Organosilicon Chemistry. Part 25.[1] Catalysis of the Reaction Between Alcohols and Silanes by Hydrido-, Dinitrogen-, and Ethylene-iron Complexes

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The reaction between alcohols, ROH (R = Me, Et, Pr^n, or Bu^n), and SiH(OEt)$_3$ or SiPh$_2$H$_2$ is strongly catalysed at room temperature by [FeH$_2$(PMePh$_2$)$_4$] or by [FeH$_2$(N$_2$)(PEtPh$_2$)$_3$]. With SiH(OEt)$_3$, reaction is complicated by alkoxy-exchange when R $\neq$ OEt. With both catalysts the reactions have induction periods but are thereafter first order in the concentration of each of the reactants and of the catalyst. Mechanisms are proposed based on the formation of iron–silyl complexes. The complex [Fe(C$_2$H$_4$)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) also catalyses the reaction but is rapidly deactivated by conversion into [FeH$_2$(dppe)$_2$].

O-SILYLATION, the reaction of an alcohol with a silane [equation (1)], can be catalysed in a variety of ways,[2-5] but homogeneous metal-catalysed systems have been little studied. Brief reports have appeared of the use of [Co$_2$(CO)$_8$],[6] [RhCl(PPh$_3$)$_3$], and [RuCl$_2$(PPh$_3$)$_3$],[7] and we have previously mentioned the somewhat limited utility of [CoH$_3$(PPh$_3$)$_3$] and [CoH(N$_2$)(PPh$_3$)$_3$].[8] We now report that the iron complex [Fe(C$_2$H$_4$)(dppe)$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane] is a moderate catalyst and that the complexes [FeH$_2$(PMePh$_2$)$_4$] and [FeH$_2$(N$_2$)(PEtPh$_2$)$_3$] are good catalysts for the reaction of triethoxysilane or diphenylsilane with a variety of alcohols.

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

RESULTS AND DISCUSSION

Catalysis by [Fe(C$_2$H$_4$)(dppe)$_2$].—When a mixture of a primary alcohol, ROH (R = Me, Et, Pr^n, or Bu^n), and a silane, SiH(OEt)$_3$ or SiPh$_2$H$_2$, was added to a toluene solution of the complex [Fe(C$_2$H$_4$)(dppe)$_2$] there was immediate vigorous evolution of dihydrogen which diminished after *ca.* 30 min. The reaction then continued slowly for *ca.* 24 h, when it was complete. No reaction was observed with SiEt$_3$H, SiMePh$_2$H, or SiPh$_3$H. G.l.c. and i.r. analysis indicated that both hydrogen atoms in SiPh$_2$H$_2$ were reactive, giving SiPh$_2$(OR)$_2$, and that SiH(OEt)$_3$ yielded all the possible alkoxy-exchange products Si(OEt)$_n$(OR)$_{4-n}$. As the reaction proceeded the initial dark red-brown colour of the solution gave way to a bright yellow, the change coinciding roughly with the change in rate of gas evolution, and i.r. spectroscopy showed the presence of the dihydrido-complex [FeH$_2$(dppe)$_2$]. Separate experiments demonstrated that this complex is a very poor catalyst.

In order to avoid complications from alkoxy-exchange in SiH(OEt)$_3$ or consecutive reactions with SiPh$_2$H$_2$, attempts were made to follow the kinetics of the reaction of SiH(OEt)$_3$ with EtOH, but the continuous deactivation of the catalyst made a proper kinetic analysis impossible. The initial rates, with the assumption that the catalyst concentration is constant, suggested first-order dependence on the concentrations of the silane, alcohol, and catalyst, with a rate constant of $4.3 \pm 0.2_2$ dm^6 mol^{-2} min^{-1}. Clearly, this result should be treated with some caution.

