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SILICA-SUPPORTED IRIDIUM-PHOSPHINE CATALYSTS FOR THE REACTION OF SILANES WITH ALCOHOLS

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Summary

Silica-supported iridium catalysts have been evaluated in the reactions of $HSiR_3$ (R = Et, OEt) and $Me_3SiO[Si(H)(Me)O]_nSiMe_3$ (PS1, $n = 1$; PS50, $n \sim 50$) with a wide variety of primary alcohols. Catalysts obtained by reaction of $IrCl(CO)[Ph_2P(CH_2)_2Si(OEt)_3]_2$ with silica are rapidly deactivated in a manner similar to the related homogeneous systems. More active catalysts are obtained by treating the silica first with $Ph_2P(CH_2)_2Si(OEt)_3$ and then with $[IrCl(C_8H_{14})_2]_2$. The order of reactivity of the silanes is PS50 $\gg$ $HSi(OEt)_3$ $>$ $HSiEt_3$ $\gg$ PS1, and that of the alcohols reflects principally the bulk of the organic group. Kinetic analysis indicates two pathways involving iridium bound to the phosphine and directly to the silica. The $^{29}Si\{^1H\}$ NMR spectra of PS50 and the product of its reaction with $Ph(CH_2)_2OH$ are reported.

Introduction

Homogeneous catalysis of the O-silylation reaction (eq. 1) has been effected with complexes of iron [1], cobalt [2—4], ruthenium [4—6], and iridium [7].

$$R_3SiH + HOR' \rightarrow R_3Si(OR') + H_2 \qquad (1)$$

However, in practice, especially for large-scale reactions, heterogeneous systems have many advantages. We have therefore attempted to bind some of the homogeneous catalysts to insoluble supports and we report now our results with the ligand $Ph_2P(CH_2)_2Si(OEt)_3$ bound to silica. Such a system was first described by Allum et al. [8] and this, or related systems, containing cobalt, nickel, rhodium or iridium have been used in hydrogenation or hydroformylation [9—12], but none has been applied to O-silylation.

Experimental

The siloxane mixture $Me_3SiO[Si(H)(Me)O]_nSiMe_3$ ($n = 1$, denoted by PS1; n = ca. 50, denoted by PS50) were gifts from Dow Corning, Ltd. The complexes $[IrCl(C_8H_{14})_2]_2$ and $IrCl(CO)_2(H_2NC_6H_4CH_3\text{-}p)$, and the ligand $Ph_2P(CH_2)_2Si(OEt)_3$ were prepared by the literature methods [8,13,14]. Analytical data were provided by the Microanalytical Laboratory of this Department: data for P and Ir in the silica-supported samples are subject to large uncertainties. ^{29}Si NMR spectra were obtained with a Bruker WP80 spectrometer.

Chlorocarbonylbis(2-triethoxysilylethyldiphenylphosphine)iridium(I)

The complex $IrCl(CO)(H_2NC_6H_4CH_3\text{-}p)$ (0.50 g, 1.3 mmol) was added to a stirred solution of $Ph_2P(CH_2)_2Si(OEt)_3$ (0.96 g, 2.6 mmol) in CH_2Cl_2 (3 cm^3) under nitrogen. Addition of MeOH (15 cm^3) precipitated the yellow product. Yield, 0.84 g (65%). $\nu(CO)$ 1961 cm^{-1}. (C, 48.5; H, 5.7; Cl, 3.4; Ir, 19.1%. Calcd.: C, 48.8; H, 5.6; Cl, 3.5; Ir, 19.1%).

Silica-supported siloxyethyldiphenylphosphine

Silica (Crossfield U_{30}) was washed with dilute hydrochloric acid and water and dried at 180°C. The washed silica (10 g) was suspended in sodium-dry toluene (40 cm^3), $(EtO)_3Si(CH_2)_2PPh_2$ (3 cm^3) was added, and the mixture was vigorously refluxed with continuous removal of ethanol from the refluxate for 6 hours. The silica was recovered by filtration and any unbound ligand removed by Soxhlet extraction with toluene.

The complex $IrCl(CO)[Ph_2P(CH_2)_2(OEt)_3]_2$ was bound to silica in an analogous manner.

Supported iridium catalyst

The silica-supported phosphine in toluene was treated with $[IrCl(C_8H_{14})_2]_2$ for two hours at room temperature. The solid was recovered, extracted with boiling toluene for 6 hours, and dried.

Catalysis experiments

Reactions were conducted at constant pressure in a flask fitted with a nitrogen inlet, a suba-seal, and a gas burette. The solvent, silane, and catalyst were placed in the flask which was then purged with nitrogen while the temperature was adjusted to that required. The nitrogen flow was stopped, the gas burette set to zero, and the alcohol injected by syringe.

Results

The complexes $IrCl(CO)L_2$ [$L = Ph_2P(CH_2)_2Si(OEt)_3$] and $IrClL_2$ (prepared in situ from $[IrCl(C_8H_{14})_2]_2 + 4L$) behaved as homogeneous catalysts in a similar manner to the previously investigated iridium complexes [7]. Their use in silica-supported systems was therefore examined.

The complex $IrCl(CO)L_2$ was anchored to silica by refluxing in toluene, the ethanol produced being continually removed by azeotropic distillation. Two batches of catalyst were thus obtained, containing ca. 1% and 5% iridium (Table 1). Both were effective in catalysing the room-temperature reaction of PS50

TABLE 1

ANALYTICAL DATA FOR SUPPORTED CATALYSTS (%)

	Batch	Ir [a]	P [a]	C	H	P : Ir
$IrCl(CO)L_2$	I	4.9				
	II	1.2				
$[IrCl(C_8H_{14})_2]_2/L$	I	1.2		5.4	1.1	
	II	1.2	0.5	6.5	1.1	2.5
	III	1.5	0.5			2.1
	IV	1.0	0.34			2.1
	V	2.6	0.46	14	2.0	1.1
	VI	1.2	1.05	6.1	1.1	5.4
	VII	1.6				

[a] ±0.3%.

with ethanol, geraniol, citronellol, and 2-phenylethanol; the rate of reaction decreased in the order given. The catalytic behaviour was qualitatively similar to the homogeneous $IrCl(CO)L'_2$ systems (L' = tertiary phosphine or arsine), in that the rate increased with increase in the concentration of either reagent or of the catalyst. When the catalyst was recovered by filtration and re-used with fresh reagents, the reaction was considerably slower and became effectively zero on further recovery and re-use. Work with this system was therefore abandoned.

A second supported catalyst was prepared by treating silica first with the ligand $(EtO)_3Si(CH_2)_2PPh_2$ and then with $[IrCl(C_8H_{14})_2]_2$. These products contained 1—2% iridium and 0.3—1.0% phosphorus, giving P : Ir ratios in the range 1 : 1 to 5 : 1 (Table 1). All were active catalysts for the reaction of $HSi(OEt)_3$ or PS50 with a range of alcohols. The reactions (in toluene solution) were monitored at constant pressure by measuring the volume of hydrogen evolved. Confirmation was obtained by quantitative GLC and IR measurements that the rate of production of hydrogen was equal to those of formation of $Si(OEt)_4$ and of consumption of the silane. With an amount of the catalyst corresponding to about ten millimoles of iridium per mole of Si—H, reactions with ethanol proceeded smoothly and rapidly at room temperature, e.g. to 50% in 80 minutes with a 2.0 : 1.0 : 0.01 EtOH : $HSi(OEt)_3$: Ir system. Higher alcohols gave slower reactions, and most experiments were conducted at 40°C.

The rate of reaction of ethanol decreased, cet. par., in the order PS50 $\gg$ $HSi(OEt)_3 > HSiEt_3 \gg$ PS1. Towards $HSi(OEt)_3$, the order of reactivity of simple alcohols was MeOH > EtOH > Pr^iOH; Bu^tOH and eugenol were completely unreactive. A wider range of alcohols was investigated with PS50 and the following order was found: EtOH $\gg$ citronellol, geraniol, *p*-anisylalcohol, 2-phenylethanol > menthol > 2-ethylhexane-1,3-diol > eugenol.

Good reproducibility was obtained with different samples of any one batch of catalyst (Fig. 1), demonstrating the homogeneity of the preparation. However, different batches gave different reactivities which correlated neither with the total iridium content nor with the P : Ir ratio (Fig. 2). Indeed, the catalyst with the greatest iridium content was the least active.

