Studies in Mössbauer Spectroscopy. Part 12.[1] Characterization of Complexes containing Iron–Silicon Bonds †

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Reactions between iron(0) and iron(II) tertiary phosphine complexes and silanes have been investigated. Only with the bidentate ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) could silyl derivatives be characterized; these are of the type $[FeH(SiR_3)(dppe)_2]$ and $[Fe(SiR_3)_2(dppe)_2]$ [R_3 = $(OEt)_3$, Cl_3, or $MeCl_2$]. From an analysis of the ^{57}Fe Mössbauer spectra, it seems likely that these complexes have *trans* configurations. The complexes $[FeH(SiPh_3)(CO)_4]$ and $[Fe(SiCl_3)_2(CO)_4]$ react with PPh_3 to give $[Fe(CO)_4(PPh_3)]$ and $SiPh_3H$ or Si_2Cl_6.

STUDIES in these laboratories have demonstrated that tertiary phosphine complexes of iron are good catalysts for the alcoholysis of silanes [equation (1)].[2] The mechanism proposed for the catalysis involves oxidative addition of $H-SiR_3$ to the iron centre, with the formation of an iron–silicon bond. While such additions are well

$$SiR_3H + R'OH \longrightarrow SiR_3(OR') + H_2 \qquad (1)$$

documented for phosphine complexes of the heavier metals, only in the cases of cobalt[3] and nickel[4] are there reports of metal–silicon bonds in complexes of ligands other than cyclopentadienyl and carbonyl groups. We therefore undertook the examination of the reactions between silanes and tertiary phosphine complexes of iron(0) and iron(II), the results of which are now presented, together with a brief study of some carbonyl complexes. During the course of our work a very brief report of similar reactions was given.[5]

RESULTS

Starting Materials.—The ^{57}Fe Mössbauer parameters of the starting materials and related complexes are given in Table 1. The high isomer shift (i.s.) of $[Fe(C_2H_4)(dppe)_2]$ is compatible with the d^8 configuration expected for an iron(0) complex. The quadrupole splitting (q.s.) is rather lower than observed for other iron(0) complexes, which are all carbonyl complexes.[6] This suggests that the contributions to the electric-field gradient (e.f.g.) of the electrons of the non-bonding and bonding orbitals (q_{val} and q_{mol}) are opposite in sign, which would be consistent with a square-pyramidal configuration, with the olefin in the apical position.

TABLE 1

Iron-57 Mössbauer data at 77 K

Complex	δ_{Fe}[a,b] mm s^{-1}	Δ[b] mm s^{-1}
$[Fe(C_2H_4)(dppe)_2]$	0.543	0.657
$[FeH_2(dppe)_2]\cdot 2C_6H_5Me$	0.033	0.567
$[FeCl_2(dppe)]$	0.680	2.852
	0.67[c]	2.57[c]
$[FeCl_2(PEtPh_2)_2]$	0.686	2.935
trans-$[FeCl_2(depe)_2]$[d]	0.40	1.42
trans-$[FeCl_2(pdep)_2]$[d]	0.38	1.16
trans-$[FeCl_2(dmpe)_2]$[d]	0.36	1.61
trans-$[FeH_2(pdep)_2]$[d]	−0.03	1.78

[a] Relative to metallic iron. [b] ±0.005 mm s^{-1}. [c] W. A. Baker and P. M. Lutz, *Inorg. Chim. Acta*, 1976, **16**, 5. [d] depe = $Et_2PCH_2CH_2PEt_2$, pdep = o-$C_6H_4(PEt_2)_2$, dmpe = $Me_2PCH_2CH_2PMe_2$; i.s. values were converted from those relative to stainless steel by subtracting 0.10 mm s^{-1} (ref. 7).

For $[FeH_2(dppe)_2]$, isolated as its toluene solvate, the q.s. is considerably lower than that of the only other reported FeH_2P_4 species, *trans*-$[FeH_2(pdep)_2]$ [pdep = o-$C_6H_4(PEt_2)_2$].[7] This could in part be due to distortion of the structure by the two molecules of toluene included in the crystal lattice, but probably also indicates a change in configuration to *cis* stereochemistry. This configuration would be compatible with the increased steric demands of the diphenylphosphino-groups and the greater flexibility of the CH_2CH_2 backbone of the ligand.

