Substitution Reactions of Dihydridotetracarbonyliron

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The i.r. [(ν(CO) and ν(Fe–H)] and Mössbauer spectra of $H_2Fe(CO)_4$ in hexane at −78 and −196° are reported. The reaction between $H_2Fe(CO)_4$ and thiols proceeds by simultaneous loss of hydrogen and carbon monoxide to the known thiolate-bridged complexes, $[Fe(CO)_3SR]_2$ (R = Ph, C_6F_5, or Pr^i). With triphenyl-phosphine and -arsine, hydrogen substitution occurs producing the complexes $Fe(CO)_4L$ and $Fe(CO)_3L_2$ (L = Ph_3P or Ph_3As). Two unstable complexes were also isolated in low yield from the Ph_3As reaction, one of which was identified by mass spectrometry as $Fe(CO)_4H_2AsPh_3$. A structure with bridging hydrogen atoms between iron and arsenic is suggested.

THE gas-phase i.r. spectrum of dihydridotetracarbonyliron in the carbonyl and metal–hydrogen stretching region has been reported briefly[1] but no absorption was assigned to ν(Fe–H). The measurements were made at room temperature, under which conditions the hydride is known to decompose. We report here the i.r. and Mössbauer spectra in hexane at −78 and −196° respectively.

Recently the preparation and chemical properties of the hydrides $H_2M(CO)_4$ (M = Ru[1] or Os[2]) have been reported. Both systems undergo similar substitution reactions with phosphine ligands forming the complexes $H_2M(CO)_3PR_3$ and $H_2M(CO)_2(PR_3)_2$ through loss of carbon monoxide. The nature of the final products formed differs in that for osmium the reaction terminates mainly at the monosubstitution product $H_2Os(CO)_3PR_3$ whilst for ruthenium the reaction continues to the disubstituted product $H_2Ru(CO)_2(PR_3)_2$. The substitution of carbon monoxide is typical of the reactions of phosphines with hydridocarbonyl complexes in general,[3] and has also been reported for the monohydrido-complexes of manganese,[4] and cobalt.[5] We report here the reactions of $H_2Fe(CO)_4$, with triphenyl-phosphine and -arsine, which, in contrast to the complexes of Ru and Os, liberates hydrogen before carbon monoxide.

We have also studied the reactions between $H_2Fe(CO)_4$ and thiols in an attempt to synthesise complexes of the type $Fe(CO)_4(SR)_2$, or sulphur-bridged derivatives of higher nuclear complexity, using the method applied to other hydridocarbonyl complexes.[6] However, we have been able to isolate only the known complexes $[Fe(CO)_3SR]_2$ from these reactions.

Dihydridotetracarbonyliron.—The i.r. spectrum of $H_2Fe(CO)_4$ in hexane solution at −78° in the 2500—1600 cm.$^{-1}$ region is recorded in Table 1. The important features are the presence of a weak and three medium or strong absorptions to higher frequencies than 2000 cm.$^{-1}$, and a weak absorption at 1887 cm.$^{-1}$ (Figure 1). The arrangement and relative intensity of the absorptions in the higher energy region are consistent with an octahedral arrangement of groups around the metal with the

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[1] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

[2] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1967, **6**, 2092.

[3] A. P. Ginsberg, *Transition Metal Chem.*, 1965, **1**, 111, and refs. therein.

[4] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 157.

[5] R. F. Heck. *J. Amer. Chem. Soc.*, 1963, **85**, 657.

[6] A. G. Osborne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1143.

TABLE 1

I.r. ($cm.^{-1}$) and Mössbauer spectra of $H_2M(CO)_4$

Complex	Form	ν(CO)	ν(M–H)
$H_2Fe(CO)_4$	Hexane soln.	2121w, 2111vw,sh, 2053m, 2042s, 2029vw,sh, 2010m	1887w,br
	Gas [a]	2071w, 2061m, 2056s, 2050m, 2018w	
$H_2Ru(CO)_4$	Gas [a]	2082vw, 2074m, 2070s, 2066m, 2018w	1980w,br
$H_2Os(CO)_4$	Heptane [b] soln.	2141w, 2067m, 2055s, 2048vs, 2016w	1942w,br
		Isomer shift δ (mm./sec.)	Quadrupole splitting Δ (mm./sec.)
$H_2Fe(CO)_4$	Hexane soln.	0·085	0·615

[a] Ref. I. [b] Ref. 2.

hydrogens in *cis*-positions, and also with distorted structures which retain the C_{2v} symmetry. The A_1 vibration which occurs to high frequency is of weak intensity and provides no information on distortion of the octahedral arrangement.