Detailed studies were made on the EtOH/$HSi(OEt)_3$ system with one batch

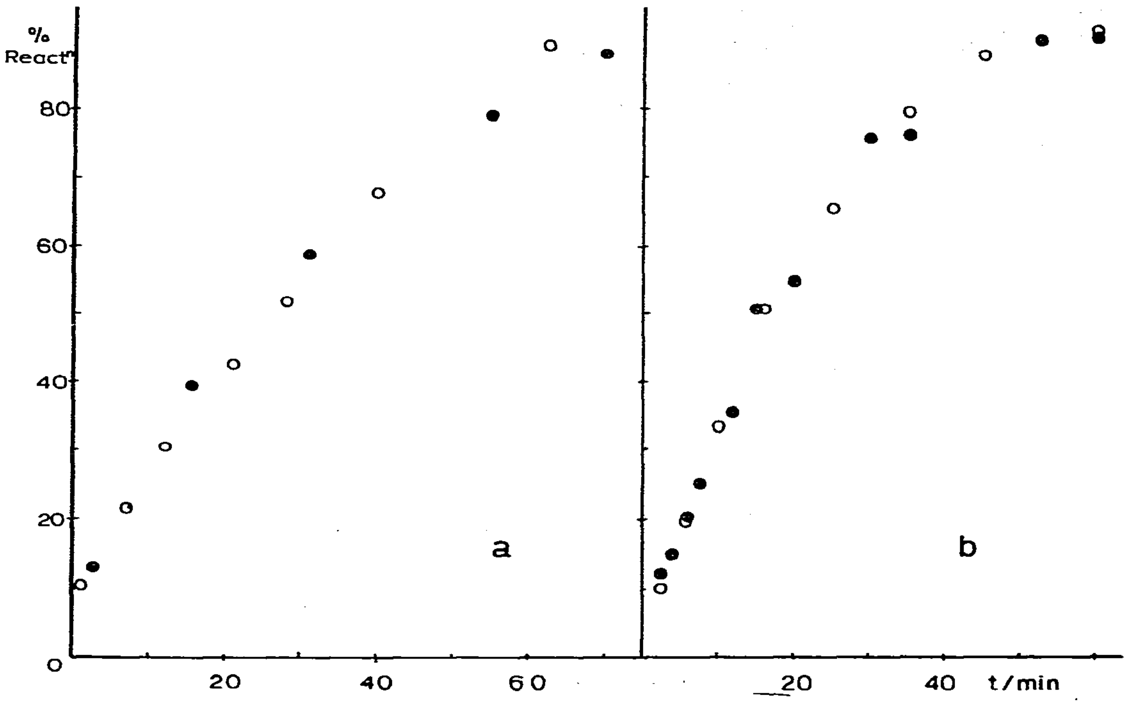

Fig. 1. Reproducibility of reactions. (a) $[EtOH]_{init}$, 0.294 mol dm^{-3}; $[HSi(OEt)_3]_{init}$, 0.717 mol dm^{-3}; catalyst, 0.7 g batch VI (0.044 mmol Ir); solvent, toluene; temperature, 40°C. (b) $[Ph(CH_2)_2OH]_{init}$, 0.147 mol dm^{-3}; $[PS50]_{init}$, 0.717 mol(Si—H) dm^{-3}; catalyst, 0.7 g batch III (0.055 mol Ir); solvent, toluene; temperature, 40°C.

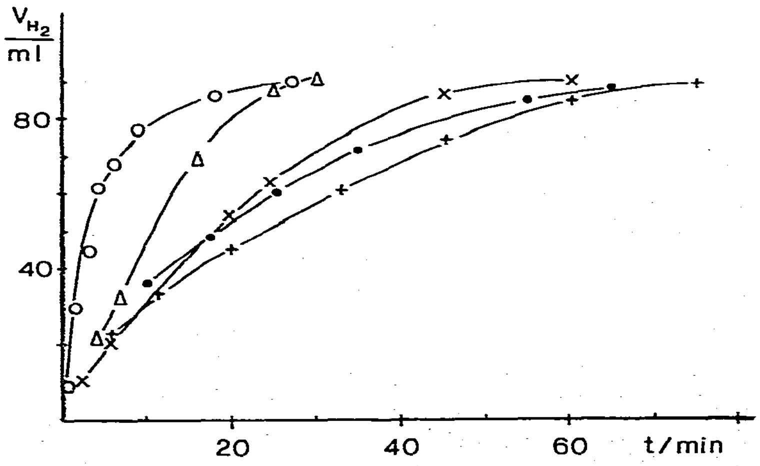

Fig. 2. Reaction profiles with different catalyst preparations. $[Ph(CH_2)_2OH]_{init}$ 0.147 mol dm^{-3}; $[PS50]_{init}$ 0.717 mol(Si—H) dm^{-3}; catalyst, 0.7 g; solvent, toluene; temperature, 55°C.