Reactions of Iron(II) *Carbonyl Complexes.*—The complexes *cis*-$[FeH(SiPh_3)(CO)_4]$ and *cis*-$[Fe(SiCl_3)_2(CO)_4]$ were prepared as described by Graham,[8] and their reactions with triphenylphosphine were examined. In both cases the substituted carbonyl complexes $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$ were isolated and identified by their i.r. spectra.[9] With the hydride, the silane $SiPh_3H$ was also formed, in agreement with Graham's observation.[8] The reaction of the bis(silyl) complex has not been reported before, but gave the iron(0) complexes and Si_2Cl_6. Presumably, in both cases the entry of the phosphine into the co-ordination sphere initiates an intramolecular rearrangement and *cis* elimination of the silane or disilane [equation (2), X = H or SiR_3]. In agreement with this, we were

$$[FeX(SiR_3)(CO)_4] + PPh_3 \longrightarrow [Fe(CO)_4(PPh_3)] + SiR_3X \qquad (2)$$

unable to obtain any reaction between $[Fe(CO)_4(PPh_3)]$ and $SiCl_3H$.

Reactions of Unidentate-phosphine Complexes.—The complex $[FeH_2(PMePh_2)_4]$ did not react with $SiEt_3H$, $SiH(OEt)_3$, $SiMePh_2H$, or $SiPh_2H_2$ at room temperature in the presence or absence of a solvent. On increasing the temperature decomposition occurred, yielding the phosphine and pyrophoric iron. With $SiCl_3H$ or $SiMeCl_2H$ vigorous reactions took place, giving $[FeCl_2(PMePh_2)_2]$.

The complex $[FeH_2(N_2)(PEtPh_2)_3]$ reacted with $SiEt_3H$, $SiH(OEt)_3$, $SiMePh_2H$, or $SiPh_3H$ with loss of dinitrogen, but no products could be isolated; attempts to work-up the reaction mixtures led to decomposition. With $SiCl_3H$ or $SiMeCl_2H$, $[FeCl_2(PEtPh_2)_2]$ was formed.

The complex $[FeCl_2(PMePh_2)_2]$ reacted with $SiCl_3H$ in the presence of an excess of triethylamine to give an air-sensitive product, the i.r. spectrum of which showed the presence of Si–Cl bonds [ν(Si–Cl) at 500—600vbr cm^{-1}] and the absence of Fe–Cl stretching bands. The ^{57}Fe Mössbauer spectrum consisted of a poorly resolved doublet with an i.s. (0.30 mm s^{-1}) characteristic of a low-spin complex; the small q.s. (0.22 mm s^{-1}) suggests low-spin iron(II) with less than cubic symmetry. There were no indications of elemental iron or any other iron-containing

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† No reprints available.

species, and we can only suggest, very tentatively, that the product might contain the ion $[Fe(SiCl_3)_4(PMePh_2)_2]^{2-}$; this formulation is consistent with the partial quadrupole splitting (p.q.s.) values given below. No reaction occurred when the amine was replaced by $PMePh_2$.

Reactions of Bidentate-phosphine Complexes.—It seemed possible that complexes of chelating ligands might be more tractable and, accordingly, we investigated the reactions of $[FeMe_2(dppe)_2]$, $[Fe(C_2H_4)(dppe)_2]$, and $[FeH_2(dppe)_2]$ with tertiary silanes. The first of these was either unreactive or decomposed to uncharacterizable products but the others, although highly reactive, allowed products to be identified.

The ethylene complex $[Fe(C_2H_4)(dppe)_2]$ in toluene or other solvents reacted with $SiH(OEt)_3$ or $SiEt_3H$ to form $[FeH_2(dppe)_2]$ and, in the former case, $Si_2(OEt)_6$. At 80 °C the rate of formation of the dihydride depended on the silane, going to completion in a few hours with $SiH(OEt)_3$ and in 24 h with $SiEt_3H$. With $SiPh_3H$ or $SiMePh_2H$ reaction was not complete after 3 months.

