711. *The Formation of Metal–Hydrogen Bonds in the Protonation of Transition-metal–Carbonyl Complexes.*

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The interaction of a variety of transition-metal carbonyls and substituted carbonyls with sulphuric, trifluoroacetic, and other strong acids has been investigated. In a number of cases it has been shown that the central metal atom of the complex is protonated in solution; typical protonated species are $[HFe(CO)_3(PPh_3)^2]^+$, $[H\{Mo(CO)_3\pi\text{-}C_5H_5\}_2]^+$ and $[HCr(CO)_3C_6H_5Me]^+$.

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.*, $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2H]PF_6$, 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 carbonyl-π-cyclopentadienyl-molybdenum and -tungsten compounds, which provide unusual examples, in protonated species, of hydrogen associated with two metal atoms.

Improved preparations of carbonyl triphenylphosphineiron compounds are given, and the triphenyl-arsine and -stibine analogues described. Tricarbonyl-π-cyclopentadienyl-molybdenum and -tungsten trifluoroacetates, and pentacarbonylrhenium trifluoroacetate, are also described.

The first example of the protonation by acids of the central metal atom in a neutral transition-metal complex was that of hydridodi-π-cyclopentadienylrhenium.[1,2] The di-π-cyclopentadienyl dihydrides of molybdenum and tungsten [3] also act as bases, as does the rhenium compound named, whose base strength in aqueous dioxan is comparable with that of ammonia. Ferrocene and ruthenocene are basic, although only weakly so, forming the corresponding ions in boron trifluoride monohydrate as a protonating solvent.[4]

It was suggested by Sternberg and Wender [5] that base behaviour of the type shown by the rhenium compound might explain the reduction of various organic substrates in ethanolic hydrochloric acid by iron and cobalt carbonyls and by the dicarbonyl-π-cyclopentadienyliron dimer. However, we have not been able to show the existence in such solutions of protonated species of the stoicheiometry envisaged by Sternberg and Wender and there is so far no evidence that a protonated species is involved in the reductions. Nevertheless, using various anhydrous strong acids as protonating solvents we have found that various complexes with strongly π-bonding ligands can be protonated.

A list of the compounds investigated is given in the Experimental section. Since the binuclear species with metal–metal bonds have shown several unusual features which illustrate some of the processes occurring in protonated species, we discuss them first.

(A) *Binuclear Carbonyl-π-cyclopentadienylmetals.*—The binuclear π-cyclopentadienyl carbonyls $[\pi\text{-}C_5H_5M(CO)_3]_2$ (M = Mo or W), $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, and $\pi\text{-}C_5H_5FeMn(CO)_7$ dissolve readily in oxygen-free 98% sulphuric acid to fairly stable solutions. These solutions are diamagnetic (demonstrated by using the Evans [6] 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 $\pi\text{-}C_5H_5$ group, is always a sharp singlet, in contrast to the $\pi\text{-}C_5H_5$ resonance line of the neutral and protonated di-π-cyclopentadienyl species of molybdenum, tungsten, rhenium, and iron,[2-4] which are multiplets due to spin coupling of the hydrogen on the metal with the ring-hydrogen atoms.

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[1] Wilkinson and Birmingham, *J. Amer. Chem. Soc.*, 1955, **77**, 3689.

[2] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.

[3] Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854.

[4] Curphey, Santer, Richards, and Rosenblum, *J. Amer. Chem. Soc.*, 1960, **82**, 5249.

[5] Sternberg and Wender, Internat. Conf. Co-ordination Chemistry, *Chem. Soc. Special Publ.* No. 13, 1959, p. 35.

[6] Evans, *J.*, 1959, 2003.

The absence of splitting in the present cases is probably not significant, and even the mononuclear π-cyclopentadienyl carbonyl hydrides, *e.g.*, $\pi\text{-}C_5H_5W(CO)_3H$, show no observable splitting of the $\pi\text{-}C_5H_5$ resonances; for the di-π-cyclopentadienyl compounds the splitting is very small, *ca.* 0·5—1·5 c./sec.

TABLE 1.

Nuclear magnetic resonance spectra of the protonated binuclear π-cyclopentadienyl carbonyl complexes.

(At 56·45 Mc./sec. in 98% " AnalaR " H_2SO_4; relative intensities in parentheses.)

Species	$\tau(\pi\text{-}C_5H_5)$	τ(M–H)
$[\pi\text{-}C_5H_5Mo(CO)_3]_2H^+$	4·28(10)	30·99(1) singlet
$[\pi\text{-}C_5H_5W(CO)_3]_2H^+$	4·20(10)	34·77(1) " triplet " (1 : 6·26 : 1); J = 38·6 c./sec.*
$[\pi\text{-}C_5H_5W(CO)_3]_2H^+PF_6^-$ †	4·10	34·8 ‡
Equimol. mixture, $[\pi\text{-}C_5H_5Mo(CO)_3]_2H^+$	~4·25	30·99 singlet
and $[\pi\text{-}C_5H_5W(CO)_3]_2H^+$		34·77 " triplet "; J = 38·6 c./sec.
$[(\pi\text{-}C_5H_5)_2MoW(CO)_6]H^+$	~4·20	32·88 " triplet " (1 : 12 : 1); J = 38 c./sec.
$[\pi\text{-}C_5H_5Fe(CO)_2]_2H^+$ §	4·76(10)	36·30(1) singlet
$[\pi\text{-}C_5H_5Fe(CO)_2]_2H^+PF_6^-$ †	4·70(10)	36·3(1) singlet
$[\pi\text{-}C_5H_5FeMn(CO)_7]H^+$	4·68(5)	38·07(1) singlet
$[\pi\text{-}C_5H_5FeMn(CO)_7]H^+PF_6^-$ †	4·55(5)	38·0(1) singlet
$[\pi\text{-}C_5H_5FeMn(CO)_7]D^+PF_6^-$ †	4·55	Absent
$[\pi\text{-}C_5H_5Ru(CO)_2]_2H^+$	4·48(10)	28·58(1)

* At 40 Mc./sec. J = 39·8 c./sec. † Spectra measured in liquid sulphur dioxide with tetramethylsilane as internal reference. ‡ ^{183}W splitting not observed because of low solubility of salt. § Measured in $CF_3{\cdot}CO_2H$ with tetramethylsilane internal reference; also measured in H_2SO_4 with dimethyl sulphate as internal reference, and in $HF\text{–}BF_3$, $BF_3,H_2O\text{–}CF_3{\cdot}CO_2H$, and aqueous–$HBF_4$ propionic anhydride mixture.