	Batch	[Ir] (mmol)	P : Ir	$10^3 k_s$ (s^{-1})	$10^3 k_{s,Ir}$ (s^{-1} mol^{-1})
○	II	0.044	2.5	4.5	41
△	IV	0.037	2.1	1.3	11
×	III	0.055	2.0	0.67	6.8
●	VI	0.044	5.4	0.67	6.8
+	V	0.095	1.1	0.50	5.0

of catalyst. The rate of reaction increased with increase in the initial concentration of the silane (Fig. 3a) and in the amount of catalyst (Fig. 3b), but was relatively insensitive to change in the initial concentration of the alcohol (Fig. 3c). These observations suggest probable first-order dependence on the silane and the catalyst, and zero or fractional order in ethanol. That the effect of change in ethanol concentration was not due to a change in the polarity of the mixture was shown by experiments with a range of solvents (toluene, chlorobenzene, 1,2-dichlorobenzene, tetrahydrofuran); the rates were identical except in THF, in which the reaction was appreciably slower. Increasing polarity thus leads to a decrease in rate, whereas increase in ethanol concentration gives an increase. The data of Fig. 3a show a good first-order dependence on the silane up to 70—80% reaction, and the rate constants, k_s, are proportional to the total amount of catalyst present (Table 2). Similar analysis of the data of Fig. 3c gives first-order rate constants which increase with increasing concentration of ethanol (Table 3). The dependence is linear but does not show direct proportionality:

$$10^3 k_s(\mathrm{s}^{-1}) = 0.26 + 0.056[\mathrm{EtOH}](\mathrm{mol\ dm}^{-3}).$$

The rate law thus has two terms, one second-order overall, the other third-order overall, suggesting two concurrent mechanisms.

