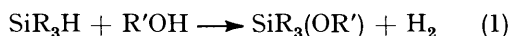


## Organosilicon Chemistry. Part 25.<sup>1</sup> Catalysis of the Reaction Between Alcohols and Silanes by Hydrido-, Dinitrogen-, and Ethylene-iron Complexes

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The reaction between alcohols, ROH (R = Me, Et, Pr<sup>n</sup>, or Bu<sup>n</sup>), and SiH(OEt)<sub>3</sub> or SiPh<sub>2</sub>H<sub>2</sub> is strongly catalysed at room temperature by [FeH<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>] or by [FeH<sub>2</sub>(N<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub>]. With SiH(OEt)<sub>3</sub>, reaction is complicated by alkoxy-exchange when R ≠ 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<sub>2</sub>H<sub>4</sub>)(dppe)<sub>2</sub>] (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) also catalyses the reaction but is rapidly deactivated by conversion into [FeH<sub>2</sub>(dppe)<sub>2</sub>].

O-SILYLATION, the reaction of an alcohol with a silane [equation (1)], can be catalysed in a variety of ways,<sup>2-5</sup> but homogeneous metal-catalysed systems have been little studied. Brief reports have appeared of the use of



[Co<sub>2</sub>(CO)<sub>8</sub>],<sup>6</sup> [RhCl(PPh<sub>3</sub>)<sub>3</sub>], and [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>7</sup> and we have previously mentioned the somewhat limited utility of [CoH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] and [CoH(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>].<sup>8</sup> We now report that the iron complex [Fe(C<sub>2</sub>H<sub>4</sub>)(dppe)<sub>2</sub>] [dppe = 1,2-bis(diphenylphosphino)ethane] is a moderate catalyst and that the complexes [FeH<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>] and [FeH<sub>2</sub>(N<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub>] are good catalysts for the reaction of triethoxysilane or diphenylsilane with a variety of alcohols.

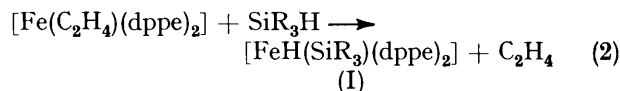
### RESULTS AND DISCUSSION

*Catalysis by [Fe(C<sub>2</sub>H<sub>4</sub>)(dppe)<sub>2</sub>].*—When a mixture of a primary alcohol, ROH (R = Me, Et, Pr<sup>n</sup>, or Bu<sup>n</sup>), and a silane, SiH(OEt)<sub>3</sub> or SiPh<sub>2</sub>H<sub>2</sub>, was added to a toluene solution of the complex [Fe(C<sub>2</sub>H<sub>4</sub>)(dppe)<sub>2</sub>] 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<sub>3</sub>H, SiMePh<sub>2</sub>H, or SiPh<sub>3</sub>H. G.l.c. and i.r. analysis indicated that both hydrogen atoms in SiPh<sub>2</sub>H<sub>2</sub> were reactive, giving SiPh<sub>2</sub>(OR)<sub>2</sub>, and that SiH(OEt)<sub>3</sub> yielded all the possible alkoxy-exchange products Si(OEt)<sub>n</sub>(OR)<sub>4-n</sub>. 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<sub>2</sub>(dppe)<sub>2</sub>]. Separate experiments demonstrated that this complex is a very poor catalyst.

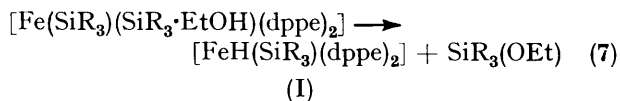
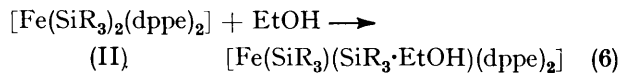
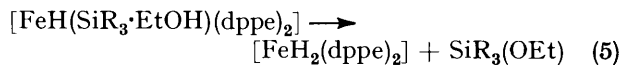
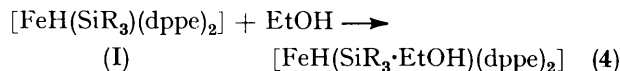
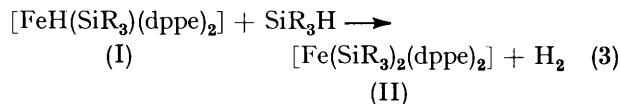
In order to avoid complications from alkoxy-exchange in SiH(OEt)<sub>3</sub> or consecutive reactions with SiPh<sub>2</sub>H<sub>2</sub>, attempts were made to follow the kinetics of the reaction of SiH(OEt)<sub>3</sub> with EtOH, but the continuous deactivation of the catalyst made a proper kinetic 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  $4.3 \pm 0.2 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$ . Clearly, this result should be treated with some caution.

