Organosilicon Chemistry. Part 24.[1] Homogeneous Rhodium-catalysed Hydrosilation of Alkenes and Alkynes: The Role of Oxygen or Hydroperoxides

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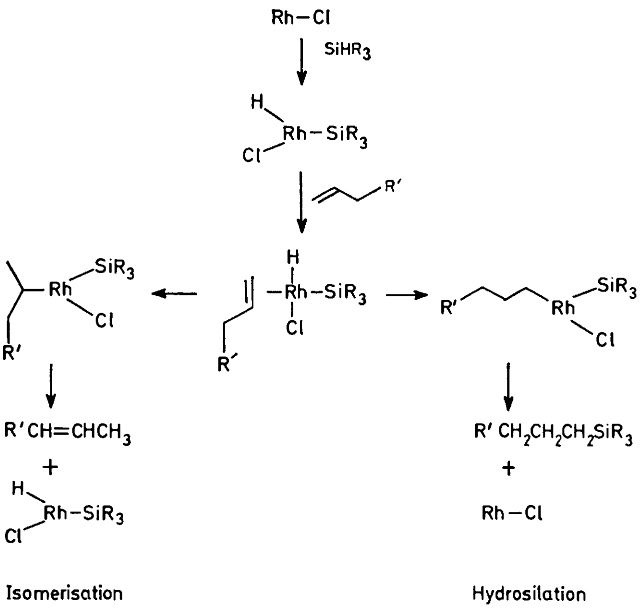
The hydrosilation of propene, hex-1-ene, and hex-1-yne, catalysed by $[RhCl(PPh_3)_3]$ has been reinvestigated. When all reagents are carefully purified, the hydrosilation reaction is completely inhibited but can be initiated by the addition of oxygen or t-butyl hydroperoxide. The rate and extent of reaction in the latter case is unaffected by the presence of phenolic radical traps. For optimum reaction, stoicheiometric quantities of hydroperoxide are required. In the hex-1-yne system, variation of the PPh_3 : Rh ratio gives maximum activity at 1 : 1 and, with this stoicheiometry, the reaction rate is relatively insensitive to purification of the reagents. It is suggested that the role of oxygen or hydroperoxide is to remove triphenylphosphine from the system, by oxidation, generating a highly active catalyst with a low PPh_3 : Rh ratio. In the ' clean ' conditions isomerisation of hex-1-ene proceeds rapidly, being catalysed by the silyl complex $[RhH(Cl)(SiR_3)(PPh_3)_2]$.

RHODIUM(I) complexes are known to be good catalysts for the hydrosilation of alkenes and alkynes, the complexes $[\{RhCl(C_2H_4)_2\}_2]$ and $[RhCl(PPh_3)_3]$ being particularly effective.[2-9] Although no detailed mechanistic studies have been made, it is generally assumed that the mechanism is similar to that of hydrogenation, *i.e.* oxidative addition of the silane to the metal (Si–H cleavage), co-ordination and insertion of the substrate into the Rh–H bond, followed by reductive elimination of the product (Scheme).[3,5] A report [8] of predominant *trans* addition to alkynes appeared to be in conflict with this mechanism, but we have recently shown [9] that the initial product of the $[RhCl(PPh_3)_3]$-catalysed addition of $SiEt_3H$ to hex-1-yne is the *trans* isomer (*i.e. cis* addition) which subsequently isomerises in the presence of the catalyst and the silane. The hydrosilation of long-chain alkenes is also complicated by isomerisation, which gives internal isomers which are unreactive to hydrosilation.[4,5] The isomerisation presumably proceeds by insertion of the alkene into the Rh–H bond of the silyl adduct, *i.e.* it involves an intermediate similar to that postulated for the hydrosilation reaction (Scheme). It was surprising to find that the rates of the two reactions were affected differently by changes in the catalyst concentration.[7] We therefore undertook a more thorough examination of the system, which proved to be unexpectedly complicated, and to demonstrate a critical dependence on the purity of the substrate.



