497. *The Broad-line Proton Resonance Spectrum of Iron Carbonyl Hydride.*

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The broad-line nuclear magnetic resonance spectrum of iron carbonyl hydride, $H_2Fe(CO)_4$, has been measured at 20° K. The expected doublet structure was not observed, probably owing to either traces of impurity or zero-point proton vibration. The second moment, treated as being due to a proton-pair signal, leads to an interproton distance of $1{\cdot}88 \pm 0{\cdot}05$ Å. This value is considered in terms of various structures for the compound and it is concluded that the hydrogen atoms are bound directly to the metal atom with the Fe–H distance being *ca.* 1·1 Å.

Since the discovery of iron carbonyl hydride, $H_2Fe(CO)_4$, by Hieber and Leutert,[1] other transition-metal carbonyl hydrides have been claimed, but of these only the cobalt [2] and manganese [3] compounds have been well characterized. Until recently, the iron and cobalt compounds were the only examples of transition-metal complex hydrides, but other types, with π-cyclopentadienyl [4,5,6] and substituted phosphine [7] and cyanide [8,9] ligands, as well as mixed π-cyclopentadienyl-carbonyl [6,10,11] hydrides, are now known.

The structure of the iron and cobalt carbonyl hydrides, and particularly the exact nature of the binding of the hydrogen atom in the compounds (a problem which applies also to the other complex hydrides), has been the subject of considerable speculation.

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[1] Hieber and Leutert, *Naturwiss.*, 1931, **19**, 360.

[2] Coleman and Blanchard, *J. Amer. Chem. Soc.*, 1936, **58**, 2160; Hieber, *Angew. Chem.*, 1936, **49**, 463.

[3] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13**b, 339.

[4] Birmingham and Wilkinson, *J. Amer. Chem. Soc.*, 1955, **77**, 3421.

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

[6] Green and Wilkinson, unpublished work.

[7] Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

[8] Griffith, Pratt, and Wilkinson, *Nature*, 1958, **182**, 466.

[9] Griffith and Wilkinson, *J.*, in the press.

[10] Fischer, Hafner, and Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

[11] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

The earliest view of the binding of hydrogen was that suggested by Hieber,[12] in which the hydrogen atoms were considered to be embedded as protons in the electronic core of the metal atom, the groups H_2Fe and HCo functioning as pseudo-metal atoms of atomic number 28; the molecules $H_2Fe(CO)_4$ and $HCo(CO)_4$ were thus comparable with $Ni(CO)_4$.

Ewens and Lister,[13] whilst proving by electron diffraction the tetrahedral disposition of CO groups in $H_2Fe(CO)_4$ and $HCo(CO)_4$, suggested that electron transfer from hydrogen to the metal occurred, with linkage of the proton to the lone pair of the oxygen atoms to give a linear C–O–H group isoelectronic with the NO group in metal nitrosyls and nitrosyl carbonyls. This suggestion, although consistent with the inert-gas rule formalism, can be ruled out by infrared studies on $HCo(CO)_4$,[14,15,16] where no hydroxyl stretching frequency was observed, by the low parachor contribution of the hydrogen atoms, which implies that they do not project beyond the van der Waals diameter of the $M(CO)_4$ skeleton,[17] by high-resolution nuclear magnetic resonance measurements on $HCo(CO)_4$,[14] $H_2Fe(CO)_4$,[16] and π-$C_5H_5M(CO)_3H$ (M = Cr, Mo, W),[11] where the observed proton shifts cannot be reconciled with bonding to oxygen, and by data discussed below.

In connection with infrared measurements on $HCo(CO)_4$,[15] Edgell and Gallup [18] suggested a structure (I) in which the hydrogen atom bridged three carbon monoxide groups, with subsidiary linkage to the metal atom, the bonding electrons being considered to occupy eight-centred molecular orbitals derived from carbon monoxide π-orbitals, the d_{z^2} orbital of the metal, and the 1*s* orbital of hydrogen in a molecule of C_{3v} symmetry. Calculations of overlap integrals showed that these become a maximum at a Co–H distance just under 2 Å, and it was inferred that the proton is located in this vicinity. Energetic considerations led to the view that little bonding between the metal and hydrogen atoms is involved. This suggestion was held to be consistent with the large proton chemical shift in $HCo(CO)_4$ [14] (15 parts per million to the high-field side in water) and with the low value, 703 cm.$^{-1}$, of the only infrared vibration attributable to hydrogen.[15,16]