We have previously shown that the ethylene complex undergoes oxidative addition with SiH(OEt)<sub>3</sub> and other silanes to form hydrido-silyl (I) and bis(silyl) (II) complexes [equations (2) and (3)],<sup>9</sup> 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 alkoxy-silane 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-coordinate. This reaction may occur as a single concerted process without affecting the arguments given.) Attack on (I) would give the inactive dihydride, a stoichiometric amount of SiR<sub>3</sub>(OEt), and no dihydrogen [equation (3)]



tions (4) and (5)]. While catalyst deactivation could occur by this route, no catalysis is possible. Reaction of (II), however, would give (I), [FeH(SiR<sub>3</sub>)(dppe)<sub>2</sub>] [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

(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  $k_8K_3$ . Since only the initial rates were used

$$d(\text{H}_2)/dt = k[\text{catalyst}][\text{SiR}_3\text{H}][\text{EtOH}]/[\text{H}_2] \quad (\text{i})$$

the expected inhibition by dihydrogen could not be detected. This reaction scheme also requires that complex (I) react more rapidly with  $\text{SiR}_3\text{H}$  than with  $\text{EtOH}$ , 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.<sup>9,10</sup> Complex (I) would presumably react similarly.

*Catalysis by  $[\text{FeH}_2(\text{PMePh}_2)_4]$ .*—In contrast to the chelated dihydride, the complex  $[\text{FeH}_2(\text{PMePh}_2)_4]$  is a very effective catalyst for the reaction of  $\text{SiH}(\text{OEt})_3$  or of  $\text{SiPh}_2\text{H}_2$  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  $\text{SiH}(\text{OEt})_3$ . At the end of the reaction the starting complex could be recovered. Tertiary silanes containing three organic substituents ( $\text{SiEt}_3\text{H}$ ,  $\text{SiMePh}_2\text{H}$ , or  $\text{SiPh}_3\text{H}$ ) did not react, and any trace of chlorosilane impurity resulted in immediate conversion of the catalyst into the inactive  $[\text{FeCl}_2(\text{PMePh}_2)_2]$ .

Kinetic studies on the  $\text{SiH}(\text{OEt})_3$ - $\text{EtOH}$  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  $[\text{FeH}_2(\text{PMePh}_2)_4]$ , with  $[\text{SiH}(\text{OEt})_3]$   
= 0.4 mol  $\text{dm}^{-3}$

$10^2[\text{catalyst}]$ mol $\text{dm}^{-3}$	$[\text{EtOH}]$	$10^3k_2$ <sup>a</sup> dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>	$k_3$ <sup>b</sup> dm <sup>6</sup> mol <sup>-2</sup> min <sup>-1</sup>
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 <sup>c</sup>	56	4.8
	8.0	54	4.6
1.9	0.80	95	5.1
	4.0	110	4.7
2.3	0.8	120	4.9
2.5	2.0	130	5.1
2.6	0.80	190	5.4
3.5	0.40	50	4.3

Av.  $4.9 \pm 0.1_3$  <sup>d</sup>

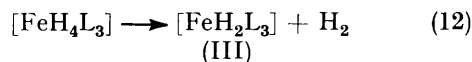
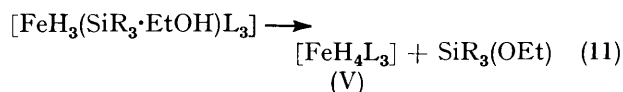
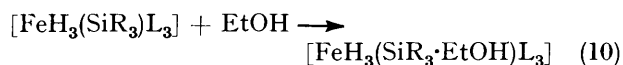
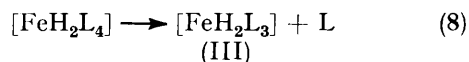
<sup>a</sup> For  $d(\text{H}_2)/dt = k_2[\text{EtOH}][\text{SiH}(\text{OEt})_3]$ . <sup>b</sup> For  $d(\text{H}_2)/dt = k_3[\text{catalyst}][\text{EtOH}][\text{SiH}(\text{OEt})_3]$ . <sup>c</sup> Pretreatment with 10:1  $\text{EtOH}:\text{SiH}(\text{OEt})_3$ . <sup>d</sup> Standard deviation of the 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<sup>6</sup> mol<sup>-2</sup> min<sup>-1</sup>. Within the limits of error this rate

$$d(\text{H}_2)/dt = k_3[\text{catalyst}][\text{SiH}(\text{OEt})_3][\text{EtOH}] \quad (\text{ii})$$

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

The complex  $[\text{FeH}_2(\text{PMePh}_2)_4]$  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,<sup>11</sup> which is consistent with the observed lack of reactivity of  $\text{SiEt}_3\text{H}$ , 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);  $\text{L} = \text{PMePh}_2$ ,  $\text{R} = \text{OEt}$ ]. Similar ruthenium(IV) silyl complexes have been prepared,<sup>12,13</sup> and (IV) is also analogous to the known  $[\text{FeH}_4(\text{PEtPh}_2)_3]$ .<sup>14</sup> Nucleophilic attack by ethanol on (IV) would give  $\text{Si}(\text{OEt})_4$  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.



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).

$$d(\text{H}_2)/dt = k_{11}K_9K_{10}[\text{FeH}_2\text{L}_3][\text{SiR}_3\text{H}][\text{EtOH}] \quad (\text{iii})$$

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

$$d(\text{H}_2)/dt = k_{10}K_9[\text{FeH}_2\text{L}_3][\text{SiR}_3\text{H}][\text{EtOH}] \quad (\text{iv})$$

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



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