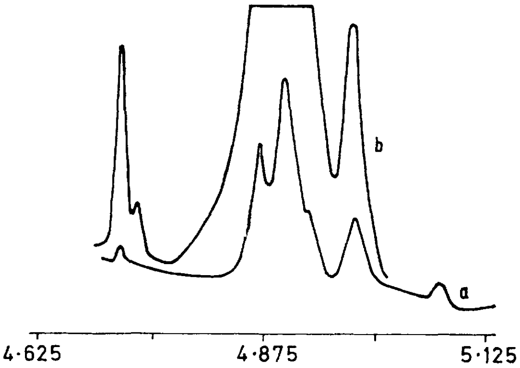

FIGURE 1 I.r. spectrum of $H_2Fe(CO)_4$ in hexane at −78°; a, dilute and b, concentrated solution

The i.r. spectrum is very similar to those of $H_2Ru(CO)_4$ [1] and $H_2Os(CO)_4$ [2] (Table 1). In general the corresponding frequencies increase from iron to ruthenium and osmium, but decrease from ruthenium to osmium.[2] Two weak absorptions occur in the spectrum of $H_2Fe(CO)_4$ at 2111 and 2029 $cm.^{-1}$, the former being detected only in concentrated solution (Figure 1b), and are assigned tentatively to ^{13}C–O stretching frequencies. The absorption at 2016 $cm.^{-1}$ for the osmium complex has been assigned also to ^{13}CO.[2] Deuterium exchange confirmed the assignment of the weak broad band at 1942 $cm.^{-1}$ in $H_2Os(CO)_4$ to metal–hydrogen stretching.[2] In general for analogous transition-metal complexes ν(M–H) increases on proceeding down a periodic group,[3] so ν(Fe–H) is expected to lower frequency than ν(Os–H), and the broad weak band at 1887 $cm.^{-1}$ in the spectrum of $H_2Fe(CO)_4$ which has similar features to ν(Os–H) is tentatively assigned to ν(Fe–H). Two metal–hydrogen stretching frequencies ($A_1 + B_1$) are expected for dihydrido-complexes, but as for $H_2Os(CO)_4$ it was not possible to resolve the broad weak peak.[2] Indeed, it has been noted[7] that all *cis*-dihydrides {except *cis*-$[CoH_2(diphos)_2]^+$, ref. 8} in which the hydrogen atoms are *trans* to the same group, exhibit only one ν(M–H) absorption, although this is sometimes broad, so that this iron complex also conforms to Adams's 'rule-of-thumb'[7] that the number of M–H bands observed is the same as the number of different groups *trans* to hydrogen.

The Mössbauer spectrum obtained from a frozen hexane solution at −196° consists of a pair of symmetrical peaks having a quadrupole splitting of 0·615 mm./sec. and an isomer shift of 0·085 mm./sec. The spectrum is well resolved with narrow linewidths (0·27 mm./sec.). The recently reported spectrum obtained for the pure solid at 80°K,[9] for which the isomer shift is quoted at 295°K, is in good agreement with the value for the frozen solution, if the estimated second-order Doppler-shift value used was the usual value of −0·08 mm./sec. The small quadrupole splitting is certainly consistent with the *cis*-octahedral structure suggested by the low-temperature i.r. data, and the isomer shift, which is very low in comparison with other octahedral iron complexes (see ref. 9) is thought to result from strong σ-donor properties of the hydride ion.

Substitution Reactions of $H_2Fe(CO)_4$.—The substitution reactions with triphenyl-phosphine and -arsine occur under mild conditions often commencing at *ca.* 0°. Using equimolar quantities of reactants, complexes of the type $Fe(CO)_4L$ are formed by loss of hydrogen, which was shown by mass spectrometry to be the only gaseous product. With excess of the ligand, displacement of both hydrogen and carbon monoxide occurs, the product being a mixture of complexes of the type $Fe(CO)_4L$ and $Fe(CO)_3L_2$. When two moles of the ligand are used the latter is the sole product.

