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XXVII *. SILYL—RUTHENIUM(IV) COMPLEXES

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Summary

Silyl—ruthenium(IV) complexes, $\text{RuH}_3(\text{SiR}_3)\text{L}_n$ ($\text{R}_3 = \text{F}_3, \text{MeF}_2, \text{Cl}_2\text{Me}, (\text{OEt})_3, \text{ClMe}_2, \text{HPh}_2, \text{MePh}_2, \text{Ph}_3$; $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$; $n = 2, 3$) are formed by reaction of an excess of HSiR_3 with $\text{RuH}_2\text{L}_4, \text{RuHClL}_3, \text{RuCl}_2\text{L}_3$, or $\text{RuCl}_3(\text{AsPh}_3)_3$. The chloro complexes react with concurrent formation of ClSiR_3 . With HSiMe_3 or HSiEt_3 , $\text{RuCl}_2(\text{PPh}_3)_3$ is reduced to $\text{RuHCl}(\text{PPh}_3)_3$ and no silyl complexes are formed; these silanes do not react with $\text{RuH}_2(\text{PPh}_3)_4$. Complexes of the type $\text{RuH}_2\text{X}(\text{SiR}_3)\text{L}_3$ ($\text{X} = \text{Cl}, \text{I}$) are obtained by reaction of the chlororuthenium(II) complexes with HSiCl_3 , or of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ with CDCl_3 or I_2 . The complexes $\text{RuH}_3(\text{SiR}_3)\text{L}_3$ undergo silyl exchange or H—D exchange with HSiR'_3 or D_2 .

Introduction

As part of our study of silylmetal complexes [2–7], we have examined the interaction between ruthenium(II) complexes and tertiary silanes. Since the completion of our work [8], two similar studies have been reported, but the results are interpreted rather differently from our findings. We formulate all our compounds as derivatives of ruthenium(IV), $\text{RuH}_3(\text{SiR}_3)\text{L}_n$ ($n = 2, 3$) and $\text{RuH}_2\text{X}(\text{SiR}_3)\text{L}_3$ ($\text{X} = \text{Cl}, \text{I}$), whereas Kono et al. [9] report some complexes of the former type together with four- and five-coordinate ruthenium(II) complexes of the type $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_n$ ($n = 2, 3$) and Svoboda et al. [10] find only the last of these, $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_3$. We therefore present here the evidence for our formulation, which is based on the spectroscopic and chemical properties of the complexes.

* Ref. 1 is regarded as Part XXVI of this series.

Results

The complexes $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuHCl}(\text{PPh}_3)_3$, and $\text{RuH}_2(\text{PPh}_3)_4$ in benzene solution react with an excess of a tertiary silane, HSiR_3 ($\text{R}_3 = \text{F}_3, \text{F}_2\text{Me}, \text{Cl}_2\text{Me}, (\text{OEt})_3, \text{ClMe}_2, \text{HPh}_2, \text{MePh}_2, \text{Ph}_3$), to give white, air-sensitive solids of composition $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$. The reaction is slow, requiring 18–24 h for completion. For a given silane, the same product is obtained from each of the starting complexes. The reaction between $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{HSi}(\text{OEt})_3$ was carried out in a constant volume apparatus, and no change in pressure was observed. When the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{HSi}(\text{OEt})_3$ was allowed to proceed for a short time only, the purple complex $\text{RuHCl}(\text{PPh}_3)_3$ was isolated.

In several cases, the molecular weights of the products indicated that some dissociation was occurring, presumably by loss of a phosphine ligand, and products were often obtained for which analysis suggested a deficiency of triphenylphosphine. The addition of the phosphine during the preparation, or the use of a benzene/hexane mixture in which the products are insoluble, gave pure triphosphine complexes. Repeated recrystallisation gave bis-phosphine complexes, $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_2$ for $\text{R}_3 = \text{F}_3, \text{MeCl}_2$, or $(\text{OEt})_3$. When $\text{RuCl}_2(\text{Ptol}_3)_3$ ($\text{tol} = p\text{-CH}_3\text{C}_6\text{H}_4$) or $\text{RuCl}_3(\text{AsPh}_3)_n$ ($n = 2, 3$) were used, bis-ligand complexes were usually obtained, except for $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{Ptol}_3)_3$.

The complexes $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$ reacted much more rapidly in the presence of triethylamine or with dimethylformamide as solvent. In the latter case use of the undried solvent gave a different product, described below.

The three ruthenium(II) complexes reacted with HSiCl_3 , in benzene solution, to give the yellow complex $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$. Starting from the dichloro complex, an orange solid was also formed which could not be fully characterised but may be a bis-silyl complex similar to that suggested by Svoboda et al. [10].

Trimethyl- and triethyl-silane did not react with $\text{RuH}_2(\text{PPh}_3)_4$ or $\text{RuHCl}(\text{PPh}_3)_3$ but with $\text{RuCl}_2(\text{PPh}_3)_3$ reaction occurred to give $\text{RuHCl}(\text{PPh}_3)_3$ (identified by analysis, IR and NMR spectroscopy) and ClSiMe_3 (IR and NMR); no dihydrogen or hydrogen chloride were detected.

Infrared spectra

The IR spectra of all the complexes show bands characteristic of the neutral ligands and of the SiR_3 groups (Table 1). In the region $1900\text{--}2010\text{ cm}^{-1}$, two or sometimes three broad bands were found, corresponding to Ru–H stretching modes, all of which were at lower frequency than those for the hydridic starting materials. The corresponding deformation modes were observed at ca. 850 cm^{-1} . In the far-IR region, no bands corresponding to Ru–Cl stretching modes were seen, but bands at $330\text{--}350\text{ cm}^{-1}$ were assigned to Ru–Si stretching, by analogy with other systems (cf, refs. 3, 6, and ref. therein).

The spectrum of $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$ showed Ru–H and Ru–Si stretching modes at $1960, 1940$ and 355 cm^{-1} and also a band at 265 cm^{-1} due to Ru–Cl stretching.

TABLE 1
IR DATA FOR $\text{RuH}_3(\text{SiR}_3)_n$ (cm^{-1} , Nujol mulls) ^a

SiR_3	L	n	$\nu(\text{Ru-H})$	$\delta(\text{Ru-H})$	$\nu(\text{Ru-Si})$	SiR_3	Assignment
SiF_3	PPh_3	3	1980s, 1950s	840m, 835m	330m,	825s, 795 s	$\nu(\text{Si-F})$
SiF_2Me	PPh_3	3	1965s, 1935s	840m	323m,	805s, 800s	$\rho(\text{Si-CH}_3)$
SiCl_2Me	PPh_3	3	1995s, 1970s, 1940s	850m	350s,	810, 795s	$\rho(\text{Si-CH}_3)$
Si(OEt)_3	PPh_3	3	2010m, 1970s	850w, 840w	315w,	1068s	$\nu(\text{Si-O-C})$
SiClMe_2	PPh_3	3	2000m, 1955s, 1935s	850m, 840s	350s,	810s	$\rho(\text{Si-CH}_3)$
SiHPh_2	PPh_3	3	1975s, 1960s, 1903m	875m, 830w	—	2010	$\nu(\text{Si-H})$
SiMePh_2	PPh_3	3	1970s, 1955s, 1935s	845m, 830w	335s,	790s	$\rho(\text{Si-CH}_3)$
SiPh_3	PPh_3	3	1970s, 1955s	850m, 810m			
SiF_2Me	Ptol_3	2	1935m, 1915m	845m	350w,	805s	$\rho(\text{Si-CH}_3)$
SiCl_2Me	Ptol_3	2	1970s, 1955s, 1940s	835m	350m,	790s	$\rho(\text{Si-CH}_3)$
SiClEt_2	Ptol_3	2	1945s, 1925s	850w, 838w	350m		
Si(OEt)_3	Ptol_3	3	1945m, 1910m	843m, 835w,	350w,	1070s	$\nu(\text{Si-O-C})$
SiF_2Me	AsPh_3	2	1965s, 1945m	835m	360w,	805s	$\rho(\text{Si-CH}_3)$
SiCl_2Me	AsPh_3	2	1950s, 1920s	850w	360m,	800s	$\rho(\text{Si-CH}_3)$
Si(OEt)_3	AsPh_3	2	1990m, 1965m	840w		1070s	$\nu(\text{Si-O-C})$
SiEt_3	AsPh_3	2	1985m, 1962m	845w	350w		

^a The complexes $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ have $\nu(\text{Ru-H})$ at 2030 and 2075 cm^{-1} , respectively, and $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$ have $\nu(\text{Ru-Cl})$ at 315 and 280 cm^{-1} , respectively.

NMR spectra

All the silyl complexes gave ^1H NMR signals in the high-field region (ca. τ 20) characteristic of hydride ligands (Table 2). The complex $\text{RuH}_3[\text{Si(OEt)}_3](\text{AsPh}_3)_2$ gave a sharp single line but the phosphine complexes gave broad bands

TABLE 2
NMR DATA FOR $\text{RuH}_3(\text{SiR}_3)_n$ (τ , ppm)

SiR_3	L	n	$\tau(\text{Ru-H})$	$\tau(\text{CH}_3)$	$\tau(\text{CH}_2)$	Solvent
SiF_2Me	PPh_3	3	20.51	9.33		CH_2Cl_2
SiCl_2Me	PPh_3	3	19.80 19.52	9.52		CH_2Cl_2 C_6H_6
Si(OEt)_3	PPh_3	3	20.41 20.05	9.25	6.70	CH_2Cl_2 C_6H_6
SiClMe_2	PPh_3	3	20.00	9.72		CH_2Cl_2
SiHPh_2 ^a	PPh_3	3	19.84			CH_2Cl_2
SiPh_3	PPh_3	3	19.82			CH_2Cl_2
SiCl_2Me	Ptol_3	2	19.87	9.49 (SiMe) 7.77 (tol)		CH_2Cl_2
Si(OEt)_3	Ptol_3	3	20.68	9.26 (OEt) 7.78 (tol)	6.73	CH_2Cl_2
Si(OEt)_3	AsPh_3	2	21.60	9.30	6.67	C_6H_6

^a Also τ 4.78 (C_6H_6) corresponding to Si-H.

with half-widths of 80–90 Hz, with some fine structure superposed on the broad envelope. The breadth and incomplete resolution suggest that exchange processes may be occurring, either by dissociation or by fluxional rearrangement.

The spectrum of $\text{RuH}_3(\text{SiCl}_2\text{Me})(\text{PPh}_3)_3$ was unaffected by the addition of three molar equivalents of the phosphine. The high-field spectrum of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{Ptol}_3)_3$ was unchanged after the addition of one molar equivalent of Ptol_3 , but the low-field region showed two distinct resonances due to the methyl groups of the coordinated and free ligand (τ 7.78 and 7.72, respectively). The latter peak increased in intensity on addition of more of the phosphine, the other signal being unaffected. These results show that phosphine dissociation or exchange does not occur rapidly on the NMR time scale. Exchange by loss of silane was also eliminated as a relaxation mechanism, since the spectra of $\text{RuH}_3[\text{Si}(\text{OEt})_3]\text{L}_3$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$) were unaffected by addition of the free silane. The spectra of these last-named complexes were examined in the temperature range -50 to $+95^\circ\text{C}$; on raising the temperature the high-field signal became slightly less broad, but a well resolved pattern was not obtained.

Integration was difficult owing to the breadth of the signals, but the spectra of $\text{RuH}_3(\text{SiR}_3)\text{L}_3$ ($\text{R}_3 = \text{Cl}_2\text{Me}, \text{L} = \text{PPh}_3; \text{R} = \text{OEt}, \text{L} = \text{Ptol}_3, \text{AsPh}_3$) showed the ratios of $\text{Ru}-\text{H}/\text{L}$ and $\text{Ru}-\text{H}/\text{SiR}_3$ to be 1/1 and 3/1, respectively. A known amount of $\text{RhHCl}[\text{Si}(\text{OEt})_3](\text{PPh}_3)_2$ ($\text{Rh}-\text{H}, \tau$ 24.85 [7]) was added to a solution of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$, and integration of the high-field signals gave a ratio of 1/2.5.

Reactions of the silyl complexes

(i) *With carbon monoxide.* On stirring a solution of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ under carbon monoxide, one molar equivalent of gas was taken up. The IR spectrum of the resulting solution showed that the bands of the starting complex had largely disappeared, and new absorptions were found characteristic of $\text{HSi}(\text{OEt})_3$ (2175 cm^{-1} , $\nu(\text{Si}-\text{H})$) and of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ ($1965, 1890\text{ cm}^{-1}$, $\nu(\text{Ru}-\text{H})$); 1940 cm^{-1} , ($\nu(\text{C}-\text{O})$). The intensity of the 2175 cm^{-1} band corresponded to 0.85 molar equivalents of $\text{HSi}(\text{OEt})_3$. The NMR spectrum of the solution gave further confirmation of the reaction, showing additional resonances at τ 6.15, 8.69 corresponding to free $\text{HSi}(\text{OEt})_3$. A white solid was precipitated on addition of hexane, identified as $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ by analysis and comparison of the IR spectrum with that of an authentic sample.

(ii) *With hydrogen chloride.* The complexes $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ ($\text{R}_3 = (\text{OEt})_3, \text{MeCl}_2$) reacted rapidly with an excess of hydrogen chloride to give the brown $\text{RuCl}_2(\text{PPh}_3)_3$, and the free silane. When equimolar portions of the reactants were combined, the same products were obtained, with no indication of intermediates such as $\text{RuH}_2\text{Cl}(\text{SiR}_3)(\text{PPh}_3)_3$ or $\text{RuHCl}(\text{PPh}_3)_3$.

(iii) *With deuteriochloroform and carbon tetrachloride.* The NMR spectrum of a solution of $\text{RuH}_3(\text{SiF}_2\text{Me})(\text{PPh}_3)_3$ in CDCl_3 showed a resonance at τ 4.8 corresponding to CH_2Cl_2 (or CHDCl_2). After some time, the purple complex $\text{RuHCl}(\text{PPh}_3)_3$ and the free silane, HSiF_2Me , were formed. It seems likely that the initial product would be $\text{RuH}_2\text{Cl}(\text{SiF}_2\text{Me})(\text{PPh}_3)_3$ (see below) which decomposed to the observed products. A similar reaction occurred when RuH_3-

$[\text{Si}(\text{OEt})_3](\text{AsPh}_3)_2$ was dissolved in CDCl_3 ; Integration of the signals at τ 4.8 (CHDCl_2), 6.67 and 9.30 $[\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ and 21.8 (Ru—H) consistently gave ratios of 1/9/6/2, suggesting the presence of equimolar quantities of CHDCl_2 and the probable product, $\text{RuH}_2\text{Cl}[\text{Si}(\text{OEt})_3](\text{AsPh}_3)_2$. When $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ in C_6F_6 was treated with CCl_4 (the complex is not soluble in pure CCl_4), a new resonance appeared at τ 2.82 ppm, corresponding to CHCl_3 , and $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{HSi}(\text{OEt})_3$ were slowly formed.

(iv) *With iodine.* A benzene solution of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ reacted with 0.5 molar equivalents of iodine to give a gas, identified by mass spectroscopy as dihydrogen, and a brown solid analysing as $\text{RuH}_2\text{I}[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$. The NMR spectrum of a CH_2Cl_2 solution of this solid showed a broad resonance centred on τ 20.14 and sharp signals at τ 6.7, 9.3 characteristic of a coordinated $\text{Si}(\text{OEt})_3$ group. The IR spectrum showed ν (Ru—H) at 1965 cm^{-1} .

(v) *With dideuterium.* A benzene solution of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ was stirred under an atmosphere of dideuterium at room temperature for 16 h. The mass spectrum of the residual gas indicated the formation of H_2 and HD, and the IR spectrum of the white solid precipitated on addition of n-hexane showed much diminished absorption at 1960 cm^{-1} and a new band at 1410 cm^{-1} , assigned as $\nu(\text{Ru—D})$. The experiment was repeated with frequent renewal of the D_2 atmosphere over three days, but it was not possible completely to remove the IR absorption at 1960 cm^{-1} . The NMR spectrum of the recovered solid, dissolved in CH_2Cl_2 , showed a broad unresolved signal at τ 20.4 identical in position and shape to that of the starting material.

(vi) *With silanes.* Solutions of $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ ($\text{R}_3 = (\text{OEt})_3, \text{Cl}_2\text{Me}$) in benzene reacted with HSiF_3 to give the F_3Si complex and free HSiR_3 . The $(\text{EtO})_3\text{Si}$ complex in benzene reacted with HSiCl_3 to give the yellow $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$, identical with that obtained from reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with HSiCl_3 .

Reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with Chlorosilanes

A benzene solution of $\text{RuH}_2(\text{PPh}_3)_4$ was shaken for 24 h with an excess of ClSiMe_3 to give the purple $\text{RuHCl}(\text{PPh}_3)_3$ and HSiMe_3 . The dihydride, in benzene/hexane, also reacted with SiCl_4 to give the brown $\text{RuCl}_2(\text{PPh}_3)_3$ and HSiCl_3 .

Discussion

The above results agree with the reports of Kono et al. [9] and Svoboda et al. [10], that the reaction of tertiary silanes with $\text{RuH}_2(\text{PPh}_3)_4$, $\text{RuHCl}(\text{PPh}_3)_3$ or $\text{RuCl}_2(\text{PPh}_3)_3$ give the silyl complexes $\text{RuH}_x(\text{SiR}_3)(\text{PPh}_3)_y$ ($y = 2, 3$), and we have also obtained corresponding AsPh_3 and Ptol_3 complexes. One neutral ligand appears to dissociate readily and is lost during recrystallisation, but is retained if additional ligand is added to the reaction mixture. The formulations differ, however, in the number of hydride ligands, x , associated with the ruthenium. For materials derived from $\text{RuH}_2(\text{PPh}_3)_4$, we agree with the suggestion of the Japanese workers [9] the oxidative-elimination has occurred to give the seven-coordinate silylruthenium(IV) derivatives $\text{RuH}_3(\text{SiR}_3)\text{L}_3$. The products we ob-

TABLE 3

COMPARISON OF IR DATA ($\bar{\nu}$, cm^{-1}) IN THE Ru—H STRETCHING REGION FOR (a) $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ (Nujol) AND (b) $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_3$ (KBr [9]) (agreement of other bands is also good)

SiClMe ₂		SiCl ₂ Me		Si(OEt) ₃		SiHPh ₂	SiClPh ₂
(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
2000	1998	1995				2010	2000
1955	1957	1970		1970	1969	1975	1980
1935	1940	1940	1945			1960	1968
						1903	1910

tain from the chlororuthenium complexes appear to be identical to those from the dihydride, and we observed the intermediate formation of $\text{RuHCl}(\text{PPh}_3)_3$ when starting from the dichloro-complex; in agreement with the other workers [9–11], we find that reaction stops at this stage when HSiEt_3 or HSiMe_3 are used. However, both the other groups formulate the products of reaction of $\text{RuCl}_2(\text{PPh}_3)$ or $\text{RuHCl}(\text{PPh}_3)_3$ as ruthenium(II) complexes, $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_y$ ($y = 2, 3$). The two formulations are not distinguishable by analysis, since they differ only by two hydrogen atoms, and no NMR data were given. Comparison of the IR spectra is not easy because few common silanes were used, different media were employed for the spectra, and most of the absorptions are not diagnostic, being those of PPh_3 or the silyl groups. Such comparisons as can be made suggest that both sets of products are the same (Table 3). While five-coordinate ruthenium(II) complexes are well known, there do not appear to be any examples of four-coordinate complexes, and we feel that formulation of all these materials as ruthenium(IV) species, $\text{RuH}_3(\text{SiR}_3)_y$ ($y = 2, 3$), is more reasonable. The evidence for the presence of three hydride ligands may be summarised as follows:

(a) Integration of NMR spectra for several complexes, including those derived from chloro complexes, e.g. $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{AsPh}_3)_2$.

(b) Integration of the NMR spectrum of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{AsPh}_3)_2$ in CDCl_3 shows the presence of equimolar amounts of CHDCl_2 and a dihydride species, presumably $\text{RuH}_2\text{Cl}[\text{Si}(\text{OEt})_3](\text{AsPh}_3)_2$.

(c) Lack of gas evolution in the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with HSiR_3 .

(d) Formation of halogen-silyl complexes which are also hydrides, e.g. $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$; $\text{RuH}_2\text{I}[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$.

(e) Evolution of dihydrogen on reaction of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ with iodine.

(f) Formation of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{HSi}(\text{OEt})_3$ from reaction of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ with carbon monoxide.

There is also a difference in formulation of the products derived from secondary silanes, H_2SiR_2 . Kono et al. report that reactions with $\text{RuCl}_2(\text{PPh}_3)_3$ result in halogen transfer and formation of $\text{RuH}(\text{SiR}_2\text{Cl})(\text{PPh}_3)_3$ [9]. These materials show up to three Ru—H stretching modes in the IR, but no Si—H modes were assigned, and the NMR spectra (in CDCl_3) integrated correctly for the above formulation ($\text{R} = \text{Et}$). We have examined only H_2SiPh_2 , but obtain the same product from $\text{RuH}_2(\text{PPh}_3)_4$ and from $\text{RuCl}_2(\text{PPh}_3)_3$ which we for-

multate as $\text{RuH}_3(\text{SiHPh}_2)(\text{PPh}_3)_3$. The IR spectrum of our product and that of the Japanese workers appear to be the same (Table 3), and a band at 2010 cm^{-1} can be assigned to the coordinated SiHPh_2 group. The NMR spectrum (in C_6H_6) showed a resonance at τ 4.78, attributable to the SiHPh_2 group (free H_2SiPh_2 appears at τ 5.12). In view of our observation that the trihydrido complexes react with CDCl_3 , it is not surprising that the NMR spectra obtained by Kono et al. using this solvent showed only a small signal due to Ru-H . We find that HSiCl_3 exerts a chlorinating effect similar to that of CHCl_3 or CCl_4 , since reactions with this silane gave $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$. The same product was obtained by the reaction of $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ with HSiCl_3 . A product of similar stoichiometry was obtained by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{HSi}(\text{OEt})_3$ in undried DMF, $\text{RuH}_2\text{Cl}[\text{Si}(\text{OEt})_3](\text{PPh}_3)_2(\text{DMF})$; in this case, the chlorinating agent was presumably a trace of HCl formed by hydrolysis of $\text{ClSi}(\text{OEt})_3$.

In conclusion, we feel that the products of reaction of silanes with ruthenium(II) complexes should be formulated as ruthenium(IV) complexes, $\text{RuH}_3(\text{SiR}_3)_3$ or $\text{RuH}_2\text{Cl}(\text{SiR}_3)_3$, the latter being unstable in solution in the absence of an excess of the silane, when they revert to $\text{RuHCl}(\text{PPh}_3)_3$.

Experimental

Solvents were dried and degassed by standard methods; reactions were performed under nitrogen. Ruthenium-containing starting materials were prepared by literature methods [12–15]. IR and NMR spectra were obtained with Perkin–Elmer 257, 621 and R20 or Varian HA100 spectrometers. Analytical data were obtained from the Microanalytical Laboratory of this Department, and are given in Table 4.

Silyl complexes were made by methods of which the following are typical.

Trihydrido(dimethylchlorosilyl)tris(triphenylphosphine)ruthenium(IV)

The complex $\text{RuCl}_2(\text{PPh}_3)_3$ (0.5 g, 0.52 mmol) was sealed in an evacuated tube with dimethylchlorosilane (5.0 mmol) and benzene/n-hexane (10% v/v, 1.0 cm^3). The tube was shaken at room temperature until the brown colour of the starting material had disappeared (18 hours). The white solid product was filtered off, washed with n-hexane and dried in vacuo.

Other complexes were obtained analogously. Dichloromethane/hexane (10%), triethylamine/benzene (50%) or dry dimethylformamide could also be used as solvents. If hexane was omitted and the solids were subsequently precipitated by the addition of hexane, consistently low C and H analyses were found. Repeated recrystallisation gave bis-phosphine complexes.

Similar procedures were used when starting from $\text{RuHCl}(\text{PPh}_3)_3$ or $\text{RuH}_2(\text{PPh}_3)_4$.

Analogous reactions with HSiMe_3 or HSiEt_3 and $\text{RuCl}_2(\text{PPh}_3)_3$, with diglyme as solvent, resulted in the formation of $\text{RuHCl}(\text{PPh}_3)_3$ and ClSiMe_3 or ClSiEt_3 , identified by IR and NMR spectroscopy ($\nu(\text{Ru-H})$, 2030 cm^{-1} ; $\nu(\text{Ru-Cl})$, 280 cm^{-1} (lit. $2020, 280\text{ cm}^{-1}$ [13]); Ru-H , τ 28.3 (CH_2Cl_2); $^2J(\text{P-H})$, 26 Hz (lit. τ 28.08, 26 Hz [16]); ClSiMe_3 : $770, 625, 485\text{ cm}^{-1}$, identical to an authentic sample; τ 9.90). Similarly, $\text{RuH}_2(\text{PPh}_3)_4$ reacted with ClSiMe_3 or SiCl_4 to form $\text{RuHCl}(\text{PPh}_3)_3$ (IR) and HSiMe_3 or HSiCl_3 (IR).

TABLE 4
 ANALYTICAL DATA

Compound	Preparation ^a	Analysis (found (calcd.) (%))			Mol. wt.
		C	H	Other	
RuH ₃ [Si(OEt) ₃](PPh ₃) ₃	b	67.7 (68.3)	5.9 (5.8)		934, 945 (1045)
	c	67.6	6.1		
	d	68.4	5.8		
RuH ₃ [Si(OEt) ₃](PPh ₃) ₂		64.5 (63.9)	5.8 (5.8)		
RuH ₃ (SiF ₃)(PPh ₃) ₃	b, d	65.6 (66.5)	5.2 (4.8)	F 5.8 (5.8)	647 (974)
RuH ₃ (SiF ₂ Me)(PPh ₃) ₃	b, c, d	67.8 (67.9)	5.5 (5.3)	F 3.8 (3.9)	
RuH ₃ (SiCl ₂ Me)(PPh ₃) ₃	b, c, d	65.6 (65.8)	5.0 (5.0)	Cl 7.0 Cl (7.1)	720, 753 (1003)
RuH ₃ (SiCl ₂ Me)(PPh ₃) ₂		59.1 (60.0)	4.8 (4.6)		
RuH ₃ (SiClMe ₂)(PPh ₃) ₃	b	67.9 (68.3)	5.7 (5.5)	Cl 4.2 (3.6)	
	d	68.2	5.4	Cl 4.3	
RuH ₃ (SiMePh ₂)(PPh ₃) ₃	b, d	73.9 (74.0)	5.8 (5.6)		
RuH ₃ (SiHPh ₂)(PPh ₃) ₃	b	72.0 (73.8)	5.7 (5.5)		
	d	73.4	5.5		
RuH ₃ (SiPh ₃)(PPh ₃) ₃	b, d	75.7 (75.3)	5.4 (5.5)		
RuH ₃ (SiF ₂ Me)(Ptol ₃) ₂		63.1 (65.0)	5.9 (6.0)	F 4.0 (4.8)	
RuH ₃ (SiCl ₂ Me)(Ptol ₃) ₂		62.9 (62.5)	6.3 (5.8)	Cl 8.1 (8.6)	
RuH ₃ [Si(OEt) ₃](Ptol ₃) ₃		69.8 (70.3)	7.1 (6.8)		
RuH ₃ (SiClEt ₂)(Ptol ₃) ₂		65.3 (66.1)	7.1 (6.8)	Cl 4.4 (4.2)	
RuH ₃ (SiCl ₂ Me)(AsPh ₃) ₂		53.9 (53.6)	4.4 (4.3)	Cl 8.9 (8.6)	
RuH ₃ [Si(OEt) ₃](AsPh ₃) ₂		58.0 (57.4)	5.5 (5.5)		
RuH ₃ (SiEt ₃)(AsPh ