°, leaving orange product in solution. This orange product was then crystallised repeatedly from benzene-petroleum ether (0.28 g.), m.p. 167°.

Black compound. (Found: C, 52.4; H, 2.9; N, 6.8).

$\nu_{max.}$ (CCl_4) 2010, 2035 and 2055 cm.$^{-1}$ and

(KCl) 1985, 1998, 2007, 2032 and 2058 cm.$^{-1}$ (MC-O)

Orange compound. (Found: C, 58.1; H, 3.8; N, 8.4 $C_{32}H_{22}Fe_2N_4O_6$ requires C, 57.3; H, 3.3; N, 8.35).

$\nu_{max.}$ (CCl_4) 1982, 1998, 2038 and 2072 cm.$^{-1}$ and

(KCl) 1970, 1990, 2025 and 2067 cm.$^{-1}$ (MC-O)

N.M.R. (C_6F_6) 2.45 τ (multiplet, relative intensity 20, aromatic protons) 3.36 and 4.14 τ (singlets, relative intensities 0.9 and 0.6 respectively, NH protons).

(2) A white solid (3.15 g.) eluted with benzene-petroleum ether (1:4). This was crystallised from benzene-petroleum ether to give benzophenone azine, m.p. 165°, undepressed on admixture with an authentic specimen.

Reaction of Diphenyldiazomethane and Triiron Dodecacarbonyl

Diphenyldiazomethane[87] (13 g., 0.067 mole) and triiron dodecacarbonyl (12 g., 0.024 mole) were stirred in benzene (300 ml.) at 70-5° for 4 hr. The reaction started at 60° with the rapid evolution of gas. The reaction mixture was filtered and then worked up as in the preceding experiment. The yields obtained were, black compound (2 g.), orange compound (0.1 g.) and benzophenone azine (2.8 g.).

Reaction of the Black Compound obtained from Diphenyldiazomethane and Iron Pentacarbonyl with Lithium Aluminium Hydride.

The compound (0.5 g.) dissolved in ether (30 ml.) and tetrahydrofuran (20 ml.) was added dropwise and with stirring to an ice-cold suspension of lithium aluminium hydride (0.076 g.) in ether (30 ml.). The reaction mixture was stirred at this temperature for 2 hr. Excess lithium aluminium hydride was decomposed by the addition of ethyl alcohol (5 ml.). The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was chromatographed in benzene-petroleum ether (1:1) on alumina to give:

(1) A white solid (0.020 g.) eluted with ether. It was crystallised from benzene-petroleum ether and the product obtained had m.p. 165°, undepressed on admixture with an authentic specimen of benzophenone azine.

(2) A colourless liquid (0.07 g.) eluted with ethyl alcohol. It was not identified.

Reaction of Diphenyldiazomethane and Chromium Hexacarbonyl under irradiation.

Diphenyldiazomethane[87] (4.3 g., 0.022 mole) and chromium hexacarbonyl (4 g., 0.018 mole) were irradiated in tetrahydrofuran (500 ml.) for 5 hr. The reaction mixture was filtered rapidly and the ~~solvent~~ evaporated at room temperature. There was extensive decomposition during this time with the formation of light green solid that did not dissolve in any organic solvent. Only traces of chromium hexacarbonyl could be sublimed from this residue.

Reaction of Diphenyldiazomethane and Nickel Tetracarbonyl under irradiation.

Diphenyldiazomethane[87] (4 g., 0.02 mole) and nickel tetracarbonyl (3.5 g., 0.02 mole) were irradiated in benzene (600 ml.) for 6 hr. There was extensive decomposition. The reaction mixture was filtered and the solvent evaporated under reduced pressure. Chromatography of the residue on alumina in benzene gave only benzophenone azine.

Reaction of Diphenyldiazomethane with Methylcyclopentadienylmanganese Tricarbonyl under irradiation.

Diphenyldiazomethane[87] (4 g., 0.02 mole) and methylcyclopentadienylmanganese tricarbonyl (4.5 g., 0.02 mole) were irradiated in benzene (500 ml.) for 5 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was chromatographed to give benzophenone azine (0.25 g.) and unchanged methylcyclopentadienylmanganese tricarbonyl (4.1 g., 91.1% recovery).

Reaction of Di-(p-tolyl) diazomethane and Iron Pentacarbonyl under Irradiation.

Di-(p-tolyl) diazomethane[88] (30 g., 0.135 mole) and iron pentacarbonyl (52.56 g., 0.268 mole) were irradiated in benzene (1400 ml.) for 6 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was crystallised from benzene-petroleum ether to give 4,4'-dimethylbenzophenone azine (11.15 g.). The residue obtained on evaporation of the filtrate was dissolved in benzene (50 ml.)

and petroleum ether (100 ml.) and chromatographed on alumina to give;

(1) A mixture of orange, black, and yellow compounds (4.07 g.) eluted with petroleum ether-benzene (9:1). Rechromatography gave a black compound (1.6 g.) eluted with petroleum ether. It was crystallised from ether-petroleum ether (b.p. 40-60°) and the product obtained had m.p. 158°. (Found: C,53.9; H,3.3; N,7.0; O,17.9).

$\nu_{max.}$ (CCl_4) 2018, 2042 and 2060 cm.$^{-1}$ and
(KCl) 1965, 1995, 2030 and 2050 cm.$^{-1}$ (MC-O)

An orange compound (0.965 g.) was eluted with benzene-petroleum ether (1:20). It was crystallised from ether-petroleum ether (b.p. 40-60°), m.p. 165-165.5°. (Found: C,62.9; H,4.5; N,6.9; O,12.2 $C_{36}H_{30}Fe_2N_4O_6$ requires C, 59.5; H,4.1; N,7.7; O,13.2).

$\nu_{max.}$ (CCl_4) 1985, 1998, 2040 and 2075 cm.$^{-1}$ and
(KCl) 1955, 1970 with shoulders at 1985 and 1998, 2037 and 2072 cm.$^{-1}$ (MC-O).

N.M.R. (CCl_4) 3τ (multiplet, relative intensity 16.8, aromatic protons) 4.4 and 5.48τ (broad, relative intensities 0.7 and 1.0 respectively, NH protons) and 7.7τ (broad multiplet, relative intensity 12, methyl protons).

(2) A yellow solid (0.54 g.) eluted with benzene-petroleum ether (1:1). This was rechromatographed in petroleum ether on ordinary alumina (6 hr. deactivated) to give a yellow solid

eluted with benzene-petroleum ether (1:1). It was crystallised from petroleum ether; m.p. 129-30°. Lassaigne's test for nitrogen was negative. (Found: C, 82.85; H, 6.3).

(3) A yellow solid (3.6 g.) eluted with ether. It was shown to be 4,4'-dimethylbenzophenone azine.

(4) A white solid (0.63 g.) eluted with ethyl acetate. It was rechromatographed in benzene on ordinary alumina (6 hr. deactivated) and eluted with ethyl acetate. It was crystallised from benzene-petroleum ether, m.p. 217-18°. Lassaigne's test for nitrogen was negative (Found: C, 78.0; H, 6.1; M., 503).

$\nu_{max.}$ (CCl_4) 1700 cm.$^{-1}$ (CO)

(5) A greyish white solid (0.3 g.) eluted with methylene chloride. It could not be purified.

