

STUDIES ON THE CHEMISTRY OF

TRANSITION METAL CARBONYLS

A Thesis submitted by

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For her love, and patient understanding,

I Dedicate this Thesis to my Wife,

FRANCES

A C K N O W L E D G M E N T S

I would like to thank Professor G. Wilkinson for his constant help, encouragement and advice during his supervision of this work.

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A. Davison

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A B S T R A C T

The interaction of a variety of transition metal carbonyls and substituted carbonyls with sulphuric, trifluoroacetic and other strong acids is described. In a number of cases it has been shown that protonation of the central metal atom of the complex occurs in solution; typical protonated species are $[\text{HFe}(\text{CO})_3(\text{PPh}_3)_2]^+$, $[\text{H}\{\text{Mo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)\}_2]^+$ and $[\text{HCr}(\text{CO})_3\text{C}_6\text{H}_5\text{CH}_3]^+$.

Although in most cases protonation to give an M-H bond can be demonstrated only by the appearance of a high-field line in the high-resolution nuclear magnetic resonance spectra of the solutions, a few salts, e.g. $[\{\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\}_2\text{H}]\text{PF}_6$, can be isolated and the infrared spectra of the solids also show the presence of an M-H bond.

The structures of the protonated species are discussed, in particular those of the binuclear π -cyclopentadienyl molybdenum and tungsten carbonyls, which provide unusual examples in protonated species of the hydrogen being associated with two metal atoms.

Improved preparations of triphenylphosphine iron carbonyls are given and the triphenyl arsine and stibine analogues described. π -Cyclopentadienyl molybdenum and tungsten tricarbonyl trifluoroacetates and pentacarbonyl rhenium trifluoroacetate are also described.

Chloro- π -cyclopentadienyldicarbonyliron has been converted by the action of carbon monoxide and triphenyl-phosphine, -arsine, or -stibine into the cationic species $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{MPh}_3]^+$ (where M = P, As, or Sb).

Reduction by sodium borohydride of the triphenylphosphine substituted ion gives dicarbonylcyclopentadienetriphenylphosphineiron, but the tricarbonyl cation gives only hydridodicarbonylcyclopentadienyl-iron.

Infrared and nuclear magnetic resonance spectra are reported.

C H A P T E R I

INTRODUCTION

Since the discovery of iron carbonyl hydride,¹ $\text{H}_2\text{Fe}(\text{CO})_4$, in 1931, a large number of transition metal hydrides have been characterised.

A recent and comprehensive review of these hydrides has been published.² These hydrides have the hydrogen bonded directly to the transition metal, and many of them contain strongly π -bonding ligands, such as CO, CN, R_3P , and $\pi\text{-C}_5\text{H}_5$. Recently, however, a hydride of rhodium was reported, $[(\text{en})_2\text{RhClH}][\text{B}(\text{Ph})_4]$,³ which has no π -bonding ligands.

PROPERTIES

The stabilities vary from thermally unstable (decomposition -10°) and readily oxidised iron carbonyl hydride to the air- and thermally-stable⁴ hydrido-chlorobis-triethylphosphineplatinum.

Transition metal hydrides are often good reducing agents,⁵ e.g. acetone can be reduced to isopropyl alcohol using the stoichiometric amount of $\text{H}_2\text{Fe}(\text{CO})_4$.

Of the physical methods used for structure determinations, infrared and proton magnetic resonance spectroscopy have proved most useful in determining the nature of the transition metal hydride complexes.

Infrared spectral studies have shown that the metal hydrogen stretching modes² occur in the region 2300-1700 cm^{-1} . All the available proton magnetic resonance spectra show a characteristic high-field resonance in the region τ 10-50 (τ 10 is the chemical shift of tetramethylsilane), which is due to the proton bonded to the transition metal. Few other types of proton have resonances in this region, except for HI and amide protons of porphyrins, so the observation of a high-field proton resonance provides a unique means of demonstrating that a hydride is present in solution, even though it may not be possible to isolate it. The proton resonance of the hydrogen bonded to nuclei of transition metals, which have a spin = $\frac{1}{2}$, e.g. rhodium ^{103}Rh abundance 100% or tungsten ^{183}W abundance 14.28%, show doublet structure, which arises from spin-coupled interaction of the proton with the metal nuclei. This is proof that the resonance is due to a hydrogen bonded to the metal. The chemical shifts of the hydridic protons indicate that they are highly diamagnetically shielded.

The theory of the origin of chemical shifts and the shielding of nuclei have been discussed by Pople, Bernstein and Schneider.⁶

A qualitative consideration of the factors involved shows that, when a molecule is placed in a magnetic field, the applied field H_0 interacts with the motions of the electrons such that the molecule acquires a diamagnetic moment, which will contribute to the nett field at the nucleus. This component is proportional to the applied field

and can be considered to be the internal diamagnetic shielding of the nucleus. The magnetic field at the nucleus i will be given by $H_i = H_0(1 - \sigma_i)$ where σ_i is the non-dimensional shielding constant of the nucleus i . Chemical shifts arise because in general σ_i is a function of the chemical environment of the nucleus. In practice shielding constants are obtained from chemical shift measurements, i.e.

δ in p.p.m. related to σ by $\delta = \sigma - \sigma_r$; a positive value corresponds to greater shielding than that for the reference compound. Saika and Slichter⁷ divide the contributions to shielding into three terms:

(A) a diamagnetic correction due to bonding electrons around the atom;

(B) a paramagnetic term which results from mixing the ground state with the excited states of the atom;

(C) contributions from other atoms in the molecule.

The chemical shifts of protons, unlike those of ^{19}F and ^{59}Co , are not dominated by any one term. The local paramagnetic term (B) will be less important because there are no low-lying p orbitals on the hydrogen atom. Variations in the electron density around the hydrogen (term A) provides some correlation of shielding of protons to the electronegativity of the groups to which it is attached.

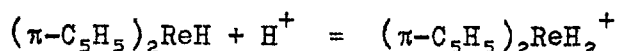
Measurements of proton shifts show that all of the shifts cannot be correlated with the ionic character of the bonds. This lack of correlation can be understood when it is considered that the total

electron density on the hydrogen is quite small and the proton will be exposed to currents flowing in other parts of the molecule. If the proton is bonded to a magnetically anisotropic group X, it will experience shielding if this neighbouring group has a greater diamagnetic susceptibility along the X-H bond rather than perpendicular to it. The major part of the anisotropy of the local susceptibility of the group is considered to arise from paramagnetic contributions from the mixing of the ground state with excited electronic states by the magnetic field. This near neighbour effect has been used to explain the increasing high-field shifts of HBr and HI,⁶ because the magnitude of the paramagnetic terms giving rise to the anisotropy will increase with increasing availability of upper orbitals (d and f, etc.). The chemical shifts of hydrogen bonded to silicon and tin are not large⁸ because, unlike transition metals, these elements have no low-lying d orbitals. d Electrons can give rise to much larger paramagnetic terms than do p or s electrons. The unusually large chemical shifts of transition metal hydrides probably arise from a large neighbour anisotropy effect, associated with the d electrons, which can give a large diamagnetic shielding to the hydride protons. As would be expected, therefore, the chemical shifts of these hydrides bear no relationship to the ionic character of the M-H bond.

ACID AND BASE BEHAVIOUR

The carbonyl hydrides of iron and manganese are weak acids,⁹
 $[\text{H}_2\text{Fe}(\text{CO})_4]: K_{a_1} = 4.15 \times 10^{-5}, K_{a_2} = 3.7 \times 10^{-14}; \text{HMn}(\text{CO})_5: K_a = 0.8 \times 10^{-7}]$,
 whereas $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$ is a weak base¹⁰ in aqueous dioxan ($K_b = 3.61 \times 10^{-9}$);
 $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$ is a very weak acid,¹¹ but when dissolved in $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{CO}_2\text{H}$
 it is a weak base (this thesis).

The first example of the protonation of a neutral transition metal complex to give a protonated hydride was that of di- π -cyclopentadienyl rhenium¹²



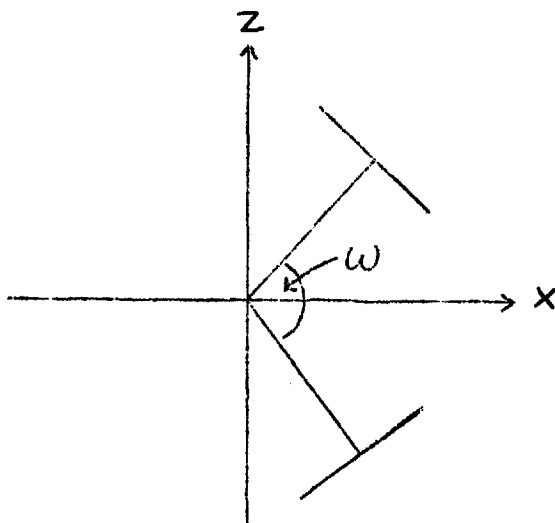
It was subsequently suggested by Sternberg and Wender⁵ that positively charged carbonyl hydrides could be produced, by protonation of carbonyl complexes, to account for the reducing properties of ethanolic hydrochloric acid solutions of $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$, and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with certain organic substrates. A preliminary study of the proton resonance spectra of some of these complexes in strong acids showed that, in some cases, protonation¹³ occurred to give cationic hydrides, although these were not always of the stoichiometry envisaged by Sternberg and Wender.

It was shown simultaneously that the neutral di- π -cyclopentadienyls of iron and ruthenium were protonated¹⁴ to give the cationic hydrides $(\pi\text{-C}_5\text{H}_5)_2\text{MH}^+$ ($\text{M} = \text{Fe}$ or Ru). The di- π -cyclopentadienyl dihydrides of molybdenum and tungsten¹⁵ function as monoacid bases when dissolved in acids to give the trihydride cations $(\pi\text{-C}_5\text{H}_5)_2\text{MH}_3^+$ ($\text{M} = \text{Mo}$ or W).

These protonated species are isoelectronic with the neutral $(\pi\text{-C}_5\text{H}_5)_2\text{TaH}_3$, which is not basic.¹⁵

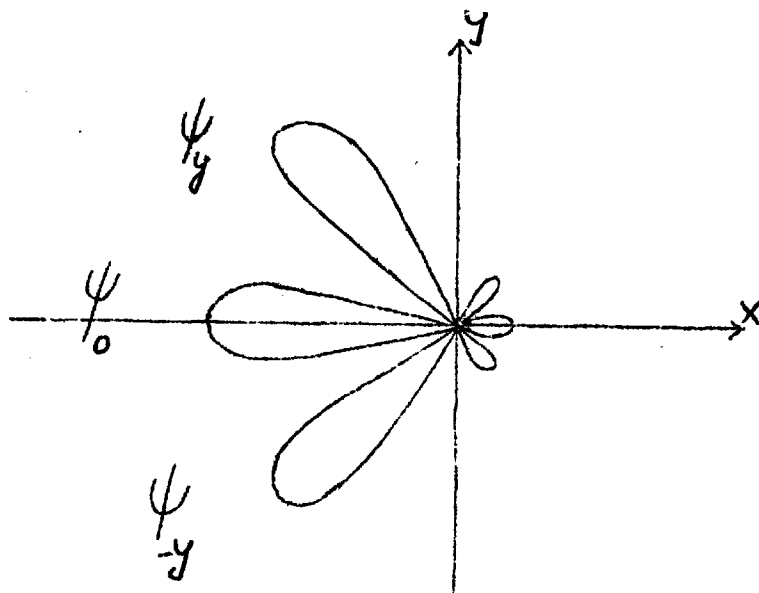
A theoretical interpretation of the ability of the neutral di- π -cyclopentadienyls and the di- π -cyclopentadienyl hydrides to take up a proton, and the structures of the hydride species, has been given by Ballhausen.¹⁶

In these complexes the cyclopentadienyl rings are twisted such that the radius vectors from the metal to the centre of the $\pi\text{-C}_5\text{H}_5$ rings make an angle ω .



All the valence orbitals of the metal atoms are used (i.e. $(n-1)$ d, ns, and np orbitals) to construct hybrid orbitals. Two sets of three mutually orthogonal hybrids, which can transform into each other by reflection in the xy plane, can be constructed. When ω is 135° , these orbitals are strongly directed towards the rings and overlap with bonding orbitals of the rings to give six bonding molecular orbitals.

The three remaining orbitals give three spatially directed hybrids ψ_0 , ψ_y and ψ_{-y} . They are orthogonal on each other and to the six ring hybrids; they are strongly spatially directed in the xy plane.



The ring bonding molecular orbitals contain twelve electrons, and the remaining electrons are treated as "chemically active" and are placed in the ψ_0 , ψ_y , and ψ_{-y} orbitals. These orbitals can be used for bonding hydrogens to the metal in the neutral di- π -cyclopentadienyl hydrides or they can be protonated just like other stereochemically active lone pairs. The maximum number of hydrogens which can be bonded in this way is three, which explains why di- π -cyclopentadienyltantalum trihydride is not protonated.

This thesis, in part, describes the behaviour of diverse organo-metallic and carbonyl complexes in strong acids with particular

reference to protonation. The behaviour of these complexes can be classified as follows:

(A) Dissolution without Decomposition. $C_7H_7Mo(CO)_3BF_4$ dissolves in concentrated sulphuric acid without decomposition.¹⁷

(B) Protonation of π -bonded Olefin Ligands. Complexes which have olefin ligands, in which there are π -electrons not utilised in bonding to the metal atom, can be protonated to give carbonium ions bonded to, and stabilised by, metal carbonyl residues,¹⁸ e.g. cyclooctatetraeneiron-tricarbonyl is protonated to give bicyclo[5,1,0]octadieniumirontricarbonyl cation.

(C) Dissolution to give Anionic Carbonyl Complexes. The binuclear halogen-bridged complexes of platinum and rhodium, $[Pt(CO)Cl_2]_2$ and $[Rh(CO)_2Cl]_2$, dissolve in concentrated hydrochloric acid to give the anionic carbonyl species¹⁹ $[Pt(CO)Cl_3]^-$ and²⁰ $[Rh(CO)_2Cl_2]^-$, respectively.

(D) Decomposition. Many complexes are decomposed by acids and in some cases hydrogen is given off.⁵ Some complexes are protonated by one acid, but are decomposed by another (see Table I). This could indicate that decomposition occurs via a protonated intermediate.

(E) Protonation to give Cationic Transition Metal Hydrides. Some metal carbonyls and organometallic carbonyls dissolve in strong acids, to give stable solutions which contain protonated cationic hydrides. These are discussed in subsequent sections.

CHAPTER II

PROTONATION STUDIES

Using various anhydrous strong acids as protonating solvents, it has been found that three classes of complex with strongly π -bonding ligands can be protonated. These are (I) binuclear π -cyclopentadienyl carbonyls which have metal-metal bonds, (II) mononuclear π -cyclopentadienyl and arene metal carbonyls, and (III) iron carbonyl and the substituted phosphine and arsine iron carbonyls.

The following acids have been used as protonating solvents: 98% AR sulphuric; trifluoroacetic; trifluoroacetic-boron trifluoride monohydrate mixtures; acetic and propionic anhydrides plus hydrofluoroboric acid; and boron trifluoride or phosphorus pentafluoride in anhydrous liquid hydrogen fluoride. Since many of the compounds studied decompose, often rapidly, in such media, salts have been isolated only in special cases, and the principal test of protonation has been the detection of a proton resonance line in the high-field region. For compounds where decomposition is so rapid (ca. 1-2 min.) that the proton resonance spectrum of the solution could not be recorded, protonated species may well be present initially; in some cases broadening by paramagnetic ions produced in decomposition could prevent observation of high-field lines. Since in at least one case intramolecular hydrogen transfer to another ligand occurs, this may be a common mode of decomposition.