If correct, this view should apply to the structurally and chemically similar iron carbonyl hydride, but it was pointed out [16] that the acid constants of $H_2Fe(CO)_4$, $pK_1 =$ *ca.* 10^{-5} and $pK_2 =$ *ca.* 10^{-14}, are more consistent with the binding of the hydrogen atom directly to the metal atom, and that the low value of the infrared vibration associated with hydrogen [confirmed by study of $DCo(CO)_4$] need imply no more than a weak metal–hydrogen bond, in keeping with the low thermal stability of $HCo(CO)_4$ and $H_2Fe(CO)_4$. In support of this view, in $HMn(CO)_5$ [19] the hydrogen vibration, assigned as a M–H stretch, lies at 1783 cm.$^{-1}$, whilst in other complex hydrides absorptions are found in the 2000 cm.$^{-1}$ region.[5,20]

Further evidence against the suggestion by Edgell *et al.* was provided by a reconsideration of their work by Cotton; [21] the original overlap calculations contained an error and a correct application of the mathematics leads to greatest total overlap at a Co–H distance of *ca.* 1·2 Å. This result thus indicates significant bonding of hydrogen to the metal atom and further alteration in this direction could be achieved by use of a $3d_{z^2}$–$4p_z$ hybrid orbital for cobalt. Cotton, with Edgell *et al.*, places the hydrogen atom on the C_3 axis of $HCo(CO)_4$.

A different view of the structure of the carbonyl hydrides was provided by Liehr; [22] direct bonding between the metal and hydrogen is again envisaged. The assumed tetrahedral symmetry of the $M(CO)_4$ skeleton involves bonding of the carbon monoxide ligands

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[12] Hieber, *Die Chemie*, 1942, **55**, 25.

[13] Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.

[14] Friedel, Wender, Shufler, and Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

[15] Edgell, Magee, and Gallup, *ibid.*, 1956, **78**, 4185.

[16] Cotton and Wilkinson, *Chem. and Ind.*, 1956, 1305.

[17] Hieber, Seel, and Schneider, *Chem. Ber.*, 1952, **85**, 647.

[18] Edgell and Gallup, *J. Amer. Chem. Soc.*, 1956, **78**, 4188.

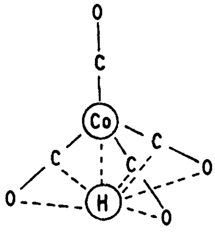
[19] Cotton, Down, and Wilkinson, *J.*, 1959, 833.

[20] Chatt, Duncanson, and Shaw, *Chem. and Ind.*, 1958, 859.

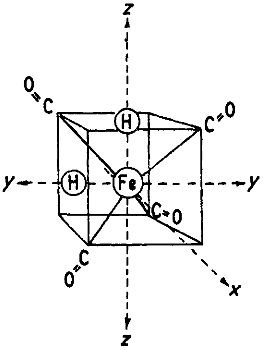
[21] Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 4425.

[22] Liehr, *Z. Naturforsch.*, 1957, **12**b, 95.

to the metal atom by sp^3 hybridized metal orbitals. The doubly occupied d_{xy}, d_{xz}, and d_{yz} orbitals of the $n = 3$ shell enter into dative π-bonding with the ligands, but the degenerate d_{z^2}–$d_{x^2-y^2}$ orbitals are non-bonding with respect to the ligands. They are, however, bonding with respect to the 1*s* orbital of hydrogen, and Liehr suggested that the protons are embedded in these orbitals in the direction of maximum electron density. In $HCo(CO)_4$ one, and in $H_2Fe(CO)_4$ two, hydrogen atoms are located on the four-fold rotation–reflection axes of the $M(CO)_4$ tetrahedron, each proton in $H_2Fe(CO)_4$ being symmetrically placed between two carbon monoxide ligands (II). No optimum metal–hydrogen distance was suggested.



(I)



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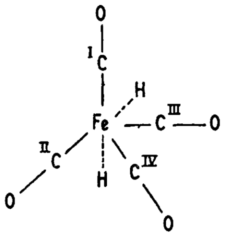

(III)

Thus we conclude that, although it is strongly suggestive of direct metal-to-hydrogen bonding, existing physical and theoretical evidence does not prove the fact for the carbonyl compounds.