Probably, there should be no less than two more organic compounds formed in this reaction as was evidenced by the fractions of chromatography. They were not studied.

Reaction of the Orange Compound obtained from Di-(p-tolyl) diazomethane and Iron Pentacarbonyl with Lithium Aluminium Hydride.

The compound (0.5 g., 0.0006 mole) dissolved in tetrahydrofuran (20 ml.) was added dropwise and with stirring to an ice-cold suspension of lithium aluminium hydride (0.078 g., 0.002 mole) in tetrahydrofuran (20 ml.). The reaction mixture was allowed to stir for 3 hr. at this temperature and excess lithium aluminium hydride was decomposed by the addition of ethyl acetate (10 ml.). The reaction mixture was filtered and the residue left on evaporation of the solvent under reduced pressure was chromatographed in petroleum ether on alumina (4 hr. deactivated) to give:

(1) A mixture of pale yellow oil and white solid (0.017 g.). It was crystallised from petroleum ether to give a solid (0.007 g.), m.p. 277-8°. It was not studied.

(2) A yellow solid (0.015 g.), m.p. 75-77°, eluted with ether.

(3) A light yellow solid (0.050 g.) eluted with ethyl acetate. It was crystallised from ethyl acetate and petroleum ether, m.p. 121-2° (Found: C,76.65; H,6.8; N,10.6; O,6.2). $\nu_{max.}$ (CCl_4) 3312 cm.$^{-1}$ (NH); 1675, 1700 cm.$^{-1}$ (CO)

Reaction of Phenyldiazomethane and Iron Pentacarbonyl under irradiation.

Phenyldiazomethane[89] (1.96 g., 0.016 mole) and iron pentacarbonyl (3.21 g., 0.016 mole) were irradiated in benzene (550 ml.) for 5 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The unstable residue was dissolved in the minimum amount of petroleum ether-benzene (1:1) and chromatographed on alumina (1 hr. deactivated) to give

(1) A mixture or red liquid and white solid (0.98 g.) eluted with petroleum ether. Rechromatography on alumina (1 hr. deactivated) did not completely separate the white solid. The impure and unstable red liquid (0.2 g.) thus separated showed metal carbonyl absorption in the infrared spectrum.

$\nu_{\text{max.}}$ (liquid) 1980 and 2053 cm.$^{-1}$ (MC=O)

The white solid (0.1 g.) had m.p. 120-3°.

(2) A light brown unstable liquid (0.317 g.) eluted with petroleum ether. It was not studied further.

Reaction of Phenylbenzoyldiazomethane and diiron enneacarbonyl

Phenylbenzoyldiazomethane[90] (6 g., 0.027 mole) and diiron enneacarbonyl (10 g., 0.027 mole) were stirred in benzene (300 ml.) for 3 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was dissolved in minimum volume of benzene-petroleum ether (1:1) and chromatographed on alumina to give:

(1) A mixture of thick gum and yellow solid eluted with benzene-petroleum ether (1:1); the gum dissolved readily in ether leaving the solid (0.2 g.) behind. It was rechromatographed in benzene on ordinary alumina (6 hr. deactivated) and crystallised from ethyl acetate to give a crystalline nitrogen-containing compound, m.p. 202-3°.

$\nu_{\text{max.}}$ ($CHCl_3$) 1668 cm.$^{-1}$ (CO)

Melting point and infrared evidence suggests that the compound is bis-benzilketazine (lit.[91] m.p. 203°).

(2) A very thick liquid eluted with ethyl acetate was not studied.

Reaction of Phenylbenzoyldiazomethane and Triiron Dodecacarbonyl.

Phenylbenzoyldiazomethane[90] (2 g., 0.009 mole) and triiron dodecacarbonyl (1.5 g., 0.003 mole) were stirred in benzene (200 ml.) at 80° for 5 hr. The reaction mixture was filtered, the filtrate evaporated to dryness under reduced pressure and the residue left was chromatographed in benzene-petroleum ether (1:1) to give a trace of an unstable metal carbonyl compound and bis-benzilketazine.

Reaction of Phenylbenzoyldiazomethane and Iron Pentacarbonyl under irradiation.

Phenylbenzoyldiazomethane[90] (4 g., 0.018 mole) and iron pentacarbonyl (3.5 g., 0.018 mole) were irradiated in benzene (600 ml.) for 4 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was chromatographed in benzene-petroleum ether (1:1) to give only bis-benzilketazine.

Reaction of Benzopheone Azine and Iron Pentacarbonyl under irradiatio

Benzophenone azine (2.5 g., 0.0069 mole) and iron pentacarbonyl (5 g., 0.025 mole) were irradiated in benzene (400 ml.) for 8 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue on chromatography in benzene on alumina gave almost quantitative recovery of benzophenone azine.

Reaction of Benzophenone Azine and Diiron Enneacarbonyl

Benzophenone azine (4 g., 0.01 mole) and diiron enneacarbonyl (2 g., 0.005 mole) were stirred with heating to reflux in benzene (200 ml.) for 6 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The petroleum ether soluble portion of the residue was chromatographed on alumina to give:

(1) An orange solid (0.025 g., 0.7%) eluted with petroleum ether. Rechromatography and crystallisation from petroleum ether gave a crystalline product, m.p. 140-141°. (Found: C,60.25; H,3.3; N, 4.5; O,15.1. $C_{32}H_{20}Fe_2N_2O_6$ requirs C,60.05; H,3.15; N,4.4; O,15.0).

$\nu_{max.}$ (CCl_4) 1988, 2035 and 2065 cm.$^{-1}$ and

(KCl) 1955, 1970, 1980, 2025 and 2065 cm.$^{-1}$ (MC-O)

(2) Traces of organic compounds eluted subsequently were not studied.

The petroleum ether insoluble portion was chromatographed in benzene on alumina to give unchanged benzophenone azine (3.5 g., 87.5% recovery).

The reaction of benzopheone azine (4 g., 0.01 mole) and excess diiron enneacarbonyl (8 g., 0.02 mole) under identical conditions furnished the above complex (0.11 g.).

Reaction of 4,4'-Dimethylbenzophenone Azine and Diiron Enneacarbonyl

4,4'-Dimethylbenzophenone azine (16 g., 0.038 mole) and diiron enneacarbonyl (28 g., 0.076 mole) were stirred in benzene (800 ml.) at 60° for 6 hr. The reaction mixture was then filtered and the solvent evaporated under reduced pressure. The petroleum ether soluble portion of the residue was chromatographed on alumina to give:

(1) An orange solid (0.57 g., 2.2%; based on the amount of azine taken) eluted with petroleum ether. Rechromatography and crystallisation from ether-petroleum ether (b.p. 30-40°) yielded a crystalline product, m.p. 178-9°. (Found: C,62.1; H,3.9; N,4.05; O,13.5. $C_{36}H_{28}Fe_2N_2O_6$ requires C,62.1; H,4.1; N,4.0; O,13.8).

$\nu_{max.}$ (CCl_4) 1975, 2020 and 2055 cm.$^{-1}$ and
(KCl) 1960, 2008 and 2050 cm.$^{-1}$ (MC=O)

N.M.R. 2.93τ (singlet, relative intensity 3.9, aromatic protons).
7.63τ (singlet, relative intensity 3, methyl protons).

(2) A white solid (0.73 g.) eluted with ether. It was rechromatographed in ether on alumina and crystallised from petroleum ether (b.p. 40-60°) to a product, m.p. 81-2°. Its infrared spectrum was superimposable with that of an authentic specimen of 4,4'-dimethylbenzophenone.

The petroleum ether insoluble portion of the residue was chromatographed in benzene on alumina to give unchanged 4,4'-dimethylbenzophenone azine (11 g., 68.7% recovery).

REACTIONS OF AZOBENZENE AND SUBSTITUTED AXOBENZENES WITH IRON CARBONYLS

Reaction of Azobenzene and Iron Pentacarbonyl under irradiation.

Azobenzene (24 g., 0.13 mole) and iron pentacarbonyl (50.4 g., 0.25 mole) were irradiated in benzene (1400 ml.) for 42 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was then chromatographed on alumina to give:

(1) Unchanged azobenzene (21 g., 87.5%) eluted with petroleum ether.

(2) A red-brown solid (2.1 g., 3.44%) eluted with petroleum ether. Rechromatography and crystallisation from ether-petroleum ether furnished the crystalline product, m.p. 163-164°. (Found: C,47.0; H,2.1; N,6.2. $C_{18}H_{10}Fe_2N_2O_6$ requires C,46.8; H,2.2; N,6.1).
$\nu_{max.}$(CCl$_4$) 3362 cm.$^{-1}$ (NH); 1985, 2035 and 2075 cm.$^{-1}$ and (KCl) 1960, 1975, 1998, 2040 and 2072 cm.$^{-1}$ (MC-O).

(3) A deep red solid (0.011 g.) eluted with benzene. It was crystallised from pentane to a product, m.p. 127-9°. It did not show any metal carbonyl absorption in the infrared spectrum.

(4) Traces of products eluted subsequently were not studied.

Reaction of Azobenzene and Triiron Dodecacarbonyl.

Azobenzene (2 g., 0.011 mole) and triiron dodecacarbonyl (2 g., 0.004 mole) were heated to reflux with stirring in benzene

(200 ml.) for 8 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was chromatographed on alumina to give:

(1) Unchanged azobenzene (1.5 g., 75% recovery) eluted with petroleum ether.

(2) An impure brown solid eluted with petroleum ether. Rechromatography and crystallisation from ether-petroleum ether gave crystalline product (0.06 g., 2.18%). Its melting point was undepressed on admixture with the complex obtained from azobenzene and iron pentacarbonyl under irradiation.

(3) The products eluted subsequently in small amounts were not studied.

Reaction of the Complex obtained from Azobenzene and Iron Pentacarbonyl with Lithium Aluminium Hydride.

The complex (0.5 g., 0.001 mole) in ether (20 ml.) was added dropwise and with stirring to an ice-cold suspension of lithium aluminium hydride (0.2 g., 0.005 mole) in ether (30 ml.). There was a vigorous reaction during addition of the complex. The reaction mixture was stirred for 2 hr. at this temperature. Excess lithium aluminium hydride was destroyed by the addition of ethyl alcohol (10 ml.). The reaction mixture was filtered, the filtrate evaporated under reduced pressure and the residue was chromatographed in petroleum ether on alumina to give:

(1) A light pink solid (0.048 g.) eluted with ether. It was crystallised from petroleum ether (b.p. 30-40°) to give o-aminodiphenylamine, m.p. 77-8°, undepressed on admixture with an authentic specimen.

(2) Traces of material, eluted before and after the main product mentioned above, were not studied.

Prolysis of the Complex obtained from Azobenzene and Iron Pentacarbonyl.

The complex (0.1 g., 0.0002 mole) taken in a sublimation apparatus at 0.08 mm. was plunged into a metal bath at 200° and kept at this temperature for 75 mins. A part of the complex sublimed instantaneously. Both sublimate and the residue were chromatographed in petroleum ether on alumina to give unchanged complex (0.070 g., 70% recovery). No other product was detected.

Reaction of Azobenzene with Methylcyclopentadienylmanganese Tricarbonyl.

Azobenzene (2 g., 0.011 mole) and methylcyclopentadienylmanganese tricarbonyl (2.4 g., 0.011 mole) were irradiated in benzene (550 ml.) for 6 hr. The solution was filtered, the solvent evaporated under reduced pressure and the residue was chromatographed in petroleum ether on alumina to give both azobenzene and methylcyclopentadienylmanganese tricarbonyl in almost quantitative amounts.

Reaction of 4,4'-Dimethoxyazobenzene and Iron Pentacarbonyl under irradiation.

4,4'-Dimethoxyazobenzene[92] (12 g., 0.049 mole) and iron pentacarbonyl (19.5 g., 0.099 mole) were irradiated in benzene (1300 ml.) for 40 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was dissolved in benzene (200 ml.) and chromatographed on alumina in petroleum ether to give:

(1) A deep brown solid contaminated with 4,4'-dimethoxyazobenzene and eluted with benzene-petroleum ether (1:1). Most of the unchanged 4,4'-dimethoxyazobenzene was sublimed at 90° at 0.08 mm. and the residue chromatographed in petroleum ether on alumina. Repeated crystallisation from petroleum ether furnished crystalline material (0.05 g., 0.19%), m.p. 170° d. (Found: C,46.35; H,3.0; N,5.5. $C_{20}H_{14}Fe_2N_2O_8$ requires C,46.0; H,2.7; N,5.4).

$\nu_{max.}$ (CCl_4) 3358 cm.$^{-1}$ (NH); 1972, 2022 and 2060 cm.$^{-1}$ and (KCl) 1965, 1978 with a shoulder at 1992, 2023, 2040 and 2065 cm.$^{-1}$ (MC=O).

(2) An impure deep red solid eluted with benzene. Repeated chromatography in benzene-petroleum ether (1:1) on alumina and repeated crystallisation from benzene-petroleum ether furnished red crystalline product (0.3 g., 0.50%), m.p. 148.5-149° (Found: C,60.8; H,4.5; N,9.4. $C_{30}H_{26}FeN_4O_6$ requires

C,60.7; H,4.4; N,9.4).

$\nu_{\text{max.}}$ (CCl_4) 1970 and 2020 cm.$^{-1}$ (MC=O)

(3) A very complicated mixture of organic products (1.59 g.) eluted with solvents of increasing polarities. They were not studied.

Reaction of 4,4'-Dimethylazobenzene and Iron Pentacarbonyl under irradiation.

4,4'-Dimethylazobenzene^{92} (4 g., 0.019 mole) and iron pentacarbonyl (7.46 g., 0.038 mole) were irradiated in benzene (600 ml.) for 20 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was dissolved in benzene (150 ml.) and chromatographed on alumina to give:

(1) A mixture of products eluted with benzene. The petroleum ether soluble portion from this was chromatographed on alumina to give:

(a) A deep brown solid (0.2 g., 2.2%) eluted with benzene-petroleum ether (1:12). Rechromatography and crystallisation for petroleum ether furnished the crystalline product, m.p. 172°. (Found: C,48.95; H,3.0; N,5.6. $C_{20}H_{14}Fe_2N_2O_6$ requires C,49.0; H,2.9; N,5.7).

$\nu_{\text{max.}}$ (CCl_4) 3358 cm.$^{-1}$ (NH); 1970, 2022 and 2060 cm.$^{-1}$(MC=O

(b) A red solid (0.05 g., 0.31 %) eluted with benzene-petroleum ether (1:6). Rechromatography and crystallisation from pentane gave a product, m.p. 167-8°. It was not possible to obtain this compound in analytical purity. $\nu_{\text{max.}}$ (CCl_4) 1970 and 2022 cm.$^{-1}$ (MC=O).