A list of the compounds investigated is given in Table I.

TABLE I. Behaviour of Carbonyl Complexes in Strong Acids.

A, 98% A.R. H_2SO_4 . B, $\text{BF}_3 \cdot \text{H}_2\text{O}$ or $\text{CF}_3\text{CO}_2\text{H} \cdot \text{BF}_3 \cdot \text{H}_2\text{O}$ mixtures (1:1, 1:2, and 2:1). C, $\text{CF}_3\text{CO}_2\text{H}$ 100%.

s = soluble; i = insoluble; ds = decomposes slowly; dr = decomposes rapidly; st = stable for at least 10 min.; p = protonation (see text); sp.s = sparingly soluble.

Compound	A	B	C
1. CHROMIUM			
$\text{Cr}(\text{CO})_6$	i	i	i
Arene $\text{Cr}(\text{CO})_3$ (a)	s, yellow; dr 1-2 min.	s, yellow; p	sp.s
$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{Cr}(\text{CO})_3$	dr	dr	dr
$\text{XC}_6\text{H}_4\text{Cr}(\text{CO})_3$ (X = F or Cl)	dr	sp.s; p?	
diphenyl $[\text{Cr}(\text{CO})_3]_2$	dr	i	
$(\text{C}_6\text{H}_6)_2\text{Cr}$	dr	dr	dr
$\text{Cr}(\text{CO})_5\text{PPh}_3$		i; ds	i; ds
$\text{Cr}(\text{CO})_4[\text{PPh}_3]_2$	i	i; ds	i; ds
2. MOLYBDENUM			
$\text{Mo}(\text{CO})_6$	i	i	i
mesitylene $\text{Mo}(\text{CO})_3$	dr	dr	dr
$[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$	s, red brown; p; st	sp.s	sp.s
$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$	dr ($\text{CH}_4 \uparrow$)		dr ($\text{CH}_4 \uparrow$)
$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}$	dr ($\text{H}_2 \uparrow$)	dr ($\text{H}_2 \uparrow$)	dr ($\text{H}_2 \uparrow$)
$[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{Hg}$	dr (b)	sp.s; ds	
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$	dr (b) ($\text{HCl} \uparrow$)		
α, α -dipyridyl $\text{Mo}(\text{CO})_4$	dr	dr	dr

Compound	A	B	C
3. <u>TUNGSTEN</u>			
$W(CO)_6$	i	i	i
$(\pi-C_5H_5)_2MoW(CO)_6$	s, red brown; p; st		
$\pi-C_5H_5W(CO)_3Cl$	dr ^(b) (HCl↑)		
$\pi-C_5H_5W(CO)_3CH_3$	dr (CH ₄ ↑)	dr (CH ₄ ↑)	dr (CH ₄ ↑)
$[\pi-C_5H_5W(CO)_3]_2Hg$	dr ^(b)	s; p ^(c)	sp.s
$[\pi-C_5H_5W(CO)_3]_2$	s, red brown; p; st	sp.s	sp.s
$\pi-C_5H_5W(CO)_3H$	dr	s, yellow; p; ds	s
4. <u>MANGANESE</u>			
$\pi-CH_3-C_5H_4Mn(CO)_3$	s, red; st	s, red; st 2 days	s, red
$\pi-C_5H_5Mn(CO)_3$	sp.s, red	sp.s	sp.s
$Mn_2(CO)_{10}$	sp.s, yellow	sp.s, yellow	sp.s, yellow
$Mn(CO)_5CH_3$	dr (CH ₄ ↑)	dr (CH ₄ ↑)	dr (CH ₄ ↑)
$Mn(CO)_5Br$	dr	dr	dr
$\pi-C_5H_5FeMn(CO)_7$	s, red; p; st		
5. <u>RHENIUM</u>			
$Re_2(CO)_{10}$	i		
$Re(CO)_5CH_3$	dr (CH ₄ ↑)	dr (CH ₄ ↑)	dr (CH ₄ ↑)
6. <u>IRON</u>			
$Fe(CO)_5$	s, green; dr	s; p; ds	s; st
$Fe_2(CO)_9$	dr	dr	i
$Fe_3(CO)_{12}$	dr	dr	s
$Fe(CO)_4PPh_3$	s; p; st		dr
$Fe(CO)_3(PPh_3)_2$	s; p; st		dr

Table I (contd.)

14.

Compound	A	B	C
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	s; p; st		dr
$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$	s; p; st		dr
$\text{Fe}(\text{CO})_3(\text{SbPh}_3)_2$	s; p? dr (1 min.)		dr
$\text{Fe}(\text{CO})_3\text{diars}^{(d)}$	s; st	s; st	
$\text{Fe}(\text{CO})_4(\text{AuPPh}_3)_2$	dr		
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$	s (e)	s; p; st	s; st
$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	s, red brown; p; st	s; p; st	s; p; st (f)
$[\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7]$	s, red; p; st		
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$	dr ($\text{HCl} \uparrow$) (g)		s
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$	dr ($\text{CH}_4 \uparrow$) (g)	dr	dr
$\text{o-phen}_2\text{Fe}(\text{CN})_2$	s, yellow; st (h)	s, yellow; st (h)	s, yellow; st (h)
7. COBALT			
$\text{Co}_2(\text{CO})_8$	dr	dr	dr
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$	dr	dr	s; st
$\text{Co}(\text{CO})_4\text{AuPPh}_3$	dr (i)		
$\text{Co}_2(\text{CO})_6\text{C}_2\text{R}_2$ (R = alkyl and aryl)	dr		dr
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CCF}_3)_4$	s, red; st		s, red; st
$\text{Co}(\text{CO})_4\text{C}_3\text{F}_7$	dr	dr	dr
$[\text{Co}(\text{CO})_3\text{PPh}_3]_2$	dr	i; ds	i

Compound	A	B	C
8. <u>NICKEL</u>			
$\text{Ni}(\text{CO})_4$	s; dr	s; st	s; st
$\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$	dr (j)	dr	dr
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$	dr		
$\pi\text{-C}_5\text{H}_5\text{NiNO}$	dr		dr
$[\pi\text{-C}_5\text{H}_5\text{NiCO}]_2$	dr		dr
$(\pi\text{-C}_5\text{H}_5\text{Ni})_2\text{C}_2\text{R}_2$ (R = alkyl and aryl)	dr		
$\text{NiBr}_2(\text{Me}_2\text{PCH}_2)_2$	dr		

(a) See Table III for protonated species.

(b) Gives $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\cdot\text{OSO}_3\text{H}$.

(c) Gives $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}_2^+$ (see text).

(d) Diars = o-phenylene bisdimethyl arsine.

(e) Slight oxidation to $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}^+$.

(f) Also in $\text{CClF}_2\text{CO}_2\text{H}$ and $\text{HBF}_4(\text{aq})$ in propionic anhydride.

(g) Gives red $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{OSO}_3\text{H}$.

(h) Protonates the cyanide groups to give o-phen₂Fe(CNH⁺)₂ - no high-field line.

(i) $\text{HCo}(\text{CO})_4$ evolved.

(j) Forms Ni^{2+} and $\text{Ph}_3\text{PH}^+\text{HSO}_4^-$; CO evolved.

C H A P T E R I I I

BINUCLEAR π -CYCLOPENTADIENYL METAL CARBONYLS

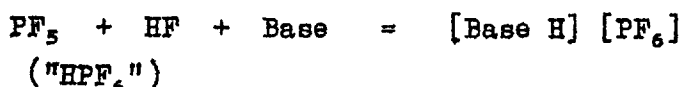
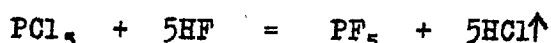
INTRODUCTION

The binuclear π -cyclopentadienyl carbonyls $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$), $[(\pi\text{-C}_5\text{H}_5)_2\text{MoW}(\text{CO})_6]$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7$ dissolve readily in oxygen-free 98% sulphuric acid to give fairly stable solutions. These solutions are diamagnetic (demonstrated using the Evans²¹ method) and their nuclear magnetic resonance spectra show resonance lines in both low- ($\tau < 10$) and high-field regions. The low-field line, due to the $\pi\text{-C}_5\text{H}_5$ group, is always a sharp singlet, in contrast to the $\pi\text{-C}_5\text{H}_5$ resonance line of the neutral and protonated di- π -cyclopentadienyl species of Mo, W, Re and Fe,^{10,14,15} which are multiplets due to spin coupling of the hydrogen on the metal with the ring hydrogens.

The absence of splitting in the present cases is probably not significant and even the mononuclear π -cyclopentadienyl carbonyl hydrides, e.g., $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$, show no observable splitting of the $\pi\text{-C}_5\text{H}_5$ resonances; for the di- π -cyclopentadienyl compounds the splitting is very small, ca. 0.5 - 1.5 cycle/sec.

The relative intensities of the $\pi\text{-C}_5\text{H}_5$ and high-field resonance lines (Table II) show that the binuclear complexes function as monoacid bases. The neutral complexes can be recovered, essentially quantitatively, by careful dilution of the sulphuric acid solutions with water. An

exception is the heptacarbonyl π -cyclopentadienyl iron manganese hydrogen cation which is stable in dilute aqueous acid, from which it can be precipitated by addition of solutions of salts of large anions such as hexafluorophosphate. Salts of the other binuclear protonated species have been obtained as hexafluorophosphates by the addition of phosphorus pentachloride to their solutions in anhydrous hydrogen fluoride, which generates PF_5 in situ giving rise to "HPF₆".



The hexafluorophosphates are sparingly soluble in liquid sulphur dioxide at room temperature (in a sealed tube).

The infrared spectra of the salts are consistent with their formulation as cationic hexafluorophosphates and the high-resolution nuclear magnetic resonance spectra of the liquid sulphur dioxide solutions show the characteristic high-field lines in positions identical to those recorded in sulphuric acid solutions.

The visible and ultraviolet absorption spectra (Fig. 1) of the protonated complexes in sulphuric acid are significantly different from those of the neutral complexes, the main features being a shift in the absorption maxima to longer wavelengths with a concomitant, approximately tenfold, decrease in the molar extinction coefficients. It may be noted that although dimanganese decacarbonyl is only sparingly soluble in concentrated sulphuric acid (saturated solution, ca. 10^{-3}M),

FIG. 1Visible and Ultraviolet Absorption Spectra

I : A, $[\pi\text{-C}_5\text{H}_5\text{W(CO)}_3]_2$ in CH_2Cl_2 .

B, $[\{\pi\text{-C}_5\text{H}_5\text{W(CO)}_3\}_2\text{H}^\oplus]^+$ in A.R. 98% H_2SO_4 .

II: A, $\text{Mn}_2(\text{CO})_{10}$ in CHCl_3 .

B, $\text{Mn}_2(\text{CO})_{10}$ in A.R. 98% H_2SO_4 .

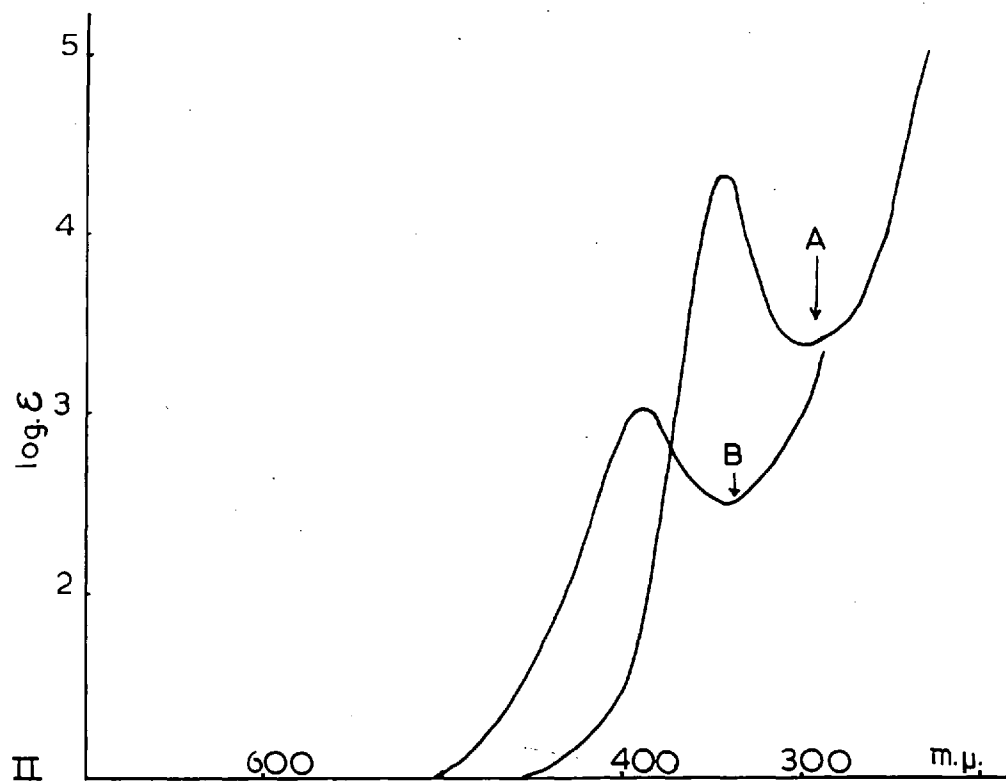
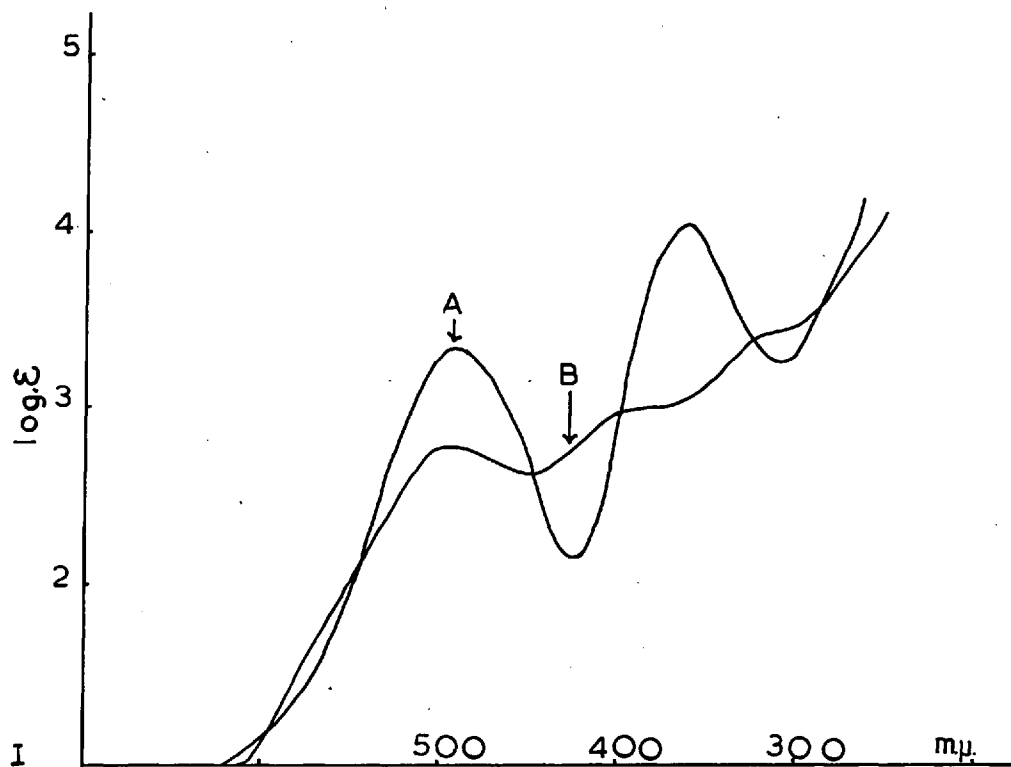


FIG. I.

giving a pale yellow solution which is too dilute for the detection of protonation by nuclear magnetic resonance, the absorption spectrum in sulphuric acid ($\lambda_{\max}$ 389 m μ , $\epsilon_{\max}$ 1,140) compared to that in chloroform ($\lambda_{\max}$ 343 m μ , $\epsilon_{\max}$ 22,800) suggests that protonation of the carbonyl occurs.