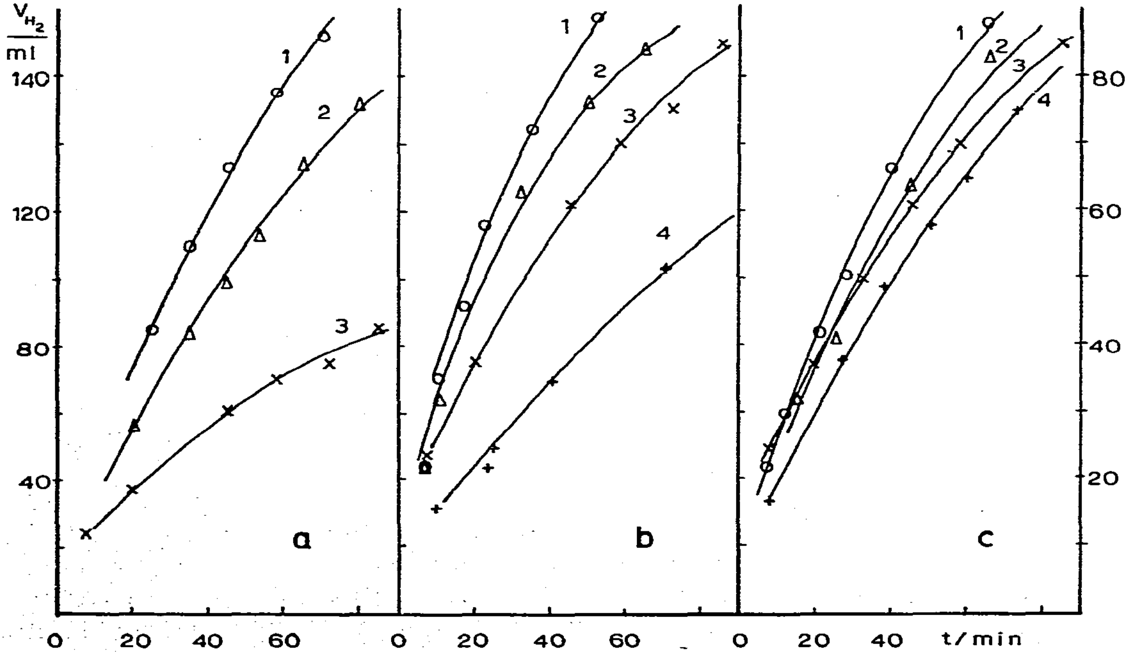

Fig. 3. Effect of varying the concentration of reagents. (a) $[\mathrm{EtOH}]_{\mathrm{init}}$, 0.147 mol dm^{-3}; catalyst 0.7 g batch IV; $[\mathrm{HSi(OEt)_3}]_{\mathrm{init}}$ (mol dm^{-3}) 0.294 (1), 0.210 (2), 0.073 (3). (b) $[\mathrm{EtOH}]_{\mathrm{init}}$ 0.147 mol dm^{-3}; $[\mathrm{HSi(OEt)_3}]_{\mathrm{init}}$ 0.0717 mol dm^{-3}; catalyst batch IV 1.5 g (1), 1.2 g (2), 0.7 g (3), 0.4 g (4). (c) $[\mathrm{HSi(OEt)_3}]_{\mathrm{init}}$ 0.0717 mol dm^{-3}; catalyst 0.7 g batch IV; $[\mathrm{EtOH}]_{\mathrm{init}}$ (mol dm^{-3}) 0.287 (1), 0.215 (2), 0.143 (3), 0.0717 (4). Note the change in vertical scale for (b) and (c).

TABLE 2

FIRST-ORDER DEPENDENCE ON [$HSi(OEt)_3$] AND [Ir] FOR THE $EtOH$—$HSi(OEt)_3$ REACTION

Catalyst (g)	[Ir] (mmol)	$10^3 k_s$ (s^{-1})	$10^3 k_{s,Ir} = 10^3 k_s/[Ir]$ (s^{-1} $mmol^{-1}$)	
0.400	0.025	0.185	7.3	Average: 7.1 s^{-1} $mmol^{-1}$
0.700	0.044	0.337	7.7	
1.20	0.075	0.482	6.5	
1.50	0.094	0.638	6.8	

Conditions: $[EtOH]_{init}$, 0.147 mol dm^{-3}; $[HSi(OEt)_3]_{init}$, 0.0717 mol dm^{-3}; solvent, toluene; catalyst, batch VI (1.2% Ir); temperature, 40°C.

In the majority of cases the reactions went rapidly to more than 80% completion. If at this stage additional reactants were added, the reaction recommenced at a rate similar to or slightly greater than that of the original reaction. Similar observations were made when the catalyst was recovered by filtration and re-used with fresh reactants.

Reactions between PS50 and citroneliol or 2-phenylethanol were carried out in the absence of a solvent at 55°C (mole ratio alcohol : Si—H : Ir 10 : 10 : 0.011). The reaction with citronellol was rapid, ca. 35% in 100 minutes and complete in less than 12 hours. 2-Phenylethanol reacted considerably more slowly, giving 30% reaction in 5 hours, but not reaching completion after 24 hours. The product of this reaction was analysed by ^{29}Si NMR spectroscopy (see below).

The ^{29}Si {^1H} NMR spectrum of PS50 shows three resonances (Fig. 4a). The main signal is at —34.1 ppm * and is due to the skeletal O—*Si*(Me)(H)—O groups. Two smaller signals have comparable intensities. That at lower field (10.6 ppm) is assigned to the terminal Me_3*Si*—O groups. The second small signal is close to the main resonance (—34.9 ppm) and is probably due to the terminal MeSiH groups, Me_3SiO—*Si*(Me)(H)—O. The spectrum of the product of reaction with $Ph(CH_2)_2OH$ is shown in Fig. 4b. The low-field band is retained, that at —34.1 ppm is considerably reduced in intensity, and that at —34.9 ppm has disappeared; strong new bands are evident at ca. —57 ppm. These last must be due to silicon atoms which have undergone O-silylation, O—*Si*(Me)(OR)—O (R = CH_2CH_2Ph). The upfield chemical shift is consistent with the presence of an additional electronegative substituent, since $Si(OEt)_4$ gave a single resonance at —81.5 ppm. The signal at —57 ppm has three components, indicating the presence of O—Si(Me)(OR)—O groups with different neighbour groups depending on whether reaction has occurred at isolated silicon atoms (A), at adjacent pairs of atoms (B), or at larger groups of adjacent atoms (C). The retention of a small band at —34.1 ppm indicates that reaction is not complete. Integration suggests that ca. 10% of the Si—H groups remain; the most intense peak thus probably corresponds to silicon atoms of type C. The smallest peak of this set may correspond to the terminal Me_3SiO—*Si*(Me)(OR)—O groups; the terminal

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* Chemical shifts are downfield from Me_4Si.