(2) A white solid (0.165 g.) eluted with ethyl acetate. Rechromatography in ether-ethyl acetate (4:1) on alumina and crystallisation from ether-petroleum ether gave crystalline product, m.p. 181-3°. (Found: C, 80.3; H, 8.1; N, 11.8). $_{\text{max.}}$ ($CHCl_3$) 3350, 3428 cm.$^{-1}$ (NH).

(3) A red solid (0.027 g.) eluted with ethyl acetate. It crystallised from ethyl alcohol, m.p. 145-6°. 4,4'-Dimethylazobenzene did not dipress its melting point.

<u>Reaction of 4,4'-Dimethylazobenzene and Diiron Enneacarbonyl</u>

4,4'-Dimethylazobenzene^{92} (15 g., 0.071 mole) and diiron enneacarbonyl (26 g., 0.071 mole) were stirred in benzene (600 ml.) at room temperature for 20 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The petroleum ether soluble portion of the residue was chromatographed on alumina to give:

(1) A deep red solid (0.050 g., 0.16%) eluted with petroleum ether. It was crystallised from petroleum ether (b.p. 40-60°) to a product, m.p. 166-7°. (Found: C, 43.4; H, 2.5; N, 5.9; O, 23.8. $C_{23}H_{14}Fe_3N_2O_9$ requires C, 43.85; H, 2.2, N, 4.45; O, 22.9). $\nu_{\text{max.}}$ (CCl_4) 1968, 1985, 2005, 2035 and 2050 cm.$^{-1}$ (MC=O)

(2) The products eluted subsequently in extremely small amounts make any further study impossible.

The petroleum ether insoluble portion of the residue only unchanged 4,4'-dimethylazobenzene (13 g., 86.6% recovery) and some polymeric products.

REACTIONS OF SCHIFF BASES WITH IRON CARBONYLS.

Reaction of N-Benzylideneaniline with Diiron Enneacarbonyl

N-Benzylideneaniline[93] (4 g., 0.002 mole) and diiron enneacarbonyl (8.27 g., 0.002 mole) were stirred in benzene (200 ml.) at room temperature for 20 hr. The reaction mixture was filtered through kieselguhr and the residue left after the evaporation of solvent under reduced pressure was chromatographed in petroleum ether on alumina to give:

(1) A deep brown solid (1.7 g., 16.7%) eluted with petroleum ether. It was rechromatographed and crystallised from petroleum ether (b.p. 30-40°) to give deep brown crystals, m.p. 82-82.5° (Found: C, 49.7; H, 2.5; N, 3.2. $C_{19}H_{11}Fe_2NO_6$ requires C, 49.5; H, 2.4; N, 3.0).

$\nu_{max.}$ (CCl_4) 1980, 2025 and 2065 cm.$^{-1}$ and

(KCl) 1935, 1955, 1968 with a shoulder at 1980, 2010 and 2055 cm.$^{-1}$ (MC-O).

N.M.R. data are reported in the Appendix.

(2) A white solid (0.052 g.) eluted with ethyl acetate. Crystallisation from ethyl acetate-petroleum ether gave white plates, m.p. 159.5-160°, undepressed on admixture with an authentic sample of benzanilide. They had superimposable infrared spectra.

(3) A mixture of liquids (1.145 g.) eluted with ethyl acetate. It was fractionally distilled to give:

(a) A colourless liquid (0.454 g.), b.p. 36° at 0.7 mm. Its infrared spectrum was superimposable with that of an authentic specimen of aniline.

(b) A colourless liquid (0.161 g.), b.p. 56° at 0.7 mm. (Found: C,74.9; H,7.2).

$\nu_{max.}$ (liquid) 1724 cm.$^{-1}$ (CO).

The thick brown liquid left behind was not investigate

Reaction of N-Benzylideneaniline with Iron Pentacarbonyl under irradiation.

N-Benzylideneaniline[93] (4 g., 0.022 mole) and iron pentacarbonyl (9 g., 0.045 mole) were irradiated in benzene (500 ml.) for 15 hr. The reaction mixture was filtered through kieselguhr and the residue left after removal of the solvent under reduced pressure was chromatographed in petroleum ether on alumina to give:

(1) A deep brown solid (0.465 g., 4.5%) eluted with petroleum ether. It was identical with the complex formed from N-benzylideneaniline and diiron enneacarbonyl.

(2) A mixture of two liquids (1.970 g.) as obtained in the preceding experiment.

Formation of benzanilide was not detected in this case.

Reaction of the Complex obtained from N-Benzylideneaniline and Diiron Enneacarbonyl with Lithium Aluminium Hydride.

The complex (1 g., 0.002 mole) dissolved in tetrahydrofuran (20 ml.) was added dropwise and with stirring to an ice-cold suspension of lithium aluminium hydride (0.16 g., 0.004 mole) in tetrahydrofuran (50 ml.). After stirring the reaction mixture for 1 hr., excess lithium aluminium hydride was decomposed by the addition of ethyl acetate (20 ml.). The reaction mixture was filtered through kieselguhr and the residue left on evaporatio of the solvent under reduced pressure was chromatographed in petroleum ether on alumina to give:

(1) A trace of unchanged complex eluted with petroleum ether.

(2) A white solid (0.240 g.) eluted with petroleum ether. This was crystallised from petroleum ether (b.p. 40-60°) to give N-benzylaniline, m.p. 35°, undepressed on admixture with an authentic specimen. They had superimposable infrared spectra.

Reaction of the Complex obtained from N-Benzylideneaniline and Diiron Enneacarbonyl with Ferric Chloride.

(a) The complex (1 g., 0.002 mole) dissolved in benzene (30 ml.) was added dropwise and with stirring to a suspension of anhydrous ferric chloride (0.7 g., 0.004 mole) in benzene (50 ml.). The reaction mixture was stirred for 4 hr. at room temperature and filtered through kieselguhr. The residue left on evaporation of the filtrate under reduced pressure was chromatographed in petroleum ether on alumina to give only unchanged complex (0.7 g., 70% recovery).

(b) The complex (1 g., 0.002 mole) dissolved in ethyl alcohol (40 ml.) was added dropwise and with stirring to a solution of anhydrous ferric chloride (0.7 g., 0.004 mole) in ethyl alcohol (30 ml.). The reaction mixture was stirred at room temperature for 3 hr. and then at 60° for 3 hr.; during this time there was no visible change. The reaction mixture was filtered and the deep red gummy residue left on evaporation of the solvent under reduced pressure did not dissolve in common organic solvents. Its solution in ethyl alcohol was filtered through alumina and the light brown solid thus eluted (0.250 g.) was chromatographed in benzene on alumina. A white solid (0.220 g.) was eluted with benzene-ether (4:1), and this on crystallisation from benzene-petroleum ether had m.p. 160-1°.

(Found: C,82.0; H,6.1; N,6.6)

$\nu_{\text{max.}}$ (CCl_4) 1675 cm.$^{-1}$ (CO).

N.M.R.($CDCl_3$) 2.47τ(multiplet) and 5.25τ(singlet)[ratio 5:1].