The study of the molybdenum and tungsten species has given information concerning the nature of the protonated binuclear species and these are discussed first.

The molybdenum and tungsten compounds. The purple-red binuclear compounds, $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]_2$, give red-brown solutions in sulphuric acid which decompose only slowly in the absence of air over a period of a few hours. For the neutral molybdenum compound, the infrared spectrum has strong bands at 1960 and 1916 cm^{-1} (the latter rather broad) assigned to the terminal carbonyl stretching modes; in sulphuric acid, there are bands at 2074, 2054 and 1988 cm^{-1} , all very strong. For the tungsten compound the corresponding values are 1958, 1928 and 1893 cm^{-1} and in sulphuric acid 2028 and 1961 cm^{-1} . The values in sulphuric acid compare favourably with those of the mull spectra of the hexafluorophosphates. For the tungsten compound the salt has bands at 2015 and 1960 cm^{-1} together with a strong band at ca. 850 cm^{-1} due to the PF_6^- ion. The differences between the neutral and protonated complexes show the expected increase in the C-O stretching frequencies for a cationic metal carbonyl complex.

The chemical shifts of the protons bound to the metal are exceptionally large, $\tau = 30-40$, and are among the highest so far recorded, a fact which lends strong support to the view²² that the magnitude of the proton shifts of hydrogen atoms bound to transition metals has little if any correlation with the electron density around the hydrogen atom or the polarity of the M-H bond. Additional conclusive evidence that the hydrogen atom is directly associated with the metal atom comes from the observation of satellite bands in the species containing tungsten atoms. These arise from spin-coupled interaction of the proton with the tungsten isotope ^{183}W (spin $\frac{1}{2}$, abundance 14.28%).

The sulphuric acid solutions containing equimolecular amounts of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ and $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ show only the separate independent lines of the components (Table II). This fact shows that there is no fission of the metal-metal bond in either binuclear species in sulphuric acid which would lead to the mixed tungsten-molybdenum complex. The mixed neutral complex with a Mo-W bond gives rise to the ion $[(\pi\text{-C}_5\text{H}_5)_2\text{MoW}(\text{CO})_6\text{H}]^+$ which shows a high-field line halfway between that of the bi-tungsten and bi-molybdenum complexes and in addition has a doublet satellite due to the spin-coupled interaction with ^{183}W . In a mixed metal complex we might have expected that the proton would be associated with either the tungsten or molybdenum atoms or both independently and that the resultant spectrum would show proton resonances having almost the same chemical shifts as the proton in the

bi-molybdenum and bi-tungsten complexes. The observed spectrum clearly indicates that the proton is associated in some way with both metal atoms in the binuclear species.

It is well known that exchange processes can modify the features of nuclear magnetic resonance spectra expected for a static model. However, it became apparent early in the studies on the $[\{\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\}_2\text{H}]^+$ cation that exchange processes need not necessarily destroy spin-coupling multiplets, provided that in the exchange the proton is never completely detached from the metal system. This feature has also recently been recognised in the spectra of boron hydrides and their derivatives.²³ The types of exchange process which can occur in the acid solvents used here and their predicted effect on nuclear magnetic resonance spectra are as follows.

1. Rapid intramolecular exchange. (a) Spin-spin coupling multiplets can be observed although they may differ in number and value from those expected in a static model. (b) Any chemical shifts between the sites will be averaged proportionately.

2. Intermolecular exchange involving solvent protons.

(i) Very slow (strong bases in strong acids). (a) Spin-spin coupling may be observed. (b) Chemical shifts will not be averaged.

Examples of such behaviour are $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_3^+$,¹⁵ $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}_2^+$,¹⁰ and $(\pi\text{-C}_5\text{H}_5)_2\text{FeH}^+$.¹⁴

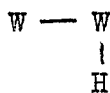
- (ii) Slow. (a) Spin-spin couplings may not be observed.
 (b) The large chemical shifts between M-H and solvent, however, will not necessarily be averaged. Examples of this type of behaviour are $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_3^+$ ¹⁵ and $(\pi\text{-C}_5\text{H}_5)_2\text{RuH}^+$ ¹⁴.
- (iii) Rapid. (a) Spin-spin coupling will not be observed.
 (b) Chemical shifts will be averaged proportionately. An example is $(\pi\text{-C}_5\text{H}_5)_2\text{OsH}^+$ ¹⁴.

For the protonated binuclear species the exchange of protons bound to metal with protons of the acid is obviously very slow. Using the separation of solvent and high-field lines, $\Delta\nu$, the average lifetime of the proton on the metal atom must be greater than about $1/2\pi\Delta \approx 8 \times 10^{-4}$ sec.

For the protonated tungsten complex $[\{\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\}_2\text{H}]^+$ there are three possible chemical structures, I, II and III, which differ in the way in which the proton is bound to the metal atom:



I



II



III

Structures I and II are static models while structure III involves exchange of the proton between the two tungsten atoms. It is possible to predict the proton resonance spectrum expected for the proton bound to the metal atom(s) for each structure. However, in making this prediction it is necessary to consider the fact that there are three isotopically different binuclear species present. Let $\text{W}^{\frac{1}{2}}$ represent the isotope ^{183}W

and W the non-magnetic isotopes. The relative abundances of the three species, $W-W$, $W-W^{\frac{1}{2}}$, $W^{\frac{1}{2}}-W^{\frac{1}{2}}$, are $85.72 \times 85.72 / 100 = 73.48$, $2 \times 85.72 \times 14.28 / 100 = 24.48$ and $14.28 \times 14.28 / 100 = 2.04\%$, respectively. The number of satellite bands and their relative intensities in the possible systems are then as follows.

I. No intramolecular exchange; proton associated with both tungsten atoms symmetrically. The calculated spectrum consists of a superposition of the following components: (i) a singlet due to $W \overset{H}{-} W$ of relative intensity 73.48%; (ii) a doublet, separation J_1 , due to $W \overset{H}{-} W^{\frac{1}{2}}$, intensity 24.48%; (iii) a triplet, separation J_1 , due to $W^{\frac{1}{2}} \overset{H}{-} W^{\frac{1}{2}}$, 2.04%. Hence we expect a "quintuplet" which has components of relative intensities: outer satellites, 1.02% (since these are the outer components of a 1:2:1 triplet), inner satellites, 24.48% and the central peak $73.48 + 1.02 = 74.5\%$. Hence the inner satellites are 32.86% (1: 3.044) of the intensity of the central peak.

II. No intramolecular exchange; proton associated with only one tungsten atom. A. The proton does not experience spin coupling to the remote tungsten nucleus when this is ^{183}W . The calculated spectrum is a superposition of four components: (i) a singlet due to $W-W-H$, intensity 73.48%; (ii) a doublet, separation J_2 , due to $W-W^{\frac{1}{2}}-H$, 12.24%; (iii) a singlet due to $W^{\frac{1}{2}}-W-H$, 12.24%; and (iv) a doublet due to $W^{\frac{1}{2}}-W^{\frac{1}{2}}-H$, 2.04%.

The resultant spectrum is now a "triplet" with the relative intensities: satellites, 14.28%; central peak, 85.72%. The satellites are hence 16.66% of the central peak in intensity.

B. The proton is coupled to the remote tungsten atom when this is ^{183}W with a small but finite spin coupling constant J_2' . The calculated spectrum now has components: (i) a singlet due to $\text{W}-\text{W}-\text{H}$, 73.48%; (ii) a doublet, separation J_2 , due to $\text{W}-\text{W}^{\frac{1}{2}}-\text{H}$, 12.24%; (iii) a doublet, separation J_2' , due to $\text{W}^{\frac{1}{2}}-\text{W}-\text{H}$, 12.24%, $J_2 > J_2'$; and (iv) a double doublet, main separation J_2 , small separation J_2' , 2.04%.

The resultant spectrum is now a multiplet whose relative intensities are: double doublet, 2.04%; outer doublet, 12.24%; inner doublet, 12.24% and central peak, 73.48%.

III. Rapid intramolecular exchange of the proton between the two tungsten atoms.

A. Model based on static system IIA. The calculated spectrum has components: (i) a singlet, 73.48%; (ii) a doublet, 24.48%, of separation J_3 where $J_3 = J_2/2$; and (iii) a doublet, separation J_2 , 2.04%. The resultant "quintuplet" has inner satellites of intensity 33.32% (1: 3.002) of the central peak.

B. Model based on static system IIB. The calculated spectrum has components: (i) a singlet, 73.48%; (ii) a doublet, 24.48%, with separation $J_4 = (J_2 + J_2')/2$; and (iii) a double doublet, 2.04%, of main separation J_2 and smaller separation J_2' . The intensity of the

* For the static system IIB we considered the signs of J_2 and J_2' to be the same. If they are of opposite sign the "time averaging" results in the separation of the inner satellites as $(J_2 - J_2')/2$ and not $(J_2 + J_2')/2$.

inner satellites is now 33.32% that of the central peak as in IIIA.

The theoretical spectra and the observed spectrum of $[\{\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\}_2\text{H}]^+$ are shown in Fig. 2. The outer satellite bands are shown at twice the calculated intensities for clarity. The observed spectrum is a "triplet" with the intensity ratio of the doublet to central peak 1:3.13. The satellites hence are 31.9% of the central peak and the observed spectrum is consistent with the cases I, IIIA or IIIB. In principle it should have been possible to distinguish between these alternatives by observation of the outer satellites and their intensities. The low intensities of the latter preclude detection above the normal background noise. Nevertheless, it seems most likely that the proton is undergoing rapid intramolecular exchange between chemically equivalent positions (cf. the situation occurring in the mesitylenium ion at room temperature),²⁴ with the resultant spectrum time averaged corresponding to IIIA or IIIB. We noted above that the spectrum of protonated species with Mo-W bond provides further evidence that proton is associated with both metal atoms. Using similar arguments to those used for the bi-tungsten species, there are again five theoretical spectra and these are shown together with the observed spectrum in Fig. 3. For the cases I, IIIA and IIIB, the calculated spectrum is a "triplet" (with relative intensities: doublet, 14.28%; singlet, 85.72%), located between the positions of the chemical shifts for $[\{\pi\text{-C}_5\text{H}_5\}\text{Mo}(\text{CO})_3\}_2\text{H}]^+$ and $[\{\pi\text{-C}_5\text{H}_5\}\text{W}(\text{CO})_3\}_2\text{H}]^+$.

FIG. 2Calculated and Observed High-field Proton ResonanceSpectra of $[\pi\text{-C}_5\text{H}_5\text{W(CO)}_3]_2\text{H}^+$.

- I. No intramolecular exchange, proton associated with both tungsten atoms symmetrically.
- II. No intramolecular exchange, proton associated with only one tungsten atom: (A) proton not coupled to remote nucleus when this is ^{183}W ; (B) proton is coupled to remote nucleus when this is ^{183}W with small but finite spin-coupling constant J_2' .
- III. Very rapid intramolecular exchange of proton: (A) based on static system IIA; (B) based on static system IIB.
- IV. Observed spectrum in 98% sulphuric acid at 56.45 Mc./sec.

The outer satellite bands are shown at twice the calculated intensity.

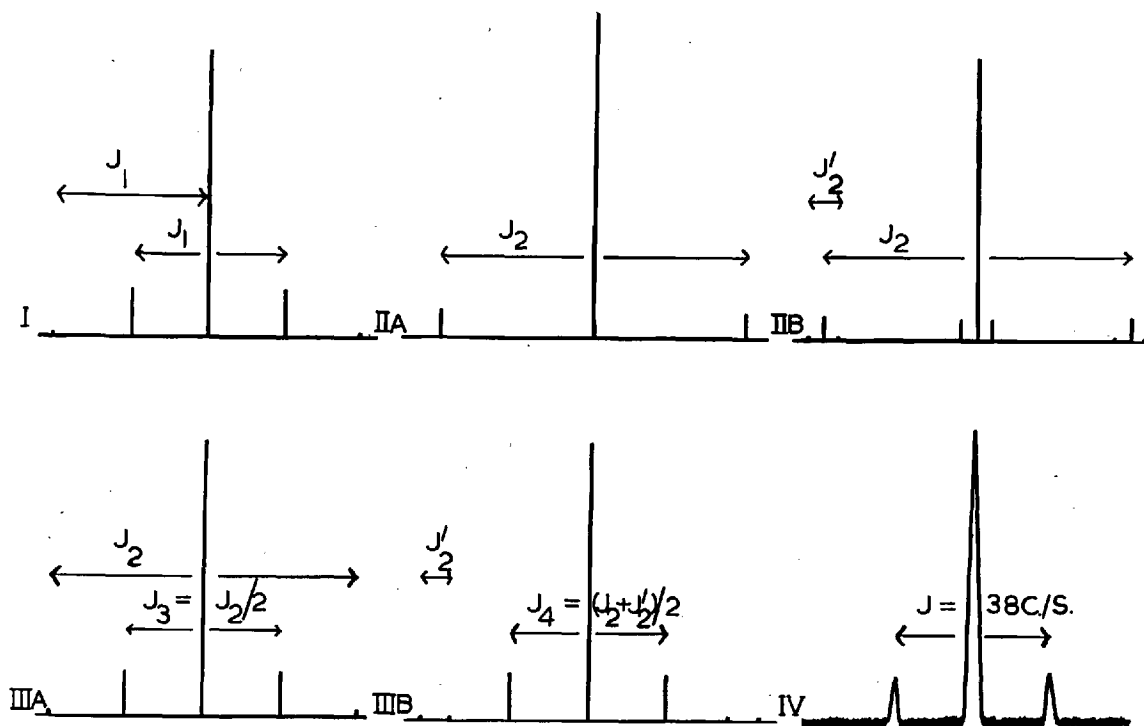


FIG. 2.

FIG. 3Calculated and Observed High-field Proton ResonanceSpectra of $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WMo}(\text{CO})_3\pi\text{-C}_5\text{H}_5]\text{H}^+$.

- I. No intramolecular exchange, proton associated with both W and Mo atoms symmetrically.
- II. No intramolecular exchange, proton associated with either W or Mo atoms singly: (A) proton on Mo atom is not spin-coupled to W atom when this is ^{183}W ; (B) proton on Mo atom is spin-coupled to W atom when this is ^{183}W .
- III. Very rapid intramolecular exchange of proton: (A) based on static system IIA; (B) based on static system IIB.
- IV. Observed spectrum in 98% sulphuric acid at 56.45 Mc./sec.
 $\delta_{\text{Mo}_2}(\text{H})$, $\delta_{\text{W}_2}(\text{H})$ and $\delta_{\text{MoW}}(\text{H})$ are the chemical shifts of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{H}^+$, $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{H}^+$, and $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WMo}(\text{CO})_3\pi\text{-C}_5\text{H}_5]\text{H}^+$, respectively.

