Organosilicon Chemistry. Part XII.[1] Stability and Catalytic Activity of some Chlorohydridobis(phosphine)(silyl)rhodium(III) Complexes

By **Robert N. Haszeldine,* R. V. (Dick) Parish,** and **Richard J. Taylor,** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

New complexes of the type $[L_2RhH(SiR_3)Cl]$ have been prepared [$L = Ph_2(tol)P$, $Ph_2(cy)P$, $Ph(cy)_2P$, or Ph_2Pr^iP; $R = OEt$, Me, or Et; tol = *p*-tolyl; cy = cyclohexyl]. Evidence for similar complexes with $L = Ph_2EtP$ and Ph_2MeP has been obtained by ligand-exchange studies. The stability to dissociation of complexes of this type increases in the orders $SiMe_3 < SiMe_2Cl < SiMeCl_2 < SiCl_3$, $SiPh_3 < SiEt_3 < Si(OEt)_3 < SiCl_3$, $(cy)_3P < Ph(cy)_2P < Ph_2(cy)P \lesssim Ph_2(tol)P \approx Ph_3P$, $Ph_2MeP < Ph_2EtP < Ph_2Pr^iP \approx Ph_3P$, and $Ph_3As < Ph_3P$. The dependence of stability on the neutral ligand reflects a combination of steric and electronic effects. The rate of addition of triethylsilane to hex-1-ene, catalysed by the complexes $[L_3RhCl]$, increases in the order $L = (cy)_3P \lll Ph_2MeP < Ph(cy)_2P \approx Ph_3P < Ph_2(cy)P \approx Ph_2EtP$.

SILYL derivatives of the transition metals have been prepared by a variety of routes,[2] but one of the simplest is the oxidation–addition or oxidation–elimination reaction involving a d^8 complex.[3-12] The rhodium(I) complex $[(Ph_3P)_3RhCl]$ gives a variety of derivatives,[6,7] and similar reactions (1)—(3) have recently been used to obtain cobalt [9] and iridium [13] complexes.

$$[(Ph_3P)_3Co(N_2)H] + HSiF_3 \longrightarrow [(Ph_3P)_3CoH_2(SiF_3)] + N_2 \qquad (1)$$

$$[(Ph_3P)_3RhCl] + HSiPh_3 \longrightarrow [(Ph_3P)_2RhH(SiPh_3)Cl] + Ph_3P \qquad (2)$$

$$[(Ph_3P)_2Ir(N_2)Cl] + HSi(OEt)_3 \longrightarrow [(Ph_3P)_2IrH\{Si(OEt)_3\}Cl] + N_2 \qquad (3)$$

The stability of the product of an oxidation–addition reaction is generally related to the nature of the metal atom and the ligands in a well defined way.[14] An increase in the σ-basicity or a decrease in the π-acidity of some or all of the ligands decreases the promotion energy of the metal atom and facilitates the oxidation. Similarly, transition metals from the third long period usually have lower promotion energies than corresponding second-row metals. These trends appear to apply to the preparation and stability of silyl derivatives. Thus, the complex $[(Ph_3P)_3RhCl]$ reacts readily with a wide range of tertiary silanes,[6,7] but $[(Ph_3P)_2Rh(CO)Cl]$ gives a very unstable adduct with trichlorosilane.[6] The use of a more basic phosphine, *e.g.* Et_3P, gives a slightly more stable product.[7] The complex $[(Ph_3P)_2Ir(CO)Cl]$ and tertiary silanes form adducts which dissociate readily in solution,[3] but the adducts $[(Ph_3P)_2Ir(CO)H_2(SiR_3)]$ and $[(Ph_3P)_2IrH(SiR_3)Cl]$ are very stable.[4,13] It has also been noted that silanes bearing the most electronegative groups [*e.g.* $HSiCl_3$ and $HSi(OEt)_3$] give the most stable adducts, presumably by forming the most stable metal–silicon bonds.[3,6]

In view of the presumed involvement of hydridosilyl complexes in rhodium-catalysed hydrosilation reactions,[3,6,7,15] it was of interest to prepare other complexes of the type $[L_2RhH(SiR_3)Cl]$ involving larger or more basic ligands and to attempt to correlate the stability of such adducts with the catalytic efficiency of $[L_3RhCl]$. The initial results of such a study are now reported.