Reaction of N-4-Methylbenzylideneaniline with Diiron Enneacarbonyl

N-4-Methylbenzylideneaniline^{94} (4 g., 0.02 mole) and diiron enneacarbonyl (7.4 g., 0.02 mole) were stirred in benzene (200 ml.) at room temperature for 24 hr. The reaction mixture was filtered through kieselguhr and the filtrate evaporated under reduced pressure. The residue thus obtained was chromatographed in petroleum ether on alumina to give:

(1) A deep brown solid (0.090 g., 0.92%) eluted with petroleum ether. It was rechromatographed and crystallised from petroleum ether (b.p. 30-40°) to give deep brown crystals, m.p. 138-9°. (Found: C,50.6; H,2.75; O,20.4. $C_{20}H_{13}Fe_2NO_6$ requires C,50.6; H,2.8; O,20.2).
$\nu_{max.}$ (CCl$_4$) 1980, 2025 and 2065 cm.$^{-1}$ and
(KCl) 1945, 1965 with a shoulder at 1980, 1995, 2010 and 2060 cm.$^{-1}$ (MC-O).

N.M.R. data are reported in the Appendix.

(2) A second brown solid (0.760 g., 7.8%) eluted with petroleum ether. It was rechromatographed and crystallised from petroleum ether (b.p. 30-40°) to give deep brown crystalline material, m.p. 127-127.5°. (Found: C,50.7; H,2.6; N,3.2; O,20.3. $C_{20}H_{13}Fe_2NO_6$ requires C,50.6; H,2.8; N,2.95; O,20.2).
$\nu_{max.}$ (CCl$_4$) 1965, 2020 and 2060 cm.$^{-1}$ and
(KCl) 1955, 1985, 2010-2015 and 2050 cm.$^{-1}$ (MC-O).

N.M.R. data are reported in the Appendix.

(3) Unchanged N-4-methylbenzylideneaniline (2.1 g., ~50% recovery) eluted with benzene.

(4) A pale yellow liquid (0.724 g.) eluted with ethyl acetate.

It was distilled to give a colourless liquid (0.349 g.). Its infrared spectrum was superimposable with that of an authentic sample of aniline.

A part of the residue left after distillation crystallised from ethyl acetate-petroleum ether to give white crystalline solid (0.015 g.), m.p. 142°.

$\nu_{\text{max.}}$ ($CHCl_3$) 3432 cm.$^{-1}$ (NH); 1735 cm.$^{-1}$ (CO).

This evidence suggests that the compound is p-toluanilide. (Lit.[95] m.p. 146°).

Reaction of the Second Complex obtained from N-4-Methylbenzylideneaniline and Diiron Enneacarbonyl with Lithium Aluminium Hydride.

The complex (1 g., 0.002 mole) dissolved in tetrahydrofuran (20 ml.) was added dropwise and with stirring to an ice-cold suspension of lithium aluminium hydride (0.250 g., 0.006 mole) in tetrahydrofuran (40 ml.). The reaction mixture was stirred for 1 hr. at this temperature and for 1 hr. at room temperature. Excess lithium aluminium hydride was decomposed by the dropwise addition of ethyl acetate (20 ml.). The reaction mixture was filtered, sovent evaporated under reduced pressure and the residue chromatographed in petroleum ether on alumina to give:

(1) Unchanged complex (0.282 g., 28.2% recovery) eluted with petroleum ether.

(2) A white solid (0.135 g.) eluted with ether. It was crystallised from petroleum ether (b.p. 30-40°) to a solid, m.p. 43-5°.

$\nu_{max.}$ (CCl_4) 3448 cm.$^{-1}$ (NH).

Evidence from melting point and infrared spectrum suggests that the compound is N-4-methylbenzylaniline. (Lit.[96] m.p. 42-45°).

Reaction of N-Benzylidene-p-toluidine with Diiron Enneacarbonyl.

N-Benzylidene-p-toluidine[94] (4 g., 0.02 mole) and diiron enneacarbonyl (7.4 g., 0.02 mole) were stirred in benzene (200 ml.) at room temperature for 24 hr. The reaction mixture was then filtered through kieselguhr and the solvent evaporated under reduced pressure. Chromatography of the residue in petroleum ether on alumina gave:

(1) A maroon solid (1.610 g., 16.3%) eluted with petroleum ether. Rechromatography and crystallisation from petroleum ether (b.p. 40-60°) gave a crystalline product, m.p. 87°. (Found: C,50.6; H,3.05; O,20.4. $C_{20}H_{13}Fe_2NO_6$ requires C,50.6; H,2.8; O,20.2).

$\nu_{max.}$ (CCl_4) 1980, 2028 and 2068 cm.$^{-1}$ and

(KCl) 1935, 1960, 1980, 2020 and 2060 cm.$^{-1}$ (MC-O).

N.M.R. data are reported in the Appendix.

(2) A number of organic compounds (1.469 g.) eluted with solvents of increasing polarities were not studied.

Reaction of N-Benzylidenemethylamine and Diiron Enneacarbonyl.

N-Benzylidenemethylamine[97] (12 g., 0.10 mole) and diiron enneacarbonyl (58 g., 0.16 mole) were stirred in benzene (600 ml.) at room temperature for 24 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The petroleum ether soluble portion of the residue was chromatographed on alumina to give:

(1) A deep brown solid (13.73 g., 34%; based on unrecovered Schiff base) eluted with petroleum ether. Rechromatography and crystallisation from petroleum ether (b.p. 30-40°) gave crystalline product, m.p. 92-92.5°. (Found: C,42.25; H,2.3; N,3.55; O,24.2. $C_{14}H_9Fe_2NO_6$ requires C,42.1; H,2.3; N,3.5; O,24.1).

$\nu_{max.}$ (CCl_4) 1985, 2035 and 2075 cm.$^{-1}$ and
(KCl) 1945, 1955, 1970 with a shoulder at 1980, 2025 and 2065 cm.$^{-1}$ (MC=O).

N.M.R. data are reported in the Appendix.

(2) Organic byproducts (3.13 g.) when the column was stripped with methyl alcohol. They were not studied.

Reaction of N-Isopropylideneaniline with Diiron Enneacarbonyl

N-Isopropylideneaniline[98] (4 g., 0.03 mole) and diiron enneacarbonyl (21.8 g., 0.06 mole) were stirred in benzene (200 ml. at room temperature for 8 hr. All diiron enneacarbonyl had been consumed during this time and there was extensive decomposition of the reaction mixture. It was filtered through kieselguhr and the solvent distilled under reduced pressure. Chromatography of the unstable residue in petroleum ether on alumina gave:

(1) An unstable orange liquid (0.07 g.) eluted with petroleum ether. It was not studied further.

$\nu_{max.}$ (liquid) 1960, 2000and 2020 cm.$^{-1}$ (MC=O).

(2) Unchanged N-isopropylideneaniline (3.068 g., 75% recovery) eluted with methylene chloride and identified by comparison of its infrared spectrum with that of an authentic specimen.

Reaction of Acetophenone Anil with Diiron Enneacarbonyl.