SCHEME Neutral ligands are omitted, and no specific stereochemistry is implied

RESULTS

Hydrosilation of Propene.—Attempts to follow the rate of consumption of the silane in the hex-1-ene–$SiEt_3H$–$[RhCl(PPh_3)_3]$ system gave erratic results and was complicated by the isomerisation of the alkene. It was therefore decided to use propene, which could not isomerise. Reactions were carried out at constant volume, with the silane and catalyst dissolved in benzene at 40 °C; the progress of the reaction was monitored by the change in pressure, assuming propene to be an ideal gas. The rate of dissolution of propene in benzene was considerably greater than the consumption rate during any of the reactions, so that limitation of the rate by diffusion was not possible. Using $[RhCl(PPh_3)_3]$ or $[\{RhCl(C_8H_{14})_2\}_2]$ (C_8H_{14} = cyclooctene) with or without the addition of PPh_3, it was not possible to obtain reproducible or consistent results. It was observed that, when reaction was slow, the solution remained a clear yellow throughout but, when reaction was rapid, the solution darkened and sometimes gave a black deposit. The darkening suggested that the catalyst was decomposing, possibly through the adventitious presence of oxygen. With systems containing 2 or 3 mol of PPh_3 per Rh atom, careful exclusion of oxygen gave a dramatic reduction in rate, effectively to zero (Table). On adding oxygen to the system, reaction immediately commenced and the solution began to darken. The darkening was thought to be due to the formation of metallic rhodium, raising the possibility that the reaction was heterogeneously catalysed. However, the reaction appeared to slow down as deposition of the solid progressed, and a sample of the solid exhibited low catalytic activity. It appears that, in the presence of oxygen, a more active catalytic species is produced but that eventually decomposition of the catalyst occurs. When the PPh_3 : Rh ratio was less than 2 : 1, rapid reaction occurred in the absence of oxygen.

*Hydrosilation of Hex-*1*-ene*.—The hex-1-ene–$SiEt_3H$–[$RhCl(PPh_3)_3$] system was reinvestigated, monitoring the consumption of the silane by the intensity of the Si–H stretching band in the i.r. spectra of the solutions. Initial results were similar to those reported previously.[7] However, when all the reagents were carefully purified, no hydrosilation was observed with $SiEt_3H$, $SiH(OEt)_3$, or $SiMePh_2H$, but isomerisation of the alkene occurred. For example, in chlorobenzene at 50 °C with mol ratios $SiEt_3H$: C_6H_{12} : [$RhCl(PPh_3)_3$] = 1 : 2 : 10^{-3}, no silane had been consumed after 30 min, but only 27% of the original hex-1-ene remained; *cis*-hex-2-ene (42.2%), *trans*-hex-2-ene (25.0%), and *trans*-hex-3-ene (3.4%), together with a trace (1.8%) of hexane, had been formed. The yellow colour of the reaction mixture suggested the presence of the silyl complex [$RhH(Cl)(SiEt_3)(PPh_3)_2$] which, being a co-ordinatively unsaturated metal hydride, might be expected to be a good isomerisation catalyst. This was confirmed by reactions conducted in sealed n.m.r. tubes. Purified hex-1-ene isomerised slowly at room temperature in the presence of the $SiEt_3$ complex or of the $Si(OEt)_3$ complex. For instance, with the latter complex in $CDCl_3$, hex-1-ene was 75% isomerised in 4 h, during which time the concentration of the silyl complex remained constant and no hydrosilation was detected. After $\geqslant$15 h, traces of a new $Si(OEt)_3$ species were observed, presumably $C_6H_{13}Si(OEt)_3$, and no hex-1-ene remained. Hexene isomers (*cis*-2, 15.8%; *trans*-2, 56.5%; *trans*-3, 18.6%) and a little hexane (9%) were found by g.l.c. analysis.