We have previously shown that the ethylene complex undergoes oxidative addition with SiH(OEt)$_3$ and other silanes to form hydrido-silyl (I) and bis(silyl) (II) complexes [equations (2) and (3)],[9] and these complexes are likely intermediates in the catalytic reactions. Nucleophilic attack by the alcohol on the co-ordinated silyl group could lead to formation of an alkoxysilane and an Fe–H bond. (In the reaction schemes shown below this reaction is shown as occurring in two separate stages, involving an intermediate in which silicon is five-co-ordinate. This reaction may occur as a single concerted process without affecting the arguments given.) Attack on (I) would give the inactive dihydride, a stoicheiometric amount of SiR$_3$(OEt), and no dihydrogen [equations (4) and (5)]. While catalyst deactivation could occur by this route, no catalysis is possible. Reaction of (II), however, would give (I), [FeH(SiR$_3$)(dppe)$_2$] [equations (6) and (7)] which by reaction with the silane [equation (3)] would regenerate (II), giving a catalytic loop. If reaction (6) or (7) were rate-determining and

$$\mathrm{[Fe(C_2H_4)(dppe)_2] + SiR_3H \longrightarrow \underset{(I)}{[FeH(SiR_3)(dppe)_2]} + C_2H_4} \qquad (2)$$

$$\mathrm{\underset{(I)}{[FeH(SiR_3)(dppe)_2]} + SiR_3H \longrightarrow \underset{(II)}{[Fe(SiR_3)_2(dppe)_2]} + H_2} \qquad (3)$$

$$\mathrm{\underset{(I)}{[FeH(SiR_3)(dppe)_2]} + EtOH \longrightarrow [FeH(SiR_3{\cdot}EtOH)(dppe)_2]} \qquad (4)$$

$$\mathrm{[FeH(SiR_3{\cdot}EtOH)(dppe)_2] \longrightarrow [FeH_2(dppe)_2] + SiR_3(OEt)} \qquad (5)$$

$$\mathrm{\underset{(II)}{[Fe(SiR_3)_2(dppe)_2]} + EtOH \longrightarrow [Fe(SiR_3)(SiR_3{\cdot}EtOH)(dppe)_2]} \qquad (6)$$

$$\mathrm{[Fe(SiR_3)(SiR_3{\cdot}EtOH)(dppe)_2] \longrightarrow \underset{(I)}{[FeH(SiR_3)(dppe)_2]} + SiR_3(OEt)} \qquad (7)$$

(3) and (6) were rapidly established equilibria with K_3 and K_6 small, the rate law would be as in (i) where $k = k_7K_3K_6$ or k_6K_3. Since only the initial rates were used

$$\mathrm{d(H_2)/d}t = k[\mathrm{catalyst}][\mathrm{SiR_3H}][\mathrm{EtOH}]/[\mathrm{H_2}] \quad \text{(i)}$$

the expected inhibition by dihydrogen could not be detected. This reaction scheme also requires that complex (I) react more rapidly with SiR_3H than with EtOH, at least under the initial conditions.

Further deactivation of the catalyst could occur by the reaction of the ethylene complex or the bis(silyl) complex with the dihydrogen produced, both of which reactions are known.[9,10] Complex (I) would presumably react similarly.

Catalysis by $[FeH_2(PMePh_2)_4]$.—In contrast to the chelated dihydride, the complex $[FeH_2(PMePh_2)_4]$ is a very effective catalyst for the reaction of $SiH(OEt)_3$ or of $SiPh_2H_2$ with alcohols, the reactions going to completion in 1—4 h at room temperature. Again, both hydrogen atoms of the tertiary silane were reactive, and alkoxy-exchange occurred with $SiH(OEt)_3$. At the end of the reaction the starting complex could be recovered. Tertiary silanes containing three organic substituents ($SiEt_3H$, $SiMePh_2H$, or $SiPh_3H$) did not react, and any trace of chlorosilane impurity resulted in immediate conversion of the catalyst into the inactive $[FeCl_2(PMePh_2)_2]$.