RESULTS

Reactions between Rhodium(I) *Complexes and Tertiary Silanes.*—The complexes $[L_3RhCl]$ (L = tertiary phosphine) are readily obtained by reaction of the appropriate phosphine with the η-olefin complex $[\{(C_2H_4)_2RhCl\}_2]$ or $[\{(C_8H_{14})_2RhCl\}_2]$.[16] The phosphine complexes were usually prepared *in situ* and used without isolation. With many such complexes an immediate colour change (from red to orange or yellow) occurred on addition of triethoxysilane to the solution, and stable complexes $[L_2RhH\{Si(OEt)_3\}Cl]$ were isolated for $L = Ph_3P$, $Ph_2(tol)P$, Ph_2Pr^iP, $Ph_2(cy)P$, and $Ph(cy)_2P$ (tol = *p*-tolyl and cy = cyclohexyl). No such adducts could be isolated for $L = (cy)_3P$, Ph_2MeP, or Ph_2EtP, although for the last of these a yellow product was obtained at −60 °C which decomposed on warming to room temperature. For $L = Ph_2(tol)P$ and $Ph_2(cy)P$ stable adducts were also obtained with trimethyl- and triethylsilane by the previously described method of reducing drastically the amount of solvent employed.[6] As with the corresponding triphenylphosphine complexes, these complexes dissociated completely in solution. No new products were obtained from the mixtures $[L_3RhCl]$–$HSiEt_3$ [$L = Ph(cy)_2P$ or $(cy)_3P$] or $[\{Ph_2(cy)P\}_3RhCl]$–$HSiPh_3$. No reaction occurred between triethoxysilane and any of the complexes $[L_2Rh]Cl$ [$L = Ph_2PCH_2CH_2PPh_2$ (dppe), or

---

[1] Part XI, R. N. Haszeldine, R. V. Parish, and J. H. Setchfield, *J. Organometallic Chem.*, 1973, **57**, 279.

[2] E. H. Brookes and R. J. Cross, *Organometallic Chem. Rev.*, 1971, **A6**, 227.

[3] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

[4] A. J. Chalk, *Chem. Comm.*, 1969, 1207.

[5] J. F. Harrod and D. F. R. Gilson, *Canad. J. Chem.*, 1969, **47**, 2205.

[6] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Chem. Soc.* (*A*), 1969, 683.

[7] F. de Charentenay, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 787.

[8] J. F. Harrod and C. A. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 2699.

[9] N. J. Archer, R. N. Haszeldine, and R. V. Parish, *Chem. Comm.*, 1971, 524.

[10] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1.

[11] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4.

[12] J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 881.

[13] R. N. Haszeldine, R. V. Parish, and J. H. Setchfield, unpublished work.

[14] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53; R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319; L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[15] A. J. Chalk, *J. Organometallic Chem.*, 1970, **21**, 207.

[16] S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1054.

$Ph_2PCH{:}CHPPh_2$ (dppen)], [$L_2Rh(CO)Cl$] [L = Ph_2MeP, Ph_2EtP, $Ph_2(cy)P$, $PhEt_2P$, $Ph(cy)_2P$, or $(cy)_3P$], [$(dppe)_2RhH$], or [$(Ph_3P)_3Rh(CO)H$]. In the presence of dichloromethane the last of these gave [$(Ph_3P)_2Rh(CO)Cl$],0·5CH_2Cl_2.

I.r. Spectra.—I.r. spectra * of the complexes [$L_2RhH(SiR_3)Cl$] showed bands typical of the L and R_3Si groups. Bands were also found at 2 050—2 100 and *ca.* 850 cm^{-1}, which can be attributed to Rh–H stretching and bending modes. The spectra were very similar to those of the corresponding triphenylphosphine complexes.[6] There seems to be a slight but consistent increase in ν(Rh–H) in the order L = $Ph_3P < Ph_2(cy)P < Ph(cy)_2P$.

N.m.r. Spectra.—Satisfactory n.m.r. spectra * were difficult to obtain because of the low solubility of the complexes. Spectra could be obtained only for the triethoxysilyl derivatives, as the trialkylsilyl complexes dissociate in solution. The spectra showed a slight upfield shift of the CH_3 and CH_2 signals of the $(EtO)_3Si$ group relative to those for the free silane, indicating co-ordination of this group to the metal atom.[6] In the high-field region (τ 20—30) signals due to a hydrido-ligand were observed, consisting of an overlapped doublet of triplets [J(Rh–H) 24—26, J(P–H) 11·5—15 Hz]. These values, and the chemical shifts, are similar to those previously reported,[6] and presumably indicate similar structures.