Reaction of propene with triethylsilane with exclusion and addition of air [a]

Catalyst	$-d[C_3H_6]/dt$ [b,c] mmol min^{-1}	Extent of reaction [c] (%)	Reaction time [c] (min)	$-d[C_3H_6]/dt$ [b,d] mmol min^{-1}	Extent of reaction [d] (%)	Reaction time [d] (min)
[$RhCl(PPh_3)_3$]	0.006	2.3	120	0.360	37	220
	0.005	1.7	140			
	0.005	3.3	240	0.270	49	130
	0.002	1.0	120	0.806	33	30
[$\{RhCl(C_8H_{14})_2\}_2$]	0.927	100	60			
[$\{RhCl(C_8H_{14})_2\}_2$] + 2 PPh_3	0.556	74	90			
[$\{RhCl(C_8H_{14})_2\}_2$] + 4 PPh_3	0.000	0	360			
[$\{RhCl(C_8H_{14})_2\}_2$] + 6 PPh_3	0.000	0	280			
Rh [e]	0.202	60	120			

[a] In benzene at 40 °C, initial pressure of propene, 650 mmHg; initial amount of $SiCl_3H$, 30 mmol. [b] Initial rate. [c] Before admission of air. [d] After admission of air. [e] Prepared from [$\{RhCl(C_8H_{14})_2\}_2$] + $SiEt_3H$, and washed with hexane.

The reaction of purified hex-1-ene with $SiEt_3H$ could be promoted by the addition of oxygen, giving a red reaction mixture which darkened and precipitated metallic rhodium, at which point the reaction stopped. When atmospheric oxygen was rigorously excluded but unpurified hexene was used, reaction again proceeded and was faster when the hexene was pretreated by exposure to u.v. light in the presence of air. The unpurified hexene would be expected to contain traces of hydroperoxide, the amount of which would be increased by the pretreatment. The addition of t-butyl hydroperoxide to a ' clean ' unreactive system gave an immediate rapid reaction. In these experiments purified hex-1-ene was used and the system was monitored for a period before addition of the hydroperoxide, to establish that no reaction was occurring. Reaction commenced immediately after the injection of Bu^tOOH, but the silane was never completely consumed. However, results were now completely reproducible. The amount of silane reacting decreased with increase in the period before addition of the hydroperoxide (Figure 1), confirming that isomerisation of the hex-1-ene was occurring in the ' clean ' system. The internal isomers are unreactive to hydrosilation,[4,7] and cyclohexene was shown not to react even in the presence of hydroperoxide. That catalyst deactivation was not the cause of the incomplete reactions was shown by adding a further amount of [$RhCl(PPh_3)_3$] to a finished reaction; no further consumption of silane occurred. However, when additional hex-1-ene was added, the reaction recommenced (Figure 1). The rate of reaction was dependent on the amount of hydroperoxide added, and optimum results were obtained at 1 : 1 $\leqslant$ Bu^tOOH : [$RhCl(PPh_3)_3$] $\leqslant$ 4 : 1. At ratios less than 1 : 1 there was no activation of the system, while at ratios greater than 10 : 1 reduced activity and decomposition of the catalyst were found. Di-t-butyl peroxide was completely ineffective as an activator.

When the hydroperoxide was added to the yellow ' clean ' system, a red colour developed which faded to yellow at the close of the reaction or when further amounts of hex-1-ene were added; thus, the red colouration is not due to colloidal metal. Precisely similar reaction profiles were observed when the addition of the silane to the C_6H_{12}–Bu^tOOH–[$RhCl(PPh_3)_3$] mixture was delayed for 20 min, and the reactions were also unaffected by the presence of phenolic radical inhibitors (2,4,6-tri-t-butylphenol or