TABLE 2

Products of reactions of silanes with iron complexes

Reaction	δ_{Fe} [a] mm s^{-1}	Δ [a] mm s^{-1}	Percentage of total area	Assignment
$[Fe(C_2H_4)(dppe)_2] + SiH(OEt)_3$	0.26	0.75	100	$[Fe\{Si(OEt)_3\}_2(dppe)_2]$
$[Fe(C_2H_4)(dppe)_2] + SiMeCl_2H$	0.31	0.43	44	$[FeH(SiMeCl_2)(dppe)_2]$
[*cf.* Figure 2(*a*)]	0.23	0.87	16	$[Fe(SiMeCl_2)_2(dppe)_2]$
	0.37	1.41	10	$[FeCl_2(dppe)_2]$
	0.80 [b]	2.52 [b]	29 [b]	$[FeCl_2(dppe)]$
$[FeH_2(dppe)_2] + SiMeCl_2H$	0.16	0.31	24	$[FeH(SiMeCl_2)(dppe)_2]$
[*cf.* Figure 2(*b*)]	0.17	0.83	58	$[Fe(SiMeCl_2)_2(dppe)_2]$
	0.79 [b]	2.93 [b]	10 [b]	$[FeCl_2(dppe)]$
	1.02 [b]	3.08 [b]	8 [b]	$[H_2(dppe)][FeCl_4]$
$[FeH_2(dppe)_2] + SiCl_3H$	0.11	0.48	92	$[FeH(SiCl_3)(dppe)_2]$
[*cf.* Figure 1(*a*)]	0.73	1.58	3	?
	0.68 [b]	3.06 [b]	4	$[FeCl_2(dppe)] + [H_2dppe][FeCl_4]$
$[Fe(C_2H_4)(dppe)_2] + SiCl_3H$	0.11	0.47	45	$[FeH(SiCl_3)(dppe)_2]$
[*cf.* Figure 1(*b*)]	0.19	0.98	19	$[Fe(SiCl_3)_2(dppe)_2]$
	0.34	1.31	11	$[FeCl_2(dppe)_2]$
	0.90 [b]	2.52 [b]	26 [b]	$[FeCl_2(dppe)]$
$[FeH_2(dppe)_2] + SiCl_3H$	0.34	1.36	54	$[FeCl_2(dppe)_2]$
(1 h)	0.38	0.42	13	$[FeCl(SiCl_3)(dppe)_2]$
[*cf.* Figure 1 (*c*)]	1.16 [b]	2.71 [b]	23 [b]	$[H_2dppe][FeCl_4]$
	0.87 [b]	2.50 [b]	10 [b]	$[FeCl_2(dppe)]$

[a] ±0.02 mm s^{-1}. [b] Large errors owing to low-velocity lines being obscured (see text).

At room temperature in the absence of solvent, $[Fe(C_2H_4)(dppe)_2]$ reacted with $SiH(OEt)_3$, giving dihydrogen and a red solid analyzing as $[Fe\{Si(OEt)_3\}_2(dppe)_2]$. The i.r. spectrum showed no bands which could be attributed to Fe–H stretching modes, but a medium band at 373 cm^{-1}, not present in the spectra of the starting complex or related materials, is assigned as an Fe–Si stretching mode. The ^{57}Fe Mössbauer spectrum showed a simple doublet, with parameters different from those of the starting material or of $[FeH_2(dppe)_2]$, but indicative of a low-spin iron(II) species with less than octahedral symmetry (Table 2). The parameters of this spectrum are discussed below.

Both the ethylene complex and the dihydride reacted extremely readily with chlorosilanes. Thus with $SiCl_3H$ a white product was formed, which became yellow on exposure to air, and the i.r. spectrum indicated the presence of P–H and Fe–Cl bonds but no trace of Si–Cl stretching modes. This material is presumably the diphosphonium salt of the tetrachloroferrate(II) anion, $[H_2dppe][FeCl_4]$, although an analytically pure sample could not be obtained. It was not found possible to obtain pure simple products of any type by any variations in reaction conditions or times. However, by keeping reaction times extremely short and examining the Mössbauer spectra of the mixtures of products it was possible to obtain evidence for the formation of new compounds which we believe to be silyl iron complexes.

An excess of $SiCl_3H$ or $SiMeCl_2H$ was distilled on to the iron complex at 77 K and removed by pumping as soon as the reaction vessel had reached room temperature. The Mössbauer spectra of the products (Figures 1 and 2, Table 2) showed two major doublets plus several minor signals in each case, except for the $[FeH_2(dppe)_2]$–$SiCl_3H$ mixture [Figure 1(*a*)] which showed only one principal doublet. All the strong signals could be assigned as quadrupole-split spectra of low-spin iron(II) species, different from the starting materials. The parameters are also different from those reported for other $[FeCl_2(diphosphine)_2]$ complexes (Table 1).

The intensities of the four peaks do not allow a clear choice of pairings into doublets, but this problem is resolved by the observation that the single doublet of Figure 1(*a*) also appears as the central doublet of Figure 1(*b*). Thus, although the reaction times were similar, the dihydride has yielded a single reaction product while the more reactive ethylene complex has given the same product and another material with similar i.s. and larger q.s. It seems likely that the second species is formed by further reaction of the first, and that both are silyl-iron complexes, $[FeH(SiCl_3)(dppe)_2]$ and $[Fe(SiCl_3)_2(dppe)_2]$ respectively. Such species would be expected to have similar i.s. and this assignment gives a consistent series of q.s. values (see below).