For other transition-metal complex hydrides, physical evidence for direct metal–hydrogen bonding is more substantial. The first case where such bonding was substantiated by infrared and high-resolution nuclear magnetic resonance measurements was for $(\pi\text{-}C_5H_5)_2ReH$ and $(\pi\text{-}C_5H_5)_2ReH_2^+$.[5] Similar studies on phosphineplatinum halogenohydrides,[7,20] π-cyclopentadienyl-molybdenum and -tungsten dihydrides,[6] and cobalt and rhodium cyanide hydride [8,9] ions, etc., have given further proof. Of particular interest is the splitting of proton resonance signals in the nuclear magnetic resonance spectra of the platinum [7] and rhodium [9] complexes due to electron coupled spin–spin interaction between the proton and metal nucleus.

The present investigation concerns the broad-line nuclear magnetic resonance spectrum of solid $H_2Fe(CO)_4$. This compound is well suited to such study since the occurrence of only two protons in a large molecule will ensure that intermolecular broadening is small; further, it is the only dihydride amenable to such study, others, *e.g.*, $(\pi\text{-}C_5H_5)_2WH_2$,[6] containing other protons. It was hoped that the determination of the interproton distance would allow, by choice of a suitable model, the metal–hydrogen distance to be estimated.

RESULTS AND DISCUSSION

Samples of $H_2Fe(CO)_4$ prepared by two different methods were examined at liquid-hydrogen temperature (~20° K). Difficulties were encountered not only because of its thermal instability, which requires that operations with sample tubes must be carried out without allowing warming to above *ca.* —30° C, but also because of the weak signals; the limits of the instrument were approached. The weakness of the signals was due to the low proton density of the material and to ease of signal saturation, so that only a very low H_1 field could be employed. In view of the rather poor signal-to-noise ratio (*ca.* 5 : 1) the results from the best three samples are reasonably concordant. Averaged derivative curves are shown in the Figure.

The expected doublet structure was not observed. This would be easily obscured by a trace of impurity [and $H_2Fe(CO)_4$ is exceptionally difficult to obtain very pure], or possibly by zero-point vibration of the protons if weakly bound.

The second moments, treated as due to a proton-pair signal, should give, by the Van Vleck formula, a reasonable approximation to the interproton distance (Table **1**). The crucial point is that intermolecular broadening of all structural models must be small, since there are only two protons in a large molecule in which all other nuclei have zero spin.

Averaged derivative curves obtained from samples **3**, **4**, *and* **6**.

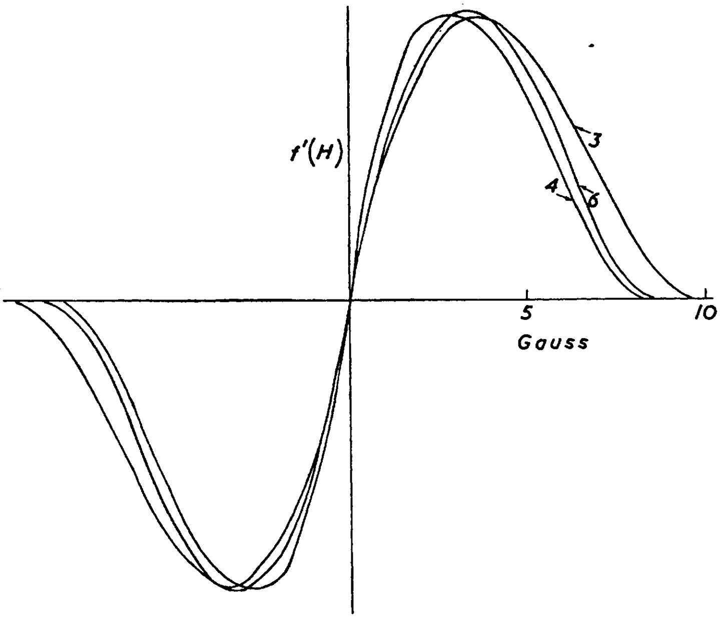

TABLE 1. *Second moments and interproton distances in* $H_2Fe(CO)_4$.

Sample No.:	**3** [a]	4	6
$(\Delta H^2)_{av.}$ (gauss²)	9·4 ± 0·7	7·1 ± 0·7	7·7 ± 1·0
H–H (Å) [b]	**1·83**	1·92	1·90

[a] Suspected slow leakage of liquid hydrogen into vicinity of coil. [b] H–H (average) = 1·88 ± 0·05 Å.

Ewens and Lister's model can, as noted above, be eliminated on several grounds. The present measurement being considered, it is unlikely that molecules with an M–C–O–H linear grouping would pack in the solid with protons adjacent, and even the exceedingly improbable arrangement in which all hydrogen atoms are packed in groups of three in van der Waals contact would cause an intermolecular broadening of only 3·75 gauss². The intramolecular H–H distance of 6·4 Å would cause a negligible broadening of 0·002 gauss². All other models would not allow close approach of more than two protons in adjacent molecules, setting an upper limit of 1·87 gauss² to the intermolecular broadening.

If the protons in $H_2Fe(CO)_4$ are equivalent and bridged in the manner suggested by Edgell *et al.* for $HCo(CO)_4$, the intra- and inter-molecular broadening would again be very small (0·30 gauss²). Thus neither this model nor Ewens and Lister's model could account for more than a small fraction of the observed second moment. Even if the remainder were due to a large amount of impurity broadening (which is unlikely and in any case would have to be fortuitously similar in the two different preparations), then the $H_2Fe(CO)_4$ signal would be superimposed as a narrow central absorption peak; such a peak is not observed.

Hence the present results show certainly that the protons are located much closer in towards the metal atom, and consequently bonded predominantly to it.

Thus Hieber's original postulates of the pseudo-metal atom nature for H_2Fe and HCo may be considered to be correct although only to the extent that they imply a close association of the hydrogen and metal atoms.

Structure of Iron Carbonyl Hydride.—In order to compute the metal–hydrogen distance from the measured interproton distance, it is necessary to assume a structural model for the compound, particularly the location of the protons relative to the CO groups and the H–Fe–H angle.

Considering first Liehr's structure, we can raise some objections. Thus the assumed tetrahedral arrangement of the carbon monoxide ligands is probably not strictly correct and an asymmetric linkage of the hydrogen atoms is implied since these are considered to be bound to the d_{z^2} and $d_{x^2-y^2}$ orbitals. The first, incurring overlap with one of the two principal lobes of the d_{z^2} orbital, would be more strongly bound than the second, which uses one of the four equivalent lobes of the $d_{x^2-y^2}$ orbital. Only one line was observed in the high-resolution nuclear magnetic resonance spectrum of $H_2Fe(CO)_4$,[16] and the protons may reasonably be assumed to be equivalent.

In constructing an adequate model for $H_2Fe(CO)_4$ on the lines of the Edgell and Cotton's model for $HCo(CO)_4$, we can consider the insertion of an extra proton into the iron tetracarbonyl anion $HFe(CO)_4^-$ which is isoelectronic with $HCo(CO)_4$. Now in $HCo(CO)_4$ the infrared spectrum [15] showed evidence for a slight perturbation of the carbonyl skeleton to C_{3v}. Study of the Raman spectrum of the $HFe(CO)_4^-$ ion by Stammreich *et al.*[23] has shown even more clearly that there is distortion of the tetrahedral symmetry to C_{3v} owing to the effect of the hydrogen atom. These lower symmetries can be associated either with a change in the M–C bond length in the M–C–O group lying along the C_{3v} axis, or with an increase over the tetrahedral angle of the C–M–C angle for the three equivalent carbon monoxide groups, or to a combination of these effects.

Thus if we admit that the proton in $HCo(CO)_4$, and, by analogy, in $HFe(CO)_4^-$, lies on the C_{3v} axis, then in $H_2Fe(CO)_4$ the second proton cannot be inserted in an equivalent position without further distortion. If we accept the equivalence of the protons then it follows merely on symmetry arguments that there must be two pairs of equivalent carbon monoxide groups, $CO^{I,II}$ and $CO^{III,IV}$, as in (III).