Thermal Stability of Triphenylphosphine Complexes.—The complex [$(Ph_3P)_2RhH(SiMe_3)Cl$] decomposed completely on heating at 100 °C for 3 h *in vacuo*, giving trimethylsilane and [$\{(Ph_3P)_2RhCl\}_2$]. The complex [$(Ph_3P)_2RhH(SiMe_2Cl)Cl$] did not decompose below 130 °C, when heated slowly *in vacuo*, but at this temperature chlorodimethylsilane was liberated. The Cl_2MeSi complex is stable at 120 °C, but decomposed slowly at 145 °C giving dichloromethylsilane. The Cl_3Si complex is stable at 145 °C (3 h). Very slow decomposition occurred at 160 °C, when trace amounts of trichlorosilane were formed. Decomposition was rapid at 200 °C, trichlorosilane and benzene being among the volatile products.

Ligand-replacement Reactions.—The complex [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$] reacted rapidly with chelating diphosphines, liberating triethoxysilane. With two moles of dppe or dppen, the complexes [L_2Rh]Cl were formed. One mole of dppe gave the new complex [$(dppe)(Ph_3P)RhCl$]. The silyl complex also reacted rapidly with an excess of methyldiphenylphosphine, liberating the silane and forming, presumably, the complex [$(Ph_2MeP)_3RhCl$].

Attempts were made to follow reactions of this type by observing i.r. spectra of a dichloromethane solution of the silyl complex in the presence of various phosphines. The addition of methyldiphenyl- or dimethylphenyl-phosphine resulted in rapid loss of the band at 2 060 cm^{-1} [ν(Rh–H)] and the appearance of a band at 2 197 cm^{-1} [ν(Si–H) for $(EtO)_3SiH$]. With ethyldiphenylphosphine reaction was much slower, the ν(Si–H) band appearing only weakly after 1 h. No change was detected in the spectrum on addition of any of the ligands Ph_3P, $Ph_2(cy)P$, or Ph_3As. These ligands form stable complexes with very similar i.r. spectra, so that ligand exchange would probably not be detected.

A more sensitive method of testing for ligand exchange is by following changes in the high-field region of the n.m.r. spectrum. Thus, the complex [$(Ph_3As)_2RhH\{Si(OEt)_3\}Cl$] gave a doublet at τ 26·3. On addition of one mole of triphenylphosphine, a second signal developed at the expense of the first, the intensities being approximately equal after 3 h. The second signal was centred at τ 25·2 and consisted of a pair of doublets, demonstrating the presence of one co-ordinated phosphine. With four moles of the phosphine, the second set of signals was found as soon as the spectrum could be run, and within 50 min the only detectable signal was a doublet of triplets centred at τ 24·6 characteristic of the bis(phosphine) complex. No free silane was observed during this sequence of reactions. The reverse reactions are also possible, and low concentrations of [$(Ph_3P)(Ph_3As)RhH\{Si(OEt)_3\}Cl$] and [$(Ph_3As)_2RhH\{Si(OEt)_3\}Cl$] were formed when two moles of the arsine were added to [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$].

Similar reactions occur between the complex [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$] and the phosphines $Ph_2(cy)P$, Ph_2EtP, and Ph_2MeP. With $Ph_2(cy)P$, three sets of signals were obtained after equilibration (2—3 h), two of which correspond to the complexes [$L_2RhH\{Si(OEt)_3\}Cl$] [L = Ph_3P and $Ph_2(cy)P$]. The remaining signals, a doublet of triplets with an intermediate chemical shift, presumably correspond to the mixed-ligand complex [$(Ph_3P)\{Ph_2(cy)P\}RhH\{Si(OEt)_3\}Cl$]. No trace of any double quartet signal was found, showing that tris(phosphine) complexes were formed in very low concentrations, if at all, and that ligand exchange is slow on the n.m.r. timescale. Again no free silane was detected.