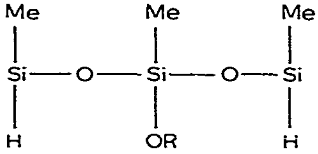
TABLE 3

FIRST-ORDER RATE CONSTANTS AS A FUNCTION OF [EtOH]

$[\mathrm{EtOH}]_{\mathrm{init}}$ (mol dm^{-3})	0.72	1.43	2.15	2.87
$10^3 k_s$(s^{-1})	0.30	0.34	0.37	0.42

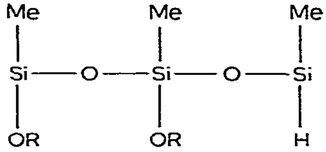
Other conditions: $[\mathrm{HSi(OEt)_3}]_{\mathrm{init}}$, 0.072 mol dm^{-3}; catalyst, 0.7 g, batch VI; solvent, toluene; temperature, 40°C.

Si—H groups would be expected to react rapidly.



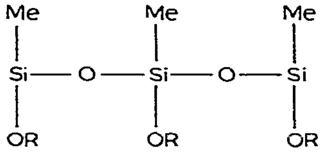
$\underset{H}{\overset{Me}{Si}}-O-\underset{OR}{\overset{Me}{Si}}-O-\underset{H}{\overset{Me}{Si}}$

(A)



$\underset{OR}{\overset{Me}{Si}}-O-\underset{OR}{\overset{Me}{Si}}-O-\underset{H}{\overset{Me}{Si}}$

(B)



$\underset{OR}{\overset{Me}{Si}}-O-\underset{OR}{\overset{Me}{Si}}-O-\underset{OR}{\overset{Me}{Si}}$

(C)

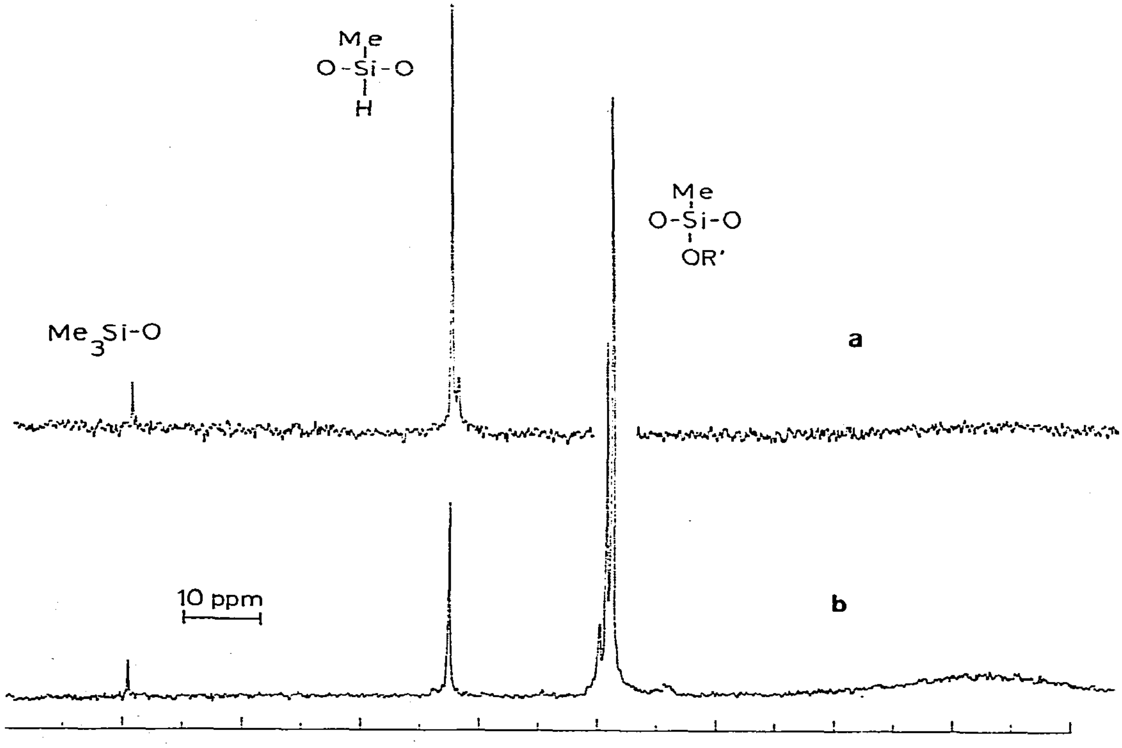


Fig. 4. ^{29}Si $\{^1$H$\}$ NMR spectra for (a) PS50 and (b) the product of reaction of PS50 with $\mathrm{Ph(CH_2)_2OH}$.