There is other evidence for the non-equivalence of the carbon monoxide groups in $HCo(CO)_4$ and in $H_2Fe(CO)_4$. Thus although in certain articles (see for example refs. 24 and 25) the metal–carbon bond distances determined by Ewens and Lister in their electron diffraction studies have been averaged (indeed it has been said [24] that there is no evidence for the existence of two different M–C and C–O bond distances), the original values (in Å):

	$H_2Fe(CO)_4$	$HCo(CO)_4$
M–C (in CO)	1·84 ± 0·03	1·83 ± 0·02
M–C (in COH)	1·79 ± 0·04	1·75 ± 0·08

indicate that two M–C bonds in $H_2Fe(CO)_4$ and one in $HCo(CO)_4$ are short. No appreciable divergence from the tetrahedral angle was observed, but with the techniques then available, divergences of a few degrees would have escaped notice. A redetermination with modern techniques is to be desired.

The non-equivalence of the carbon monoxide groups in $HCo(CO)_4$, $HFe(CO)_4^-$, and $H_2Fe(CO)_4$ therefore seems well grounded; it may be assumed that a similar situation exists for $HMn(CO)_5$ where infrared studies have shown that the molecule has only low symmetry,[26] and for other carbonyl hydride systems. The extent of the distortion of the

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[23] Stammreich, Sala, Tavares, Krumholtz, and Behmoiras, *J. Chem. Phys.*, in the press.

[24] Bailar (Editor), " Chemistry of the Co-ordination Compounds," Reinhold Publishing Co., New York, 1956, p. 530.

[25] Moeller, " Inorganic Chemistry," Wiley, New York, 1952, p. 703.

[26] Wilson, *Z. Naturforsch.*, 1958, **13**b, 349.

$M(CO)_4$ skeleton, and in $H_2Fe(CO)_4$ the divergence of the H–Fe–H angle from the tetrahedral angle to be expected in the absence of distortion, cannot be directly determined. Some light can be thrown on this problem, however, by a consideration of the possible electronic structures of $H_2Fe(CO)_4$. From these considerations, it seems likely that the H–Fe–H angle lies between 109° 28′ and *ca* 125°. In Table 2 are given the computed Fe–H distances for these extremes and for one intermediate (120°) angle, together with the distance for the 90° angle of Liehr's model. The estimated Fe–H distance is hence *ca.* 1·1 Å. Whilst a good estimate of the covalent radius of iron in mononuclear carbonyl compounds is difficult to make, it is probably somewhat smaller than half the Fe–Fe distance in dinuclear species,[27] *i.e.*, $\leqslant 1{\cdot}23$ Å. We can conclude therefore that the Fe–H distance is of the same order, if not actually smaller than the covalent radius of the metal atom, and that the concept of the proton's being buried in the electron density of the metal atom is not unreasonable.

TABLE 2. *Computed* Fe–H *distances in* $H_2Fe(CO)_4$, H–H *being taken as* 1·88 ± 0·05 Å.

H–Fe–H angle	90°	109° 28′	120°	125° 44′
Fe–H Å	1·33 ± 0·04	1·15 ± 0·03	1·09 ± 0·03	1·06 ± 0·03

Electronic Structure of the Carbonyl Hydrides.—The nature of the orbitals involved in the bonding of hydrogen in these compounds cannot be as simple as might have been expected, since distortions of unknown magnitude from the tetrahedral symmetry are evident.

For Edgell and Cotton's model of $HCo(CO)_4$, the hydrogen atom is regarded as being bound to the d_{z^2} orbital (Note: the C_{3v} and z axes are taken as coincident), with the possible incorporation of some $4p$ character. This scheme may be questioned, since there would be strong overlap between the reverse lobe of the d_{z^2} orbital and the carbonyl group diametrically opposite across the metal atom. This objection can readily be met by rehybridization of the d_{z^2} with the opposing sp^3 hybrid orbital to give

$$\psi_A = g\, sp^3 + h\, d_{z^2} \qquad \text{(bonding to CO)}$$
$$\psi_B = -h\, sp^3 + g\, d_{z^2} \qquad \text{(bonding to H)}$$

where $g^2 + h^2 = 1$ (normalization), and g and h will be of the same order of magnitude (probably $g > h$). Extending the problem to $H_2Fe(CO)_4$, we see that the binding of a second hydrogen atom at a position approximately tetrahedral to the first would present considerable difficulty, since the bonding could hardly be to the $d_{x^2-y^2}$ orbital which lies at 90° to the d_{z^2} orbital. Indeed any use of pure d orbitals for bonding to the hydrogen atoms also has the objection of strong non-bonding overlap with the ligands opposite and of non-equivalent bonding of the hydrogen atoms. Hence any attempt to overcome this difficulty must require the use of mixed d orbitals which can then be rehybridized with the appropriate sp^3 orbitals as above.