The initial spectrum of a solution containing equimolar amounts of [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$] and Ph_2MeP showed the presence of the starting complex and some free silane. After 30 min, use of the time-averaging computer showed three sets of high-field signals, the intensity decreasing rapidly with increasing chemical shift. After 2 h the first two sets were of comparable intensity but that at highest field was undetectable without the time-averaging computer. The low-field H_3C region (τ 7—9·5) was very complex, and the H_2C region showed a quartet at τ 6·2 [free $HSi(OEt)_3$] and a quintet at τ 6·6 presumably due to overlapping quartets of two co-ordinated $(EtO)_3Si$ groups. When the experiment was repeated with the addition of two moles of triethoxysilane, all three high-field signals were clearly discernible, and after 1·5 h the relative intensities were *ca.* 4 : 6 : 3 in order of increasing chemical shift. This ratio suggests that the ligand distribution is not random and the enhancement of all the intensities shows that the ligand-substituted complexes are in equilibrium with a dissociated species and the silane. With larger quantities of methyldiphenylphosphine (5—6 moles) no hydride signals could be detected at any time.

Reaction between equimolar amounts of the complex [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$] and Ph_2EtP occurred much more slowly, a second set of signals appearing with no apparent liberation of the silane. With an excess of this phosphine, the hydride signals were lost and the free silane was formed, but again more slowly than with Ph_2MeP. When a phosphite, $(PhO)_3P$ or $\{EtC(CH_2O)_3\}P$, was added to a solution of [$(Ph_3P)_2RhH\{Si(OEt)_3\}Cl$], rapid decomposition took place, the silane was liberated, and some gas was evolved.

Hydrosilation of Hex-1-ene.—The complexes [L_3RhCl] [L = Ph_3P, $Ph_2(tol)P$, $Ph_2(cy)P$, Ph_2Pr^iP, or $Ph(cy)_2P$] all catalysed the addition of triphenylsilane to hex-1-ene (mole ratio catalyst : silane : olefin = 10^{-4} : 2 : 3, 60 °C, 6 days) to give n-hexyltriphenylsilane in yields of 40—80%. Simi-

---

* I.r. and n.m.r. spectral data for the silyl complexes are to be found in Supplementary Publication No. SUP 21105 (3 pp.). For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

larly the complexes [L_nRhCl] (L = Ph_3P or Ph_2MeP; n = 2 or 3) catalysed the addition of trimethylsilane (10^{-3} : 1 : 1, room temperature, 4 days) to give n-hexyltrimethylsilane in yields of 50—80%. In these last reactions, a marked temperature rise occurred 20—30 min after mixing, indicating that the reaction is rapid and exothermic. With triethylsilane and hex-1-ene (10^{-3} : 1 : 2) at 60 °C, reaction was 70% complete in 15 min and 90% complete in 1 h. The rate of consumption of hex-1-ene is greater than that of the silane, since considerable isomerisation is occurring [Figure 1(*a*)]. Isomerisation followed the usual pattern, *cis*-hex-2-ene being produced initially, followed by *trans*-hex-2-ene and *trans*-hex-3-ene. With a catalyst : silane : hexene ratio of 10^{-4} : 1 : 2 at 60 °C, 70% hydrosilation occurred in 1 h and 90% in 2 h, but the rate of isomerisation was considerably reduced [Figure 1(*b*)]. No reaction was detected after 1·5 h at 30 °C, and with a reactant ratio of 10^{-5} : 1 : 2 no reaction was detected after 7 h at 60 °C. Reaction between triethylsilane and a mixture of *cis*- and *trans*-hex-2-ene (10^{-4} : 1 : 2) was very slow, less than 5% after 7 h at 60 °C.

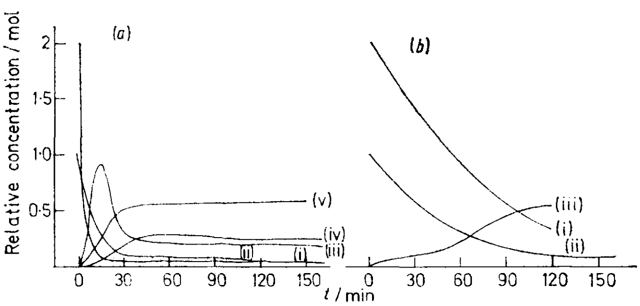

FIGURE 1 Progress of the reaction between hex-1-ene and triethylsilane catalysed by [$(Ph_3P)_3RhCl$]. Triethylsilane: [$(Ph_3P)_3RhCl$] ratio (*a*) 1 : 10^{-3}, (*b*) 1 : 10^{-4}. (*i*), Hex-1-ene; (*ii*), triethylsilane; (*iii*), *cis*-hex-2-ene; (*iv*), *trans*-hex-3-ene; (*v*), *trans*-hex-2-ene