The preferential loss of the hydride groups from $H_2Fe(CO)_4$ by neutral ligands is in sharp contrast to other hydridocarbonyl complexes which invariably undergo carbonyl substitution reactions. $HMn(CO)_5$ [4] and $HCo(CO)_4$ [5] give the complexes $HMn(CO)_4(PPh_3)$ and $HCo(CO)_3(PPh_3)$ which have greater thermal and oxidative stability than the parent complexes; the effect has been attributed to a depolarisation of the M–H bond through the greater σ-donor ability but poorer π-acceptor properties of the phosphine ligand as compared with CO.[3] The osmium and ruthenium complexes, $H_2Os(CO)_4$ [2] and $H_2Ru(CO)_4$,[1] are also reported to undergo carbonyl rather than hydrogen substitution, forming, under mild conditions, the complexes $H_2Os(CO)_3PR_3$ and $H_2Ru(CO)_2(PR_3)_2$, whose i.r. and ^1H n.m.r. spectra were consistent with retention of the *cis*-arrangement of the hydrogen atoms. A *cis*-octahedral structure has been proposed for $H_2Fe(CO)_4$ on the basis of ^1H n.m.r.,[10] i.r., and Mössbauer studies, and it may

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[7] D. M. Adams, 'Metal Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 16.

[8] A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.

[9] G. M. Bancroft, M. J. Mays, and B. E. Prater, Abstract of Faraday Soc. Discussion, Cambridge, March 1969.

[10] F. A. Cotton and G. Wilkinson, *Chem. and Ind.*, 1956, 1305.

therefore be concluded that the anomalous behaviour of $H_2Fe(CO)_4$ is not a consequence of an inherent weakness of two M–H bonds in *cis*-positions. Also, the value of the Fe–H stretching frequency (1887 cm.$^{-1}$) is only slightly lower than ν(Os–H) at 1942 cm.$^{-1}$ (ref. 2) and ν(Ru–H) at 1980 cm.$^{-1}$ (ref. 1) and indicates that the strength of the Fe–H bond is of the order of other transition-metal–hydrogen bonds.

A factor of importance in the course of the substitution reactions is the apparent stability of the five-co-ordinate iron(0) complexes $Fe(CO)_4L$ ($L = PR_3$ or AsR_3).[11] The two most likely reactions (1) and (2) both result in complexes whose symmetry and formal oxidation are

$$cis\text{-}H_2M(CO)_4 + L \longrightarrow cis\text{-}H_2M(CO)_3L + CO \quad (1)$$

$$cis\text{-}H_2M(CO)_4 + L \longrightarrow M(CO)_4L + H_2 \quad (2)$$

optimum for stabilisation by formation of π-bonds and by ligand-field effects (six-co-ordinate d^6 and five-co-ordinate d^8). Thus the actual product of the reaction will depend on the differences in the relative stabilities of the two possible derivatives $M(CO)_4L$ or $M(CO)_3LH_2$ for each metal on passing down the given group. For a d^8 system, five-co-ordination is most favoured for the first-row metal as shown, *e.g.*, by the existence of several five-co-ordinate phosphine and carbonyl derivatives of Co^I and Ni^{II}, whereas the number of corresponding complexes is low [12] for the heavier congeners. For a d^6 system in octahedral stereochemistry there is greatest stabilisation of the heavy-metal derivatives as is shown particularly by the halogenocarbonyl complexes of the iron group elements. Thus, on balance, one might expect to obtain a d^8 five-co-ordinate complex for iron but a d^6 six-co-ordinate complex for the heavier members of the triad.

In the reaction between $Fe(CO)_4H_2$ and Ph_3As at 0°, an additional hexane-soluble material remains in solution after all the $Fe(CO)_4AsPh_3$ and $Fe(CO)_3(AsPh_3)_2$ have precipitated. Black crystals, which are believed to be a mixture of two complexes, (1) and (2), are obtained by cooling the solution to $-20°$. Complex (1) is more thermally stable than complex (2) and was obtained free of the latter complex by handling and recrystallising the material between 0° and room temperature. Complex (2) was obtained as very dark, almost black crystals by recrystallisation of the second crop of crystals from the original hexane solution. The temperature of the solution was never $> -20°$.