We assume first, for simplicity, that the carbon monoxide groups in $H_2Fe(CO)_4$ are tetrahedral about the metal atom, with conventional sp^3 bonds and d_π bonding. Now the general d orbital with a maximum along the z axis (again taken as lying along an M–C–O bond as in the Edgell–Cotton model) is given by

$$\psi = a\, d_{z^2} + b\, d_{x^2-y^2} + c\, d_{xy}$$

where $a^2 + b^2 + c^2 = 1$ (normalization condition) and also $b^2 + c^2 \leqslant 3a^2$. If the latter condition is not satisfied, there is a saddle-point on the z-axis instead of a true maximum; this contingency will, however, never be permitted to arise. Inclusion of contributions from the d_{xz} and d_{yz} orbitals would not generalize the case further since these would deflect the maximum from the z direction. This orbital is now required to be orthogonal to a similar combination of d orbitals in co-ordinates x', y, t, formed by rotating the xz axes

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[27] Mills, *Acta Cryst.*, 1958, **11**, 620; Powell and Ewens, *J.*, 1939, 286.

about the y axis through the angle $\cos^{-1}\frac{1}{3}$ (the supplement to the tetrahedral angle) to $x't$. Thus

$$\psi_1 = a_1\, d_{z^2} + b_1\, d_{x^2-y^2} + c_1\, d_{xy}$$

$$\psi_2 = a_2\, d_{t^2} + b_2\, d_{x'^2-y^2} + c_2\, d_{x'y}$$

The condition for equivalent orbitals requires $a_1 = a_2 = a$. Normalization requires $a^2 + b_1{}^2 + c_1{}^2 = a^2 + b_2{}^2 + c_2{}^2 = 1$, and orthogonality requires $-a^2 + (4/\sqrt{3})a(b_1 + b_2) + \frac{5}{3}\, b_1b_2 + c_1c_2 = 0$. The only satisfactory orbitals appear by trial and error to be of the form $b_1 = b_2 = b$; $-c_1 = c_2 = c$. Since the d_{z^2} orbital is the only component having a non-zero value in the z direction, its contribution must be maximized to give the most strongly directed orbitals. It is, however, impossible to derive a pair of orbitals mutually inclined at 70° 32′ and the equivalent to the d_{z^2} orbital alone ($a = 1$; $b = c = 0$), the d_{z^2} orbital orthogonalizing with itself on rotation through an angle $\cos^{-1}\sqrt{\frac{1}{3}} = 54°\,44'$. The most strongly directed orbitals satisfying the conditions in fact have $a = 0{\cdot}9803$, $b = 0{\cdot}1978$, $c = 0$. Reduced to the same co-ordinate system, these can be expressed in the form: $\psi_{1,2} = p\, d_{z^2} \pm q\, d_{xz} + r\, d_{x^2-y^2}$; where $q^2 = \frac{1}{2}$; $p^2 + r^2 = \frac{1}{2}$ (for normalization and orthogonality) and $\sqrt{3}p + (q/\sqrt{2}) - r = 0$ (to give maxima at 70° 32′). Thus written, they are mirror images in the yz plane, with the maximal directions bisected by the z axis.

There is a further consideration which modifies our view as to the most probable bonding scheme. Mixing the $d_{x^2-y^2}$, d_{xy} orbitals with the d_{z^2} orbital causes the equatorial " belt " associated with the latter to expand somewhat and assume directional character. It is helpful in visualizing this to consider the ϕ dependence in this plane. Thus the value of ψ_1 in the xy plane is

$$\sqrt{\left(\frac{15}{16\pi}\right)}\left(-\frac{a}{\sqrt{3}} + b\cos 2\phi - c\sin 2\phi\right) = \sqrt{\left(\frac{15}{16\pi}\right)}\left\{-\frac{a}{\sqrt{3}} + \gamma\cos(2\phi + \alpha)\right\}$$

where $\gamma = \sqrt{(b^2 + c^2)}$; $\tan\alpha = c/b$.