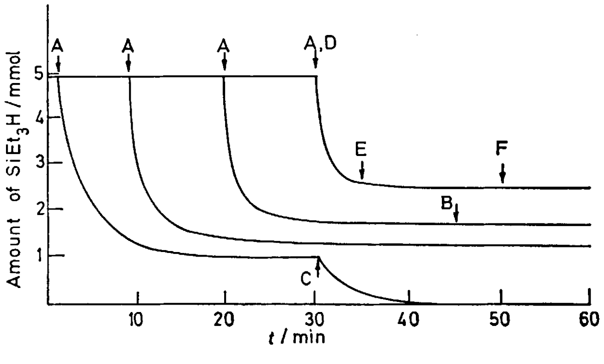


FIGURE 1 Reaction between purified hex-1-ene (10 mmol) and triethylsilane (5 mmol) at 50 °C with [$RhCl(PPh_3)_3$] as catalyst (0.005 mmol). At points marked A, Bu^tOOH (0.02 mmol) was added; at B, [$RhCl(PPh_3)_3$] was added; at C, hex-1-ene and Bu^tOOH were added. The composition of the hydrocarbon present at points D, E, and F were: hex-1-ene, 27.6, 2.1, and 0.0%; *cis*-hex-2-ene, 42.2, 39.3, and 33.6%; *trans*-hex-2-ene, 25.0, 49.4, and 50.4%; *trans*-hex-3-ene, 3.4, 8.5, and 9.6%; n-hexane, 1.8, 0.7, and 6.4%, respectively

2,6-di-t-butyl-*p*-cresol, 10 : 1 relative to Bu^{t}OOH). The reaction was completely inhibited by the hydroperoxide-decomposition agent tetraphenylbis(dithiene)nickel[10,*] (present at 0.125 of the concentration of Bu^{t}OOH and 0.5 of that of the rhodium complex), but in this case the hexene isomerisation was also inhibited, suggesting that the catalyst had been poisoned.

That the hydroperoxide did not influence the course of the reaction was demonstrated by isolation of the products. G.l.c. and n.m.r. analyses showed that the major product was triethyl-n-hexylsilane. A minor product appeared to be a triethylhexenylsilane; the position of the double bond could not be established, but it is presumably in the 1-position.

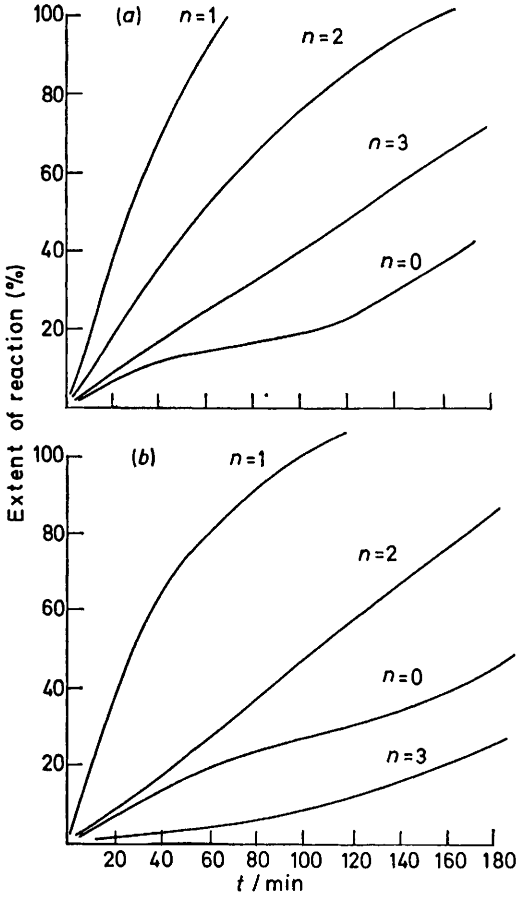


FIGURE 2 Reaction between hex-1-yne (12.5 mmol) and triethylsilane (12.5 mmol) at 60 °C with $[\{RhCl(C_8H_{14})_2\}_2] + 2n\ PPh_3$ as catalyst (0.04 mmol of Rh); (*a*) unpurified reagents; (*b*) purified reagents