The relative intensities of the $\pi\text{-}C_5H_5$ and high-field resonance lines (Table 1) 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 hydridoheptacarbonyl-π-cyclopentadienylironmanganese cation which is stable in dilute aqueous acid, from which it is precipitated by addition of solutions of salts with large anions such as hexafluorophosphate. Salts of the other binuclear protonated species have been obtained as hexafluorophosphates by addition of phosphorus pentachloride to their solutions in anhydrous hydrogen fluoride. The hexafluorophosphates are sparingly soluble in liquid sulphur dioxide at room temperature in a sealed tube).

The visible and ultraviolet absorption spectra of the protonated complexes in sulphuric acid differ significantly from those of the neutral complexes, the main features being a shift in the absorption maxima to longer wavelengths with concomitant, approximately ten-fold decrease in the molar extinction coefficients. It may be noted here that although dimanganese decacarbonyl is only sparingly soluble in concentrated sulphuric acid (saturated solution = *ca.* 10^{-3}M), 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 mμ, ε 1140) compared with that in chloroform ($\lambda_{max.}$ 343 mμ, ε 22,800) suggests that protonation of the carbonyl occurs.

Study of the molybdenum and tungsten species has given information concerning the nature of the protonated binuclear species and we discuss them first.

Molybdenum and tungsten compounds. The purple-red binuclear compounds, $[\pi\text{-}C_5H_5M(CO)_3]_2$, give red-brown solutions in sulphuric acid which decompose only slowly in the absence of air (during 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 hexafluorophosphate ion. The differences between the neutral and the protonated complexes show the expected increase n 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 strongly supports the view[7] that the magnitude of the proton shifts of hydrogen atoms bound to transition metals is little if at all correlated 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 high-resolution nuclear magnetic resonance spectra of equimolecular amounts of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $[\pi\text{-}C_5H_5W(CO)_3]_2$ dissolved in sulphuric acid, of $\{[(\pi\text{-}C_5H_5)_2MoW(CO)_6H]^+\}$, and of $[\{\pi\text{-}C_5H_5W(CO)_3\}_2H]^+$ show clearly that the proton is associated in some way with *both* metal atoms in these binuclear complexes.

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 our studies on the $[\{\pi\text{-}C_5H_5W(CO)_3\}_2H]^+$ 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.[8] 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.

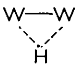
(2) Intermolecular exchange involving solvent protons. (i) Very slow (strong bases in strong acids). (*a*) Spin–spin coupling may be observed. (*b*) Chemical shifts will not be averaged. Examples showing such behaviour are $(\pi\text{-}C_5H_5)_2WH_3^+$,[3] $(\pi\text{-}C_5H_5)_2ReH_2^+$,[2] and $(\pi\text{-}C_5H_5)_2FeH^+$.[4]

(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 showing this type of behaviour are $(\pi\text{-}C_5H_5)_2MoH_3^+$,[3] and $(\pi\text{-}C_5H_5)_2RuH^+$.[4]

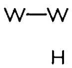
(iii) Rapid. (*a*) Spin–spin coupling will not be observed. (*b*) Chemical shifts will be averaged proportionately. An example here is $(\pi\text{-}C_5H_5)_2OsH^+$.[4]

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

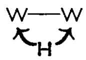
For the protonated tungsten complex $[\{\pi\text{-}C_5H_5W(CO)_3\}_2H]^+$ there are three possible chemical structures, (I)—(III), which differ in the way in which the proton is bound to the metal atom:



(I)



(II)



(III)

Structures (I) and (II) are static models; structure (III) involves exchange of the proton between the two tungsten atoms. It is possible to predict the proton resonance spectrum

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[7] Wilkinson, in " Advances in the Chemistry of Coordination Compounds," p. 50, ed. Kirschner, Macmillan, New York, 1961.

[8] Williams, *J. Inorg. Nuclear Chem.*, 1961, **20**, 198.

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. If $\mathrm{W}^{\frac{1}{2}}$ represents the isotope $^{183}\mathrm{W}$, the relative abundances of the three species, W–W, $\mathrm{W{-}W}^{\frac{1}{2}}$, $\mathrm{W}^{\frac{1}{2}}{-}\mathrm{W}^{\frac{1}{2}}$, will be respectively 73·48, 24·48, and 2·04%. The number of satellite bands and their relative intensities for the three principal systems can be derived 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 $\mathrm{W}\overset{\mathrm{H}}{\text{——}}\mathrm{W}$ of relative intensity 73·48%; (ii) a doublet, separation J_1, due to $\mathrm{W}\overset{\mathrm{H}}{\text{——}}\mathrm{W}^{\frac{1}{2}}$, intensity 24·48%; (iii) a triplet, separation J_1, due to $\mathrm{W}^{\frac{1}{2}}\overset{\mathrm{H}}{\text{——}}\mathrm{W}^{\frac{1}{2}}$, 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 $73{\cdot}48 + 1{\cdot}02 = 74{\cdot}5\%$. 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 $^{183}\mathrm{W}$. 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 $\mathrm{W{-}W}^{\frac{1}{2}}\mathrm{{-}H}$, 12·24%; (iii) a singlet due to $\mathrm{W}^{\frac{1}{2}}\mathrm{{-}W{-}H}$, 12·24%; and (iv) a doublet due to $\mathrm{W}^{\frac{1}{2}}{-}\mathrm{W}^{\frac{1}{2}}\mathrm{{-}H}$, 2·04%.

The resultant spectrum is now a " triplet " with the relative intensities: satellites, 14·28%; central peak, 85·72%. The satellites have 16·66% of the intensity of the central peak.

B. The proton is coupled to the remote tungsten atom when this is $^{183}\mathrm{W}$ with a small but finite spin coupling constant J_2'. The calculated spectrum now has components: (i) a singlet due to W–W–H, 73·48%; (ii) a doublet, separation J_2, due to $\mathrm{W{-}W}^{\frac{1}{2}}\mathrm{{-}H}$, 12·24%; (iii) a doublet, separation J_2', due to $\mathrm{W}^{\frac{1}{2}}\mathrm{{-}W{-}H}$, 12·24%, $J_2 > J_2'$; and (iv) a doublet 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 doublet doublet, 2·04%, of main separation J_2 and smaller separation J_2'. The intensity of the inner satellites is now 33·32% of that of the central peak, as in IIIA.

The theoretical spectra and the observed spectrum of $[(\pi\text{-}\mathrm{C_5H_5})\mathrm{W(CO)_3}]_2\mathrm{H}^+$ are shown in Fig. 1. 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 satellite intensities are thus 31·9% of that of the central peak and the observed spectrum is consistent with the cases I and IIIA or B. In principle we should have been able to distinguish between these possibilities 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 [9]), with the resultant

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* 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 $(J_2 + J_2')/2$.