The spectra of the products of reaction of the two iron complexes with $SiMeCl_2H$ (Figure 2) are more difficult to assign. In view of the general similarity in the reactivity of the silanes,[10] similar products to those from $SiCl_3H$ are to be expected, and the Mössbauer parameters should not be very different from those of the Fe–$SiCl_3$ complexes. Accordingly, the inner peaks are taken as one doublet and the outer pair as another. As will be seen below, this assignment gives smooth trends in the parameters throughout the whole series. In this case there was a difference in reaction times, that for the ethylene complex being kept very short and the dihydride being allowed rather longer. This difference is reflected in the intensities of the doublets, the area ratio inner : outer changing from *ca.* 3 : 1 to *ca.* 1 : 3.

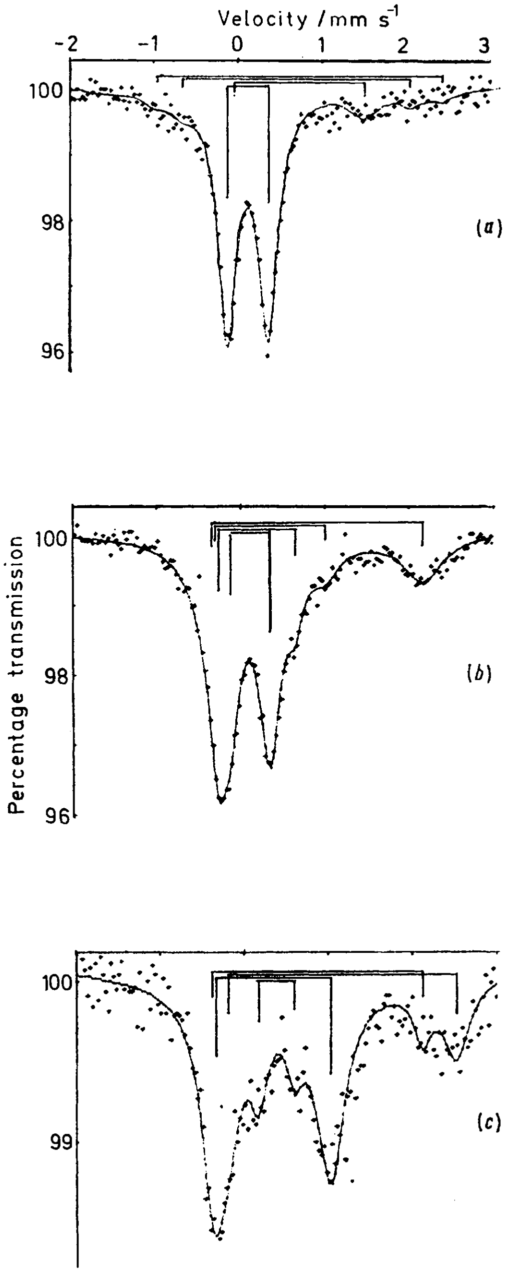


FIGURE 1 Iron-57-Mössbauer spectra of reaction products from $SiCl_3H$ and (*a*) $[FeH_2(dppe)_2]$, (*b*) $[Fe(C_2H_4)(dppe)_2]$, and (*c*) $[FeH_2(dppe)_2]$ for 1 h. The bars show peak positions at half intensity

By analogy with the $SiCl_3H$ system, the inner doublet is attributed to $[FeH(SiMeCl_2)(dppe)_2]$ and the outer doublet to $[Fe(SiMeCl_2)_2(dppe)_2]$.

In three of the spectra [Figure 1(*b*), Figure 2(*a*) and (*b*)] two of the lines are close to those of $[FeH_2(dppe)_2]$, which is a possible product or contaminant. However, the fourth spectrum [Figure 1(*a*)] is of the product of a short-term reaction starting from the dihydride, but shows no trace of these lines. In the other cases, the intensity ratios suggest that, even if some dihydride were present, there must be some other species present with lines overlapping those of the dihydride.

When the reaction of $[FeH_2(dppe)_2]$ with $SiCl_3H$ was allowed to continue for 1 h at room temperature a product with an entirely different Mössbauer spectrum was obtained [Figure 1(*c*)]. No trace is seen of the signals attributed to the two Fe–$SiCl_3$ complexes, but two new low-spin iron(II) species are present. The major component also appears as a minor constituent of the products of the short-term reactions of the ethylene complex, Figures 1(*b*) and 2(*a*). Despite the fact that, in the latter cases, the low-velocity line is overlapped by other much stronger lines, the consistency in the parameters is good. Since this species occurs in reaction mixtures derived from different silanes, and is not observed when $SiH(OEt)_3$ is used, it is unlikely to be a silyl complex, and we suggest that it is $[FeCl_2(dppe)_2]$. Dichloroiron complexes of other bidentate phosphines give similar Mössbauer parameters (Table 1), and have been assigned *trans* structures.[11]

The minor component has a very small q.s. and an i.s. close to that of the major species but higher than those of the iron silyls. Both parameters suggest the presence of a relatively poor donor, such as Cl^-, and likely assignments are to $[FeH(Cl)(dppe)_2]$ or $[FeCl(SiCl_3)(dppe)_2]$; on the basis of the p.q.s. values derived below the latter is preferred.

In all the products obtained from chlorosilanes small signals are observed at high velocities, characteristic of high-spin iron(II) species. The lower-velocity components are buried beneath much larger peaks, and their positions are not well defined. The i.s. and q.s. values are therefore not

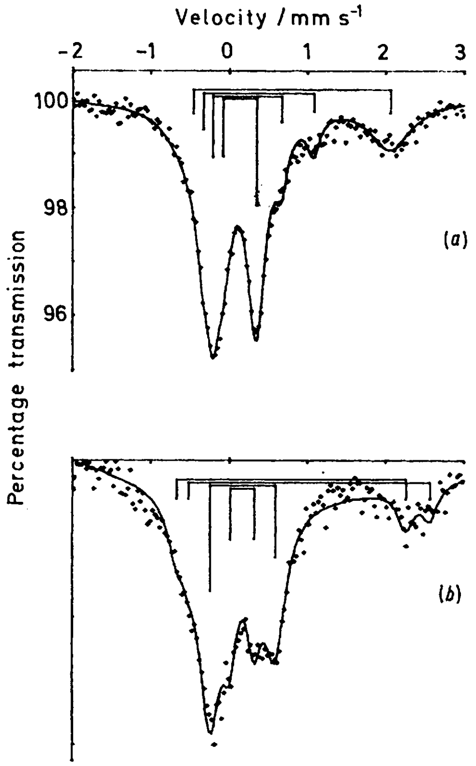


FIGURE 2 Iron-57 Mössbauer spectra of reaction products from $SiMeCl_2H$ and (*a*) $[Fe(C_2H_4)(dppe)_2]$, (*b*) $[FeH_2(dppe)_2]$. The bars show peak positions at half intensity

very reliable, but assignments can be made from the positions of the high-velocity lines, which are *ca.* 2.0 and *ca.* 2.4 mm s^{-1}. The first of these corresponds to the position of the high-velocity line for the four-co-ordinate complex [$FeCl_2$(dppe)]. The other line is often associated with the appearance in the i.r. spectrum of bands at *ca.* 2 500 and *ca.* 330 cm^{-1}, attributable to ν(P–H) of a phosphonium cation and ν(Fe–Cl) of an $[FeCl_4]^{2-}$ anion. It seems likely, therefore, that this species is [H_2dppe][$FeCl_4$].

When the ethylene complex was heated under reflux with trichlorosilane in tetrahydrofuran a white product was obtained which appears from its Mössbauer and i.r. spectra to be [$FeCl_2$(dppe)]. This complex was formed readily at higher temperatures and also appears as a minor component of room-temperature reaction mixtures.

Structures and p.q.s. Values.—The structures of the silyl complexes are not known. From the probable mechanism of formation (oxidative elimination, see below), *cis* configurations are likely but *trans* geometry cannot be ruled out. The stereochemistry can be inferred from a calculation of the p.q.s. values for the silyl groups.

A value of -0.68 mm s^{-1} for p.q.s.($\frac{1}{2}$ dppe) was obtained by Bancroft and Libbey,[11] but was thought to be uncertain and a less negative value was more likely. The value calculated from the q.s. of [FeH_2(dppe)$_2$] is -0.76 mm s^{-1}, which is considerably more negative than those for other diphosphines (-0.59 to -0.70 mm s^{-1}). This deviation probably reflects the distortion from regular geometry forced by the steric demands of the ligand and of the toluene molecules included in the lattice. Using data for the complex thought to be *trans*-[$FeCl_2$(dppe)$_2$] a value of -0.64 mm s^{-1} is derived, which is consistent with the values for similar ligands and slightly less negative than Bancroft's value.