Kinetic studies on the $SiH(OEt)_3$–EtOH system (in toluene solution) demonstrated that reaction was initially slow but increased with time, becoming quite rapid after 10—15 min. When the reaction had gone to completion the remaining solution was still catalytically active, and addition of more of the silane and the alcohol gave immediate rapid evolution of hydrogen with no induction period. Kinetic studies were therefore made on the 'activated' system. When ethanol was present in large excess, a good pseudo-first-order dependence on the silane concentration was shown up to 80—90% completion of reaction. When the concentrations of the silane and ethanol were comparable, first-order plots were unsatisfactory but a second-order treatment gave good linear plots, again over 80—90% completion of reaction.

TABLE 1

Catalysis by $[FeH_2(PMePh_2)_4]$, with $[SiH(OEt)_3]$ = 0.4 mol dm^{-3}

10^2[catalyst]	[EtOH]	10^3k_2 [a]	k_3 [b]
mol dm^{-3}		dm^3 mol^{-1} min^{-1}	dm^6 mol^{-2} min^{-1}
0.58	0.80	35	6.0
	4.0	29	5.0
1.2	0.80	57	4.9
	4.0	51	4.4
	4.0 [c]	56	4.8
	8.0	54	4.6
1.9	0.80	95	5.1
2.3	4.0	110	4.7
2.5	0.8	120	4.9
2.6	2.0	130	5.1
3.5	0.80	190	5.4
1.2	0.40	50	4.3
			Av. 4.9 ± 0.1$_3$ [d]

[a] For $\mathrm{d(H_2)/d}t = k_2[\mathrm{EtOH}][\mathrm{SiH(OEt)_3}]$. [b] For $\mathrm{d(H_2)/d}t = k_3[\mathrm{catalyst}][\mathrm{EtOH}][\mathrm{SiH(OEt)_3}]$. [c] Pretreatment with 10 : 1 EtOH : $SiH(OEt)_3$. [d] Standard deviation of the mean.

The rate constants derived from the second-order treatments were proportional to the catalyst concentration (Table 1). The rate law is thus (ii) where $k_3 = 4.9 \pm 0.1$ dm^6 mol^{-2} min^{-1}. Within the limits of error this rate

$$\mathrm{d(H_2)/d}t = k_3[\mathrm{catalyst}][\mathrm{SiH(OEt)_3}][\mathrm{EtOH}] \quad \text{(ii)}$$

constant was the same as that obtaining in the final part of the first-stage reaction.

The complex $[FeH_2(PMePh_2)_4]$ does not react with ethanol (it is prepared in this solvent), so that likely mechanisms would again involve interaction of the complex with the silane. Oxidative addition of tertiary silanes containing electronegative groups is known to occur more readily than that of triorganosilanes,[11] which is consistent with the observed lack of reactivity of $SiEt_3H$, *etc.* Addition would probably occur with loss of a co-ordinated phosphine to form a 16-electron complex, (III), which could add the silane to give an 18-electron silyl complex, (IV), formally containing iron(IV) [equations (8) and (9); L = $PMePh_2$, R = OEt]. Similar ruthenium(IV) silyl complexes have been prepared,[12,13] and (IV) is also analogous to the known $[FeH_4(PEtPh_2)_3]$.[14] Nucleophilic attack by ethanol on (IV) would give $Si(OEt)_4$ and a tetrahydride (V) similar to that mentioned above [equations (10) and (11)]. If (V) now loses hydrogen, the starting dihydride (III) is regenerated [equation (12)] and the catalytic loop is completed.

$$[\mathrm{FeH_2L_4}] \longrightarrow \underset{\text{(III)}}{[\mathrm{FeH_2L_3}]} + \mathrm{L} \quad (8)$$

$$[\mathrm{FeH_2L_3}] + \mathrm{SiR_3H} \longrightarrow \underset{\text{(IV)}}{[\mathrm{FeH_3(SiR_3)L_3}]} \quad (9)$$

$$[\mathrm{FeH_3(SiR_3)L_3}] + \mathrm{EtOH} \longrightarrow [\mathrm{FeH_3(SiR_3{\cdot}EtOH)L_3}] \quad (10)$$

$$[\mathrm{FeH_3(SiR_3{\cdot}EtOH)L_3}] \longrightarrow \underset{\text{(V)}}{[\mathrm{FeH_4L_3}]} + \mathrm{SiR_3(OEt)} \quad (11)$$

$$[\mathrm{FeH_4L_3}] \longrightarrow \underset{\text{(III)}}{[\mathrm{FeH_2L_3}]} + \mathrm{H_2} \quad (12)$$