Complex (1) dissolves in hexane to produce a deep brown solution, and decomposes slowly at room temperature, the volatile products being identified by mass spectrometry as carbon monoxide and hydrogen. The presence of hydrogen in the complex is thus indicated although the presence of a terminal metal–hydrogen bond is not consistent with the ability of the complex to dissolve unchanged in chloroform.[13] The other thermal decomposition products are $Fe_3(CO)_{12}$, free $AsPh_3$, and a small amount of $Fe(CO)_4AsPh_3$. Complex (1) decomposes very rapidly in air, yielding some $Fe_3(CO)_{12}$ and $AsPh_3$, and it was not possible to analyse the complex in a conventional combustion apparatus because of its tendency to explode in oxygen. The values given are for the one sample which was slowly heated in the oxygen stream without explosion.

Decomposition into $Fe_3(CO)_{12}$ and $AsPh_3$ also occurred in the mass spectrometer, but a high-resolution search showed that peaks arising normally from $Fe_3(CO)_n$ ($n = 9$ or 11) also contained peaks corresponding within 3 p.p.m. to a species $H_2Fe(CO)_4AsPh_3$ and its fragmentation products by loss of carbon monoxide (Table 2).

TABLE 2

Mass measurements on complex (1)

Nominal mass	Mass * found	Assignment	Mass calc.	ΔM † (p.p.m.)
476	475·9705	$^{56}Fe(CO)_4(AsPh_3)H_2$	475·9692	3
	475·7500	$(^{56}Fe)_3(CO)_{11}$	475·7489	2
474	473·7536	$(^{56}Fe)_2(^{54}Fe)(CO)_{11}$	473·7535	2
448	447·7518	$(^{56}Fe)_3(CO)_{10}$	447·7540	5
420	419·7586	$(^{56}Fe)_3(CO)_9$	419·7590	1
	419·9782	$^{56}Fe(CO)_2(AsPh_3)H_2$	419·9794	3

* Temperature corrected. † $\Delta M = [M_{obs} - M_{calc}]$/Nominal mass.

TABLE 3

Possible ions with *m/e* 475·9705

Ion	M_{calc}	ΔM (p.p.m.)
$^{56}Fe(CO)_4(AsPh_3)H_2$	475·9692	3
$^{57}Fe(CO)_4(AsPh_3)H$	475·9616	15
$^{56}Fe^{13}CC_{21}H_{16}AsO_4$	475·9647	10
$^{56}Fe^{13}C_2C_{20}H_{15}AsO_4$	475·9606	19

Of the many possible ions giving rise to a peak of *m/e* 475·9705 by combinations of ^{13}C, ^{54}Fe, ^{56}Fe, and ^{57}Fe, the other most likely combinations are those listed in Table 4. All the individual parts of the isotope combination pattern of the $[Fe_3(CO)_{11}]^+$ ion are at least 400 p.p.m. distant from the observed peak. A search for the ions listed in Table 3 which were expected to be less intense than the peaks corresponding to a combination of the most abundant isotopes of the elements was unsuccessful. Since the mass discrepancy ΔM for each is outside the limits of the accuracy of the measurements (<5 p.p.m.), it is concluded that the peak observed cannot be assigned to these ions, and that the peak at *m/e* 475·9705 is best assigned to the ion $[H_2Fe(CO)_4AsPh_3]^+$. Ions corresponding to $[HFe(CO)_4AsPh_3]^+$, $[Fe(CO)_4\text{-}AsPh_3]^+$, and $[H_2Fe(CO)_3AsPh_3]^+$ were not found.

TABLE 4

I.r. spectra (cm.$^{-1}$) of the triphenylarsine derivatives

Complex	Form	ν(CO) (cm.$^{-1}$)
Complex (1)	Hexane soln.	2052w, 2027s, 2007s, 1953m
Complex (2)	Hexane soln.	2054s, 1991m, 1950s
$Fe(CO)_3(AsPh_3)Cl_2$	Nujol mull	2049s, 2004s
$Fe(CO)_3(PPh_3)I_2$ [17]		2095vw, 2050s, 2035s

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[11] T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181.