Discussion

Catalysts based on silica-supported complexes of the type $\mathrm{IrCl(CO)L_2}$ were initially very active but rapidly lost their activity. Similar behaviour was observed in the homogeneous systems [7], where deactivation was attributed to the formation of complexes of the type $IrHCl_2(CO)L_2$ and $IrH_2(SiR_3)(CO)L_2$, which are not catalytically active. It is likely that similar processes occur in the present case.

Catalysts prepared by the reaction of $[IrCl(C_8H_{14})_2]_2$ with a silica-supported tertiary phosphine showed slightly lower initial activity but greater longevity. The several batches of catalyst examined showed a range of activities which did not correlate with the P : Ir ratio or even with the total iridium content. In the homogeneous systems, activity decreased with increase in the P : Ir ratio, and became almost zero at P : Ir = 3 : 1. In the present case, iridium may be bound to the support in several ways: by direct absorption on the silica surface or by coordination to one or more phosphine groups. Each type of iridium would display different activity, and the variations observed between different batches of catalyst may reflect different distributions of the metal.

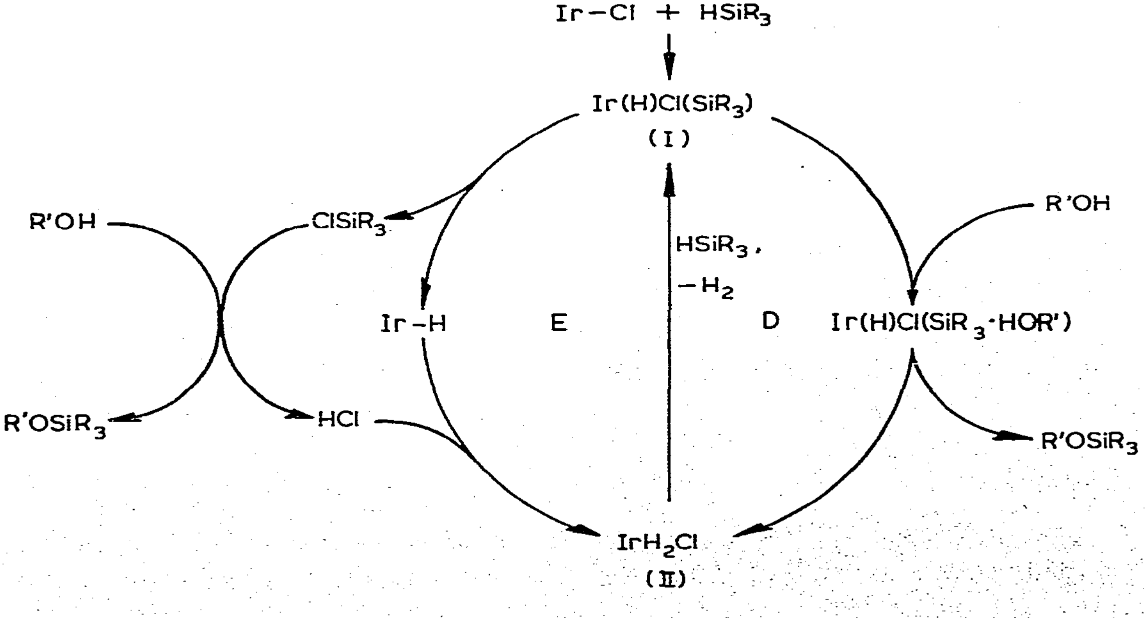
A simple kinetic analysis of the catalysed reaction between EtOH and $HSi(OEt)_3$ gave a two-term rate law of the type

$$d[H_2]/dt = k[Ir][HSi(OEt)_3]\{a + b[EtOH]\}.$$

This suggests the occurrence of two simultaneous mechanistic pathways, presumably involving iridium in different sites. One route appears to give first-order dependence on the silane and iridium, but is zero-order with respect to the alcohol. Such behaviour is reminiscent of the homogeneous systems involving $IrClL_2$ as catalyst, for which the rates were also independent of the concentration of the alcohol [7]. This route may thus be tentatively identified with catalysis by phosphine-bound iridium. The second route shows first-order dependence on the concentrations of both reactants and of iridium, and must involve