This sequence of reactions is consistent with the observed kinetics if it is assumed that reaction (12) is fast, (11) is rate-determining, and (9) and (10) are rapidly established equilibria with small values for the equilibrium constants. With these assumptions we obtain (iii).

$$\mathrm{d(H_2)/d}t = k_{11}K_9K_{10}[\mathrm{FeH_2L_3}][\mathrm{SiR_3H}][\mathrm{EtOH}] \quad \text{(iii)}$$

Alternatively, if reaction (11) is also fast and (10) is rate-determining, or steps (10) and (11) are inseparable, then expression (iv) is obtained.

$$\mathrm{d(H_2)/d}t = k_{10}K_9[\mathrm{FeH_2L_3}][\mathrm{SiR_3H}][\mathrm{EtOH}] \quad \text{(iv)}$$

It is also possible that (IV) would lose dihydrogen before reacting with ethanol, giving the sequence of reactions (13)—(15). This sequence would display similar kinetics if reaction (14) and (15) were rate-determining, except that inhibition by the product dihydrogen might be expected if (**13**) were reversible. Such inhibition is not apparent. This mechanism is also unattractive in that it involves three 16-electron species, (III), (VI), and (VII), unless the last is formulated either with EtOH co-ordinated to iron or as the oxidative-addition product $[FeH_2(OEt)(SiR_3)L_3]$, neither of which seems very likely.

$$\underset{\text{(IV)}}{[FeH_3(SiR_3)L_3]} \longrightarrow \underset{\text{(VI)}}{[FeH(SiR_3)L_3]} + H_2 \quad (13)$$

$$[FeH(SiR_3)L_3] + EtOH \longrightarrow \underset{\text{(VII)}}{[FeH(SiR_3)L_3]\cdot EtOH} \quad (14)$$

$$[FeH(SiR_3)L_3]\cdot EtOH \longrightarrow \underset{\text{(III)}}{[FeH_2L_3]} + SiR_3(OEt) \quad (15)$$

Further reaction of (IV) or (VI) with the silane to form a bis(silyl) $[FeH_2(SiR_3)_2L_3]$ (VIII) cannot be ruled out. As with the dppe system, the bis(silyl) compound might be more reactive, and similar catalytic schemes can be drawn. Indeed, it is possible that the increase in reactivity observed in the early stages of the reaction could be due to the building up of (VIII). If this were the case, however, the second-stage reaction would show an increase in rate constant similar to that of the first stage, since depletion of the silane (used in deficiency) would lead back to (III).

The induction period was reduced, but not eliminated, by pretreatment of the catalyst solution with the silane. Pretreatment with dihydrogen, dinitrogen, argon, or ethanol was ineffective, and addition of the phosphine increased the induction period. It therefore seems likely that the induction period is due to the slow dissociation of the phosphine [equation (8)].

Consumption of all the silane would leave the iron as $[FeH_2L_3]$ or $[FeH_4L_3]$, which would allow the catalytic cycle to restart immediately on addition of more silane. These complexes would react with the dissociated molecule of the phosphine on standing or during isolation of the iron complex to reform $[FeH_2L_4]$, as the corresponding complexes of $PEtPh_2$ and $PBuPh_2$ are known to do.[14]