Similarly the value of ψ_2 in the $x'y$ plane is

$$\sqrt{\left(\frac{15}{16\pi}\right)}\left\{-\frac{a}{\sqrt{3}} + \gamma\cos(2\phi - \alpha)\right\}$$

The large negative lobes of ψ_1 and ψ_2 thus have maxima in the positions $\phi = (\pi/2) - (\alpha/2)$; $\phi' = (\pi/2) + (\alpha/2)$ respectively, and the repulsion between these two values must be considered. The above scheme for optimum directional character along z and t unfortunately corresponds to $\alpha = 0$, so that the subsidiary maxima coincide along the y-axis and the repulsion is greatest. By increasing the contributions of $d_{x^2-y^2}$ and d_{xy}, it is possible to separate the subsidiary maxima somewhat, but at the expense of some directional character along the bonding axes ($\theta = \theta' = 0$). The behaviour for three values of α is given in Table 3.

TABLE 3.

α	γ	a	b	c	$\psi_{(\theta=0)}\sqrt{(16\pi/5)}$	$\psi_{\max\,(\theta=\pi/2)}\sqrt{(16\pi/5)}$
0	0·1978	0·9803	0·1978	0	1·961	−1·321
$\pi/4$	0·2854	0·9585	0·2018	0·2018	1·917	−1·453
$\pi/3$	0·4208	0·9153	0·2104	0·3642	1·831	−1·664

No solutions can be found for $\alpha \geqslant$ *ca.* 78°. As electron density is proportional to ψ^2 (real coefficients) it seems that the maximum stability for this system bonded to hydrogen atoms along z and t might reasonably be achieved for $\alpha =$ *ca.* $\pi/4$ to attain a balance between maximum directional character and minimum coulombic repulsion. It seems that little, if any, advantage could be gained by use of complex coefficients.

So far we have considered bonding only for the strictly tetrahedral angle. It can be shown that for a fairly large decrease in the acute angle between the d-orbital bonding maxima, thereby mitigating the repulsion discussed above, only a small distortion of the skeleton need occur. Suppose now that two modified *d* orbitals hybridize each with an sp^3 orbital to bond to a proton and to a carbonyl group not quite opposite to it. Then, since the negative lobe of an sp^3 orbital is only about half the size of the positive lobe, the hydrogen atom will be bonded very nearly in the direction of the *d* orbital, whereas the carbonyl group will be bonded roughly half-way between the sp^3 direction and the *d*-orbital direction. The use of pure d_{z^2} and the $d_{z'^2}$ orbital, which is equivalent to and orthogonal with it, would therefore constitute an extreme case of optimum directional character and minimum repulsion between the *d* orbitals (there being no subsidiary maxima in the equatorial belt). Since these orthogonalize at 54° 44′, the protons would be displaced by *ca.* 8° from the tetrahedral positions and the appropriate carbonyl groups by *ca.* 4°. The actual state of the molecule is very probably intermediate between this extreme and that of the strict tetrahedral case above. Thus if the *d* orbitals are at 60°, the distortion of the tetrahedron is 2—3° and a suitable combination, separation of the anti-bonding lobes being neglected, would be

$$d_1 = 0{\cdot}996d_{z^2} + 0{\cdot}091d_{x^2-y^2}$$
$$d_2 = 0{\cdot}996d_{z'^2} + 0{\cdot}091d_{x'^2-y^2}$$

The magnitude of ψ along the principal and subsidiary maxima are then $(1{\cdot}99 : 1{\cdot}16)\sqrt{(5/16\pi)}$, so that the directional character is not very different from that of the pure d_{z^2} orbital $= (2 : 1)\sqrt{(5/16\pi)}$. Evidently it is impossible to be precise regarding the H–Fe–H angle upon which the estimation of the Fe–H distance depends. From Table 2 it is clear, however, that the most probable value of the Fe–H bond length is close to 1·1 Å. This estimate agrees rather fortuitously with Cotton's estimate of *ca.* 1·2 Å for the Co–H bond length in $HCo(CO)_4$. The lowering of the symmetry in $[HFe(CO)_4]^-$ and $HCo(CO)_4$ to C_{3v} agrees well with the hydridization scheme

$$\psi_A = g\,sp^3 + h\,dz^2;\;\; \psi_B = -h\,sp^3 + g\,dz^2$$

which we have suggested, when there would be little or no distortion of the bond angles and only the metal-carbon monoxide bond length opposite the hydrogen atom would be modified (if we accept Ewens and Lister's data, shortened).