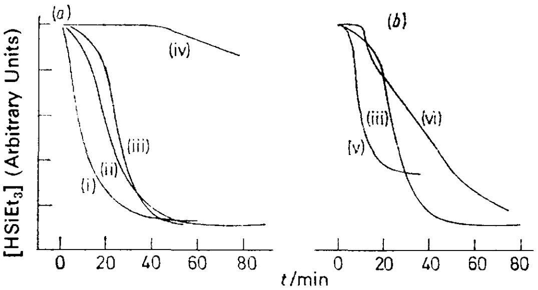

FIGURE 2 Rate of reaction of triethylsilane and hex-1-ene in benzene with various catalysts [L_3RhCl]. In (*a*) the amount of *cis*-hex-3-ene was less than 0·04 mol throughout. Irregularities in the profiles (*b*) are due to temperature fluctuations during the initial strongly exothermic stage. [L_3RhCl] : triethylsilane : hex-1-ene : benzene = 10^{-4} : 1 : 2 : 4·5; L = $Ph_2(cy)P$ (*i*), $Ph(cy)_2P$ (*ii*), Ph_3P (*iii*), $(cy)_3P$ (*iv*), Ph_2EtP (*v*), and Ph_2MeP (*vi*)

Similar reactions occurred using [$(Ph_2MeP)_3RhCl$] as catalyst, the rates being similar to those with [$(Ph_3P)_3RhCl$]. The reactions were all so fast that it was not possible to compare the rates. Reducing the temperature resulted in incomplete dissolution of the catalyst, but the reactions could be retarded successfully by dilution. A series of reactions between hex-1-ene and triethylsilane were carried out at 50 °C in benzene (catalyst : silane : hexene : benzene = 10^{-4} : 1 : 2 : 4·5) using the catalysts [L_3RhCl] [L = Ph_3P, $Ph_2(cy)P$, $Ph(cy)_2P$, $(cy)_3P$, Ph_2EtP, or Ph_2MeP]. The reactions were followed by the disappearance of the i.r. band at 2 097 cm^{-1} [ν(Si–H) of Et_3SiH], and the results are displayed in Figure 2. In many cases the reactions were so exothermic that the temperature of the reaction mixture rose 2—3 °C above the bath temperature. The order of increasing catalytic efficiency for [L_3RhCl] is L = $(cy)_3P \lll Ph_2MeP < Ph(cy)_2P \approx Ph_3P < Ph_2(cy)P \approx Ph_2EtP$.

DISCUSSION

Stability of the Silyl Complexes.—Several new silyl derivatives of rhodium(III) of the type [$L_2RhH(SiR_3)Cl$] have been obtained by the oxidation–elimination reaction of silanes $HSiR_3$ with the appropriate rhodium(I) complex [L_3RhCl]; these are summarised in Table 1.

TABLE 1

Isolation of the complexes [$L_2RhH(SiR_3)Cl$]

L \ R	OEt	Et	Ph
Ph_3P	*a*	*a*	*a*
$Ph_2(cy)P$	*a*	*a*	*b*
$Ph(cy)_2P$	*a*	*b*	*c*
$(cy)_3P$	*b*	*b*	*c*
$Ph_2(tol)P$	*a*	*a*	*c*
Ph_2Pr^iP	*a*	*c*	*c*
Ph_2EtP	*d*	*c*	*c*
Ph_2MeP	*b*	*c*	*c*

[a] Complex isolated. [b] No complex isolated. [c] Not attempted. [d] Complex isolated at low temperature.

In several cases no complex could be isolated, or even detected. The n.m.r. study of the replacement reactions shows that in these cases the silyl complexes are unstable to dissociation (*i.e.* reductive elimination of the silane), but this process is inhibited by an excess of the silane. The replacement reactions proceed in two stages, and the intermediate mixed-ligand complexes can be identified by their n.m.r. spectra. Presumably the equilibria (4)—(6) (R = OEt) are set up, although

$$[(Ph_3P)_2RhH(SiR_3)Cl] + L \rightleftharpoons [(Ph_3P)LRhH(SiR_3)Cl] + Ph_3P \quad (4)$$

$$[(Ph_3P)LRhH(SiR_3)Cl] + L \rightleftharpoons [L_2RhH(SiR_3)Cl] + Ph_3P \quad (5)$$