Catalysis by $[FeH_2(N_2)(PEtPh_2)_3]$.—The dinitrogen complex $[FeH_2(N_2)(PEtPh_2)_3]$ reacts with alkyl- and alkoxy-silanes (in the absence of an alcohol) but no products could be isolated.[9] In the presence of an alcohol, the complex functions as a catalyst very similar to $[FeH_2(PMePh_2)_4]$. Triethoxysilane and diphenylsilane both reacted with the same range of alcohols to give the products described above. The reaction of $SiH(OEt)_3$ with EtOH showed a somewhat less marked induction period, going to completion in 1—5 h at room temperature, and addition of further amounts of the reactants gave immediate reaction. The rate law for this second-stage reaction was the same as for the previous complex, with a rate constant of 2.6 ± 0.1 $dm^6\ mol^{-2}\ min^{-1}$ (Table 2). The induction period was similarly independent of pretreatment with dinitrogen, argon, dihydrogen, or ethanol, was reduced but not eliminated by pretreatment with the silane, and was lengthened by the addition of $PMePh_2$; presumably, slow loss of N_2 or $PMePh_2$ is occurring.

TABLE 2

Catalysis by $[FeH_2(N_2)(PEtPh_2)_3]$ with $[SiH(OEt)_3]$ = 0.4 mol dm^{-3}

10^2[catalyst]	[EtOH]	10^3k_2 [a]	k_3 [b]
mol dm^{-3}		$dm^3\ mol^{-1}\ min^{-1}$	$dm^6\ mol^{-2}\ min^{-1}$
0.67	2.0	21	3.1
	4.0	15	2.2
1.4	2.0	34	2.5
	4.0	35	2.6
1.5	0.80	42	2.8
1.9	4.0	48	2.5
2.6	2.0	63	2.4
2.8	0.80	68	2.5
	4.0	74	2.7
4.1	0.80	103	2.5
			Av. 2.6 ± 0.1 [c]

[a] For $d(H_2)/dt = k_2[EtOH][SiH(OEt)_3]$. [b] For $d(H_2)/dt = k_3[catalyst][EtOH][SiH(OEt)_3]$. [c] Standard deviation of the mean.

It seems likely that a mechanism similar to that described above will apply. Reaction of the catalyst with the silane [equation (16), L = $PMePh_2$] would lead to a complex analogous to (IV), and the same cycles could then be invoked.

$$[FeH_2(N_2)L_3] + SiR_3H \longrightarrow [FeH_3(SiR_3)L_3] + N_2 \quad (16)$$

EXPERIMENTAL

All reactions were carried out under an atmosphere of purified nitrogen. The iron complexes were prepared by literature methods.[10,14,15] Alkoxysilanes were identified by g.l.c. using a Perkin-Elmer 451 fractometer with a 15% w/w SE 30–Celite column (length 1.6 m).

Kinetics of the Catalysis.—Runs were carried out at constant pressure (1 atm),* using a flask (50 cm^3) immersed in a water-bath at 25 °C and connected to a gas burette. The apparatus was purged with nitrogen and the catalyst, solvent (toluene), and alcohol were introduced and stirred under nitrogen for 15 min. The nitrogen flow was stopped, the apparatus sealed, and the silane injected through a serum cap. The quantity of solvent used was adjusted so that the total volume of the final mixture was always 10 cm^3. The rate of evolution of hydrogen was monitored as a function of time and of the initial concentrations of the reactants and catalyst. Orders of reaction were established by plotting $\log(a - x)$, $\log(s - x)$, and $\log[(a - x)/(s - x)]$ against time [a,s = initial concentrations of EtOH and $SiH(OEt)_3$ respectively, x = amount of H_2 evolved] or, when $a = s$, by the time-to-half-reaction method. First-order plots were curved except for $\log(s - x)$ when a large excess of EtOH was present. The second-order plots were linear over at least 80% completion of reaction, with slopes which were proportional to the catalyst concentration. Rate constants were derived by least-squares fits to the second-order points.

For the complexes $[FeH_2(PMePh_2)_4]$ and $[FeH_2(N_2)(PEtPh_2)_3]$, the initial reaction [2 : 1 EtOH : $SiH(OEt)_3$] was allowed to go to completion, and kinetic data were obtained by injecting further quantities of reactants into the resulting mixture.

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* Throughout this paper: 1 atm = 101 325 Pa.

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