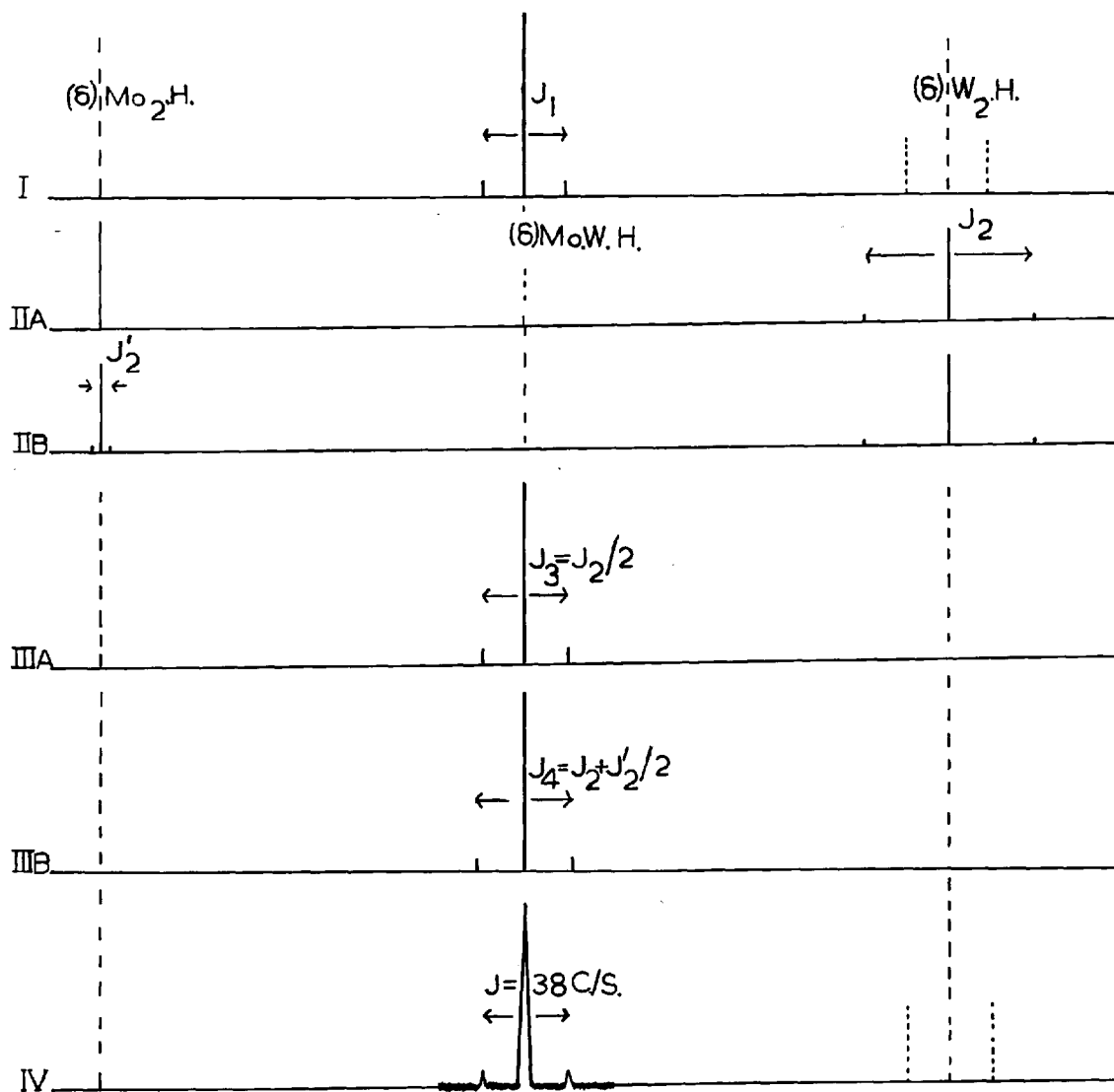


FIG.3.

In cases IIIA and IIIB the line position is halfway between these shifts. The observed spectrum is a "triplet" with the expected intensities whose chemical shift lies halfway between those of the bi-tungsten and bi-molybdenum species and is therefore consistent with models IIIA,B and possibly with I. It is not certain, however, that a proton associated with both a tungsten and molybdenum atom without exchange would experience the averaged chemical shifts of tungsten and molybdenum species.

It is often possible to slow exchange processes by cooling the samples to low temperatures. The sulphuric acid solutions cannot be cooled sufficiently and unfortunately the solubility of the hexafluorophosphates in cooled liquid hydrogen fluoride is too low for the high-field lines to be observed. In solutions of the salts in liquid sulphur dioxide, the high-field line is only just discernible in saturated solutions at 23°C.

Although it is not possible to distinguish spectroscopically between models I, IIIA and IIIB, it seems reasonable to exclude the static model which requires the proton to be located symmetrically between the two metal atoms in a bridging position. The X-ray crystal structure²⁵ of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ shows that the two halves of the molecule are linked by a metal-metal bond of length 3.222 Å. The tungsten compound has not been studied in detail, but it is isomorphous with the molybdenum compound; the W-W bond length is probably slightly longer than the Mo-Mo bond length. The metal-metal bonds here and in the similar binuclear carbonyls²⁶ $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ thus appear to be of the σ' -type, in

contrast to the metal-metal bond in the proposed structure for $\text{Co}_2(\text{CO})_8$,²⁷ and there is evidently no means of binding a hydrogen atom symmetrically between the metal atoms as envisaged in model I. In the next section it is shown, however, that compounds of the type $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{X}$ can be protonated showing that a $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3$ -grouping possesses one or more non-bonding electron pairs. In the binuclear compounds where $\text{X} = \pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3$ or $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3$ it can be assumed that each metal atom has such protonatable electron pairs not involved in bonding to the $\pi\text{-C}_5\text{H}_5$ and CO ligands. Each metal atom thus has a potential energy minimum as far as the proton is concerned and the situation is somewhat analogous to that in the hydrogen bond.

The iron compounds. The compound $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ²⁹ is readily soluble in sulphuric acid, and (in contrast to the behaviour of the Mo and W compounds) it is soluble in other strong acids to give red-brown solutions whose proton resonance spectra show the presence of $\pi\text{-C}_5\text{H}_5$ and high-field resonance lines. It had previously been noted that the compound is soluble in concentrated sulphuric acid and cryoscopic measurements³⁰ in this solvent suggested a Van't Hoff i factor of three. Sternberg and Wender⁵ suggested that this result could be interpreted as protonation to give the ion $[\{\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\}_2\text{H}_2]^{2+}$ and two bisulphate ions. However, the relative intensity measurements of the $\pi\text{-C}_5\text{H}_5$ and high-field lines are found to be 10:1 in several different acids, clearly showing that $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ is monobasic. In view of this fact, additional cryoscopic studies in sulphuric acid have now been made³¹

TABLE II

Nuclear Magnetic Resonance Spectra of the Protonated
Binuclear π -cyclopentadienyl Carbonyl Complexes.

(At 56.45 Mc./sec. in 98% A.R. H_2SO_4 ; relative intensities in brackets)

Species	τ $\pi-C_5H_5$	τ M-H
$[\pi-C_5H_5Mo(CO)_3]_2H^+$	4.28(10)	30.99(1) singlet
$[\pi-C_5H_5W(CO)_3]_2H^+$	4.20(10)	34.77(1) "triplet" (1: 6.26: 1); J = 38.6 c./sec. (a)
$[\pi-C_5H_5W(CO)_3]_2H^+PF_6^{-(b)}$	4.10	34.8 (c)
equimolar mixture $[\pi-C_5H_5Mo(CO)_3]_2H^+$ and $[\pi-C_5H_5W(CO)_3]_2H^+$	4.25	30.99 singlet 34.77 triplet; J = 38.6 c./sec.
$[(\pi-C_5H_5)_2MoW(CO)_6]H^+$	4.20	32.88 triplet (1: 12: 1); J = 38 c./sec.
$[\pi-C_5H_5Fe(CO)_2]_2H^{+(d)}$	4.76(10)	36.30(1) singlet
$[\pi-C_5H_5Fe(CO)_2]_2H^+PF_6^{-(b)}$	4.70(10)	36.3 (1) singlet
$[\pi-C_5H_5FeMn(CO)_7]H^+$	4.68 (5)	38.07(1) singlet
$[\pi-C_5H_5FeMn(CO)_7]H^+PF_6^{-(b)}$	4.55 (5)	38.0 (1) singlet
$[\pi-C_5H_5FeMn(CO)_7]D^+PF_6^{-(b)}$	4.55	absent

(a) At 40 Mc./sec. J = 39.8 cycle/sec.

(b) Spectra measured in liquid SO_2 with tetramethylsilane as internal reference.

(c) ^{183}W splitting not observed because of low solubility of salt.

(d) Measured in CF_3COOH with tetramethylsilane internal reference;
 also measured in H_2SO_4 with dimethyl sulphate as ⁱⁿ internal reference
 and in HF/BF_3 , $BF_3 \cdot H_2O - CF_3COOH$, and HBf_4 -aqueous propionic anhydride
 mixtures.

using a highly purified sample of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$; i values, for successive additions, about 2.3 and 2.4 were obtained. It is difficult to draw any reliable conclusions from these measurements and it is possible that some of the difficulties are due to traces of oxygen in the acid solutions, since it has been observed that these solutions are air-sensitive.

The infrared spectrum of the protonated species in 98% H_2SO_4 shows strong bands due to terminal C-O stretching modes at 2022, 2045 and 2068 cm^{-1} . The neutral compound has bands at 2054, 2005, 1958, and 1785 cm^{-1} in carbon tetrachloride and in carbon disulphide; the 1785 cm^{-1} band has been assigned²⁹ to the bridging carbonyl groups, the presence of which in the crystal was confirmed by X-ray diffraction study.³² The absence of any bridging carbonyl groups in the sulphuric acid solution spectrum is confirmed by the mull spectrum of $[\{(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}_2\text{H}]\text{PF}_6$ (Fig. 4) obtained by treatment of the compound dissolved in anhydrous hydrogen fluoride with added phosphorus pentachloride. It must be concluded that the bridging carbonyl disappears on dissolution of the neutral complex in strong acid but is readily re-formed when the compound is recovered by dilution of the acid solutions or by hydrolysis of salt with aqueous acetone. The possibility that the bridging "ketonic" carbonyl groups have undergone protonation to form $\text{>C}^+\text{-OH}$ groups, which could account for the disappearance of the 1785 cm^{-1} band, is unlikely, since this would require the formation of a tripositive cation which should have given an initial i factor of 4. The sulphuric acid and mull spectra of

protonated species show three strong carbonyl bands. The protonated species hence appears to have two $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ units linked by a metal-metal bond and the proton can be considered as being in a situation comparable to that in the tungsten and molybdenum species and undergoing rapid intramolecular exchange. It may be noted that the ability of the carbonyl groups to readily interchange reversibly from bridging to non-bridging positions supports the evidence, based on differences between the infrared spectra in solution and the solid state^{29,33} and on the Raman spectrum³⁴ of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, that the structure of the compound in solution and the crystal are not the same.

The bright-red compound $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-Mn}(\text{CO})_5$ ³⁵ for which the infrared spectrum shows the absence of carbonyl stretching bands below 1945 cm^{-1} , indicating that there are no bridging carbonyl groups, dissolves in concentrated sulphuric acid to give a cherry-red solution. In contrast to the other protonated binuclear species the base is not liberated on careful dilution of the sulphuric acid solution with water. The red aqueous solutions persist for several hours. These solutions give precipitates with solutions containing large anions (e.g., silicotungstate, reineckate, etc.) and a crystalline hexafluorophosphate has been isolated. The stability of the aqueous acid solutions and the possibility of isolating the hexafluorophosphate in this case enabled the salt $[\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7\text{D}]\text{PF}_6$ to be isolated. In sulphur dioxide the latter shows no high-field proton resonance line and a comparison of the infrared spectra of the hydrogen and deuterium salts (Fig. 4) shows that weak bands

at 1760 and 1270 cm^{-1} respectively can be assigned to metal-hydrogen and metal-deuterium stretching frequencies.

Since the ligand dispositions about the two metals are dissimilar in the iron-manganese compound, it is possible that the proton spends most of its time on one metal atom. Since di(manganese pentacarbonyl) is only sparingly soluble in acids and there is so far no evidence for the protonation of other manganese pentacarbonyl compounds, it is possible that the proton is located predominantly on the iron atom. The band at 1760 cm^{-1} in the infrared spectrum of the protonated salt is tentatively assigned as a Fe-H stretching mode.

The spectrum of $[\{\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\}_2\text{H}]\text{PF}_6$ also shows a weak band at 1767 cm^{-1} which may be due to the Fe-H stretch.

The nuclear magnetic resonance spectrum of $[\{\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5\}_2\text{H}]\text{PF}_6$ in liquid SO_2 , unchanged at -70°C , is consistent with the proton being attached to the $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ residue.

Other binuclear complexes such as $\text{Co}_2(\text{CO})_8$, $[\text{Ph}_3\text{PCo}(\text{CO})_3]_2$, $[\pi\text{-C}_5\text{H}_5\text{NiCO}]_2$, $[\pi\text{-C}_5\text{H}_5\text{Ni}]_2\text{RC}\equiv\text{CR}$, $\text{Ph}_3\text{PAuCo}(\text{CO})_4$, and $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{Hg}$ which have metal-metal bonds are decomposed by strong acids. The complexes with gold or mercury atoms bound to a transition metal probably have metal-metal bonds with some polar character due to the different electronegativities of the two halves of the molecules. With the anhydrous acids as well as with aqueous acids,³⁶ the transition metal carbonyl hydride is liberated,

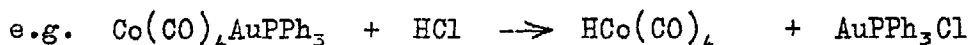


FIG. 4

Infrared Spectra of Binuclear Complexes
of Iron and Manganese

(in region 2500-1200 cm.⁻¹, Nujol mulls)

- A. $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5\text{H}]\text{PF}_6$
B. $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5\text{D}]\text{PF}_6$
C. $[\{\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\}_2\text{H}]\text{PF}_6$.