[9] Maclean and Mackor, *J. Chem. Phys.*, 1961, **34**, 2208.

spectrum time-averaged corresponding to IIIA or B. The spectrum of the protonated species with a Mo–W bond (the hydride-proton resonance line shows a doublet satellite structure owing to spin-coupled interaction with ^{183}W) provides additional evidence that the proton is associated with both metal atoms. Arguments similar to those used for the bi-tungsten species show that there are again five theoretical spectra and these are shown together with the observed spectrum in Fig. 2. For the cases I and IIIA and B, the calculated spectrum is a "triplet" (with relative intensities: doublet, 14·28%; singlet, 85·72%), located between the positions of the chemical shifts for $[\{(\pi\text{-}C_5H_5)Mo(CO)_3\}_2H]^+$ and $[\{(\pi\text{-}C_5H_5)W(CO)_3\}_2H]^+$. 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 bitungsten and bimolybdenum species and is therefore consistent with models IIIA and B and possibly with I.

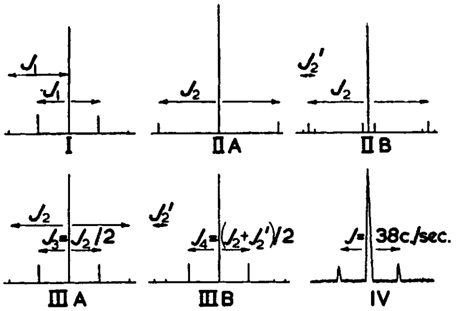

FIG. 1. Calculated and observed high-field proton resonance spectra of $[\pi\text{-}C_5H_5W(CO)_3]_2H^+$. For key to I, II, and III see text. IV, Observed spectrum in 98% sulphuric acid at 56·45 Mc./sec.

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

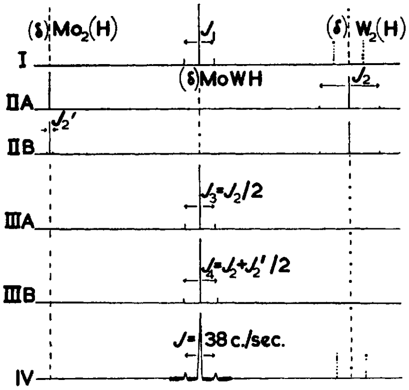

FIG. 2. Calculated and observed high-field proton resonance spectra of $[\pi\text{-}C_5H_5(CO)_3WMo(CO)_3\pi\text{-}C_5H_5]H^+$. For key to I, II, and III see text. IV, Observed spectrum in 98% sulphuric acid at 56·45 Mc./sec. $\delta Mo_2(H)$, $\delta W_2(H)$, and $\delta MoW(H)$ are the chemical shifts of $[\pi\text{-}C_5H_5Mo(CO)_3]_2H^+$, $[\pi\text{-}C_5H_5W(CO)_3]_2H^+$, and $[\pi\text{-}C_5H_5(CO)_3WMo(CO)_3\pi\text{-}C_5H_5]H^+$, respectively.

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°.

Although we cannot unequivocally 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 structure [10] of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ 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 carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [11] thus appear to be of the σ-type, in contrast to the metal–metal bond in the proposed structure for

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[10] Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

[11] Dahl, Ishishi, and Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

$Co_2(CO)_8$,[12] 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 π-$C_5H_5W(CO)_3X$ can be protonated, showing that a π-$C_5H_5W(CO)_3$ grouping possesses one or more non-bonding electron pairs. In the binuclear compounds where X = π-$C_5H_5Mo(CO)_3$ or π-$C_5H_5W(CO)_3$ we can thus assume that each metal atom has such protonatable electron pairs not involved in bonding to the π-C_5H_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.

Iron compounds. The compound $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is soluble in concentrated sulphuric acid [13] and cryoscopic measurements [14] in this solvent suggested a van't Hoff *i* factor of three. Sternberg and Wender [5] suggested that this result could be interpreted as protonation to give the ion $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2H_2]^{2+}$ and two bisulphate ions. However, the relative intensity measurements of the π-C_5H_5 and the high-field lines are found to be 10 : 1 in several different acids, clearly showing that $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is monobasic. In view of this fact, additional cryoscopic studies in sulphuric acid have now been made [15] with a highly purified sample of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$; *i* values, for successive additions, about 2·3 and 2·4 were obtained. It is difficult to draw reliable conclusions from these measurements.

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 assigned [13] to the bridging carbonyl groups, the presence of which in the crystal was confirmed by an *X*-ray diffraction study.[16] The absence of a bridging carbonyl group indicated by the spectrum of the sulphuric acid solution is confirmed by the mull spectrum of $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2H]PF_6$ obtained by treatment of the compound dissolved in anhydrous hydrogen fluoride with added phosphorus pentachloride. The bridging carbonyl groups disappear on dissolution of the neutral complex in strong acid but are 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 $>\overset{+}{C}\text{–OH}$ 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 π-$C_5H_5Fe(CO)_2$ 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 change readily and reversibly from bridging to non-bridging positions supports the evidence, based on differences between the infrared spectra in solution and the solid state [13,17] and on the Raman spectrum [18] of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, that the structures of the compound in solution and the crystal are not the same.

The bright-red compound π-$C_5H_5Fe(CO)_2$–$Mn(CO)_5$ [19] 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

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[12] For references and discussion see Nyholm, *Proc. Chem. Soc.*, 1961, 273.
[13] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.
[14] Leisten, quoted by Hallam *et al.*, *J. Inorg. Nuclear Chem.*, 1955, **1**, 313.
[15] Leisten, personal communication.
[16] Mills, *Acta Cryst.*, 1958, **11**, 620.
[17] Cotton, Liehr, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.
[18] Cotton, Stammreich, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 3.
[19] King, Treichel, and Stone, *Chem. and Ind.*, 1961, 747.

liberated on 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 us to obtain the salt $[\pi\text{-}C_5H_5FeMn(CO)_7D]PF_6$. In sulphur dioxide the latter shows no high-field proton resonance line and a comparison of the infrared spectra of the hydrogen and the deuterium salt shows that weak bands at 1760 and 1270 $cm.^{-1}$ can be assigned to metal–hydrogen and metal–deuterium stretching frequencies, respectively.

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 $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2H]PF_6$ also shows a weak band at 1767 $cm.^{-1}$, which may be due to the Fe–H stretch.

The nuclear magnetic resonance spectrum of the salt $[\{\pi\text{-}C_5H_5Fe(CO)_2Mn(CO)_5\}H]PF_6$ in liquid sulphur dioxide, unchanged at —70°, is consistent with the proton's being attached to the $\pi\text{-}C_5H_5Fe(CO)_2$ residue.