The concurrence of hydrosilation and isomerisation was also demonstrated by changing the $C_6H_{12} : SiEt_3H$ ratio. At 2 : 1, with Bu^{t}OOH added after 20 min, 30% of the silane was consumed, while at 4 : 1, 80% was consumed. This difference represents the greater amount of hex-1-ene remaining after isomerisation during the 'clean' period. Isomerisation was eliminated by using triethylvinylsilane as alkene. Under 'clean' conditions, the vinylsilane did not react with $SiEt_3H$, $SiH(OEt)_3$, or $SiMePh_2H$. When Bu^{t}OOH was added, reaction with $SiMePh_2H$ went rapidly to completion.

The complexes $[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir) were also investigated briefly as catalysts for the C_6H_{12}–$SiEt_3H$ reaction. Under 'clean' conditions neither complex catalysed the reaction. With the addition of Bu^{t}OOH, the rhodium complex gave a reaction which was considerably slower than that with $[RhCl(PPh_3)_3]$, while the iridium complex remained ineffective. The bis(phosphine) complex $[RhCl(PPh_3)_2]$ was formed by *in situ* reaction of $[\{RhCl(C_8H_{14})_2\}_2]$ with the stoicheiometric amount of PPh_3, but was also ineffective under 'clean' conditions. The addition of Bu^{t}OOH gave results identical to those with the tris(phosphine) complex. The use of higher PPh_3 : Rh ratios (up to 10 : 1) gave progressive diminution in the effectiveness of the hydroperoxide. The hydroperoxide alone, in the absence of the rhodium complexes, gave no hydrosilation.

*Hydrosilation of Hex-*1*-yne.*—The reaction between hex-1-yne and $SiEt_3H$ or $SiH(OEt)_3$ is similarly quenched by purification of the alkyne. Under 'clean' conditions, neither $[RhCl(PPh_3)_3]$ nor $[IrCl(CO)(PPh_3)_2]$ exhibited any catalytic activity, although with unpurified hex-1-yne both are highly effective. In both cases, the system was activated by Bu^{t}OOH, a 4 : 1 ratio with respect to the catalyst being the most effective; 1 : 1 was ineffective and 10 : 1 led to catalyst decomposition. The hydroperoxide was ineffective in the absence of the complexes. Di-t-butyl peroxide did not activate the complexes but, curiously, phenol exhibited an effect similar to that of Bu^{t}OOH.

The effect of varying the PPh_3 : Rh ratio was investigated by adding various amounts of the phosphine to $[\{RhCl(C_8H_{14})_2\}_2]$. With unpurified hex-1-yne and $SiEt_3H$ at 60 °C in toluene, the rate of reaction increased in the order $PPh_3 : Rh = 0 : 1 < 3 : 1 < 2 : 1 < 1 : 1$ [Figure 2(*a*)]. When the hex-1-yne was purified, the rate of reaction was again very dependent on the PPh_3 : Rh ratio. At a ratio of 3 : 1 very little reaction occurred, as with the preformed tris(phosphine) complex. At other ratios, some slowing of the reaction was evident (by 20—40%), but the 1 : 1 system was relatively unaffected and remained the most effective [Figure 2(*b*)].

The effect of changing the order of addition of the reagents was also briefly examined. In all previous work, including that with hex-1-ene, the rhodium complex and the alkene or alkyne were mixed first and then the silane was added. If the silane was added before the hex-1-yne (the only system investigated in this way), reaction was extremely rapid and much less sensitive to the purity of the hexyne. At the close of the reaction, the i.r. spectrum of the solution showed a band at 2 175 cm^{-1} suggestive of a metal hydride. Similar results were obtained by treating the catalyst solutions with hydrogen before adding the silane and hexyne.

DISCUSSION

Rhodium-catalysed hydrosilation reactions are more complicated than previously thought. It is obvious that hydrosilation and isomerisation of alk-1-enes proceed by different mechanisms. Isomerisation proceeds independently of hydrosilation, under conditions when hydrosilation does not occur, presumably by the conventional route outlined in the Scheme with a hydrido-silyl metal complex as intermediate. Although the complex $[RhH(Cl)(SiCl_3)(PPh_3)_2]$ (R = Cl) reacts

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[*] Bis(1,2-diphenylethylene-1,2-dithio)nickel.

with ethylene to give $SiCl_3H$ and $[\{RhCl(C_2H_4)_2\}_2]$,[4] there is no indication of corresponding reactions of the complexes with R = Et or OEt with hex-1-ene. However, the silyl complexes appear not to be active participants in the hydrosilation reaction. With hindsight, of course, it appears unlikely that complexes stable enough to be isolated would be effective catalytic intermediates in reactions requiring their rapid reaction.

The quenching of the hydrosilation reaction by the purification of the substrate was most surprising. However, there seems no doubt that, when $[RhCl(PPh_3)_3]$ is used as the catalyst, the reaction will proceed only in the presence of oxygen or hydroperoxides. The activating effect of oxygen has been previously mentioned[5] but nothing is known of its mode of action. The rhodium complex has been extensively used to catalyse reactions between alkenes and oxygen,[11–19] which usually seem to involve catalytic breakdown of a hydroperoxide to give radicals which initiate autoxidation. The reactions are generally inhibited by phenolic radical traps,[11,20] although recent reports suggest that oxidation of straight-chain alk-1-enes is unaffected by conventional inhibitors.[18,19] The rhodium cyclo-octene complex has been shown to give a dioxygen complex which can form radicals by hydrogen abstraction.[21] It is therefore possible that the oxygen or hydroperoxide promotion of hydrosilation is due to radical formation. However, we consider this unlikely for the following reasons. First, the reaction of hex-1-ene proceeds unabated in the presence of phenolic inhibitors. Secondly, hex-1-yne has been shown to yield a *trans* adduct as the primary product, even when not purified.[9] This is the result of *cis* addition; radical processes would be expected to give *trans* addition. Thirdly, the reaction of hex-1-ene is not catalysed by $[IrCl(CO)(PPh_3)_2]$, with or without added hydroperoxide; this complex has been shown to decompose hydroperoxides by radical processes.[22]

Another possibility is that the additives are causing the breakdown of the complexes to metallic rhodium to give a heterogeneously catalysed system. This, too, seems unlikely since by the time that the metallic precipitate is visible the reaction has lost its vigour. The deposited metal does catalyse the reaction, but at a much lower rate than that observed during the initial stages of the homogeneous reaction. While this could simply mean that aggregation reduces the activity of the metal, we believe that the reversibility of the colour changes and the small stoicheiometric amounts of hydroperoxide required for maximum activation argue against the heterogeneous process. The metal appears only when oxygen or hydroperoxide are present in excess.

The role of these impurities is revealed by the effect of changing the PPh_3 : Rh ratio. In the hex-1-yne system the maximum activity is observed when the ratio is *ca.* 1 : 1. At this level the sensitivity to purification of the system is also low. We believe, therefore, that the function of oxygen or hydroperoxide is to remove PPh_3, presumably as its oxide, to give a mono-phosphine complex which is highly catalytically active. It has been shown that the aerial oxidation of PPh_3 is catalysed by low-valent metal complexes [platinum(0) or ruthenium(II)].[23,24] In these reactions it is thought that a dioxygen complex of stoicheiometry $M(O_2)(PPh_3)_2$ reacts with a molecule of PPh_3 from the solution, forming two molecules of PPh_3O. Under conditions similar to those used here, only 1 mol of dioxygen is taken up per mol of $[RhCl(PPh_3)_3]$,[19] and in autoxidation reactions catalysed by $[RhCl(PPh_3)_3]$ all the metal-containing products isolated at the close of the reaction had PPh_3 : Rh ratios of 1 : 1.[15] It thus seems very likely that a monophosphine complex could be formed in our system.

Hydroperoxide activation of alkenes has been observed in hydrogenation,[25] hydroformylation,[26] and isomerisation.[27,28] In the last of these, catalytic activity was shown to be due to the conversion of the initial complex, $[RuCl_2(PPh_3)_2]$, into a bis(phosphine)-carbonyl complex. Although it is possible that a carbonyl complex could be formed in our system, for example by CO-abstraction from ketones produced by decomposition of alkenyl hydroperoxides, we have shown that the complex $[RhCl(CO)(PPh_3)_2]$ is less active than $[RhCl(PPh_3)_3]$, even when activated by hydroperoxide. However, it is significant that, in many cases, hydroperoxides react with triphenylphosphine complexes to form PPh_3O,[26,28,29] but with $[RhCl(CO)(PPh_3)_2]$ the carbonyl ligand is oxidised in preference to the phosphine.[29] Oxidation of the phosphine by hydroperoxide is presumably stoicheiometric, which would account for the fact that the optimum concentration of hydroperoxide is low, 2 : 1 to 4 : 1 relative to $[RhCl(PPh_3)_3]$, while larger quantities lead to decomposition of the catalyst and the deposition of rhodium metal. The inhibition by excess of PPh_3 is presumably due to removal of the hydroperoxide and the maintenance of a high PPh_3 : Rh ratio. The successful hydrosilation of unpurified alkenes and alkynes must be due to the hydroperoxide normally present.

It thus seems probable that the beneficial effect of oxygen or hydroperoxide is due to the reduction of the PPh_3 : Rh ratio to *ca.* 1 : 1, the resulting complex being an efficient catalyst. In hydrogenation there is evidence that reduction in this ratio below 3 : 1 gives enhanced reactivity.[30] The mono-phosphine complex presumably participates in a mechanism similar to that outlined in the Scheme. The operation of such a mechanism would depend critically on the stability and ease of rearrangement of the intermediate complexes, particularly those of the silyl adducts $[RhH(Cl)(SiR_3)(PPh_3)_n]$, which would be very dependent on the number of co-ordinated PPh_3 molecules. The complex $[RhH(Cl)(SiEt_3)(PPh_3)_2]$ is sufficiently stable to be isolated, although it shows some tendency to dissociate in solution,[4] but species containing less triphenylphosphine would be more reactive, and we have been unable to isolate any silyl complexes from reactions of tertiary silanes with $[\{RhCl(C_8H_{14})_2\}_2]$. The corresponding iridium complex reacts rapidly with $SiH(OEt)_3$, evolving a gas (H_2?) and forming a hydrido-species containing co-ordinated $Si(OEt)_3$ groups.[31]

While the above is a satisfactory explanation of the major features of the hydrosilation reactions, the actual mechanism may be rather more complex. With hex-1-ene, some hexane and a hexenylsilane were always obtained, suggesting a minor pathway involving a dehydrogenation or disproportionation step. In the hex-1-yne system, the catalytic activity depended on the order of addition of the reagents, being faster when the catalyst and the silane were mixed first. We have observed similar effects in the catalysed reactions of silanes with alcohols, but the mechanism is not understood. Possibly the silane interacts with the rhodium complex to form an active hydrido-complex but, when hex-1-yne is present, this pathway is blocked by prior co-ordination of the alkyne. These possibilities require further investigation. In these systems also, catalysis is most effective at low PPh_3 : Rh ratios.

EXPERIMENTAL

The complexes $[RhCl(PPh_3)_3]$,[32] $[\{RhCl(C_8H_{14})_2\}_2]$,[33] and $[Ni(S_2Ph_2)_2]$,[34] and $SiEt_3H$ [35] were prepared by literature methods. Hex-1-ene and hex-1-yne were purified by washing with iron(II) sulphate (hex-1-yne) and passage through activated alumina. Solvents were dried and degassed by standard methods. G.l.c. analyses were made with $Ag[NO_3]$-polyethylene glycol or Apiezon-L columns.