[12] F. Piacenti, M. Bianchi, E. Benedelti, and G. Braca, *Inorg. Chem.*, 1968, **7**, 1815.

[13] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 121.

The i.r. spectrum in the carbonyl region consists of three strong bands and one weak band to high frequency (Figure 2 and Table 4). These are all assigned to C–O stretching modes, rather than Fe–H modes since the latter would be expected to occur below 1950 cm.$^{-1}$ by comparison with $H_2Fe(CO)_4$ itself and with other hydridocarbonyl systems.[3] Attempted deuteriation experiments had no effect on the position and intensity of these bands. The spectrum therefore suggests that all four carbonyl groups are still present in this product, and that two are in *trans*-positions. We were unable definitely to detect Fe–H bands in the spectrum and attempts to detect an ^1H n.m.r. signal of the M–H proton were unsuccessful using saturated solutions of the complex in toluene, hexane, and chlorobenzene at $-30°$. Up to 300 accumulations were made but the region τ 10—40 was completely clear.

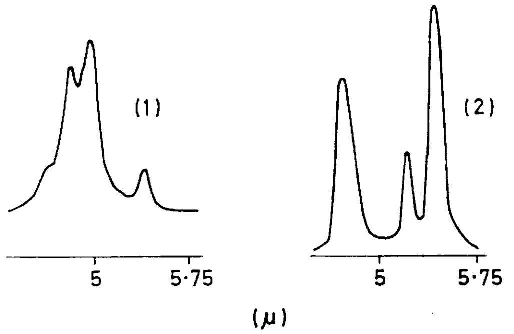
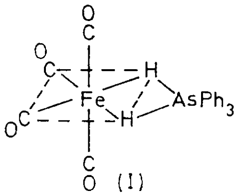


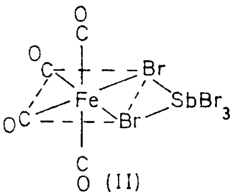
FIGURE 2 I.r. spectra of hexane solutions of complexes (1) and (2)

The Mössbauer spectrum, obtained for a mull in silicone grease at $-196°$, consists of a pair of peaks having a quadrupole splitting of 0·42 mm./sec. and an isomer shift of 0·37 mm./sec. The quadrupole splitting is consistent with octahedral co-ordination of the iron, and its decrease in magnitude compared to the parent hydride $H_2Fe(CO)_4$ suggests that distortion from the octahedral symmetry has been reduced. The increase in the isomer shift from that of the parent hydride, indicates a decrease in *s*-electron density at the nucleus consistent with a weakening of the σ-donor properties of the hydrogens. Thus the Mössbauer spectrum can be interpreted in terms of the groups, other than carbonyl being in *cis*-positions and being more stereoactive, yet more weakly bonded to the metal than is the hydrogen in $H_2Fe(CO)_4$.

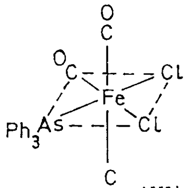
Complex (1) thus contains triphenylarsine and hydrogen groups, and because of the mass spectral data and the similarity of the i.r. spectrum to that of the parent $H_2Fe(CO)_4$, it is believed the complex is mononuclear and contains four carbonyl groups. We have studied the chemical and spectroscopic properties of the series of mono- and poly-nuclear carbonyl and hydridocarbonyliron complexes in another context,[14] and conclude that a formulation involving anions of this type and the cation $[AsPh_3H]^+$ is unlikely. Also, the apparent ease with which free triphenylarsine is formed during decomposition of the complex makes any formulation as a normal arsine-substituted hydridocarbonyl complex seem unlikely, particularly since a terminal Fe–H bond would be expected to react with chloroform to form the Fe–Cl bond. A possible structure which is consistent with all the observations is shown (I) and involves an $Fe(CO)_4$ moiety linked *via* two hydrogen bridges to triphenylarsine. Other structures based upon Fe·H·As·H·Fe bridges are probably not consistent with the mass spectral data, but further discussion is premature at this stage without more definitive data.