Other binuclear complexes such as $Co_2(CO)_8$, $[Ph_3PCo(CO)_3]_2$, $[\pi\text{-}C_5H_5NiCO]_2$, $[\pi\text{-}C_5H_5Ni]_2RC{\equiv}CR$, $Ph_3PAuCo(CO)_4$, and $[\pi\text{-}C_5H_5W(CO)_3]_2Hg$ 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 owing to the different electronegativities of the two halves of the molecules. With the anhydrous acids as well as with aqueous acids,[20] the transition-metal carbonyl hydride is liberated. For $[\pi\text{-}C_5H_5W(CO)_3]_2Hg$ in $BF_3,H_2O\text{–}CF_3\cdot CO_2H$, the liberated hydride is protonated, giving the ion $\pi\text{-}C_5H_5W(CO)_3H_2^+$ discussed below. We note, however, that despite its decomposition by anhydrous acids, even at low temperatures, $Co_2(CO)_8$ has been shown to act as a Lewis base, and the adduct $Co_2(CO)_8AlBr_3$ has been characterised.[21] It is possible that some of the complexes which can be protonated, *e.g.*, $(\pi\text{-}C_5H_5)_2ReH$, will also show similar Lewis base behaviour, for example, towards BH_3 or BCl_3.

B. *Mononuclear π-Cyclopentadienyl and Arene–Metal Carbonyls.*—The study of the hydridodi-π-cyclopentadienylmetals [2,3] led to the view, confirmed by molecular-orbital calculations,[22] 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 $(\pi\text{-}C_5H_5)_2ReH$ and $(\pi\text{-}C_5H_5)_2WH_2$. 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 with that of the rhenium and tungsten compounds. The view that in these di-π-cyclopentadienylmetal compounds there are six orbitals involved in primary bonding to the ligands, and three filled, " chemically active " [22] orbitals being non-bonding or partially involved in back-bonding to the ligands, can be extended to compounds with only one $\pi\text{-}C_5H_5$ ring present, and also to isoelectronic arene complexes. Thus $\pi\text{-}C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$ are isoelectronic with ferrocene, and $\pi\text{-}C_5H_5W(CO)_3H$ can be considered analogous to

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[20] Lewis, personal communication.

[21] Chini and Ercoli, *Gazzetta*, 1958, **88**, 1171; cf. also Cotton and Monchamp, *J.*, 1960, 1882.

[22] Ballhausen and Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333.

$(\pi\text{-}C_5H_5)_2ReH$. We have shown that several such carbonyl compounds can be protonated in anhydrous strong acids; the proton resonance data are collected in Table 2.

TABLE 2.

Nuclear magnetic resonance spectra of π-cyclopentadienyl- and arene-metal carbonyls.

[At 56·45 Mc./sec. in BF_3,H_2O (1 : 1 mol.) unless otherwise stated.]

Compound	τ M–H	τ Ligands
$\pi\text{-}C_5H_5W(CO)_3H_2^+$	* 11·93(1) singlet, broad width ½ ht. ~9 c./sec. † 11·90(1) singlet, broad, ~15 c./sec.	4·03(2·9) $\pi\text{-}C_5H_5$ singlet 3·99(3) $\pi\text{-}C_5H_5$ singlet
Compounds $ArCr(CO)_3$		
Benzene	13·55 ± 0·3 broad (~95 c./sec.)	
Toluene	13·98 ± 0·2(1) broad (~40 c./sec.)	3·35 ± 0·2 aromatic 7·14 ± 0·2 (3·2) CH_3
Mesitylene	14·27 ± 0·2 broad (~35 c./sec.)	4·13 ± 0·2 aromatic 7·78 ± 0·2 CH_3
1,2-Diphenylethane	14·06 ± 0·3	
o-Fluorotoluene	13·54 ± 0·3	
p-Fluorotoluene	13·58 ± 0·3	
o-Chlorotoluene	13·74 ± 0·3	
p-Chlorotoluene	14·0 ± 0·3	
Chlorobenzene	Insoluble	
Fluorobenzene	,,	
$[\pi\text{-}C_5H_5W(CO)_3]_2Hg$	11·95 ‡ (1)	3·99 (2·9)

* $BF_3,H_2O : CF_3{\cdot}CO_2H$ 1·23 : 1. † $BF_3,H_2O : CF_3{\cdot}CO_2H$ 1 : 1·73. ‡ $BF_3,H_2O : CF_3{\cdot}CO_2H$ 2 : 1; due to $\pi\text{-}C_5H_5W(CO)_3H_2^+$ produced by decomposition to hydride followed by protonation.

The compound $\pi\text{-}C_5H_5W(CO)_3H$ dissolves in trifluoroacetic acid without protonation to give stable yellow solutions. However, in the stronger acid mixture, $BF_3,H_2O\text{–}CF_3{\cdot}CO_2H$, protonation to give the ion $[\pi\text{-}C_5H_5W(CO)_3H_2]^+$ occurs. The high-field line is fairly broad, however, *ca.* 8 c./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), section A], showing that $\pi\text{-}C_5H_5W(CO)_3H$ is a much weaker base than its analogue, $(\pi\text{-}C_5H_5)_2ReH$. The yellow solutions of $[\pi\text{-}C_5H_5W(CO)_3H_2]^+$ became red over a period of several hours, evolving hydrogen and leaving in solution the previously unknown trifluoroacetate, $\pi\text{-}C_5H_5W(CO)_3O{\cdot}CO{\cdot}CF_3$. This slow decomposition appears to be an intramolecular hydrogen transfer:

$$\pi\text{-}C_5H_5W(CO)_3H_2]^+ + CF_3{\cdot}CO_2^- = \pi\text{-}C_5H_5W(CO)_3O{\cdot}CO{\cdot}CF_3 + H_2$$

The compound $\pi\text{-}C_5H_5Mo(CO)_3H$ behaves similarly: 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 $[\pi\text{-}C_5H_5Mo(CO)_3H_2]^+$.

For the methyl derivative, $\pi\text{-}C_5H_5W(CO)_3CH_3$, decomposition occurs in trifluoroacetic acid, methane being rapidly evolved; the other product is 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:

$$\begin{aligned}\pi\text{-}C_5H_5W(CO)_3CH_3 + CF_3{\cdot}CO_2H &= [\pi\text{-}C_5H_5W(CO)_3CH_3{\cdot}H]^+ + CF_3{\cdot}CO_2^- \\ &= \pi\text{-}C_5H_5W(CO)_3O{\cdot}CO{\cdot}CF_3 + CH_4\end{aligned}$$

Other alkyls of transition-metal carbonyls and π-cyclopentadienylmetal carbonyls, *e.g.*, $\pi\text{-}C_5H_5Fe(CO)_2CH_3$, $\pi\text{-}C_5H_5Mo(CO)_3CH_3$, and $CH_3{\cdot}M(CO)_5$ (M = Re and Mn), behave similarly.