It is also necessary to estimate the sign of the e.f.g. in the silyl complexes. It may be assumed that the donor power of the silyl groups would decrease from $[Si(OEt)_3]^-$ to $[SiMeCl_2]^-$ to $[SiCl_3]^-$, which is also the order of increasing q.s. for the bis(silyl) complexes. If the complexes have *trans* configurations, the observed order of q.s. requires (with the assumed order of donicities) that the e.f.g. be positive, *i.e.* that the silyl groups are less effective donors, and have more positive p.q.s. values, than the phosphine. A negative e.f.g. would imply that the silyl groups were donors comparable to or better than the hydride ligand, which is unlikely, and that the order of donicities is the reverse of that expected. Similar arguments lead to the assignment of a negative e.f.g. to the *cis*-bis(silyl) structure. The p.q.s. values derived on these bases are shown in Table 3. The values obtained on the assumption of *cis* geometry suggest that the silyl groups are similar donors to, or even less effective than, the chloride ion, which seems most improbable. The assumption of a *trans* configuration places the silyl groups between chloride and the phosphines in donor ability to iron, and also gives values close to that for $[SnCl_3]^-$ (-0.43 mm s^{-1}).[11] On that basis, *trans* structures are assigned to the bis(silyl) complexes.

TABLE 3

Average Mössbauer parameters and p.q.s. values

Complex	δ_{Fe} / mm s^{-1}	Δ / mm s^{-1}	p.q.s. (SiR_3^-) [a]/mms^{-1} *cis* [b]	p.q.s. (SiR_3^-) [a]/mms^{-1} *trans* [c]
[$FeCl_2$(dppe)$_2$]	0.35	1.36		
[Fe{Si(OEt)$_3$}$_2$(dppe)$_2$]	0.26	0.75	-0.27	-0.45
[Fe($SiMeCl_2$)$_2$(dppe)$_2$]	0.20	0.85	-0.22	-0.43
[Fe($SiCl_3$)$_2$(dppe)$_2$]	0.14	0.88	-0.20	-0.43
[FeH($SiMeCl_2$)(dppe)$_2$]	0.14	0.37		
[FeH($SiCl_3$)(dppe)$_2$]	0.11	0.48		

[a] Values derived from p.q.s.(Cl^-) = -0.30 mm s^{-1} and p.q.s.($\frac{1}{2}$ dppe) = -0.64 mm s^{-1}. [b] Assuming $eq < 0$. [c] Assuming $eq > 0$.

If these values are used in turn to calculate the q.s. of *trans*-[FeH(SiR_3)(dppe)$_2$], values of ($-$)0.38 and ($-$)0.36 mm s^{-1} are obtained for the $SiMeCl_2$ and $SiCl_3$ derivatives, in satisfactory agreement with the observed q.s.

Reactions of the Silyl Complexes.—The complex [Fe{Si(OEt)$_3$}$_2$(dppe)$_2$], in toluene solution, reacted with dihydrogen to give [FeH_2(dppe)$_2$] and SiH(OEt)$_3$. The bis(silyl) complex also catalyzed the reaction between SiH(OEt)$_3$ and EtOH, to give dihydrogen and Si(OEt)$_4$. The iron complex is converted into [FeH_2(dppe)$_2$], which is not catalytically active.

DISCUSSION

Although only one complex was isolated in even moderately pure condition, the Mössbauer spectra indicate the formation of five new complexes, most reasonably formulated as silyl-iron complexes of the type *trans*-[Fe(SiR_3)$_2$(dppe)$_2$] and *trans*-[FeH(SiR_3)(dppe)$_2$]. During the course of our work, Lappert and Speier[5] reported similar reactions, the products of which were characterized only by analyses for carbon and hydrogen and by Fe–H stretching frequencies. However, their results (summarized in Table 4) are in broad agreement with our findings, and the sum total of evidence makes the formulations of the silyl complexes plausible. The complexes are most probably formed by oxidation-elimination reactions, a well known route to metal silyl derivatives;[3,10,12] the reactions are summarized in the Scheme. The ethylene complex reacts by loss of ethylene and addition of the silane to the resulting co-ordinatively unsaturated 16-electron complex. The dihydrido- and hydridosilyl complexes presumably also react by oxidative addition followed by elimination of dihydrogen. If the intermediates in these reactions are to be 18-electron species, as is usual, one ligand must be lost and it seems likely that one phosphine group would dissociate to give a seven-co-ordinate iron(IV) complex. Although iron(IV) complexes of ' innocent ' ligands are