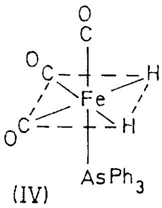
(I)



(II)



(III)



(IV)

A comparable bridge structure (II), with bromine bridging iron and antimony, has been suggested for the complex $Fe(CO)_4SbBr_5$.[15] Also, in the substitution reactions of $Fe(CO)_4X_2$ (X = Br, Cl, or I), with tertiary phosphines, arsines, and stibines, similar bridged complexes are believed to be formed in the first stage of the reaction, and to dissociate into, *e.g.* $Fe(CO)_4$ and X_2PR_3.[16] The presence of this equilibrium has been demonstrated by the decrease in rate of the reaction following the addition of the latter phosphorus(V) compound. No comparable equilibrium is apparent for $Fe(CO)_4H_2AsPh_3$. The species H_2AsPh_3 would be unstable at room temperature especially in chloroform solution, yet the iron complex appears to be unchanged over several hours.

Complex (2) could not be isolated but has been studied by i.r. spectroscopy in solution at low temperatures. In the metal carbonyl stretching region, the spectrum (Table 4, Figure 2) consists of three absorptions of strong or medium intensity, but no absorptions which can be assigned to Fe–H stretching frequencies were observed. Attempts to obtain the ^1H n.m.r. spectrum in hexane and toluene using a saturated solution at $-30°$ were unsuccessful although up to 200 accumulations were made. The presence of metal–hydrogen bonds is inferred from the reaction with chloroform which gave red crystals of $Fe(CO)_3AsPh_3Cl_2$. This complex is assigned

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[14] K. Farmery, M. Kilner, N. N. Greenwood, and R. Greatrex, *J. Chem. Soc.* (*A*), 1969, 2339.

[15] W. Hieber and A. Wirsching, *Z. anorg. Chem.*, 1940, **245**, 35.

[16] F. Basolo and I. A. Cohen, *J. Inorg. Nuclear Chem.*, 1966, 511.

the *trans*-structure (III)[17] on the basis of its i.r. spectrum (Table 2). No weak absorption expected to high frequency of these bands was detected.

The chloroarsine complex may arise in the following ways consistent with the limited data available: (i) by replacement of hydride for chloride in the complex $H_2Fe(CO)_3AsPh_3$, or (ii) by dissociation of a complex of the type $H_2Fe(CO)_4AsPh_3$ into $H_2Fe(CO)_4$ and $AsPh_3$, followed by the reaction of the hydride with chloroform and subsequent replacement of carbonyl by $AsPh_3$. Other routes are less likely, but we believe complex (2) to be of the type $H_2Fe(CO)_xAsPh_3$ ($x = 3$ or 4). The i.r. spectrum is consistent with both formulations if the tricarbonyl has the *cis*-configuration (IV). The latter, which is analogous to the derivatives of other hydridocarbonyl complexes, is preferred since it more readily explains the reaction with chloroform which appears to be free of the possible competing reactions of (ii). However a change of configuration must occur in the reaction with chloroform.

Reaction of $Fe(CO)_4H_2$ *with Thiols*.—The formation of the thiolate-bridged dinuclear derivatives $[Fe(CO)_3SR]_2$ from $Fe(CO)_4H_2$ and the thiols studied occurs smoothly and quantitatively at or just below room temperature when the reactants are mixed alone or in hexane solution. There was no evidence for the existence of a monomeric intermediate generated by elimination of hydrogen alone, even in the formation of the pentafluorophenyl derivative $[Fe(CO)_3SC_6F_5]_2$.

By analogy with monohydridocarbonyl systems, which initially undergo substitution of hydride by thiolate, the intermediates in this reaction might be expected to take the form $Fe(CO)_4(SR)_2$, particularly since the *cis*-arrangement of the hydride groups in the parent hydridocarbonyl would favour the formation of a *cis*-dithiolate corresponding to the halogenocarbonyls of iron, $Fe(CO)_4X_2$ (X = halogen). The complex $Fe(CO)_4(SC_6F_5)_2$, for example, should display similar properties to these halides in view of the often demonstrated pseudohalide character of the C_6F_5S group.[18] However, the nature of the products obtained does not suggest that such an intermediate was formed. $Fe(CO)_4(SR)_2$ complexes would tend to lose carbon monoxide and polymerise but no $[Fe(CO)_2(SR)_2]_n$[19] species were detected in these reactions.

The initial product may be formed either by elimination of hydrogen from one molecule of each reactant [to give $HFe(CO)_4(SR)$] or by co-ordination of a neutral thiol ligand with elimination of hydrogen from the hydridocarbonyl [to give $Fe(CO)_4(RSH)$]. In view of the ease with which $Fe(CO)_4H_2$ is known to lose molecular hydrogen in its reactions with neutral ligands, we suggest that the latter process is more likely. An intermediate of the form $Fe(CO)_4L$, being a derivative of five-co-ordinate iron(0) might be expected to display reasonable stability. However, co-ordinated thiols are known to lose hydrogen very readily so that they are only rarely found in complexes which are stable at normal temperatures.[20] Thus, loss of hydrogen from this type of intermediate, accompanied by the formation of thiolate bridges by elimination of carbonyl groups would result in the formation of the observed products.

EXPERIMENTAL

The reactions were carried out in darkness or subdued light, in the absence of oxygen. Temperatures were kept low to minimise thermal decomposition of $Fe(CO)_4H_2$. I.r. spectra were obtained using a Grubb–Parsons Spectromaster, and low-temperature spectra were made on a version of the equipment described by Adams.[21] Mass spectra were obtained using an AEI MS 9 spectrometer at 70 ev with a source temperature at insertion of 80°, and ^1H n.m.r. spectra recorded at 60 MHz on a Perkin-Elmer R10 spectrometer in conjunction with a Digico C.A.T. Mössbauer spectra were recorded on mulls in silicone grease and frozen hexane solutions.

PhSH, C_6F_5SH, and Pr^iSH were freshly distilled before use, and PPh_3 and $AsPh_3$ recrystallised from hexane solutions. Hexane and toluene were dried over sodium and dichloromethane distilled from phosphorus pentoxide. All solvents were pumped to remove oxygen, stored under nitrogen, and transferred by syringe against a counter current of nitrogen.

Preparation of Dihydridotetracarbonyliron.—Potassium hydroxide (10 gm., 180 mmole) and barium hydroxide (13 gm., 76 mmoles) were stirred with water (60 ml.) and pentacarbonyliron (10 ml., 75 mmoles) for 12 hr.[22] The pale orange solution was filtered, and 2·5M sulphuric acid (100 ml.) added dropwise *in vacuo* to the reaction mixture over 2 hr. The product vapours were collected in a trap at −196°. After *ca*. 3 hr., the contents of the trap were pumped at −96°, when the hydridocarbonyl remained as a pale yellow or white residue (typically 8—10 ml.). The hydride was distilled *in vacuo* when required into the reaction vessel cooled to −196° from the trap which was maintained at −36°. It was found to be more thermally stable in hydrocarbon solvents, solutions decomposing only slowly during several hr. at 0°.

Reactions of Dihydridotetracarbonyliron with Triphenylphosphine.—(a) *Formation of* $Fe(CO)_3(PPh_3)_2$. The hydridocarbonyl (*ca*. 1 ml.) was condensed on triphenylphosphine (3·5 gm., 13·4 mmoles) and toluene (20 ml.). At 0°, slow gas evolution accompanied by deposition of pale yellow crystals occurred. At room temperature the reaction ceased after about 45 min. Yellow crystals of the product, m.p. 269° (decomp.) (lit.,[23] 272°), were obtained and were recrystallised from hexane–dichloromethane (Found: C, 69·6; H, 4·5. Calc. for $C_{39}H_{30}FeO_3P_2$: C, 70·5; H, 4·5%).

(b) *Formation of* $Fe(CO)_4(PPh_3)$. From triphenylphosphine (1 g., 3·8 mmoles) under identical conditions, the hydridocarbonyl (*ca*. 1 ml.) gave yellow crystals of $Fe(CO)_4(PPh_3)$, m.p. 200—204° (decomp.) (lit.,[23] 201—203°)

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[17] M. Pankowski and M. Bigorgne, *Compt. rend.*, 1966, **263**, 239.

[18] E. W. Abel and B. C. Crosse, *Organometallic Chem. Rev.*, 1967, **2**, 443.