Since $\pi\text{-}C_5H_5W(CO)_3H$ is a much weaker base than $(\pi\text{-}C_5H_5)_2ReH$, probably owing to the demands of the carbonyl groups for *d*-electron density for metal–carbon π-bonding, we can expect π-$C_5H_5Mn(CO)_3$ to be a weaker base than ferrocene. Although this manganese compound is only sparingly soluble in acids, yellow tricarbonyl-π-methylcyclopentadienylmanganese, which should be a stronger base, is soluble in BF_3,H_2O–$CF_3{\cdot}CO_2H$ mixtures, giving a red solution which is stable for at least two days. The proton resonance spectrum shows lines due to the π-C_5H_5 and CH_3 groups, but no high-field line. We conclude that rapid intermolecular exchange between Mn–H and solvent protons is occurring [process 2(iii), section A] as in acid solutions of the compound $(\pi\text{-}C_5H_5)_2Os$.[4] The compound is thus an extremely weak base.

Although dibenzenechromium 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°). During our studies it has been noticed [23] that tricarbonylarenechromiums dissolve in concentrated sulphuric acid to give yellow solutions which rapidly decompose, but we found that in BF_3,H_2O–$CF_3{\cdot}CO_2H$ deep yellow protonated species, $ArCr(CO)_3H^+$, are formed. This is consistent with the well-known fact that benzene is a weaker back-bonding π-acceptor ligand than the π-C_5H_5 group, and hence compounds such as $C_6H_6Cr(CO)_3$ should be stronger bases than π-$C_5H_5Mn(CO)_3$. All the arene compounds are weak bases and in all cases the high-field proton resonance lines (Table 2) are broad (40—90 c./sec. at half-height). In the same solutions the corresponding alkyl and phenyl resonance lines were 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 section A.

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$Cr(CO)_3$ (*ca.* 35 c./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 c./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 $\sim$ 1,2-diphenylethane $>$ *o*- and *p*-fluoro- and -chloro-toluene $>$ benzene $>$ fluoro- and chloro-benzene.

(C) *Iron Pentacarbonyl and Substituted Carbonyls.*—When iron pentacarbonyl is dissolved in cold concentrated sulphuric acid a green solution is obtained, which decomposes violently within 1—2 minutes. However, a 1 : 1 molar mixture of BF_3,H_2O–$CF_3{\cdot}CO_2H$ gives rise to a more stable green solution which persists for about half an hour at 25°. The proton magnetic resonance spectrum (Table 3) shows a characteristic, rather broad, high-field line at τ 18·14; the broadening is due to the weakly basic nature of $Fe(CO)_5$ and the spectrum corresponds to the slow exchange 2(ii) of section A.

TABLE 3.

Nuclear magnetic resonance of protonated iron carbonyls.

(At 56·45 Mc./sec. in 98% " AnalaR " H_2SO_4; dimethyl sulphate as internal reference.)

Species	τ Fe–H	τ C_6H_5
* $HFe(CO)_5^+$	18·14	
$HFe(CO)_4PPh_3^+$	17·75(1), Doublet, J = 35·3 c./sec.	2·33(15), Broad singlet
$HFe(CO)_3(PPh_3)_2^+$	17·78, Triplet, J = 30·2 c./sec.	2·58, Broad singlet
$HFe(CO)_4AsPh_3^+$	18·11 ± 0·1(1), Singlet	2·61 ± 0·1(15)
$HFe(CO)_3(AsPh_3)_2^+$	18·11 ± 0·1, Singlet	2·68 ± 0·1

* In BF_3,H_2O–$CF_3{\cdot}CO_2H$ with C_6H_{12} as external reference.

The triphenylphosphine- and triphenylarsine-metal carbonyls $XPh_3Fe(CO)_4$ and $(XPh_3)_2Fe(CO)_3$ (X = P or As) give stable yellow solutions in 98% sulphuric acid. The

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[23] Nesmeyanov and Vol'kenau, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, **1961**, 367.

arsine complexes are less stable than the phosphine ones, but tricarbonylbistriphenylstibineiron, 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 3) at τ *ca.* 18. The relative intensities of the high-field lines and the phenyl groups show that the carbonyls function as monoacid bases, *e.g.*:

$$\mathrm{Fe(CO)_4PPh_3 + H_2SO_4 = [HFe(CO)_4PPh_3]^+ + HSO_4^-}$$

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 c./sec.), and a triplet (*J* 30·2 c./sec.) in the hydridotetracarbonyltriphenylphosphineiron and hydridotricarbonylbistriphenylphosphineiron cation, respectively. The spectra show that these complexes are strong bases [corresponding to the very slow intermolecular exchange 2(i) of section A]. The greater base strength of the substituted carbonyls than of pentacarbonyliron can be attributed to the stronger σ-donor properties and weaker π-acceptor properties of triphenyl-arsine and -phosphorus ligands than of carbon monoxide. The ^{31}P resonance spectra should also show a structure which would have uniquely confirmed the stoicheiometry of the ions. However, the concentration of phosphorus in saturated solutions sufficed to give only a barely perceptible ^{31}P resonance line at 16·5 Mc./sec.

The structures of pentacarbonyliron and the triphenylphosphine carbonyls appear to be well established [12,24] as trigonal bipyramidal with the phosphine ligands in the axial positions. The triphenyl-arsine and -stibine analogues have infrared spectra similar to those of 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 hydridopentacarbonylmanganese, $HMn(CO)_5$. The latter has been shown [25] to gave a rather low symmetry where the hydrogen atom does not occupy a normal (*i.e.*, in this case, octahedral) bond position.

In contrast to $(Ph_3As)_2Fe(CO)_3$, the chelate $DiarsFe(CO)_3$ (Diars = *o*-phenylenebisdimethylarsine) 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 pyramidal structure.[26] 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 owing to lower availability of non-bonding electrons in this complex.

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College.

The compounds studied were prepared by standard methods. We thank the following industrial companies for gifts of materials: Albright and Wilson (Mfg.) Ltd. (triphenylphosphine), Climax Molybdenum Co. (molybdenum and tungsten carbonyls), and Ethyl Corporation (chromium and manganese carbonyls). We also thank Professor R. S. Nyholm, Dr. J. Lewis, Dr. M. C. Whiting, and Dr. W. R. McClellan (Du Pont) for gifts of *o*-phenylenebisdimethylarsineiron tricarbonyl, triphenylphosphinegold metal carbonyls, several arenechromium carbonyls and tetracarbonylperfluoropropylcobalt, respectively.