TABLE 4

Products of reactions with trichlorosilane

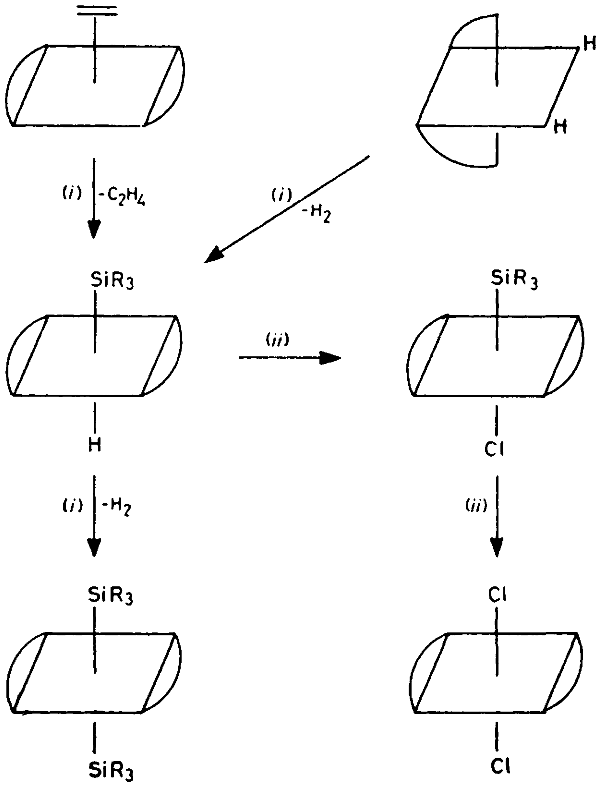
Solvent	Temperature	Products Ref. 5	Products This work
(*a*)	From	[Fe(C_2H_4)(dppe)$_2$]	
thf	room	[FeH($SiCl_3$)(dppe)]	
thf	reflux	[FeH($SiCl_3$)(dppe)$_2$]	[$FeCl_2$(dppe)]
None	room	[Fe($SiCl_3$)$_2$(dppe)$_2$]	[FeH($SiCl_3$)(dppe)$_2$] + [Fe($SiCl_3$)$_2$(dppe)$_2$]
(*b*)	From	[FeH_2(dppe)$_2$]	
None	room	[Fe($SiCl_3$)$_2$(dppe)$_2$]	[FeH($SiCl_3$)(dppe)$_2$] + [Fe($SiCl_3$)$_2$(dppe)$_2$]
(*c*)	From	[FeH(Cl)(dppe)$_2$]	
None	room	[FeCl($SiCl_3$)(dppe)$_2$]	

rare, these intermediates would be analogous to the known $[FeH_4(PEtPh_2)_3]$;[13] similar ruthenium(IV) complexes have also been isolated, of the type $[RuH_3(SiR_3)(PPh_3)_3]$, which are stable to loss of dihydrogen.[14] In the iron case the relative instability of the high oxidation state and of the half-dissociated phosphine molecule would encourage the elimination of dihydrogen and the formation of the silyl-iron(II) complexes.

The reaction of the hydridosilyl complex with the silane appears to be a finely balanced equilibrium. With $SiH(OEt)_3$ in excess, the bis(silyl) complex is formed [equation (3)] but, in the presence of an excess of dihydrogen and with the silane diluted by a solvent, the products are the dihydride and $Si_2(OEt)_6$ [equation (4)].

$$[\mathrm{FeH(SiR_3)(dppe)_2}] \longrightarrow [\mathrm{FeH_2(SiR_3)_2(dppe)_2}] \longrightarrow \begin{cases} [\mathrm{Fe(SiR_3)_2(dppe)_2}] + \mathrm{H_2} & (3) \\ [\mathrm{FeH_2(dppe)_2}] + (\mathrm{SiR_3})_2 & (4) \end{cases}$$

This represents a delicate balance between the strengths of the Fe–H and Fe–Si bonds. With triorganosilanes only reaction (4) is observed, which is consistent with the generally easier dissociation of M–H–$SiEt_3$ complexes.[10]



SCHEME (*i*) SiR_3H; (*ii*) SiR'_3Cl

The observed chloro-complexes could arise from trace amounts of hydrogen chloride present by adventitious hydrolysis, or by reaction of the chlorosilanes as chlorinating agents to replace Fe–H and Fe–Si bonds by Fe–Cl bonds. Chlorocarbon compounds are well known chlorinating agents, especially for metal–hydrogen bonds, and chlorosilanes are known to act similarly in reactions with $[CoH(dppe)_2]$.[15] The most direct route for chlorination would be by addition of Cl–SiR_2H to the metal hydride, followed by elimination of SiR_2H_2 [equation (5)]. Such a mode of addition has never been observed, but would account for the chlorination of $[CoH(dppe)_2]$ by $SiCl_4$.[15] The alternative would be an intramolecular rearrangement following the addition of H–SiR_2Cl to the metal, with M–H/Si–Cl exchange [equation (6)]. Our observation of Fe–H–SiR_2Cl complexes early in the reaction sequence, before significant quantities of chloro-complexes had formed, makes the second path more likely.