$$[L_2RhH(SiR_3)Cl] + L \rightleftharpoons [L_3RhCl] + HSiR_3 \quad (6)$$

direct dissociation of the silyl complexes as in equation (7) cannot be ruled out. From the n.m.r. studies the

$$[L_2RhH(SiR_3)Cl] \rightleftharpoons [L_2RhCl] + HSiR_3 \quad (7)$$

extent of dissociation appears to increase with the number of triphenylphosphine ligands replaced. The n.m.r. experiments confirm the results of the (attempted) syntheses, in that no dissociation was observed with ligands for which stable complexes can be isolated, but with ligands for which no silyl complexes could be isolated extensive or complete dissociation occurred. These effects are thus thermodynamic in origin.

The thermal-degradation reactions confirm the earlier suggestion[6] that, for any one ligand, the stability of the complexes [$L_2RhH(SiR_3)Cl$] to dissociation increases as the groups on silicon become more electronegative, in the order $SiMe_3 < SiMe_2Cl < SiMeCl_2 < SiCl_3$. The order $SiPh_3 < SiEt_3 < Si(OEt)_3 < SiCl_3$ probably also holds. Using these results together with those of the preparative and spectroscopic studies, it seems that the orders of stability as a function of the neutral ligands are $(cy)_3P < Ph(cy)_2P < Ph_2(cy)P \lesssim Ph_2(tol)P \approx Ph_3P$, $Ph_2MeP < Ph_2EtP < Ph_2Pr^iP \approx Ph_3P$, and $Ph_3As < Ph_3P$. The earlier suggestion,[6] based on decomposition points of the solids, that stability increases in the order $L = Ph_3P < Ph_3As$, does not hold for solutions; the n.m.r. results show that equilibria (4) and (5) ($L = Ph_3As$) favour the bis(triphenylphosphine) complex.

The dependence of the stability of the silyl complexes on the nature of the neutral ligands is not that expected on purely electronic grounds. With the series of ligands $(cy)_nPh_{3-n}P$, the displacement reactions show that as the basicity of the phosphine increases (n increasing) so does the co-ordinating power to rhodium, which would be expected to inhibit loss of the silane by reductive elimination. The reverse trend was observed, which presumably indicates that steric effects over-ride electronic effects. The crystal-structure determination for [$(Ph_3P)_2RhH(SiCl_3)Cl$] shows considerable steric crowding about the rhodium atom,[17] which would increase on substitution of cyclohexyl groups for phenyl on the phosphine and of ethoxy-groups for chloride on the silyl ligand, thus destabilising the complex. The same effect may account for our inability to obtain [$\{Ph_2(cy)P\}_2RhH(SiPh_3)Cl$] (the corresponding Et_3Si complex was isolated without difficulty), and for the general stability order $Ph_3Si < R_3Si$ (R = Me or Et). The importance of steric effects in reduction–elimination reactions is well known for iridium(III) complexes.[18] The effect is clearly rather subtle, since with alkyldiphenylphosphines the observed stabilities seem to be determined more by electronic than steric factors, increasing with increasing α-branching and basicity, $Me < Et < Pr^i$. The stability of the iso-propylphosphine complex is comparable to that of the triphenylphosphine compound.

The lower stability of the triphenylarsine silyl complex than the triphenylphosphine analogue contrasts with those of the corresponding complexes [$L_2Rh(H)Cl_2$], for which stability to loss of hydrogen chloride increases in the order $L = Ph_3P < Ph_3As < Ph_3Sb$.[19] This difference probably reflects a steric effect in that the $(EtO)_3Si$ group is considerably larger than Cl. There is evidence from Mössbauer spectroscopy that similar effects may operate in the five-co-ordinate rhodium(I)–tin complexes [$L_2(C_7H_8)Rh(SnCl_3)$] ($L = Ph_3P$, Ph_3As, or Ph_3Sb).[20] As L becomes larger, the Rh–Sn bond involves more tin $5p$ and less $5s$ character; greater involvement of a higher-energy orbital suggests less-stable bonding,[21] and similar effects may operate for silicon.