Acetophenone anil[99] (6 g., 0.03 mole) and diiron enneacarbonyl (22.4 g., 0.06 mole) were stirred in benzene (300 ml.) at room temperature for 24 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was chromatographed in petroleum ether on alumina to give:

(1) A maroon solid (2.165 g., 22.3%; based on unrecovered acetophenone anil) eluted with petroleum ether. Rechromatography and crystallisation from ether-petroleum ether (b.p. 40-60°) gave a crystalline product, m.p. 129-30°. (Found: C,50.6; H,3.0; N,3.1; O,20.4. $C_{20}H_{13}Fe_2NO_6$ requires C,50.6; H,2.8; N,2.95; O,20.2).

$\nu_{max.}$ (CCl_4) 1990 with a shoulder at 2000, 2040 and 2080 cm.$^{-1}$ and

(KCl) 1950, 1970, 1980, 2000, 2035 and 2075 (MC=O)

N.M.R. data are reported in the Appendix.

(2) The organic byproducts (3.28 g.) subsequently eluted were not studied.

MISCELLANEOUS REACTIONS

Reaction of Benzaldehyde Phenylhydrazone with Diiron Enneacarbonyl.

Benzaldehyde phenylhydrazone[100] (16 g., 0.08 mole) and diiron enneacarbonyl (29.6 g., 0.08 mole) were stirred in benzene (800 ml.) at 60° for 3 hr. and then at room temperature overnight. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. Petroleum ether and a trace of benzene removed all the coloured material from the residue and this was chromatographed in petroleum ether on alumina to give;

(1) An orange solid eluted with petroleum ether-benzene (9:1). Rechromatography and crystallisation from ether-petroleum ether furnished crystalline product (0.740 g., 1.9%), m.p. 117-8°. (Found: C, 47.9; H, 2.9; N, 6.0; O, 20.3. $C_{19}H_{12}Fe_2NO_6$ requires C, 47.9; H, 2.55; N, 5.9; O, 20.2).

$\nu_{max.}$ (CCl_4) 1980, 2030 and 2068 cm.$^{-1}$ and

(KCl) 1945, 1955, 1970, 1985, 2015 and 2058 cm.$^{-1}$ (MC=O)

(2) A series of seven bands were eluted with solvents of increasing polarities. These products were in insufficient amounts for any study.

The petroleum ether insoluble portion contained no metal carbonyl derivatives and was not studied.

Reaction of Diphenylketene and Iron Pentacarbonyl under irradiation.

Diphenylketene[101] (9 g., 0.046 mole) and iron pentacarbonyl (18.396 g., 0.093 mole) were irradiated in benzene (650 ml.) for 20 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was chromatographed in benzene on alumina (6 hr. deactivated). Re-chromatography in petroleum ether-benzene (10:1) and crystallisation from ether afforded an orange product, m.p. 129-30°. (Found: C,51.4; H,2.2; O,24.9. $C_{21}H_{12}Fe_2O_8$ requires C,50.0; H,2.4; O,25.4).

$\nu_{max.}$ (CCl_4) 2010, 2058 and 2103 $cm.^{-1}$ and

(KCl) 1970, 1980, 2002, 2025 and 2090 $cm.^{-1}$ (MC=O).

N.M.R.(CCl_4) 2.78 τ(singlet, aromatic portons).

There was extensive decomposition of the complex on alumina (not deactivated) with consequent loss of the material.

Reaction of Diethyl Azodicarboxylate and Diiron Enneacarbonyl.

Diethyl azodicarboxylate (4 g., 0.023 mole) and diiron enneacarbonyl (8.4 g., 0.023 mole) were stirred in benzene (200 ml.) at room temperature for 20 hr. Actually, a deep blue solid started precipitating out almost instantaneously when the reactants were brought together. The reaction mixture was filtered. This blue solid was unstable, changing to brown in about 2 hr.; it did not show metal carbonyl absorptions in the infrared spectrum. It was insoluble in all organic solvents and was not studied further. The filtrate was evaporated under reduced pressure and residue chromatographed on alumina in benzene-petroleum ether (9:1) to give;

(1) Traces of colourless liquids (0.090 g.) eluted with solvents of increasing polarities.

(2) A white solid (0.040 g.) eluted with methylene chloride. It was crystallised from ethyl acetate-petroleum ether to a product, m.p. 129°.

$\nu_{max.}$ (KCl) 3279 cm.$^{-1}$ (NH).

Evidence from its infrared spectrum and melting point suggests that the compound is diethyl hydrazine dicarboxylate. (Lit.[102] m.p. 131°).

This experiment carried out under irradiation yielded the same products.

Reaction of Diazocyclopentadiene and Iron Pentacarbonyl under irradiation.

Diazocyclopentadiene[103] (2.4 g., 0.026 mole) and iron pentacarbonyl (5.1 g., 0.026 mole) were irradiated in benzene (400 ml.) for 2 hr. The reaction mixture was rapidly filtered and the solvent evaporated under reduced pressure. There was extensive decomposition during this time. The benzene soluble portion of the residue was again filtered and the solvent rapidly evaporated; the infrared spectrum of the unstable red oil thus left behind showed both terminal and bridging metal carbonyl absorption.

$\nu_{max.}$ (liquid) 2114, 2045 and 1976 cm.$^{-1}$ (Terminal MC=O);
1792 cm.$^{-1}$ (Bridging MC=O).

An attempt to chromatograph it on alumina in benzene resulted in complete decomposition.

Reaction of Diazofluorene and Iron Pentacarbonyl under irradiation.

Diazofluorene[90] (7 g., 0.036 mole) and iron pentacarbonyl (14.5 g., 0.073 mole) were irradiated in benzene (650 ml.) for 24 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was dissolved in benzene (150 ml.) and chromatographed on alumina (4 hr. deactivated) in petroleum ether to give:

(1) A deep violet compound (0.518 g.) eluted with petroleum ether. Quite a lot of it decomposed. Rechromatography gave crystalline material (0.10 g.). It was rapidly crystallised from ether-petroleum ether to a product m.p. 146-7°. (Found: C,50.2; H,1.8; O,25.6). It was fairly stable in the dry state. It was later found to be much more stable in carbon tetrachloride than in ether or petroleum ether.

$\nu_{max.}$ (CCl_4) 2012, 2052 and 2088 cm.$^{-1}$ (Terminal MC=O);
1840 cm.$^{-1}$ (Bridging MC=O).

(2) A number of organic products eluted subsequently were not studied.

Reaction of Diazofluorene and Diiron Enneacarbonyl.

Diazofluorene[90] (4 g., 0.02 mole) and diiron enneacarbonyl (15.2 g., 0.04 mole) were stirred in benzene (200 ml.) at room temperature for 24 hr. There was a little unchanged diiron enneacarbonyl. The reaction mixture was filtered and the solvent evaporated under reduced pressure. Addition of petroleum ether to the residue caused precipitation of a deep red solid (1.8 g.), sparingly soluble in most organic solvents. It was identified as fluorenone azine by its melting point and mixed melting with an authentic sample. The petroleum ether soluble part was chromatographed on alumina in petroleum ether to give:

(1) A deep violet solid (0.010 g.), rather sticky, eluted with benzene-petroleum ether (1:1). It did not melt $< 300^\circ$. $\nu_{max.}$ (KCl) 1934, 1972, 2000, 2020 and 2040 cm.$^{-1}$ (MC-O).