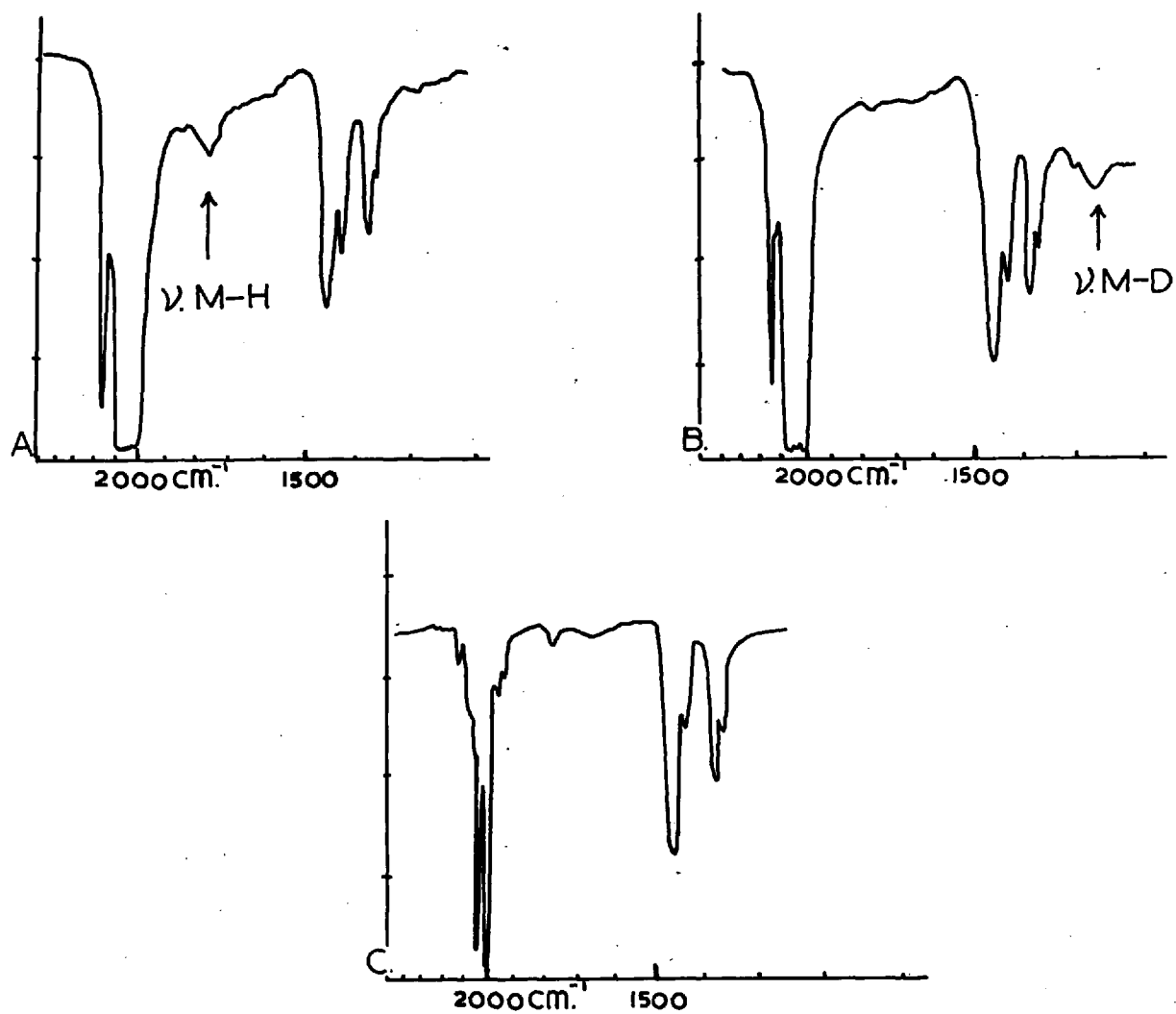
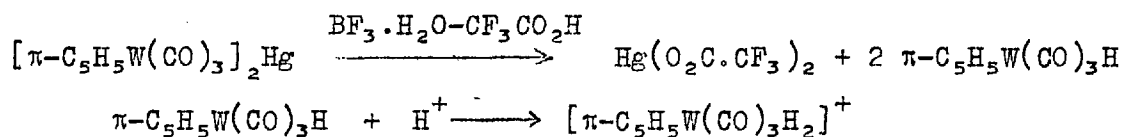


FIG. 4.

When the complex $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{Hg}$ is dissolved in $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{COOH}$, analogous behaviour occurs and the liberated hydride $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$ is protonated, to give the ion $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}_2]^+$ (which is discussed in the next section).



It should be noted, however, that despite its decomposition by anhydrous acids, even at low temperatures, $\text{Co}_2(\text{CO})_8$ has been shown to act as a Lewis base, and the adduct $\text{Co}_2(\text{CO})_8\text{AlBr}_3$ has been characterised.³⁷

It is quite possible that some of the complexes which can be protonated, e.g., $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$, will also show similar Lewis base behaviour, for example towards BH_3 .

C H A P T E R I VMONONUCLEAR CARBONYL COMPLEXES(A) Mononuclear π -Cyclopentadienyl and Arene Metal CarbonylsINTRODUCTION

The study of the di- π -cyclopentadienyl metal hydrides^{10,15} led to the view, confirmed by molecular orbital calculations,¹⁶ that in these compounds the metal-to-ring axes must be non-linear and that there are three spatially directed hybrid orbitals which can be occupied by hydrogen atoms or by lone pairs of electrons. This is in accord with the strong basicity of $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$. The feebly basic nature of ferrocene probably results from the fact that non-bonding (or partially non-bonding) orbitals become spatially directed only when the metal-to-ring bond axes are distorted from linearity in molecular vibrations. If the metal-to-ring axes in a ferrocene derivative were distorted angularly, by an intra-annular bridging group, the base strength should become comparable to that of the rhenium and tungsten compounds. The view that in these di- π -cyclopentadienyl metal compounds there are six orbitals involved in primary bonding to the ligands, and three filled, "chemically active",¹⁶ orbitals being non-bonding or partially involved in back-bonding to the ligands, can be extended to compounds with only one $\pi\text{-C}_5\text{H}_5$ ring present, and also to isoelectronic arene complexes. Thus $\pi\text{-C}_5\text{H}_5\text{Mn(CO)}_3$ and

$C_6H_6Cr(CO)_3$ are isoelectronic with ferrocene, and $\pi-C_5H_5W(CO)_3H$ can be considered analogous to $(\pi-C_5H_5)_2ReH$. Several such carbonyl compounds have been protonated in anhydrous strong acids; the proton resonance data are collected in Table III.

Cyclopentadienyl Metal Carbonyl Complexes.

The compound $\pi-C_5H_5W(CO)_3H$ dissolves in trifluoroacetic acid without protonation to give stable yellow solutions. However, using the stronger acid mixture, $BF_3 \cdot H_2O - CF_3COOH$, protonation to give the ion $[\pi-C_5H_5W(CO)_3H_2]^+$ occurs. The high-field line is fairly broad, however, ca. 8 cycle/sec. at half height, and does not show the expected "triplet" structure due to spin-coupling with the ^{183}W nucleus. These results suggest that there is slow intermolecular exchange with solvent protons (process 2(ii), Chap. III) showing that $\pi-C_5H_5W(CO)_3H$ is a much weaker base than its analogue, $(\pi-C_5H_5)_2ReH$. The yellow solutions of $[\pi-C_5H_5W(CO)_3H_2]^+$ turn red over a period of several hours, evolving hydrogen and leaving in solution the previously unknown trifluoroacetate, $\pi-C_5H_5W(CO)_3OCOCF_3$. This slow decomposition appears to be an intramolecular hydrogen transfer reaction:

$$[\pi-C_5H_5W(CO)_3H_2]^+ + CF_3CO_2^- = \pi-C_5H_5W(CO)_3OCOCF_3 + H_2.$$

The compound $\pi-C_5H_5Mo(CO)_3H$ behaves similarly but the hydrogen evolution is so rapid that no spectroscopic evidence for protonation could be obtained, but it seems certain that decomposition occurs through a protonated intermediate $[\pi-C_5H_5Mo(CO)_3H_2]^+$.

TABLE III

Nuclear Magnetic Resonance Spectra of π -cyclopentadienyl
and Arene Metal Carbonyls

(at 56.45 Mc./sec. in $\text{BF}_3 \cdot \text{H}_2\text{O}$ 1:1 mole ratio unless otherwise stated)

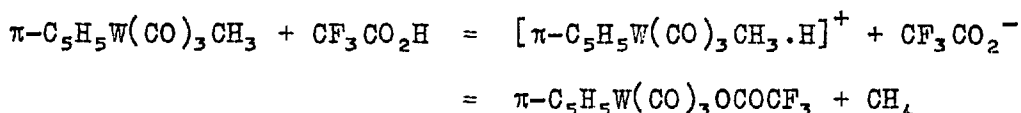
Compound	τ H	τ ligands
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}_2^+$	^a 11.93(1) singlet, broad width $\frac{1}{2}$ ht. ~ 9 c./sec. ^b 11.90(1) singlet, broad, ~ 15 c./sec.	4.03(2.9) $\pi\text{-C}_5\text{H}_5$ singlet 3.99 (3) $\pi\text{-C}_5\text{H}_5$ singlet
ArCr(CO) ₃		
benzene	13.55 ± 0.3 broad (~ 95 c./sec.)	
toluene	$13.98 \pm 0.2(1)$ " (~ 40 c./sec.)	3.35 ± 0.2 aromatic 7.14 ± 0.2 (3.2) CH ₃
mesitylene	14.27 ± 0.2 " (~ 35 c./sec.)	4.31 ± 0.2 aromatic 7.78 ± 0.2 CH ₃
1,2-diphenylethane	14.06 ± 0.3	
<u>o</u> -fluorotoluene	13.54 ± 0.3	
<u>p</u> -fluorotoluene	13.58 ± 0.3	
<u>o</u> -chlorotoluene	13.74 ± 0.3	
<u>p</u> -chlorotoluene	14.0 ± 0.3	
chlorobenzene	insoluble	
fluorobenzene	"	
$[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{Hg}$	$11.95^{\text{c,d}}$ (1)	3.99 (2.9)

^a $\text{BF}_3 \cdot \text{H}_2\text{O} : \text{CF}_3\text{COOH}$ 1.23 : 1. ^b $\text{BF}_3 \cdot \text{H}_2\text{O} : \text{CF}_3\text{COOH}$ 1 : 1.73.

^c $\text{BF}_3 \cdot \text{H}_2\text{O} : \text{CF}_3\text{CO}_2\text{H}$ 2 : 1.

^d Due to $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}_2^+$ produced by decomposition to hydride followed by protonation.

For the methyl derivative, $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$, decomposition occurs in trifluoroacetic acid, methane being rapidly evolved giving rise to the trifluoroacetate. Since the hydride can be regarded as the parent of the series of alkyls, it seems most likely that the acid decomposition involves initial protonation of the metal followed by intramolecular hydrogen transfer:



The orange π -cyclopentadienyltrifluoroacetotungstentricarbonyl is monomeric and readily soluble in common organic solvents. Other alkyls of transition metal carbonyls and π -cyclopentadienyl carbonyls, e.g., $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$, $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$, and $\text{CH}_3\text{M}(\text{CO})_5$ ($\text{M} = \text{Re}$ and Mn), behave similarly. The trifluoroacetates are stable, and unlike the perfluoroacyl compounds, do not decompose on heating in vacuo to give the perfluoromethyl derivatives.

The infrared spectra of these complexes show strong absorptions in the region $2080\text{--}1970\text{ cm}^{-1}$, which can be assigned to the terminal C-O stretching modes; a strong absorption at $\sim 1700\text{ cm}^{-1}$ can be assigned to the C-O stretching mode of a $-\text{O.CO.CF}_3$ group bonded to the metal. The complexes also show strong absorptions in the C-F stretching region from a $-\text{CF}_3$ group. These are the first reported examples of monomeric complexes of transition metals which have a trifluoroacetate group bonded to the metal.

Since $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$ is a much weaker base than $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$, probably owing to the demands of the carbonyl groups for d-electron density for metal-to-carbon π -bonding, we can expect $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ to be a weaker base than ferrocene. Although this manganese compound is only sparingly soluble in acids, yellow π -methylcyclopentadienyl manganese tricarbonyl, which should be a stronger base, is soluble in $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{COOH}$ mixtures giving a red solution which shows no decomposition after two days. The proton resonance spectrum shows lines due to the $\pi\text{-C}_5\text{H}_5$ and CH_3 groups, but no high-field line, however. It can only be concluded that rapid intermolecular exchange between Mn-H and solvent protons is occurring (Chapter III, process 2(iii)) as in the acid solutions of $(\pi\text{-C}_5\text{H}_5)_2\text{Os}$.¹⁴ The compound is thus an extremely weak base.

Arene Chromium Tricarbonyls.

During the course of these studies it has been noticed³⁸ that arene chromium tricarbonyls dissolve in concentrated sulphuric acid to give yellow solutions which rapidly decompose, but in $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{COOH}$ mixtures the deep yellow protonated species, $\text{ArCr}(\text{CO})_3\text{H}^+$, are formed. This is consistent with the fact that benzene is a weaker back-bonding π -acceptor ligand than the $\pi\text{-C}_5\text{H}_5$ group and hence compounds such as $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ should be stronger bases than $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$. All of the arene compounds are weak bases and in all cases the high-field proton resonance lines (Table III) are broad, 40-90 cycle/sec. at half height. In the same solutions the corresponding alkyl and phenyl group resonance lines were quite sharp so that the breadth of the high-field line is due to exchange with the solvent at a rate intermediate between that of processes 2(ii) and 2(iii) of Chapter III.

The arene carbonyls which have electron-releasing substituents on the ring (those not sensitive to acid) are the most soluble and have the sharpest high-field lines, e.g., mesitylene $\text{Cr}(\text{CO})_3$ (ca. 35 cycle/sec., half height), and are therefore the strongest bases, while compounds with electron-withdrawing groups ortho or para to a methyl group are of intermediate solubility, have broad lines (ca. 70-80 cycle/sec.), and are weaker bases. The complexes with electron-withdrawing groups are only sparingly soluble in the acid; the solutions of chlorobenzene and fluorobenzene were too weak to be studied. We can make a qualitative estimate of the base strength (and also solubility): mesitylene > toluene ~ 1:2 diphenylethane > o and p fluoro- and chloro-toluenes > benzene > fluoro- and chloro-benzene.

Although dibenzene chromium is isoelectronic with ferrocene, it is decomposed at once by strong acids; even if trifluoroacetic acid is condensed on to the solid at low temperatures, decomposition occurs when the acid melts (-15°C).

(B) Iron Pentacarbonyl and Substituted Carbonyls

When iron pentacarbonyl is dissolved in cold concentrated sulphuric acid a green solution is obtained, which decomposes violently within one or two minutes. However, a 1:1 molar mixture of $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{CO}_2\text{H}$ gives rise to a more stable green solution which persists for about half an hour at 25°C . The proton magnetic resonance spectrum (Table IV) shows a characteristic, rather broad, high-field line at $\tau = 18.14$; the

TABLE IVNuclear Magnetic Resonance of Protonated Iron Carbonyls

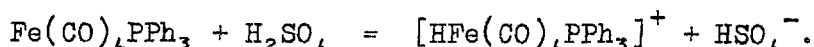
(At 56.45 Mc./sec. in 98% A.R. H_2SO_4 ; dimethyl sulphate as internal reference)

Species	$\tau_{\text{Fe-H}}$	$\tau_{\text{C}_6\text{H}_5}$
$\text{HFe}(\text{CO})_5^+ \text{ (a)}$	18.14	
$\text{HFe}(\text{CO})_4\text{PPh}_3^+$	17.75 (1) doublet, $J = 35.3 \text{ c./sec.}$	2.33 (15) broad singlet
$\text{HFe}(\text{CO})_3(\text{PPh}_3)_2^+$	17.78 triplet, $J = 30.2 \text{ c./sec.}$	2.58 broad singlet
$\text{HFe}(\text{CO})_4\text{AsPh}_3^+$	18.11 ± 0.1 (1) singlet	2.61 ± 0.1 (15)
$\text{HFe}(\text{CO})_3(\text{AsPh}_3)_2^+$	18.11 ± 0.1 singlet	2.68 ± 0.1

(a) In $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{COOH}$ with C_6H_{12} as external reference.

broadening is due to the weakly basic nature of $\text{Fe}(\text{CO})_5$ and the spectrum corresponds to the slow exchange process 2(ii) of Chapter III.