Reactions.—Propene with triethylsilane. Several sets of apparatus were used, but all involved a round-bottomed three-necked reaction vessel (500 cm^3) fitted with a magnetic stirrer and connected through a condenser to a manometer, a reservoir (5 l), and a vacuum system. In order to exclude oxygen, Teflon-tapped tipping tubes were used to add solvent and silane to the reaction vessel. A typical procedure was as follows. The catalyst (0.03 mmol) was placed in the reaction flask and benzene (10 cm^3) and $SiEt_3H$ (3.48 g, 30 mmol) in two tipping tubes. The benzene and the silane were frozen and the entire apparatus was evacuated and the liquids degassed. The system was then flushed with nitrogen and re-evacuated. The taps on the tipping tubes were closed and propene was admitted to the reaction vessel to a pressure of 650 mmHg.* The benzene was added to the reaction vessel and stirred until the catalyst had dissolved (5—10 min), and then the silane was added. The reaction was followed by the decrease in pressure, assuming propene to be an ideal gas. The total volume of the system was 6.03 l.

Hex-1-ene with triethylsilane. The reaction vessel consisted of a tube (volume 13 cm^3) fitted with a nitrogen inlet, a double-surface condenser, a tipping bucket, a neck with a serum cap, and a magnetic stirrer, and was immersed in a thermostat at 50 or 55 °C. Two such vessels were normally used at the same time, to allow control and duplicate reactions to be carried out. The catalyst (0.005 mmol) was weighed into the tipping bucket which was then fitted to the reaction vessel. The apparatus was flushed with nitrogen and the solvent (chlorobenzene, benzene, or toluene, 3 cm^3) was added by syringe. The catalyst was tipped into the solvent and stirred for 10 min. Purified hex-1-ene (1.25 cm^3, 10 mmol) and triethylsilane (0.80 cm^3, 5.0 mmol) were added by syringe. Samples of the reaction mixture (*ca.* 0.25 cm^3) were periodically withdrawn by syringe and immediately cooled to -79 °C to quench the reaction. Freshly prepared solutions of Bu^tOOH in the appropriate solvent were added, when necessary, by syringe. The temperature of the reaction mixture, checked independently, varied by no more than 0.1 °C. The concentration of the silane in the samples was estimated by measurement of the intensity of the i.r. band at 2 097 cm^{-1} in relation to that for standard solutions of the silane in the same solvent.

The hydrosilation products in one case were separated by preparative g.l.c. The major component had the same retention time as an authentic sample of $C_6H_{13}SiEt_3$ and a mass spectrum showed the following peaks [*m/e* (intensity)]: 171 (69.2), 143 (17.4), 115 (28.4), 87 (100), 59 (39.2), and 57 (13.7). The parent peak (*m/e* 201) was not observed. The mass spectrum of the minor product showed peaks at *m/e* 198 (5.4), 169 (100), 141 (83.6), 113 (23.1), 85 (16.4), 59 (28.3), and 57 (37.4), consistent with $C_6H_{11}SiEt_3$. The i.r. spectrum showed a band at 1 620 cm^{-1} [ν(C=C)] and the ^{1}H n.m.r. spectrum confirmed the presence of vinylic protons.

Hex-1-yne and triethylsilane. Reactions were carried out in a nitrogen-filled Schlenk tube with magnetic stirring, immersed in a thermostat at 60 °C. The catalyst (0.125 mmol) was dissolved in toluene (2 cm^3). Purified hex-1-yne (1.025 g, 12.5 mmol) and $SiEt_3H$ (1.45 g, 12.5 mmol) were added by syringe, and the progress of the reaction was followed by i.r. analysis as described above. The products were identified by g.l.c.

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* Throughout this paper: 1 mmHg $\approx 13.6 \times 9.8$ Pa.

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