(2) A deep red solid (0.350 g.) eluted with benzene-petroleum ether (1:1). Rechromatography on alumina in benzene-petroleum ether (1:4) gave first a deep red compound (0.240 g.); it was crystallised from ether-petroleum ether into long needles, m.p. 187-8°. Lassaigne's test for nitrogen was negative and it did not contain any iron. This evidence suggests that the compound is bifluorenylidene. (lit.[105] m.p. 190-1°). It was followed by an orange solid (0.006 g.), eluted with benzene-

petroleum ether (1:4). It did not melt $\leq$ 300°, $\nu_{\text{max.}}$ (CCl_4) 1980, 2027 and 2062 cm.$^{-1}$ (MC-O).

(3) A yellow solid (0.20 g.) eluted with benzene. Rechromatography on ordinary alumina (6 hr. deactivated) in benzene gave crystalline material, m.p. 82-3°, undepressed by an authentic sample of fluorenone. Infrared spectral comparison also showed that this was fluorenone.

(4) A deep red solid (0.50 g.) eluted with ether-benzene (1:9), m.p. 278°, undepressed by an authentic specimen of fluorenone azine.

<u>Reaction of Tetramethyl-2-tetrazene with Iron Pentacarbonyl</u>

Tetramethyl-2-tetrazene^{106} (10 g., 0.074 mole) and iron pentacarbonyl (14.6 g., 0.086 mole) were irradiated in benzene (550 ml.) for 20 hr. There was extensive decomposition in the reaction mixture. It was rapidly filtered and the solvent evaporated under reduced pressure. The residue, partly decomposed during this time, was chromatgoraphed in petroleum ether on alumina. An unstable light orange solid (0.50 g.) eluted with petroleum ether. It was rapidly crystallised from petroleum ether (b.p. 30-40°), m.p. 115-16°. It appeared to be stable in the dry state. (Found: C,35.4; H,32.; N,7.1; O,27.3).

$\nu_{\text{max.}}$ (CCl_4) 1940, 1950, 1970, 1985, 2005 and 2055 cm.$^{-1}$ (MC-O).

Reaction of Tetramethyl-2-tetrazene with Diiron Enneacarbonyl

Tetramethyl-2-tetrazene[106] (4 g., 0.034 mole) and diiron enneacarbonyl (20.6 g., 0.056 mole) were stirred in benzene (200 ml.) at room temperature for 20 hr. There was extensive decomposition in the reaction mixture. It was rapidly filtered through kieselguhr and the filtrate evaporated under reduced pressure. The residue containing considerable amounts of decomposed material was chromatographed in petroleum ether on alumina to give a highly unstable orange liquid (0.080 g.). $\nu_{max.}$ (liquid) 1972, 2016 and 2061 cm.$^{-1}$ (MC-O).

Reaction of Fluorenone and Iron Pentacarbonyl under irradiation.

Fluorenone (4 g., 0.022 mole) and iron pentacarbonyl (4.4 g., 0.022 mole) were irradiated in benzene (600 ml.) for 8 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was dissolved in benzene (20 ml.) and petroleum ether (60 ml.) and chromatographed on alumina in petroleum ether. A yellow solid (3.5 g., 87.5% recovery) was eluted with petroleum ether and was shown to be unchanged fluorenone by mixed melting point with authentic sample.

Reaction of Fluorene and Iron Pentacarbonyl under irradiation

Fluorene (4 g., 0.024 mole) and iron pentacarbonyl (4.7 g., 0.024 mole) were irradiated in benzene (600 ml.) for 8 hr. There was practically no change in the colour of the reaction mixture. It was filtered and the solvent evaporated under reduced pressure.

The infrared spectrum of the residue was superimposable with that of an authentic sample of fluorene and the recovery was quantitative.

Reaction of Tetraphenylethylene and Diiron Enneacarbonyl.

Tetraphenylethylene[107] (4 g., 0.012 mole) and diiron enneacarbonyl (4.4 g., 0.012 mole) were heated to reflux in benzene (200 ml.) with stirring for 6 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. On addition of benzene to the residue, triiron dodecacarbonyl (0.5 g.) was thrown out. It was filtered and the saturated solution of the filtrate was chromatographed in benzene on alumina. Unchanged tetraphenylethylene (3.8 g., 95% recovery) was eluted with benzene.

Reaction of Tetraphenylethylene and Iron Pentacarbonyl under irradiation.

Tetraphenylethylene[107] (4 g., 0.012 mole) and iron pentacarbonyl (4.7 g., 0.024 mole) were irradiated in benzene (500 ml.) for 8 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. Chromatography of the residue in benzene on alumina gave unchanged tetraphenylethylene in nearly quantitative amounts.

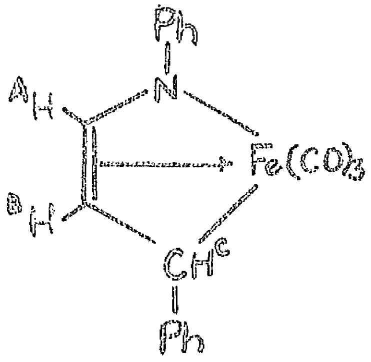
ADDENDUM

Reaction of N-Cinnamylideneaniline with Diiron Enneacarbonyl.- N-Cinnamylideneaniline[108] (2 g., 0.009 mole) and diiron enneacarbonyl (3.5 g., 0.009 mole) were stirred in benzene (200 ml.) at room temperature for 24 hr. The reaction mixture was filtered through kieselguhr and the solvent evaporated under reduced pressure. The residue was dissolved in the minimum volume of a mixture of benzene-petroleum ether (1:4) and chromatographed on alumina (4 hr. deactivated) to give

(1) A red solid (1.58 g., 47.1% ; based on anil taken), eluted with benzene-petroleum ether (1:4). Rechromatography and crystallisation from ether gave a product, m.p. 130-131° (Found: C,62.1; H,3.75; N,4.2; O,14.1. $C_{18}H_{13}FeNO_3$ requires C,62.3; H,3.8; N,4.0; O,13.8).

$\nu_{max.}(CCl_4)$ 1985 with a shoulder at 1995, 2060 $cm.^{-1}$ (MC-O)

The structure given below is analogous to that of π-cinnamaldehydeiron tricarbonyl[109] and consistent with the n.m.r. spectrum. The n.m.r. spectrum (carbon disulphide) shows

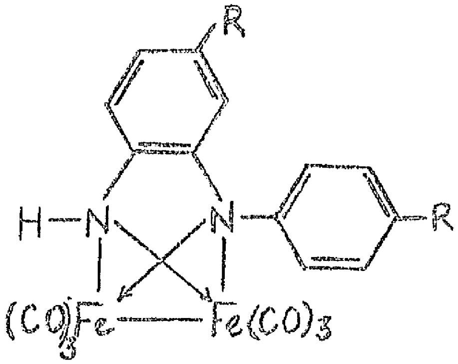


peaks at 2.95 τ (multiplet, relative intensity 10.6, aromatic protons + proton A), 4.42 τ (symmetrical quadruplet, relative intensity 1, proton B; $J_{AB} \simeq 3$ c/s; $J_{BC} \simeq 9.1$ c/s), 6.72 τ (symmetrical quadruplet, relative intensity 1, proton C; $J_{BC} \simeq 9.1$ c/s; $J_{AC} \simeq 1.1$ c/s).