The triphenylphosphine and triphenylarsine substituted carbonyls, $\text{MPh}_3\text{Fe}(\text{CO})_4$ and $(\text{MPh}_3)_2\text{Fe}(\text{CO})_3$ ($\text{M} = \text{P}$ or As), give stable yellow solutions in 98% sulphuric acid. The arsine complexes are less stable than the phosphine ones, but bistrisphenylstibine iron tricarbonyl, although dissolving to give a yellow solution, decomposes with effervescence within a minute. The proton resonance spectra of these solutions show high-field proton resonances attributable to Fe-H (Table IV) at τ values ca. 18. The relative intensities of the high-field lines and the phenyl groups show that the carbonyls function as mono-acid bases, e.g.,



The high-field resonance line in the spectra of the phosphine complexes shows that the added proton is spin-coupled to the ^{31}P nuclei giving rise to a doublet, $J = 35.3$ cycle/sec., and a triplet, $J = 30.2$ cycle/sec., in the triphenylphosphine iron tetracarbonyl hydrogen cation, and bistrisphenylphosphine iron tricarbonyl hydrogen cation, respectively. The coupling constants for hydrogen atoms bound directly to phosphorus are about 200 cycle/sec. The spectra show that these complexes are strong bases (corresponding to the very slow intermolecular exchange process 2(i) of Chapter III). The greater base strength of the substituted carbonyls compared to iron pentacarbonyl can be attributed to the stronger σ -donor properties and weaker π -acceptor properties of triphenylarsine and phosphorus ligands compared to carbon monoxide. The ^{31}P resonance

spectra should also show a structure which would have uniquely confirmed the stoichiometry of the ions. However, the concentration of phosphorus in saturated solutions was insufficient to give more than a barely perceptible ^3P resonance line at 16 Mc./sec.

The structures of iron pentacarbonyl and the triphenylphosphine substituted carbonyls appear to be well established^{27,39} as trigonal bipyramidal ones with the phosphine ligands occupying the axial positions. The triphenylarsine and stibine analogues have infrared spectra (Table V) similar to the triphenylphosphine compounds and the structures are presumably analogous. Since there is apparently no stereochemically active lone pair in these molecules, the basic character results from protonation of electron pairs on the iron which are only partially involved in multiple bonding to the carbonyl ligands. Slight distortion of the trigonal bipyramid structure on protonation will lead to a structure for the cations which is isosteric and isoelectronic with the neutral manganese hydrocarbonyl $\text{HMn}(\text{CO})_5$. The latter has been shown⁴⁰ to have a rather low symmetry where the hydrogen atom does not occupy a normal (i.e. in this case octahedral) bond position.

In contrast to $(\text{Ph}_3\text{As})_2\text{Fe}(\text{CO})_3$, the chelate $\text{DFe}(\text{CO})_3$ (D = o-phenylene bisdimethyl arsine) dissolves in sulphuric acid to give yellow solutions which show proton resonance lines attributable to phenyl and methyl groups but no high-field lines. This chelate is believed to have a square pyramidal⁴¹ structure. Since the multiple bonding requirements may well be different in this configuration, failure to observe a high-field line indicates that it is a much weaker base, presumably due to lower availability of non-bonding electrons in this complex.

TABLE V

Infrared Spectra of Triphenyl Phosphine, Arsine,
and Stibine Iron Carbonyls
 (in region 2100-1600 cm.⁻¹)

Compound	Carbonyl stretching frequencies in cm. ⁻¹
$\text{Ph}_3\text{PFe}(\text{CO})_4$ (a)	2062vs, 1982vs, 1940vs (Lit. ³⁹ 2059vs, 1984vs, 1946vs) (b)
$\text{Ph}_3\text{AsFe}(\text{CO})_4$ (b)	2064vs, 1984vs, 1946vs
$(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ (a)	1883vs (Lit. ³⁹ 1887vs) (c)
$(\text{Ph}_3\text{As})_2\text{Fe}(\text{CO})_3$ (a)	1878vs
$(\text{Ph}_3\text{Sb})_2\text{Fe}(\text{CO})_3$ (a)	1874vs

(a) CH_2Cl_2 solution.

(b) CCl_4 solution.

(c) CHCl_3 solution.

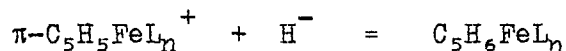
C H A P T E R V

π -CYCLOPENTADIENYL AND CYCLOPENTADIENE IRON CARBONYLS

INTRODUCTION

The interaction of iron pentacarbonyl with cyclopentadiene or its dimer produces the binuclear carbonyl $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, and it has been suggested^{5,42} that a cyclopentadiene olefin-type complex, $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_3$, is an intermediate in the preparation. An unsuccessful attempt⁴³ has been made to isolate such a complex from spiro[4,4]nona-1,3-diene, but rearrangement occurred producing tetracarbonyl di- π -tetrahydroindenyl di-iron.

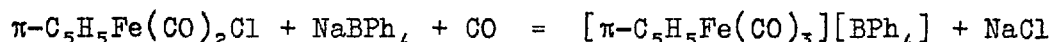
It has been shown⁴⁴ that suitable π -cyclopentadienyl metal cations can be reduced by lithium aluminium hydride or sodium borohydride to give cyclopentadiene olefin-type complexes, e.g., $\pi\text{-C}_5\text{H}_5\text{CoC}_5\text{H}_6$. It seemed reasonable to expect that if cations such as $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$ could be obtained, their reduction by hydride ion should lead to the corresponding olefin complexes:



π -CYCLOPENTADIENYL CARBONYL IRON CATIONS.

Cations of this type had not been reported previously, although the yellow aqueous solutions of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ undoubtedly contain the ion $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}_2\text{O}]^+$. If the dicarbonyl chloride in acetone solution in

the presence of sodium tetraphenylborate is treated with carbon monoxide under pressure, fine yellow crystals of the tetraphenylborate of the ion $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$ are obtained in almost quantitative yield:



The tetraphenylborate decomposes only slowly in air; it is insoluble in non-polar solvents and is sparingly soluble in acetone from which it crystallises with difficulty. It decomposes without melting when heated. Conductivity measurements in nitrobenzene⁴⁵ show that it is a 1:1 electrolyte. The ion completes the isoelectronic series $[\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_3]^{2-}$, $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]^{1-}$, $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$.

Since other ligands, particularly tertiary phosphines, could be expected to act similarly to carbon monoxide in the above reaction, the interaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ and triphenylphosphine,⁴⁶ which gave a small yield of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$, was re-examined. This observation has been confirmed, but if the benzene-insoluble portion of the reaction mixture is extracted with water, a solution of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3]^+$ is obtained from which the chloride can be isolated as a trihydrate. This yellow solid decomposes without melting; it is sparingly soluble in cold water but readily soluble in hot water. Aqueous solutions give the usual precipitation reactions with large anions, and conductivity measurements in nitrobenzene showed that the chloride is a 1:1 electrolyte and the hexachloroplatinate(IV) a 1:2 electrolyte. Similar salts were characterised with triphenylarsine and triphenylstibine as ligands, but these are less stable in air than the very stable phosphine derivatives.

The infrared spectra of the isoelectronic π -cyclopentadienyl tricarbonyl compounds, $\text{Cs}_2[\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_3]$, $\text{Na}[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]$, $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$, and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{BPh}_4]$, show two strong bands due to terminal C-O stretching modes. The formal oxidation state of the metals in this series are V(-1), Cr(0), Mn(+1), and Fe(+2). The values of the C-O stretching frequencies can be interpreted as showing the degree of electron-transfer from the metal orbitals into vacant orbitals of the carbon monoxide by metal-carbon π -bonding. The stretching frequencies for this series are: 1748, 1645; 1876, 1695; 2035, 1953;⁴⁷ and 2120, 2070 cm^{-1} . These show the expected increase in π -bonding with increasing negativity of the oxidation state ($\text{Fe} \rightarrow \text{V}$) of the central metal atom in a manner analogous to that of the N-O stretching frequencies in the isoelectronic series $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]$, $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]$, $\text{K}_5[\text{V}(\text{CN})_5\text{NO}]$.⁴⁸ In the triphenyl-phosphine, -arsine, and -stibine complexes the carbonyl stretching modes occur at 2070, 2030; 2062, 2017; and 2005, 2050 cm^{-1} , respectively. The lowering of these values from 2120 cm^{-1} for the tricarbonyl to about 2060 cm^{-1} for the phosphorus, arsenic, and antimony compounds may be associated with decreasing π -bonding capacity here, with a resultant increase in π -bonding between metal and carbon monoxide. The C-O frequencies increase in the order $\text{SbPh}_3 < \text{AsPh}_3 < \text{PPh}_3$ but the differences are small, ca. 12 cm^{-1} , and are probably of little real significance except that they confirm the observations⁴⁹ that there is little difference in π -acceptor properties of phosphorus, arsenic, and antimony as ligand atoms.

DICARBONYLCYCLOPENTADIENETRIPHENYLPHOSPHINE IRON.

Although we have failed to obtain a cyclopentadiene derivative by reduction of the ion $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$, reduction of the triphenylphosphine derivative, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3]\text{Cl}$, by sodium borohydride in tetrahydrofuran-ether gives the olefin-type complex, $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_2\text{PPh}_3$.

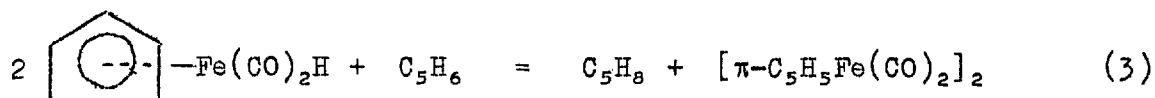
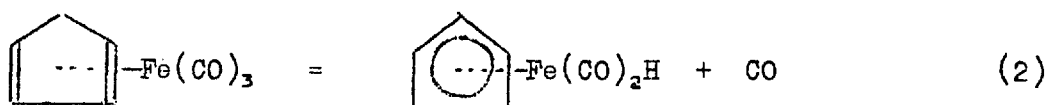
The physical and chemical properties of dicarbonylcyclopentadiene-triphenylphosphine iron show that cyclopentadiene is bound to the iron atom in the same manner as in the cobalt and rhodium compounds,⁴⁴ and that the methylene group ($>\text{CH}_\alpha\text{H}_\beta$) of the cyclopentadiene has the same unusual features that have been described for these complexes. The compound decomposes appreciably when left in air but is stable in nitrogen or in vacuo at room temperature. With carbon tetrachloride it reacts, to give chloroform and the $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3^+$ ion. In boiling xylene the compound decomposes to give $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and a small amount of ferrocene (which probably results from the decomposition of the binuclear carbonyl in xylene⁴⁶). Interaction between the compound and triphenylmethyl tetrafluoroborate is very slow, the reactive H_α being removed essentially quantitatively to give the crystalline salt $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3]\text{BF}_4$; the infrared spectrum of the latter is consistent with formulation as an ionic tetrafluoroborate.⁵⁰

The infrared spectrum of $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_2\text{PPh}_3$ shows an intense band at 2765 cm.^{-1} assignable to the C-H_α stretching mode; other assignments are also similar to those of other cyclopentadiene derivatives.

The high-resolution nuclear magnetic resonance spectrum is also similar in its general features to those of the other derivatives.⁴⁴ There are three groups of lines in the spectrum, indicating the presence of at least three types of hydrogen atom. A sharp doublet (τ 2.73, relative intensity 15) is clearly due to the protons of the triphenylphosphine portion, the proton line being split by coupling with the ^{31}P nuclear spin. The band at τ 4.87 (relative intensity 2) is assigned to the two equivalent protons on C_3 and C_4 . The resonance of each of these protons is split into a doublet by the nearest proton on C_2 (or C_5) and again into a doublet by the more distant proton of C_5 (or C_2). The two separate splittings are both roughly 2 cycles/sec. and the two middle lines of the doublets overlap, under the resolution obtained, to give the observed triplet structure with a total splitting of about 4 cycles/sec. The third band at τ 7.5 (relative intensity 4) is due to the remaining protons on the C_5H_6 group. The lines at τ 7.19, τ 7.38, and τ 8.0 appear to be part of an AB pair due to the protons of the non-equivalent methylene group, $>\text{CH}_\alpha\text{H}_\beta$; the endo-proton, H_α , is in a different magnetic environment from that of the exo-proton H_β . The poorly resolved lines at τ 7.66 and τ 7.79 are due partly to H_α and to the protons on $\text{C}_{(2)}$ and $\text{C}_{(5)}$.

DISCUSSION

In the interaction of cyclopentadiene with iron pentacarbonyl, the following reactions have been proposed:^{5,42}



It is known that $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$, which is readily obtained by the action of sodium borohydride on $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$, is thermally unstable, decomposing in the liquid state to give the binuclear carbonyl and hydrogen.⁵¹ However, all attempts to isolate $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_3$ by borohydride reduction of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+[\text{BPh}_4]^-$ in tetrahydrofuran failed, even at low temperatures, the reaction leading only to the dicarbonyl hydride with loss of carbon monoxide. It appears that $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_3$ is unstable with respect to $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ and that the transition-state activated complex $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{LH}]$ ($\text{L} = \text{CO}$) decomposes by loss of carbon monoxide in preference to forming the neutral compound $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_3$. In the case where $\text{L} = \text{PPh}_3$, only a small amount of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$, which was detected by its high-field proton-resonance line and by its decomposition to $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, is produced and the main product is the neutral cyclopentadiene complex. The latter is stable with respect

to ligand-loss and hydrogen-transfer to metal to give $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$, and there is no evidence of decomposition below 113° to $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$; a sample sealed under vacuum remained unchanged during 18 months.

Although the complex $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_3$ is unstable, there appears to be no inherent instability in diolefin-iron tricarbonyl systems and tricarbonyl compounds of norbornadiene, butadiene, cycloheptadiene, etc., are known, although these compounds do not contain a reactive $>\text{CH}_2\text{H}_\beta$ group.

The readier loss of carbon monoxide in the reduction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$ than in that of the triphenylphosphine complex, and similar differences in reactivities between acyl-cobalt carbonyls and their triphenylphosphine analogues,⁵² may be due to the non-volatility of triphenylphosphine and its weaker π -bonding capacity which tends to strengthen the remaining Fe-C bonds.

The results appear to be consistent with the above reaction scheme.

After the completion of this work,[⌘] π -cyclopentadienyl cations of iron, molybdenum and tungsten, e.g. $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_x\text{L}]^+$ (M = Mo, W, or Fe; $x = 2$ or 3 ; L = C_2H_4 or CO), were reported by Fischer et al.^{53,54}

The complexes were prepared by the interaction of the corresponding cyclopentadienylcarbonyl chlorides with aluminium chloride and either ethylene or carbon monoxide under pressure. This method has recently^{54,55} been used to give cationic complexes of the group 7 and 8 metal carbonyls, e.g. $\text{C}_2\text{H}_4\text{Mn}(\text{CO})_5\text{AlCl}_4$, $\text{Re}(\text{CO})_6\text{AlCl}_4$, and $\text{Fe}(\text{CO})_6[\text{AlCl}_4]_2$. In a preliminary communication Hübel and Weiss have mentioned

[⌘] For a published account see ref. 28.

π -(diphenylmethylcyclopentadiene)irontricarbonyltetraphenyl borate, which was prepared from (ω , ω)-diphenylfulveneirontricarbonyl, by protonation with hydrochloric acid. π -Cyclopentadienyl olefin iron cations have also been produced either by protonation⁵⁷ of σ -allyl- π -cyclopentadienyl-iron dicarbonyl or by hydride abstraction⁵⁸ from π -cyclopentadienyl- σ -ethyliron dicarbonyl. None of these workers, however, reduced the cationic species in an attempt to make a cyclopentadiene derivative of iron.

The complexes $C_{11}H_{12}Fe$ and $C_{10}H_{12}Ni$ were originally formulated as benzenecyclopentadieneiron,⁵⁹ and bis-cyclopentadienenickel,⁶⁰ respectively. It has recently been shown that they are not cyclopentadiene complexes; $C_{11}H_{12}Fe$ is reformulated as π -cyclohexadienyl- π -cyclopentadienyliron,⁶¹ in which the cyclohexadienyl group is π -bonded to the iron atom in a similar manner to that described for π -cyclohexadienyl-manganesetricarbonyl;⁶² $C_{10}H_{12}Ni$ is reformulated⁶³ as π -cyclopentadienyl π -cyclopentenylnickel, and the cyclopentenyl group contains, and is bonded to the metal by, a delocalised π -allylic system similar to that described for π -allyl cobalt⁵² and manganese carbonyls.⁶⁴ This, together with the chemical reactivity of the known cyclopentadiene complexes, suggests that the inherent instability of C_5H_6 , when bonded to a transition metal, is a direct consequence of the very great stability of C_5H_5 π -bonded to a transition metal. A cyclopentadiene group will be readily converted, by rearrangement or reaction, into a π - C_5H_5 group.

CHAPTER VI

EXPERIMENTAL

GENERAL

Microanalyses and molecular weights (ebullioscopic in benzene) are by the Microanalytical Laboratories, Imperial College.

Infrared Spectra. Measurements were made using a Perkin-Elmer Model 21 spectrometer with sodium chloride and calcium fluoride optics.

High-resolution Nuclear Magnetic Resonance Spectra. - Spectra were taken on a Varian Associates spectrometer V4311 at 56.45 Mc./sec. or, in some cases, at 40 Mc./sec. on a V4300B. Line positions were measured by the conventional side-band technique. Samples were usually measured in 5-mm. o.d. spinning pyrex tubes (polytetrafluoroethylene for HF studies), but in a few cases solutions were examined using a larger insert. For the concentrated sulphuric acid solutions, dimethylsulphate was used as internal reference; dimethylsulphate was referred to tetramethylsilane in $\text{CF}_3\text{CO}_2\text{H}$ as solvent and gave $\tau = 5.97$. For SO_2 , $\text{CF}_3\text{CO}_2\text{H}$ and $\text{BF}_3 \cdot \text{H}_2\text{O}$ - $\text{CF}_3\text{CO}_2\text{H}$ mixtures, tetramethylsilane was used directly as internal reference.

Absorption Spectra. - The spectra were recorded on a Perkin-Elmer Spectracord 4000 using degassed solvents and silica cells.

PREPARATIONS AND REACTIONS

The compounds used in the protonation studies were prepared by standard methods or by slight modifications of the published methods, where these were found to give easier preparations of the required complexes.

Protonation Studies. The solutions of the various compounds in the strong acids were prepared in test-tubes under nitrogen using oxygen-free acids and were transferred to 5-mm. o.d. tubes (afterwards sealed) for nuclear magnetic resonance measurements. For liquids or volatile solids, the trifluoroacetic acid solutions were prepared on a vacuum line as were solutions of solids in liquid sulphur dioxide. A list of compounds studied and their behaviour in three acids is given in Table I (Chapter II).

Attempts to isolate crystalline salts were made as follows. The benzene solution of the test compound containing boron trichloride, aluminium trichloride or antimony trichloride was saturated with hydrogen chloride; alternatively, a solution of the compound in wet benzene was treated with boron trifluoride. Although protonated species may well be present, intractable oils were the invariable products. The binuclear π -cyclopentadienyl carbonyls of molybdenum and tungsten were either very sparingly soluble or insoluble in anhydrous halogen acids; for example, $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$ was insoluble in liquid HBr and only sparingly soluble in anhydrous HF at room temperature. The addition of PCl_5 to the HF

solution increased the solubility somewhat and evaporation of the solution gave a brown solid which undoubtedly contained some of the protonated species as the hexafluorophosphate, as shown by the spectroscopic studies. Analyses were not too satisfactory since it was impossible to remove the free base completely by solvent extraction without causing decomposition.

Triphenylphosphine Substituted Iron Carbonyls. The following procedure gives better products than previous methods.³⁹ A solution of triphenylphosphine (9 g.) in dry, distilled tetrahydrofuran (30 ml.) was added to a hot solution of dodecacarbonyltri-iron (3 g.) in tetrahydrofuran (30 ml.), and the mixture heated under reflux. After 7 min. the solution, which had become yellow brown, was filtered through deactivated alumina (10 g.) which was washed with tetrahydrofuran (2 x 10 ml.). The clear yellow solution was concentrated (steam bath) in a rapid stream of nitrogen until crystals appeared. Cooling gave the tricarbonyl (4.2 g., 29%). The yellow filtrate was concentrated to ca. 10-20 ml. when on cooling a pale yellow solid, which was a mixture of the tri- and tetra-carbonyls, was obtained. The solid was dissolved in benzene-petroleum (100 ml., 1:1, 100-120°) and the solution filtered through Kieselguhr. Addition of petroleum (100 ml., 30-40°) and cooling to 0° gave more tricarbonyl (0.9 g.). The combined yield was recrystallised from benzene-petroleum (1:1 40-60°) to give golden-yellow crystals (4.8 g., 33%), m.p. 264-270° (with decomp.). [Found: C, 70.5; H, 4.5%; M, 678.4. Calc. for $C_{39}H_{30}FeO_3P_2$: C, 70.6; H, 4.6%; M, 664.1.]

Concentration of the pale yellow filtrate after removal of the tricarbonyl gave triphenylphosphine iron tetracarbonyl, which was recrystallised from petroleum (100-120°) as pale yellow crystals (3.1 g., 40%), m.p. 203-204° (decomp.). [Found: C, 62.4; H, 3.8%; $\underline{M}$, 415.9. Calc. for $C_{22}H_{15}FeO_4P$: C, 61.5; H, 3.5%; $\underline{M}$, 430.2.] Subsequent preparations have shown that the yields of the two products depend upon the time of refluxing of the reaction mixture; after ca. 15 min. the yield of tricarbonyl is about 40% and the tetracarbonyl 30%.

Triphenylarsine Iron Carbonyls. These compounds were prepared in a manner analogous to that described above. The reaction of $Fe_3(CO)_{12}$ and triphenylarsine is slower than that with triphenylphosphine and the mixture was refluxed for 15-20 min. Triphenylarsine iron tetracarbonyl is soluble in hot petroleum (100-120°) and can be readily separated from bis(triphenylarsine)iron tricarbonyl which is insoluble. The tetracarbonyl was recrystallised from petroleum as pale yellow crystals, m.p. 175-176° (with decomp.). [Found: C, 56.1; H, 3.3; As, 16.1; O, 13.8%; $\underline{M}$, 483 (ebullioscopic in benzene). $C_{22}H_{15}AsFeO_4$ requires C, 55.6; H, 3.2; As, 15.8; O, 13.5%; $\underline{M}$, 474.1.]

The tricarbonyl was recrystallised from benzene as golden-yellow crystals, m.p. 225-226° (decomp.). [Found: C, 63.5; H, 4.7; As, 19.7; O, 6.2%. $C_{39}H_{30}As_2FeO_3$ requires C, 62.3; H, 4.0; As, 19.9; O, 6.4%.]

Bis(triphenylstibine) Iron Tricarbonyl. Triphenylstibine (4.3 g.) and $\text{Fe}_3(\text{CO})_{12}$ (1 g.) in tetrahydrofuran (30 ml.) were heated under reflux for 45 min. The red-brown solution was filtered through deactivated alumina (10 g.) which was then washed with tetrahydrofuran (10 ml.). Evaporation to low bulk gave a red-brown solid which, on repeated recrystallisation (5 x) from benzene gave golden-yellow crystals (0.2 g., 4%), m.p. 195-196°, of bis(triphenylstibine) iron tricarbonyl. [Found: C, 54.5; H, 3.8%. $\text{C}_{39}\text{H}_{30}\text{FeO}_3\text{Sb}_2$ requires C, 54.4; H, 3.6%.]

Bis(π -cyclopentadienyl dicarbonyl iron) Hydrogen Hexafluorophosphate. Bis(π -cyclopentadienyl dicarbonyl iron) (5 g.) was dissolved in anhydrous hydrogen fluoride (ca. 75 ml.) and to the red-brown solution was carefully added in small portions with stirring sufficient phosphorus pentachloride to reduce the volume of the solution to ca. 30 ml. The excess solvent was removed in a stream of nitrogen until a red-brown solid remained. The solid was extracted with hot dichloromethane to remove unreacted $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, until the extract was pale yellow (3 x 100 ml.), and then with anhydrous ether (2 x 100 ml.). The residue was collected on a sintered crucible, washed with further portions of ether (2 x 20 ml.), and dried in vacuum to leave bis(π -cyclopentadienyl dicarbonyl iron) hydrogen hexafluorophosphate as a dark-brown powder (4.5 g., 62%) [Found: C, 31.5; H, 2.3; P, 6.8%. $\text{C}_{14}\text{H}_{11}\text{F}_6\text{Fe}_2\text{O}_4\text{P}$ requires C, 33.7; H, 2.2; P, 6.2%]. The salt is insoluble in ether, very sparingly soluble in dichloromethane and sparingly soluble in liquid SO_2 . It is decomposed by acetone-water mixtures to give $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ quantitatively.

π -Cyclopentadienyl Heptacarbonyl Iron Manganese Hydrogen Hexafluorophosphate. $\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7$ (0.5 g.) was dissolved in cold 98% sulphuric acid. The cherry-red solution was poured onto ice (ca. 7 g.). Addition of ammonium hexafluorophosphate solution (0.25 g. in 3 ml. water) to the red aqueous solution gave an orange precipitate which was collected, washed with iced-water (4 x 5 ml.) and anhydrous ether (2 x 100 ml.); drying in vacuum gave π -cyclopentadienyl heptacarbonyl iron manganese hydrogen hexafluorophosphate (0.65 g., 93%). [Found: C, 28.2; H, 1.5; F, 21.2; P, 6.1%. $\text{C}_{12}\text{H}_6\text{F}_6\text{FeMnO}_7\text{P}$ requires C, 28.0; H, 1.2; F, 22.0; P, 6.0%.] The salt is sparingly soluble in water and in dichloromethane. It is decomposed quantitatively by acetone to give $\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7$. The corresponding deuterio compound was prepared similarly but using D_2SO_4 and D_2O ; the ammonium hexafluorophosphate precipitant was dissolved in dilute (ca. 0.01N) D_2SO_4 to minimise exchange and added to the solution quickly (ca. 30 sec.) after being made up. Infrared and nuclear magnetic resonance measurements indicated that isotopic substitution was greater than 90%.

Trifluoroacetate Complex Carbonyls of Mo, W and Re. Tricarbonyl π -cyclopentadienyl methyl molybdenum (0.5 g.) was treated with trifluoroacetic acid (7 ml.). The compound slowly dissolved with evolution of methane to form a clear red solution. After removal of excess acid (0.2 mm., 20°) the solid was dissolved in diethyl ether (25 ml.) and extracted with water (2 x 25 ml.). The ethereal layer was dried (Na_2SO_4) and evaporated. Recrystallisation from petroleum ($60\text{--}80^\circ$) under

nitrogen gave red needles of π -cyclopentadienyl trifluoroaceto molybdenum tricarbonyl, m.p. 83.5-84.5° (0.59 g., 86%) [Found: C, 33.8; H, 1.42; F, 16.2%; $\underline{M}$, 371 (ebullioscopic in benzene). $C_{10}H_5F_3MoO_5$ requires C, 33.5; H, 1.41; F, 15.9%; $\underline{M}$, 358.1].

In a similar manner π -cyclopentadienyl trifluoroacetyl tungsten tricarbonyl, m.p. 90.5-91.5°. [Found: C, 26.9; H, 1.4; F, 12.6%; $\underline{M}$, 443 (ebullioscopic in benzene). $C_{10}H_5F_3O_5W$ requires C, 26.9; H, 1.1; F, 12.8%; $\underline{M}$, 446.]

The compounds are moderately stable in air, the tungsten one being most stable. There is no thermal decomposition at 100°C. in a vacuum.

Similarly from methylrhenium pentacarbonyl, trifluoroacetato rhenium tricarbonyl, white needles, m.p. 93.5-94.5°. [Found: C, 19.3; F, 13.0%. $C_7F_3O_7Re$ requires C, 19.2; F, 13.0%.]

Tricarbonyl- π -cyclopentadienyliron Tetraphenylborate. Method 1.

Chlorodicarbonyl- π -cyclopentadienyliron (0.5 g.) and sodium tetraphenylborate (0.85 g.) were dissolved in anhydrous acetone (2-3 ml.). The solution was placed in a small autoclave with carbon monoxide (90 atm.; 25-30°) for 48 hr. The product crystallised in the autoclave as large golden-yellow triangular plates; these were crushed and washed with air-free water. Recrystallisation from acetone at -78° and drying in a vacuum gave the yellow complex, decomp. 184° (1.07 g., 85%). [Found: C, 73.3; H, 5.0; O, 9.5. $C_{32}H_{25}BFeO_3$ requires C, 73.35; H, 4.8; O, 9.2%.] The crystals slowly darken in air; they are insoluble in water, ether, alcohol, benzene, and light petroleum but

soluble in acetone and nitrobenzene [conductance in nitrobenzene ($1.08 \times 10^{-3}M$), $\Lambda = 22.8 \text{ ohm}^{-1}$ at 23°].

Method 2. The chloro-compound (0.509 g.) and sodium tetraphenylborate (0.903 g.) in acetone (3 ml.) were held at 25° under nitrogen for 6 days; the product gave yellow plates (0.157 g., 12.6%). The formation of the salt under these conditions must involve intermolecular transfer of carbon monoxide.

Chlorodiacarbonyl- π -cyclopentadienyltriphenylphosphineiron Trihydrate.