Our catalytic studies[2] require the postulation of silyl-iron complexes as intermediates. The above results show that the formation of such complexes is quite feasible. The chelated complexes reported here

$$\mathrm{M{-}H + ClSiR_2H \longrightarrow MH(Cl)(SiR_2H) \longrightarrow M{-}Cl + SiR_2H_2} \qquad (5)$$

$$\mathrm{M{-}H + HSiR_2Cl \longrightarrow MH_2(SiR_2Cl) \longrightarrow M{-}Cl + SiR_2H_2} \qquad (6)$$

are themselves highly reactive and the postulated complexes of unidentate phosphines might be expected to be even more reactive, and hence are likely intermediates in rapid catalytically cyclic reactions.

EXPERIMENTAL

Starting materials were prepared by literature methods.[8,13,16-18] Chlorosilanes were purified by repeated trap-to-trap distillation immediately before use.

Bis[1,2-bis(diphenylphosphino)ethane]bis(triethoxysilyl)-iron(II).—The complex $[Fe(C_2H_4)(dppe)_2]$ (1.0 g) and $SiH(OEt)_3$ (1 cm^3) were stirred together at room temperature under a rapid flow of nitrogen for 2 h, during which time the orange colour of the starting material changed to red. The excess of $SiH(OEt)_3$ was removed under reduced pressure and the residue dissolved in toluene (25 cm^3) and filtered. The volume of the solution was halved under reduced pressure and a red *solid* was precipitated by addition of n-hexane. The solid was washed with n-hexane and dried *in vacuo*, yield 0.61 g (47%). Analyses were poorly reproducible but the values 64.2% C and 5.3% H are representative ($[Fe\{Si(OEt)_3\}_2(dppe)_2]$ requires C, 65.5; H, 6.5%).

Reactions of Iron Complexes with Chlorosilanes.—An excess of $SiCl_3H$ or $SiMeCl_2H$ was distilled on to the iron complex at 77 K and the mixture allowed to warm to room temperature, when the volatiles were rapidly removed by pumping. Longer-term reactions were conducted in sealed tubes. No consistent analytical data could be obtained and the mixtures of products were analyzed by i.r. and Mössbauer spectroscopy. The i.r. spectrum of the product from $[FeH_2(dppe)_2]$ + $SiMeCl_2H$ showed absorptions at 2 180 and 1 915 [ν(Fe–H)] and 538 cm^{-1} [ν(Si–Cl)], and that from the ethylene complex had bands at *ca*. 1 920 and 535 cm^{-1}.

Reactions of Carbonyl Complexes with Triphenylphosphine.—A mixture of $[FeH(SiPh_3)(CO)_4]$ (0.5 g, 1.2

mmol) and PPh_3 (0.31 g, 1.17 mmol) in toluene (15 cm^3) was stirred under nitrogen for 24 h. Addition of n-hexane gave a light yellow solid which was extracted with hot 95% ethanol. The residual solid was identified by its i.r. spectrum as a mixture of $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$, and $SiPh_3H$ was recovered from the ethanol extract (i.r. identification).

The complex $[Fe(SiCl_3)_2(CO)_4]$ (1.2 g, 2.8 mmol) and PPh_3 (0.72 g, 3.0 mmol) in toluene (30 cm^3) were sealed *in vacuo* and shaken for 4 d at room temperature. Volatile components were removed and trapped at 77 K, leaving a yellow solid residue which was washed with n-hexane and shown to be a mixture of $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$ (i.r. spectroscopy). The volatile fraction had b.p. 140—146 °C and 77.6% Cl; Si_2Cl_6 has b.p. 145 °C and 79.1% Cl.

Mössbauer spectra were obtained at liquid-nitrogen temperature with a ^{57}Co–Rh source at room temperature, using a Harwell 6000 series spectrometer. The i.s. and velocity-scale standard was an iron foil used at room temperature. In nearly all cases the spectra of the reaction products contained many signals, heavily overlapped, and it was necessary to apply fitting constraints to obtain meaningful analyses. The two peaks of the low-intensity doublets of high-spin iron(II) species were constrained to have equal widths and intensities. In several cases it was also necessary to apply a width constraint to the major doublets, but the intensities were left free. In two cases, minor doublets gave one linewidth <0.2 mm s^{-1}; since it was evident that genuine signals were present at these positions the widths were constrained to a fixed value of 0.25 mm s^{-1}.

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