Triphenylphosphineiron–Carbonyl Complexes.—The following procedure gives better products than previous methods.[24] A solution of triphenylphosphine (9 g.) in dry, distilled

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[24] Cotton and Parrish, *J.*, 1960, 1440.

[25] Cotton, Down, and Wilkinson, *J.*, 1959, 833.

[26] Nyholm, personal communication.

tetrahydrofuran (30 ml.) was added to a hot solution of dodecacarbonyltri-iron (3 g.) in tetrahydrofuran (30 ml.), and the mixture was 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 × 10 ml.). The clear yellow solution was concentrated on a 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.; on cooling, a pale yellow solid, which was a mixture of the tri- and tetra-carbonyls, was obtained. The solid was dissolved in 1 : 1 benzene–light petroleum (b. p. 100—120°) (100 ml.) and filtered through kieselguhr. Addition of light petroleum (100 ml.; b. p. 30—40°) and cooling to 0° gave more tricarbonyl (0·9 g.). The combined products were recrystallised from 1 : 1 benzene–light petroleum (b. p. 40—60°) to give golden-yellow crystals (4·8 g., 33%), m. p. 264—270° (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 tetracarbonyl triphenylphosphineiron, which from light petroleum (b. p. 100—120°) formed pale yellow crystals (3·1 g., 40%), m. p. 203—204° (decomp.) (Found: C, 62·4; H, 3·8%; *M*, 415·9. Calc. for $C_{22}H_{15}FeO_4P$: C, 61·5; H, 3·5%; *M*, 430·2). 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 of tetracarbonyl 30%.

Triphenylarsineiron–Carbonyl Complexes.—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. *Tetracarbonyltriphenylarsineiron* is soluble in hot light petroleum (b. p. 100—120°) and can be readily separated from tricarbonyl bis(triphenylarsine)iron which is insoluble therein. The pale yellow tetracarbonyl, recrystallised from light petroleum, had m. p. 175—176° (decomp.) [Found: C, 56·1; H, 3·3; As, 16·1; O, 13·8%; *M*, 482 (ebullioscopic in benzene). $C_{22}H_{15}AsFeO_4$ requires C, 55·6; H, 3·2; As, 15·8; O, 13·5%; *M*, 474·1].

The *tricarbonyl* formed golden-yellow crystals, m. p. 225—226° (decomp.) from benzene (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%).

Tricarbonylbis(triphenylstibine)iron.—Triphenylstibine (4·3 g.) and $Fe_3(CO)_{12}$ (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 recrystallisation five times from benzene gave golden-yellow crystals (0·2 g., 4%), m. p. 195—196°, of *tricarbonylbis(triphenylstibine)iron* (Found: C, 54·5; H, 3·8. $C_{39}H_{30}FeO_3Sb_2$ requires C, 54·4; H, 3·6%).

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 instrument. Line positions were measured by the conventional side-band technique. Samples were usually measured in spinning Pyrex tubes of 5-mm. outside diameter (polytetrafluoroethylene tubes for studies with hydrogen fluoride), but in a few cases solutions were examined by using a larger insert. For the concentrated sulphuric acid solutions, dimethyl sulphate was used as internal reference; dimethyl sulphate was referred to tetramethylsilane in trifluoroacetic acid and gave τ 5·97. For sulphur dioxide, trifluoroacetic acid, and $BF_3,H_2O–CF_3\cdot CO_2H$, tetramethylsilane was used directly as internal reference.

We thank Dr. A. R. Katritzky, of Cambridge, for a ^{31}P resonance measurement at 16·5 Mc./sec.

Protonation Studies.—The solutions of the various compounds in the strong acids were prepared in test-tubes under nitrogen with oxygen-free acids and were transferred to 5-mm. 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 4 (1 : 1, 1 : 2, and 2 : 1 $BF_3,H_2O–CF_3\cdot CO_2H$ were used).

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 very sparingly soluble or insoluble in anhydrous halogen acids; for example, $[\pi\text{-}C_5H_5W(CO)_3]_2$ was insoluble in liquid hydrogen bromide and only sparingly soluble in anhydrous hydrogen fluoride at room temperature. The addition of phosphorus pentachloride to the hydrogen fluoride solution increased the solubility somewhat and evaporation then gave a brown solid which undoubtedly contained some of the protonated species as the hexafluorophosphate, as shown by the spectroscopic studies. Analyses were not satisfactory since we were unable to remove the free base completely by solvent-extraction without causing decomposition.

Bis(dicarbonyl-π-cyclopentadienyliron) Hydrogen Hexafluorophosphate.—Bis(dicarbonyl-π-cyclopentadienyliron) (5 g.) was dissolved in anhydrous hydrogen fluoride (*ca.* 75 ml.), and to the red-brown solution was added, in small portions with stirring, sufficient phosphorus pentachloride to reduce the volume of the solution to *ca.* 30 ml. The excess of solvent was removed in a stream of nitrogen until a red-brown solid remained. The solid was extracted with hot dichloromethane to remove unchanged $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, until the extract was pale yellow (3 × 100 ml.), and then with anhydrous ether (2 × 100 ml.). The residue was collected on a sintered crucible, washed with ether (2 × 20 ml.), and dried in a vacuum, to leave *bis(dicarbcnyl-π-cyclopentadienyliron) hydrogen hexafluorophosphate* as a dark-brown powder (4·5 g., 62%) (Found: C, 31·5; H, 2·3; P, 6·8. $C_{14}H_{11}F_6Fe_2O_4P$ 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 sulphur dioxide. It decomposes in acetone–water giving $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ quantitatively.

Heptacarbonyl-π-cyclopentadienylironmanganese Hydrogen Hexafluorophosphate.—$\pi\text{-}C_5H_5FeMn(CO)_7$ (0·5 g.) was dissolved in cold 98% sulphuric acid. The cherry-red solution

TABLE 4.

Behaviour of carbonyl complexes in strong acids.

[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; ev = evolved.]