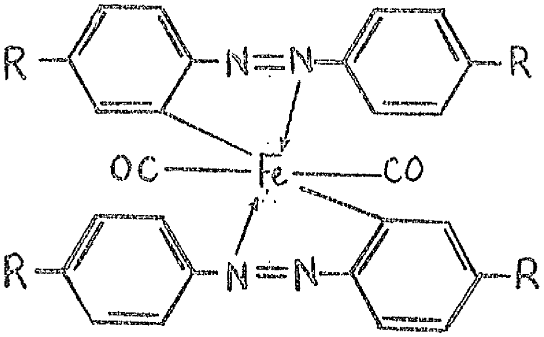
(2) The organic products (0.71 g.) eluted subsequently were not studied.

APPENDIX

Infrared maxima for Iron Carbonyl Complexes from Azobenzene and Substituted Azobenzenes between 1666 cm.$^{-1}$ and 2500 cm.$^{-1}$ (carbon tetrachloride)

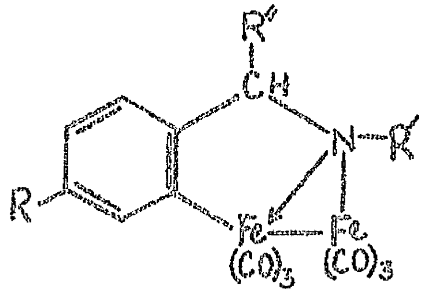


Complex	max. (cm.$^{-1}$)
R = H	1985, 2035 and 2075
R = OCH_3	1972, 2022 and 2060
R = CH_3	1970, 2022 and 2060



Complex	max. (cm.$^{-1}$)
R = OCH_3	1970, 2020
R = CH_3	1970, 2020

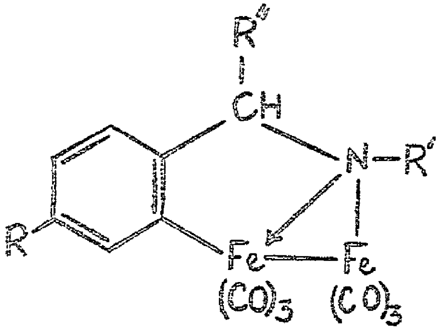
Infrared Maxima for Iron Carbonyl Complexes of Schiff Bases between 1666 cm^{-1} and 2500 $cm.^{-1}$ (carbon tetrachloride).



Schiff Base Complex	max. ($cm.^{-1}$)
$R'' = R = H$; $R' = Ph$	1980, 2025 and 2065
$R'' = H$; $R = CH_3$; $R' = Ph$ (minor)	1980, 2025 and 2065
$R'' = H$; $R = CH_3$; $R' = Ph$ (major)	1965, 2020 and 2060
$R'' = R = H$; $R' = C_6H_4CH_3$-p	1980, 2028 and 2068
$R'' = R = H$; $R' = CH_3$	1985, 2035 and 2075
$R'' = CH_3$; $R = H$; $R' = Ph$	1990, 2000[b], 2040 and 2080

b = shoulder

N.M.R. Spectra of Iron Carbonyl Complexes of Schiff Bases



Schiff Base Complex	Value	Relative Intensity	Assignment	
$R'' = R = H$; $R' = Ph$	2.45 (m) 5.59 (s)	10.4 2.0	Aromatic - Methylene-	- 9 - 2
$R = CH_3$; $R' = Ph$ $R'' = H$ (minor)	2.55 (m) 5.68 (s) 7.55 (s)	7.7 2.0 3.0	Aromatic- Methylene- Methyl-	- 8 - 2 - 3
$R = CH_3$; $R' = Ph$ $R'' = H$ (major)	2.67 (m) 5.63 (s) 7.63 (s)	8.1 2.0 3.0	Aromatic- Methylene- Methyl-	- 8 - 2 - 3
$R'' = R = H$; $R' = C_6H_4CH_3$-p	2.35 (m) 5.60 (s) 7.68 (s)	8.0 1.7 3.0	Aromatic- Methylene- Methyl-	- 8 - 2 - 3
$R'' = R = H$; $R' = CH_3$	2.45 (m) 5.96 (s) 7.16 (s)	4.2 1.8 3.0	Aromatic- Methylene- Methyl-	- 4 - 2 - 3
$R = H$; $R'' = CH_3$; $R' = Ph$	2.45 (m) 5.65 (q) 8.8 (d)	8.70 1.0 3.0	Aromatic- Methylene- Methyl-	- 9 - 1 - 3

s = singlet; m = multiplet; d = doublet; q = quadruplet.

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SUMMARY

Schiff bases of aromatic aldehydes and ketones react with diiron enneacarbonyl at room temperature giving complexe with the molecular formula (base) $Fe_2(CO)_6$. Azines and hydrazones afford analogous complexes. Schiff bases give lo yields of the same complexes when irradiated with iron pentacarbonyl, whereas azines do not react under these conditions. Azobenzene reacts with iron pentacarbonyl when irradiated to give a metal carbonyl complex corresponding to the formula "(azobenzene)$Fe_2(CO)_6$", which in fact is a derivative of orth semidine; in addition to this type, substituted azobenzenes also give products of the type (azobenzene)$_2$Fe(CO)$_2$. Reactio of azotoluene with diiron enneacarbonyl at room temperature gi yet another type of complex in extremely low yield. The mas spectral and chemical degradation and probable structures of these complexes are discussed.

Diphenyldiazomethane reacts with iron pentacarbonyl whe irradiated giving two different types of complexes; its react with triiron dodecacarbonyl gives predominantly one of these. 4,4'-Ditolyldiazomethane affords similar complexes, but phenyldiazomethane and phenylbenzoyldiazomethane give only unstable products in low yields. The most notable feature of this work is that diphenylketene, an irradiation product of

phenylbenzoyldiazomethane reacts smoothly with iron pentacarbonyl when irradiated to give complex in fairly high yiel Based on analytical, mass spectral and chemical degradation work, possible structures are proposed for these complexes. Diphenyldiazomethane does not react to give any complexes whe irradiated with nickel tetracarbonyl, methylcyclopentadienylmanganese tricarbonyl and chromium hexacarbonyl.

Tetramethyl-2-tetrazene reacts with iron pentacarbonyl when irradiated giving a complex in low yield; its reaction with diiron enneacarbonyl at room temperature gives an unstab liquid complex. Diazofluorine affords two complexes in very low yields, on treatment with diiron enneacarbonyl and a diffe complex when irradiated with iron pentacarbonyl; the latter compound shows both bridging and terminal metal carbonyl absorptions in the infrared spectrum. Diazocyclopentadiene gives an unstable liquid complex when irradiated with iron pentacarbonyl. No complexes are formed from ethyl azodicarbox late and iron pentacarbonyl or diiron enneacarbonyl. In view of the instability and low yields of these complexes, it has not been possible to carry out any chemical work on them. Attempts to form complexes from fluorene, fluorenone or tetraphenylethylene and iron pentacarbonyl by irradiation are not successful.

Some reactions between the complex obtained from acetyl and the iron tetracarbonyl anion and the following reagents are carried out in order to study the chemistry of this rather interesting compound. Its reaction with dichlorophenylphosphi does not give any phosphole. When irradiated, it yields an unstable complex. In order to see whether it is possible to replace one or more carbonyl groups by diphenylcarbene it is irradiated with diphenyldiazomethane. No such reaction occurs; instead two nitrogen containing complexes are obtained Its reaction with phenylacetylene gives a metal complex in very low yield. Although the study of these compounds is incomplet some data are presented on them.