Hydrosilation.—The complexes [L_3RhCl] act as efficient catalysts for addition of silanes to hex-1-ene. Our early experiments with [$(Ph_3P)_3RhCl$] suggested[6] that considerable isomerisation of the olefin was occurring at the same time as the hydrosilation, whereas Chalk reported[15] that, with a lower catalyst concentration, relatively little isomerisation of pent-1-ene occurred. As Figure 1 shows, the relative rates of hydrosilation and isomerisation depend on the catalyst concentration, the isomerisation decreasing rapidly with decreasing catalyst concentration. The final degree of hydrosilation (as measured by the consumption of triethylsilane) is similar with both concentrations. The extent of isomerisation was not measured for the other catalysts, but in no case did the silane react completely. This is presumably due to isomerisation of the olefin, since the hex-2-enes do not react. The slower reaction of pent-2-enes than pent-1-ene has also been reported,[15] and no hydrosilation of cyclohexene was found.[6]

It has been assumed previously[6,7,15] that these reactions are homogeneously catalysed, and a reasonable mechanism can be formulated to correlate the observed rates of hydrosilation with the stability of the intermediate silyl complexes. Such a mechanism does not account for the different orders of the hydrosilation and isomerisation reactions with respect to the rhodium complex, however, and recent experiments suggest that other mechanisms may be involved.[22] We prefer, therefore, to defer speculation until further evidence is available.

EXPERIMENTAL

The following instruments were used: Perkin-Elmer 251 and 621 i.r. spectrometers; Perkin-Elmer R10 and Varian HA100 n.m.r. spectrometers. Solvents were dried and deoxygenated. Rhodium(I) complexes[23] and tertiary phosphines and silanes were prepared by standard methods. Samples of the ligands $\{EtC(CH_2O)_3\}P$ and $Ph_2PCH{:}CHPPh_2$ were kindly provided by Drs. B. L. Booth and C. A. McAuliffe. All reactions were carried out under a dinitrogen atmosphere. Analytical data are recorded in Table 2.

The silyl complexes were obtained by methods of which the following are typical.

Chlorobis(dicyclohexylphenylphosphine)hydrido(triethoxysilyl)rhodium(III).—To a solution of dicyclohexylphenylphosphine (0·55 g, 2 mmol) in dichloromethane (20 cm^3) was

---

[17] K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 440.

[18] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716; *J.C.S. Dalton*, 1972, 223.

[19] C. E. Betts, R. N. Haszeldine, and R. V. Parish, unpublished work.

[20] R. V. Parish and P. J. Rowbotham, *J.C.S. Dalton*, 1973, 37.

[21] R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1296.

[22] N. J. Archer, H. M. Dickers, R. N. Haszeldine, L. S. Malkin, and R. V. Parish, unpublished work.

[23] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711; M. A. Bennett and P. A. Longstaff, *Chem. and Ind.*, 1965, 846; R. D. Cramer, *Inorg. Chem.*, 1962, **1**, 722; L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Comm.*, 1965, 336; A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274; A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597; D. Evans, G. Yagupsky, and G. Wilkinson, *ibid.*, 1968, 2660.

added the complex $[\{(C_8H_{14})_2RhCl\}_2]$ (0·19 g, 0·5 mmol), and the mixture was stirred for 1 h. Triethoxysilane (0·5 cm^3) was added, giving a colour change from dark red to orange over *ca.* 30 min. The solution was concentrated under vacuum and hexane (50 cm^3) was added. The resulting yellow *solid* was filtered off, washed with hexane, and dried under vacuum.

Chlorobis(cyclohexyldiphenylphosphine)hydrido(triethylsilyl)rhodium(III).—To a solution of cyclohexyldiphenylphosphine (0·30 g, 1·1 mmol) in dichloromethane (15 cm^3) was added the complex $[\{(C_2H_4)_2RhCl\}_2]$ (0·10 g, 0·25 mmol), and the mixture was stirred for 2 h. The solution was then concentrated under vacuum to *ca.* 4 cm^3 and triethylsilane (15 cm^3) was added. On further stirring (1·5 h), a yellow *solid* separated, which was filtered off, washed with hexane, and dried under vacuum.

TABLE 2

Analytical data for the new complexes

	Decomp. p., θ_c/°C	Analyses (%) Found C	Found H	Calc. C	Calc. H
$[\{Ph_2(tol)P\}_2RhH\{Si(OEt)_3\}Cl]$	122—128	61·6	6·1	61·9	5·9
$[(Ph_2Pr^iP)_2RhH\{Si(OEt)_3\}Cl]$	126—132	57·3	6·8	57·0	6·6
$[\{Ph_2(cy)P\}_2RhH\{Si(OEt)_3\}Cl]$	145—150	58·8	6·6	60·1	6·9
$[\{Ph_2(cy)P\}_2RhH(SiEt_3)Cl]$		62·7	7·1	62·7	7·3
$[\{Ph(cy)_2P\}_2RhH\{Si(OEt)_3\}Cl]$	132—136	59·2	7·9	59·3	8·3
$[(dppe)(Ph_3P)RhCl]$		65·4	5·4	66·1	4·9

Chloro[1,2-*bis(diphenylphosphino)ethane*]*triphenylphosphinerhodium*(I).—The diphosphine (dppe) (0·12 g, 0·3 mmol) was added to a solution of the complex $[(Ph_3P)_2RhH\{Si(OEt)_3\}Cl]$ (0·23 g, 0·28 mmol) in dichloromethane (5 cm^3). The i.r. spectrum showed loss of the band at 2 060 cm^{-1} [ν(Rh–H)] and the appearance of a band at 2 177 cm^{-1} [ν(Si–H)]. After 1 h hexane (50 cm^3) was added and the resulting yellow *solid* was filtered off, washed with hexane, and dried under vacuum. The n.m.r. spectrum of this product gave signals at τ 2·7 and 7·9 with intensity ratio 35 : 4·6, suggesting slight contamination with $[(dppe)_2Rh]Cl$. The latter complex was obtained when two moles of dppe were used.

Hydrosilation of Hex-1-*ene*.—(a) *With triphenylsilane*. The complex $[L_2RhH\{Si(OEt)_3\}Cl]$ (0·05 mmol), triphenylsilane (10 mmol), and hex-1-ene (15 mmol) were sealed in an evacuated tube and kept at 60 °C for 6 days. The residual olefin was removed by evacuation and the solid product recrystallised from ethanol to remove unreacted silane. The yields of n-hexyltriphenylsilane, m.p. 77 °C (lit.,[24] 77 °C), for the various complexes were: L = Ph_3P, 69; $Ph_2(tol)P$, 38; $Ph_2(cy)P$, 62; $Ph(cy)_2P$, 81; and Ph_2Pr^i, 51%. Losses during recrystallisation could not be assessed.

(b) *With trimethylsilane*. A solution of the complex $[L_nRhCl]$ (L = Ph_3P or Ph_2MeP; n = 2 or 3; 0·02 mmol) in benzene (20 cm^3) was prepared from appropriate quantities of the ligand and $[\{(C_8H_{14})_2RhCl\}_2]$. This solution (2 cm^3), trimethylsilane (30 mmol), and hex-1-ene (30 mmol) were sealed in an evacuated tube and kept at room temperature for 4 days, after which the residue was distilled. The b.p. of the highest-boiling fraction showed it to be n-hexyltrimethylsilane, b.p. 163 °C (lit.,[24] 163 °C). The n.m.r. spectrum was also consistent with this formulation (τ, intensity: 8·42, 7·5; 8·84, 3; 9·12, 2; and 9·74, 9). Yields obtained were: L = Ph_3P, n = 2, 52, n = 3, 77; Ph_2MeP, n = 2, 54, n = 3, 76%. Losses during distillation could not be assessed.

(c) *With triethylsilane*. A typical procedure was as follows. A small round-bottomed flask was fitted with a dinitrogen inlet and outlet, a reflux condenser, a thermometer pocket dipping into the contents, and a serum cap. An aliquot portion (4 cm^3) of a solution of cyclohexyldiphenylphosphine (0·3 mmol) and $[\{(C_8H_{14})_2RhCl\}_2]$ (0·1 mmol) in benzene (40 cm^3), which had been heated under reflux for 2 h, was added to the reaction vessel. Benzene (36 cm^3) and triethoxysilane (15·9 cm^3, 0·1 mmol) were added and the mixture stirred at 50 °C for 10 min. Hex-1-ene (16·8 g, 0·2 mmol) was then added and the reaction followed by withdrawing samples with a syringe through the serum cap. The samples were immediately cooled to −78 °C, and the extent of reaction subsequently assessed by measuring the intensity of the i.r. band at 2 097 cm^{-1}, compared with a suitable calibration graph.

[4/764 *Received*, 17*th April*, 1974]

---

[24] V. Bazant, V. Chvalovsky, and J. Rathousky, ' Organosilicon Chemistry,' Academic Press, London, 1965.