[19] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1587.

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(Found: C, 55·6; H, 3·6. Calc. for $C_{22}H_{15}FeO_4P$: C, 55·9; H, 3·5%).

Concentrations of reactants between those specified resulted in a mixture of the two products.

Reaction of $H_2Fe(CO)_4$ *with Triphenylarsine.*—(i) The reaction was carried out similarly giving either $Fe(CO)_4AsPh_3$ or $Fe(CO)_3(AsPh_3)_2$, or a mixture of the two depending upon quantity of arsine used; longer reaction times were required. $Fe(CO)_4AsPh_3$, m.p. 175—176° (decomp.) (lit.,[24] 178°) (Found: C, 55·2; H, 3·1. Calc. for $C_{22}H_{15}AsFeO_4$: C, 55·1; H, 3·2%); ν(CO), 2052s, 1975m, and 1942s (lit.,[24] 2054, 1977, and 1945 cm.$^{-1}$). $Fe(CO)_3(AsPh_3)_2$ (Found: C, 62·4; H, 4·1. Calc. for $C_{39}H_{30}As_2FeO_3$: C, 62·3; H, 4·0%); ν(CO) 1883s (lit.,[24] 1884 cm.$^{-1}$).

(ii) Triphenylarsine (12 g., 40 mmoles) in hexane (60 ml.) was added to frozen $H_2Fe(CO)_4$ at −196°, and the mixture allowed to warm to 0° and maintained at this temperature for *ca.* 72 hr. The yellow crystals obtained were identified by i.r. spectroscopy as a mixture of $Fe(CO)_4AsPh_3$ and $Fe(CO)_3(AsPh_3)_2$. On cooling the filtrate to −20° for several hr. large black crystals of complex (1) were obtained. Further crops of black crystals were obtained when the bulk of the mother liquor was reduced in volume, and later crops contained a difference complex, (2) (0—5%). The crops of crystals were recrystallised from hexane solution at *ca.* −20° for complex (2), but at room temperature for complex (1) [Found, complex (1): C, 56·0; H, 3·4. Calc. for $C_{22}H_{17}AsFeO_4$: C, 55·5; H, 3·6%].

Reactions of Complex (2) *with Chloroform.*—Addition of chloroform to complex (2) produced a greenish solution which was filtered and cooled to −20°. The red crystals which formed were washed with chloroform, and dried *in vacuo* (Found: C, 48·5; H, 2·9. Calc. for $C_{21}H_{15}AsCl_2FeO_3$: C, 48·7; H, 2·9%).

Attempted sublimation (100°/10^{-3} mm. Hg) of the complex, gave a white sublimate of triphenylarsine, and in the mass spectrometer only the decomposition products triphenylarsine, carbon monoxide, and chlorine were detected.

Reaction with Benzenethiol and Perfluorobenzenethiol. An excess of thiol was degassed and cooled to −196°. The hydridocarbonyl was then condensed on the thiol and the temperature allowed to rise slowly. The mixture became red at 0°, and was maintained at this temperature until gas evolution ceased (*ca.* 12 hr.), when a bright red crystalline product was obtained. On addition of hexane to the filtrate and cooling to −40° a second crop of crystals was obtained. I.r. and mass spectroscopy showed the products from benzene-thiol and perfluorobenzenethiol to be $[Fe(CO)_2SPh]_2$ and $[Fe(CO)_3SC_6F_5]_2$ (Found: C, 43·6; H, 2·12. Calc. for $C_{18}H_{10}Fe_2O_6S_2$: C, 43·4; H, 2·00%.

When the same reactions were carried out in hexane solutions, reaction did not commence until the temperature was *ca.* 10° but the same products were obtained.

Reaction with Propane-2-thiol.—The reaction was carried out as before, but reaction was more rapid at 0° and was complete after 3—4 hr. The excess of thiol was removed *in vacuo* and the brown residue recrystallised from pentane at −78°. The deep red crystalline product was shown by i.r. and mass spectroscopy to be $[Fe(CO)_3SPr^i]_2$ (Found: C, 36·7; H, 3·75. Calc. for $C_{12}H_{14}Fe_2O_6S_2$: C, 37·0; H, 3·66%.

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