Rehybridization of the *d*-orbital set on the loss of one proton from $H_2Fe(CO)_4$ to maximize the use of the d_{z^2} orbital in this way would then contribute to the high ratio of the primary and secondary acid dissociation constants.

Finally, although it is possible to arrive at equivalent hybrid *d*-orbitals mutually at 90° which could be used in the Liehr structure for $H_2Fe(CO)_4$, the scheme would be less favourable since (*a*) they are less strongly directed, (*b*) the directional property cannot be improved as before by rehybridization with sp^3, and (*c*) the bonding axes lie closer to the carbonyl groups on either side.

All transition-metal–hydrogen complex compounds, whether they behave chemically as weak or strong acids, or as bases, and irrespective of the strength of the M–H bond as indicated by the metal–hydrogen stretching frequency in the infrared spectra, show, under high resolution, proton resonances well shifted to the high-field side at 14—20 p.p.m. *vs.* water. Since even in $H_2Fe(CO)_4$ which is one of the least thermally stable of these compounds and in which the metal–hydrogen bond must be rather weak, the metal–hydrogen distance is, as estimated herein, only *ca.* 1·1 Å, the high shielding of the protons in all cases is understandable. However, it seems likely that the shifts are due to paramagnetic circulation on the metal atom as well as diamagnetic electron shielding of the proton.

EXPERIMENTAL

Preparation of Iron Carbonyl Hydride.—Iron pentacarbonyl was added to sodium–potassium eutectic suspended in ethylene glycol dimethyl ether at −10° C in a nitrogen atmosphere, and the mixture stirred. When gas evolution ceased, the solvent was removed. The residue was dissolved in water, and the solution acidified by dilute sulphuric acid added dropwise. The gas evolved was passed through a calcium chloride tube and collected in a trap at $-80°$. The compound was also prepared by treating the pentacarbonyl with aqueous barium hydroxide and potassium hydroxide, with subsequent acidification of the resulting solution.

The crude carbonyl hydroxide was purified by trap-to-trap distillation and condensed in a constricted thin-walled Pyrex tube. After being sealed off, the sample was stored in liquid nitrogen.

Measurements.—The broad-line nuclear magnetic resonance instrument and the method of use have been described.[28] A small correction (0·29 gauss^2) for field modulation and inhomogeneity broadening was deducted from the observed second moments. The first three samples to be examined were prepared by the ether method. No. 1 gave a broad signal ($\langle \Delta H^2_{\text{av.}} \rangle = 18{\cdot}5 \pm 3$ gauss^2; 11 traces) which was very weak, presumably owing to partial decomposition during handling. No. 2 likewise gave a broad signal ($\langle \Delta H^2_{\text{av.}} \rangle = 22{\cdot}5 \pm 0{\cdot}8$ gauss^2; 9 traces) but with excellent signal-to-noise ratio; this allowed observation of features which could not be reconciled with the spectrum of pure $H_2Fe(CO)_4$, namely outer shoulders to the main-derivative peak and slight inflexions inside it. Both the above samples almost certainly contained ether, since No. 3, which was obtained by acidification of the $(Na,K)_2Fe(CO)_4$ after prolonged evacuation, gave narrower traces mutually consistent with those from later samples prepared by the aqueous procedure. Of the latter, No. 5 gave, inexplicably, no detectable signal. For No. 6, closely similar traces were obtained by two runs on successive days; the mean second moments agreed to within $\frac{2}{3}$ gauss^2.

The signal-to-noise ratio deteriorates at 90° K, as expected, but the traces then appear to have a substantially unaltered second moment. On subsequent warming to room temperature, all sample tubes save one exploded and inflamed.

A blank run using carbon tetrachloride in a sample tube cooled and sealed under the same conditions as the carbonyl hydride samples gave a negligible signal.

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[28] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; Pratt and Richards, *ibid.*, 1953 **49**, 744.