SCHEME 1

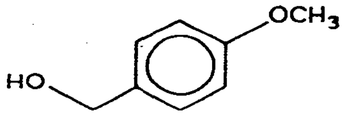
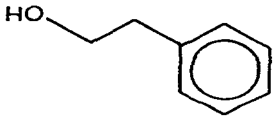
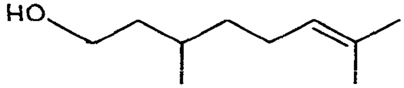
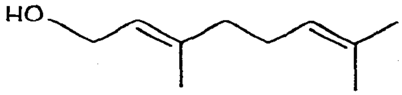
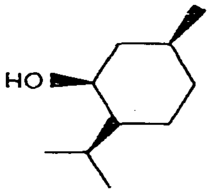
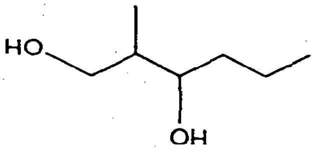
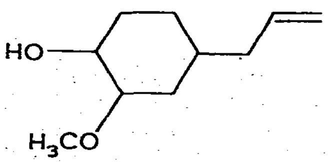
(The phosphine ligands have been omitted for the sake of clarity)



a different site, possibly formed by direct absorption of the iridium complex on the silica surface. Separate experiments showed that the iridium complex was absorbed by silica which had not been treated with the phosphine. The complex was also absorbed by silica which had been pretreated with $MeSiCl_3$. Both materials were active catalysts.

TABLE 4

REACTIVITY SEQUENCE OF ALCOHOLS

Alcohol	Structure
p-anisyl alcohol	
2-phenylethanol	
citronellol	
geraniol	
menthol	
2-ethylhexane-1,3-diol	
eugenol	

Two major mechanisms have been suggested for the catalysis of O-silylation reactions by transition metals (Scheme 1). Both involve initial oxidative addition of the silane to the metal to give a hydridosilyl complex (I). Complex I may then undergo direct nucleophilic attack at the coordinated silicon (loop D), or elimination of a chlorosilane which reacts with the alcohol (loop E). In the latter case, an unstable iridium(I) hydrido complex is formed which rapidly reacts with the hydrogen chloride liberated by the alcohol-chlorosilane reaction. In both cases, a dihydridoiridium(III) complex, II, is finally produced which can lose hydrogen in reacting with the silane to regenerate I. The chlorosilane-elimination route is thought to operate with catalysts of the type $IrCl(CO)L_2$ [7], and the direct-attack route has been suggested for catalysis by $IrClL_2$ [7] and by iron or cobalt complexes [1,3]. First-order dependence on the silane and the catalyst would be expected for either mechanism. First- or zero-order dependence on the alcohol is also compatible with either mechanism, depending on the relative rates of the initial and subsequent steps.

When the initial concentration of the silane was increased, the reaction rate increased but not in direct proportion. This may mean that one mechanistic route is inhibited by an excess of the silane. In the homogeneous $IrCl(CO)L_2$-catalysed systems, inhibition by the silane occurs by formation of the catalytically inactive $IrH_2(SiR_3)(CO)L_2$, and an analogous process may operate in the present case. If this is so, it is likely that the two concurrent mechanisms observed here are different in type, since it seems unlikely that the direct-attack mechanism would show this type of inhibition.

As observed previously [7], the polysilane PS50 reacted considerably more rapidly than $HSi(OEt)_3$. Since $HSiEt_3$ reacted more slowly than $HSi(OEt)_3$, the reactivity of PS50 cannot be an electronic effect, but could be due to the proximity of the Si—H bonds. On the direct attack mechanism, cleavage of the Ir—Si bond is rapidly followed by the formation of a new Ir—Si bond, and this might be facilitated by the involvement of adjacent silicon atoms of the polysilane.

In the reactions of any one silane with a range of alcohols, the reactivity order reflects principally the size of the organic group (Table 4), but also accords with the expected nucleophilicities.

Acknowledgements

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