Method 1. Chlorodiacarbonyl- π -cyclopentadienyliron (1.3 g.) and triphenylphosphine (2.5 g.) in tetrahydrofuran (20 ml.) were heated under reflux until a vigorous reaction set in (ca. 5 min.) and a brown solid separated; heating was continued for a further 5 min. Filtration gave a brown amorphous powder which was extracted with hot water (2 x 10 ml.); the filtrate, on cooling, deposited yellow crystals. Repeated crystallisation from hot water and drying in a vacuum-desiccator gave a golden-yellow trihydrate, decomp. 120° (0.93 g., 30%) [Found: C, 56.7; H, 4.9; P, 5.8; Cl, 6.7; Fe, 10.4. $C_{25}H_{20}ClFeO_2P, 3H_2O$ requires C, 56.8; H, 4.9; P, 5.9; Cl, 6.7; Fe, 10.6%]. The salt is stable in air and readily soluble in hot but sparingly soluble in cold water. All the chloride is ionic and can be precipitated with silver ion. Addition of chloroplatinic acid to a solution gives a white precipitate of the chloroplatinate [Found: C, 46.2; H, 3.3; Cl, 16.6. $C_{50}H_{40}Cl_6Fe_2O_4Pt$ requires C, 46.6; H, 3.1; Cl, 16.5%]. Ammonium reineckate solution gave a pale pink reineckate which was crystallised from acetone-water [Found: C, 46.2;

H, 3.6; N, 11.1. $C_{29}H_{26}CrFeN_6O_2P$ requires C, 46.0; H, 3.5; N, 11.1%]. Bromine water gave a pale orange precipitate of the tribromide, which crystallised from chloroform [Found: C, 44.3; H, 3.2. $C_{25}H_{20}Br_3FeO_2P$ requires C, 44.2; H, 2.9%]. In nitrobenzene at 23° , $0.83 \times 10^{-3}M$ $\pi-C_5H_5Fe(CO)_2PPh_3Cl \cdot 3H_2O$ had $\Delta 19.56 \text{ ohm}^{-1}$; $1.02 \times 10^{-3}M$ $[\pi-C_5H_5Fe(CO)_2-PPh_3]_2PtCl_6$ had $\Delta 37.6 \text{ ohm}^{-1}$.

Method 2. Equivalent amounts of the chloride reactant and triphenylphosphine were heated in a sealed tube. Extraction of the product with benzene and chromatography on alumina gave tricarbonylbistriphenylphosphineiron, m.p. $272-275^\circ$ (decomp.), in low yield. Extraction of the benzene-insoluble matter with hot water gave a yellow solution from which the cation was precipitated as the reineckate which crystallised as above [Found: C, 46.5; H, 3.6; N, 10.9%].

Triphenyl-arsine and -stibine Analogues. The triphenylarsine and triphenylstibine cations could be prepared only by the sealed-tube method above. They were precipitated from their aqueous solutions as the hexachloroplatinates [Found: C, 43.2; H, 3.4; O, 5.1; Cl, 16.0. $C_{50}H_{40}As_2Cl_6Fe_2O_4Pt$ requires C, 43.6; H, 2.9; O, 4.7; Cl, 15.5%. Found: C, 41.0; H, 3.3; O, 5.3. $C_{50}H_{40}Cl_6Fe_2O_4PtSb_2$ requires C, 41.0; H, 2.8; O, 4.4%]. They are less stable in air than the triphenylphosphine complex.

Dicarbonylcyclopentadienetriphenylphosphineiron. Chlorodicarbonyl- π -cyclopentadienyltriphenylphosphine iron trihydrate (1.5 g.) was suspended in 2:1 tetrahydrofuran-ether (40 ml.) at ca. -10° under nitrogen and treated with small portions (ca. 0.25 g.) of sodium borohydride until the suspended salt was completely dissolved (ca. $\frac{1}{2}$ hr.) and the solution was yellow. [This solution showed a weak high-field proton-resonance line identical with that of π -C₅H₅Fe(CO)₂H.] The solution was treated with air-free water (100 ml.) and extracted with light petroleum (b.p. 30-40°; 50 ml.). The petroleum layer [which rapidly darkened even under nitrogen owing to decomposition of π -C₅H₅Fe(CO)₂H] was washed with water, dried (CaCl₂), and concentrated to low bulk at 20°/2 mm. Chromatography on alumina (Brockmann, grade 3) under nitrogen gave a yellow weakly absorbed band which was rapidly eluted with ether and a dark red-brown strongly absorbed band from which, after extrusion, tetracarbonyldi- π -cyclopentadienyldi-iron was extracted with acetone (0.08 g., 7-8%; m.p. and mixed m.p. 193-194°). After removal of solvent from the yellow eluate at 20°/0.2 mm. a yellow solid (0.9 g., 75%) remained. Crystallization from light petroleum (b.p. 30-40°) at -78° gave a golden-yellow complex, m.p. 113-114° (decomp.) [Found: C, 68.2; H, 4.8; P, 7.4; Fe, 12.4%; M, 420. C₂₅H₂₄FeO₂P requires C, 68.25; H, 4.8; P, 7.05; Fe, 12.7%; M, 440). The compound decomposes within a few hours in air. On melting, it evolves a non-condensable gas and leaves a red oil. It is readily soluble in non-polar solvents, and the solutions darken over a

period of days in absence of oxygen. Solutions in carbon disulphide begin to darken after 1 hr., whilst in carbon tetrachloride rapid decomposition (ca. 1 min.) occurs, producing chloroform and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3\text{Cl}$, which was isolated as the chloroplatinate. The compound is moderately stable (ca. 1-2 days) in dichloromethane.

Thermal Decomposition of $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_2\text{PPh}_3$. A solution of the compound (0.23 g.) in xylene (4-5 ml.) was heated under reflux for 5 min. After 1 min. the solution became deep red-brown. Chromatography with benzene eluate allowed the isolation of ferrocene, m.p. $171\text{--}173^\circ$; the compound $[\pi\text{-C}_5\text{H}_6\text{Fe}(\text{CO})_2]_2$ (0.052 g., 60%), m.p. and mixed m.p. $189\text{--}192^\circ$, was recovered from the column by extraction with acetone.

Abstraction of Hydrogen from $\text{C}_5\text{H}_6\text{Fe}(\text{CO})_2\text{PPh}_3$. Triphenylmethyl tetrafluoroborate (0.15 g.) in dichloromethane (1-2 ml.) was added to a solution of the compound (0.123 g.) in dichloromethane (2 ml.). The reaction is only slow; after 12 hr. at ca. 5° the yellow crystals of $\pi\text{-cyclopentadienyldicarbonyltriphenylphosphineiron tetrafluoroborate}$ were removed, washed with solvent and dried (0.102 g., 69%), decomp. $> 250^\circ$ [Found: C, 56.0; H, 4.4. $\text{C}_{25}\text{H}_{20}\text{BF}_4\text{FeO}_2\text{P}$ requires C, 56.9; H, 3.8%].

Reduction of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{BPh}_4]$. A suspension of the salt (2.4 g.) in tetrahydrofuran (50 ml.) at -20° under nitrogen, on treatment with sodium borohydride, gave a deep yellow solution. This solution, which is similar in appearance to that obtained by reduction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ under the same conditions, shows a strong proton-resonance

line at a position identical with that given by $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$. Treatment of the solution with air-free water followed by extraction with light petroleum (b.p. 30-40°) caused rapid darkening of the organic layer. After removal of solvent at ca. 0°/0.1 mm., there remained purple crystals of the compound $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (0.62 g., 75%), m.p. and mixed m.p. 194°; some of the readily volatile yellow complex $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ condensed in the cold trap during removal of solvent, and on melting decomposed with effervescence to give more of the binuclear product.

This experiment has been repeated several times and no evidence for a cyclopentadiene compound has been obtained.

Other Reactions of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$. Refluxing this compound in tetrahydrofuran for 15 hr. under nitrogen afforded ferrocene and ferrous chloride; this reaction also occurs when the chloride is heated at 220°. If equivalent amounts of phenyl- or diphenyl-acetylene are added, the products are the same. The addition of 2,2'-bipyridyl or 1,10-phenanthroline causes complete disruption, resulting in octahedral ferrous complexes such as chlorotris-1,10-phenanthrolineiron(II).

INFRARED SPECTRA

Details of the spectra not given in the text are as follows.

(A) Protonation Studies. Sulphuric acid solutions were studied between AgCl plates. Values in cm.^{-1} :

$[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{H}^+$. H_2SO_4 film: 2074vs, 2054vs, 1988vs (CO str.).

$[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{H}^+$. H_2SO_4 film: 2028vs, 1961vs (CO str.).

$[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{HPF}_6$. Nujol mull: 2015vs, 1960vs (CO str.); 850vs (νPF_6^-).

$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{H}^+$. H_2SO_4 film: 2068ms, 2045vs, 2022vs (CO str.).

$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{HPF}_6$. Nujol mull: 2138s, 2068sh, 2050vs, 2018vs (CO str.); 847 (νPF_6^-). CH_2Cl_2 : 2079s, 2053s, 2026s (CO str.).

$\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7\text{HPF}_6$. CH_2Cl_2 : 2147m, 2065vs, 2055ms, 2015m, 1995m.sh (CO str.). Nujol mull: 1760w (Fe-H str.); 842s (νPF_6^-); 1425m, 1365m, 1113w, 1068w, 1005w, 971w, 905m ($\pi\text{-C}_5\text{H}_5$).

$\pi\text{-C}_5\text{H}_5\text{FeMn}(\text{CO})_7\text{DPF}_6$. Same: 1270w (Fe-D; $\nu\text{H}/\nu\text{D} = 1.386$); 840s (νPF_6^-); 1425m, 1363m, 1113w, 1068w, 1003w, 973m, 904m ($\pi\text{-C}_5\text{H}_5$).

$\text{Ph}_3\text{PFe}(\text{CO})_4\text{H}^+$. H_2SO_4 film: 2143vs, 2075vs (CO str.).

$(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3\text{H}^+$. H_2SO_4 film: 2028vs (CO str.).

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{OCOCF}_3$. CS_2 : 2072vs, 1992vs, 1975vs (CO str.); 1705vs (carboxyl); 1194vs, 1180vs, 1142vs (νCF_3).

$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{OCOCF}_3$. CS_2 : 2068vs, 1975vs (CO str.); 1712vs (carboxyl); 1201vs, 1183vs, 1146vs (νCF_3).

$\text{Re}(\text{CO})_5\text{OCOCF}_3$. Nujol mull: 2065s, 2045vs, 1995vs (CO str.); 1685vs (carboxyl), 1190vs, 1155vs (νCF_3).

(B) Cyclopentadienyl and Cyclopentadiene Iron Carbonyl Complexes.

The spectra are in hexachlorobutadiene and Nujol mulls where appropriate.

The assignments listed (in cm^{-1}) are (a) C-H phenyl, (b) C-H olefin, (c) C-H $_{\beta}$, (d) C-H $_{\alpha}$, (e) C $_6$ H $_5$ out-of-plane deformation on PPh $_3$, (f) the same on BPh $_4^-$, (g) and (h) the same on AsPh $_3$ and SbPh $_3$, respectively, (i) O-H stretch, (j) O-H deformation, (k) C-O stretch, (l) BF $_4^-$ asymmetric stretch, (m) spectra in CS $_2$ solution.

C $_5$ H $_5$ Fe(CO) $_2$ PPh $_3$ ^m: 3072w^a, 3010m, 2965w, 2765s^d, 1978vs^k, 1912vs^k, 1380vw, 1338vw, 1306vw, 1245vw, 1217w, 1186m, 1095m, 1073vw, 1055vw, 1030vw, 1000vw, 926vw, 830vw, 745s^e, 695s^e.

[C $_5$ H $_5$ Fe(CO) $_3$][BPh $_4$]: 3092vw, 3053vw; 2070vs^k, 2120vs^k; 1580w, 1477m, 1433m, 1425m, 1305w, 1184w, 1153w, 1115w, 1067w, 1033w, 1016vw, 1004w, 876w, 849w, 747s^f, 709s^f.

[C $_5$ H $_5$ Fe(CO) $_2$ PPh $_3$]Cl $_2$ ·3H $_2$ O: 3320vsⁱ; 2030vs^k; 2066vs^k; 1635m^j, 1435m, 1308w, 1115w, 1095m, 1075vw, 998w, 875w, 745ms^e, 695s^e.

[C $_5$ H $_5$ Fe(CO) $_2$ PPh $_3$]2PtCl $_6$: 3080, 3100w; 2030vs^k, 2070s^k; 1432m, 1310w, 1115w, 1096m, 1070vw, 998w, 875w, 750ms^e, 693ms^e.

[C $_5$ H $_5$ Fe(CO) $_2$ AsPh $_3$]2PtCl $_6$: 2017vs^k, 2062vs^k; 1432m, 1303w, 1183vw, 1155vw, 1073vw, 1018vw, 998w, 865vw, 740vs^g, 690s^g.

[C $_5$ H $_5$ Fe(CO) $_2$ SbPh $_3$]2PtCl $_6$: 2005vs^k, 2050vs^k; 1475m, 1435m, 1304vw, 1180vw, 1155vw, 1065vw, 1017vw, 997w, 874vw, 734ms^h, 690ms^h.

[C $_5$ H $_5$ Fe(CO) $_2$ PPh $_3$]BF $_4$: 2033vs^k, 2069vs^k; 1484m, 1438m, 1316w, 1288w, 1192w, 1172w, 1075vs^l, 873w, 750s^e, 695s^e.

HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA

The spectra of the protonated species are listed in Tables II, III, and IV.

The spectrum of $C_5H_5Fe(CO)_2PPh_3$ at 56.45 Mc./sec. (in benzene and CS_2 , with tetramethylsilane added as an internal reference): 2.73, doublet (5.2 cycles/sec.), phenyl protons; 4.87, "triplet" (4.2 cycles/sec.), H_3 , H_4 ; 7.18, 7.38, H_F , 7.66, 7.79, part of H_{α} and H_2, H_5 ; 8.0, part of H_{α} .

ABSORPTION SPECTRA

$Mn_2(CO)_{10}$: $CHCl_3$. λ_{max} , 343 m μ ; ϵ_{max} , 22,800.

$Mn_2(CO)_{10}$: H_2SO_4 98% A.R. λ_{max} , 389 m μ ; ϵ_{max} , 1,140.

$\pi-C_5H_5FeMn(CO)_7$: $CHCl_3$. λ_{max} , 388 m μ ; ϵ_{max} , 13,250; λ_{max} , 480(sh); ϵ_{max} , 1,520.

$\pi-C_5H_5FeMn(CO)_7H^+HSO_4^-$: H_2SO_4 98% A.R. λ_{max} , 395 m μ ; ϵ_{max} , 2,740; λ_{max} , 485 m μ ; ϵ_{max} , 775.

$[\pi-C_5H_5Fe(CO)_2]_2$: $CHCl_3$. λ_{max} , 343 m μ ; ϵ_{max} , 7,620; λ_{max} , 402 m μ (sh); ϵ_{max} , 1,990; λ_{max} , 520 m μ ; ϵ_{max} , 654.

$[\pi-C_5H_5Fe(CO)_2]_2H^+HSO_4^-$: H_2SO_4 98% A.R. λ_{max} , 287 m μ ; ϵ_{max} , 3,200; λ_{max} , 340 m μ ; ϵ_{max} , 2,300; λ_{max} , 426 m μ ; ϵ_{max} , 1,619; λ_{max} , 565 m μ (sh); ϵ_{max} , 206.

$[\pi-C_5H_5Mo(CO)_3]_2H^+HSO_4^-$: H_2SO_4 . λ_{max} , 325 m μ (sh); ϵ_{max} , 2,140; λ_{max} , 400 m μ ; ϵ_{max} , 900; λ_{max} , 493 m μ (sh); ϵ_{max} , 420.

$[\pi-C_5H_5W(CO)_3]_2H^+HSO_4^-$: H_2SO_4 . λ_{max} , 315 m μ (sh); ϵ_{max} , 2,590; λ_{max} , 396 m μ ; ϵ_{max} , 955; λ_{max} , 497 m μ ; ϵ_{max} , 584.

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