Compound	98% H_2SO_4 (" AnalaR ")	BF_3,H_2O or $BF_3,H_2O–CF_3{\cdot}CO_2H$	$CF_3{\cdot}CO_2H$ (100%)
Chromium derivatives			
$Cr(CO)_6$	i	i	i
Arene $Cr(CO)_3$ (*a*)	s, yellow; dr 1—2 min.	s, yellow; p	sp.s
$(CH_3)_2N{\cdot}C_6H_4Cr(CO)_3$	dr	dr	dr
$X{\cdot}C_6H_4{\cdot}Cr(CO)_3$ (X = F or Cl)	dr	sp.s; p	
Diphenyl$[Cr(CO)_3]_2$	dr	i	
$(C_6H_6)_2Cr$	dr	dr	dr
$Cr(CO)_5PPh_3$		i; ds	i; ds
$Cr(CO)_4[PPh_3]_2$	i	i; ds	i; ds
Molybdenum derivatives			
$Mo(CO)_6$		i	i
Mesitylene$Mo(CO)_3$	dr	dr	dr
$[\pi\text{-}C_5H_5Mo(CO)_3]_2$	s, red brown; p; st	sp.s	sp.s
$(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$	dr (CH_4 ev)		dr (CH_4 ev)
$(\pi\text{-}C_5H_5)Mo(CO)_3H$	dr (H_2 ev)	dr (H_2 ev)	dr (H_2 ev)
$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$	dr (*b*)	sp.s; ds	
$\pi\text{-}C_5H_5Mo(CO)_3Cl$	dr (HCl ev) (*b*)		
2,2′-Bipyridyl$Mo(CO)_4$	dr	dr	dr
Tungsten derivatives			
$W(CO)_6$	i		
$(\pi\text{-}C_5H_5)_2MoW(CO)_6$	s, red brown; p; st (*b*)		
$\pi\text{-}C_5H_5W(CO)_3Cl$	dr HCl ev)		
$\pi\text{-}C_5H_5W(CO)_3CH_3$	dr (CH_4 ev)	dr (CH_4 ev)	dr (CH_4 ev)
$[\pi\text{-}C_5H_5W(CO)_3]_2Hg$	dr (*b*)	s; p (*c*)	sp.s
$[\pi\text{-}C_5H_5W(CO)_3]_2$	s, red brown; p; st	sp.s	sp.s
$\pi\text{-}C_5H_5W(CO)_3H$	dr	s, yellow; p; ds	s
Manganese derivatives			
$\pi\text{-}CH_3{\cdot}C_5H_4Mn(CO)_3$	s, red; st	s, red; st ~2 days	s, red
$\pi\text{-}C_5H_5Mn(CO)_3$	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 ev)	dr (CH_4 ev)	dr (CH_4 ev)
$Mn(CO)_5Br$	dr	dr	dr
$\pi\text{-}C_5H_5FeMn(CO)_7$	s, red; p; st		

TABLE 4. (*Continued.*)

Compounds	98% H_2SO_4 ("Analar")	BF_3,H_2O, or $BF_3,H_2O–CF_3CO_2H$	$CF_3{\cdot}CO_2H$ (100%)
Rhenium derivatives			
$Re_2(CO)_{10}$	i		
$Re(CO)_5CH_3$	dr (CH_4 ev)	dr (CH_4 ev)	dr (CH_4 ev)
Iron derivatives			
$Fe(CO)_5$	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
$Fe(CO)_4AsPh_3$	w; p; st		dr
$Fe(CO)_3(AsPh_3)_2$	s; p; st		dr
$Fe(CO)_3(SbPh_3)_2$	s; p? dr (1 min.)		dr
$Fe(CO)_3$Diars (*d*)	s; st	s; st	
$Fe(CO)_4(AuPPh_3)_2$	dr		
$(\pi-C_5H_5)_2Fe$	s (*e*)	s; p; st	s; st
$[\pi-C_5H_5Fe(CO)_2]_2$	s, red brown; p; st	s; p; st	s; p; st (*f*)
$[\pi-C_5H_5FeMn(CO)_7]$	s, red; p; st		
$\pi-C_5H_5Fe(CO)_2Cl$	dr (HCl ev) (*g*)		s
$\pi-C_5H_5Fe(CO)_2CH_3$	dr (CH_4 ev) (*g*)	dr	dr
o-$phen_2Fe(CN)_2$	s, yellow; st (*h*)	s, yellow; st (*h*)	s, yellow; st (*h*)
Cobalt derivatives			
$Co_2(CO)_8$	dr	dr	dr
$\pi-C_5H_5(CO)_2$	dr	dr	s; st
$Co(CO)_4AuPPh_3$	dr (*i*)		
$Co_2(CO)_6C_2R_2$ (R = alkyl and aryl)	dr		dr
$\pi-C_5H_5Co(C{\cdot}CF_3)_4$	s, red; st		s, red; st
$Co(CO)_4C_3F_7$	dr	dr	dr
$[Co(CO)_3PPh_3]_2$	dr	i; ds	i
Nickel derivatives			
$Ni(CO)_4$	s; dr	s; st	s; st
$Ni(CO)_2(PPh_3)_2$	dr (*j*)	dr	dr
$(\pi-C_5H_5)_2Ni$	dr		
$\pi-C_5H_5NiNO$	dr		dr
$[\pi-C_5H_5NiCO]_2$	dr		dr
$(\pi-C_5H_5Ni)_2C_2R_2$ (R = alkyl and aryl)	dr		
$NiBr_2(Me_2P{\cdot}CH_2)_2$	dr		

(*a*) See Table 3 for protonated species. (*b*) Gives $\pi-C_5H_5M(CO)_3{\cdot}O{\cdot}SO_3H$. (*c*) Gives $\pi-C_5H_5W(CO)_3H_2^+$ (see text). (*d*) Diars = *o*-phenylenebisdimethylarsine. (*e*) Slight oxidation to $(\pi-C_5H_5)_2Fe^+$. (*f*) Also in $CClF_2{\cdot}CO_2H$ and HBF_4(aq) in propionic anhydride. (*g*) Gives red $\pi-C_5H_5Fe(CO)_2{\cdot}O{\cdot}SO_3H$. (*h*) Protonates the cyanide groups to give *o*-$phen_2Fe(CNH^+)_2$; no high-field line; *o*-phen = 1,10-phenanthroline. (*i*) $HCo(CO)_4$ evolved. (*j*) Forms Ni^{2+} and $Ph_3Ph^+HSO_4^-$, CO evolved.

was poured on ice (*ca.* 7 g.). Addition of ammonium hexafluorophosphate solution (0·25 g. in 3 ml.) to the red aqueous solution gave an orange precipitate which was collected, and washed with iced-water (4 × 5 ml.), and anhydrous ether (2 × 100 ml.); drying in a vacuum gave the *hexafluorophosphate* (0·65 g., 93%) (Found: C, 28·2; H, 1·5; F, 21·2; P, 6·1. $C_{12}H_6F_6FeMnO_7P$ 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 $\pi-C_5H_5FeMn(CO)_7$. The corresponding deutero-compound was prepared similarly by using D_2SO_4 and D_2O; the ammonium hexafluorophosphate precipitant was dissolved in *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%.

Trifluoroacetato-molybdenum, -tungsten, and -rhenium Carbonyl Complexes.—Tricarbonylmethyl-π-cyclopentadienylmolybdenum (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 the excess of acid (at 20°/0·2 mm.) the solid was dissolved in diethyl ether (25 ml.)

and extracted with water (2 × 25 ml.). The ethereal layer was dried (Na_2SO_4) and evaporated. Recrystallisation from light petroleum (b. p. 60—80°) under nitrogen gave red needles of *tricarbonyl-π-cyclopentadienyltrifluoroacetatomolybdenum*, m. p. 83·5—84·5° (0·59 g., 86%) [Found: C, 33·8; H, 1·42; F, 16·2%; *M*, 371 (ebullioscopic in benzene). $C_{10}H_5F_3MoO_5$ requires C, 33·5; H, 1·41; F, 15·9%; *M*, 358·1].

In a similar manner *tricarbonyl-π-cyclopentadienyltrifluoroacetatotungsten*, m. p. 90·5—91·5° [Found: C, 26·9; H, 1·4; F, 12·6%; *M*, 443 (ebullioscopic in benzene). $C_{10}H_5F_3O_5W$ requires C, 26·9; H, 1·1; F, 12·8%; *M*, 446], was prepared.

The compounds are moderately stable in air, the latter the more stable. There is no thermal decomposition at 100° in a vacuum.

Similarly pentacarbonylmethylrhenium gave *pentacarbonyltrifluoroacetatorhenium*, white needles, m. p. 93·5—94·5° (Found: C, 19·3; F, 13·0. $C_7H_3O_7Re$ requires C, 19·2; F, 13·0%).

Infrared Spectra.—Spectra were taken on a Perkin–Elmer model 21 instrument with sodium chloride or calcium fluoride optics as appropriate. Sulphuric acid solutions were studied between silver chloride plates. Values in cm.$^{-1}$.

[π-$C_5H_5Mo(CO)_3]_2H^+$. H_2SO_4 film. 2074vs, 2054vs, 1988vs (CO str.).

[π-$C_5H_5W(CO)_3]_2H^+$. H_2SO_4 film. 2028vs, 1961vs (CO str.).

[π-$C_5H_5W(CO)_3]_2HPF_6$. Nujol mull. 2015vs, 1960vs (CO str.); 850vs (νPF_6^-).

[π-$C_5H_5Fe(CO)_2]_2H^+$. H_2SO_4 film. 2068ms, 2045vs, 2022vs (CO str.).

[π-$C_5H_5Fe(CO)_2]_2HPF_6$. Nujol mull. 2138s, 2068sh, 2050vs, 2018vs (CO str.); 847 (νPF_6^-). CH_2Cl_2: 2079s, 2053s, 2026s (CO str.).

π-$C_5H_5FeMn(CO)_7HPF_6$. 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 (π-C_5H_5).

π-$C_5H_5FeMn(CO)_7DPF_6$. Same: 1270w (Fe–D; $\nu H/\nu D = 1·386$); 840s (νPF_6^-); 1425m, 1363m, 1113w, 1068w, 1003w, 973m, 904m (π-C_5H_5).

$Ph_3PFe(CO)_4$. CH_2Cl_2: 2062vs, 1982vs, 1940vs (lit.,[22] CCl_4: 2059vs, 1984vs, 1946vs) (CO str.).

$(Ph_3P)_2Fe(CO)_3$. CH_2Cl_2: 1883vs (lit.,[22] $CHCl_3$: 1887vs) (CO str.).

$Ph_3AsFe(CO)_4$. CCl_4: 2064vs, 1984vs, 1946vs (CO str.).

$(Ph_3As)_2Fe(CO)_3$. CH_2Cl_2: 1878vs (CO str.).

$(Ph_3Sb)_2Fe(CO)_3$. CH_2Cl_2: 1874vs (CO str.).

$Ph_3PFe(CO)_4H^+$. H_2SO_4 film: 2143vs, 2075vs (CO str.).

$(Ph_3P)_2Fe(CO)_3H^+$. H_2SO_4 film: 2028vs (CO str.).

π-$C_5H_5Mo(CO)_3{\cdot}O{\cdot}CO{\cdot}CF_3$. CS_2: 2072vs, 1992vs, 1975vs (CO str); 1705vs ($>$C=O); 1194vs, 1180vs, 1142vs (νCF_3).

π-$C_5H_5W(CO)_3{\cdot}O{\cdot}CO{\cdot}CF_3$. CS_2: 2068vs, 1975vs (CO str.); 1712vs ($>$C=O); 1201vs, 1183vs, 1146vs (ν CF_3).

$Re(CO)_5{\cdot}O{\cdot}CO{\cdot}CF_3$. Nujol mull: 2065vs, 2045vs, 1995vs (CO str.); 1685vs ($>$C=O), 1190vs, 1155vs (ν CF_3).

Ultraviolet Absorption Spectra.—The spectra were recorded on a Perkin–Elmer Spectracord 4000 instrument, with degassed solvents and silica cells. ε are given below in parentheses.

$Mn_2(CO)_{10}$: $CHCl_3$. $\lambda_{max.}$ 343 mμ (22,800).

$Mn_2(CO)_{10}$: 98% " AnalaR " H_2SO_4. $\lambda_{max.}$ 389 mμ (1140).

π-$C_5H_5FeMn(CO)_7$: $CHCl_3$. $\lambda_{max.}$ 388 mμ (13,250), 480(sh) (1520).

π-$C_5H_5FeMn(CO)_7H^+$: 98% " AnalaR " H_2SO_4. $\lambda_{max.}$ 395 (2740), 485 mμ (775).

[π-$C_5H_5Fe(CO)_2]_2$: $CHCl_3$. $\lambda_{max.}$ 343 (7620), 402sh (1990), 520 mμ (654).

[π-$C_5H_5Fe(CO)_2]_2H^+$: H_2SO_4 (as above) $\lambda_{max.}$ 287 (3200), 340 (2300), (426), (1619), 565sh mμ (206).

[π-$C_5H_5Mo(CO)_3]_2H^+$: H_2SO_4 (as above). $\lambda_{max.}$ 325sh (2140), 400 (900), 493sh mμ (420).

[π-$C_5H_5W(CO)_3]_2H^+$: H_2SO_4 (as above). $\lambda_{max.}$ 315sh (2590), 396 (955), 497 mμ (584).

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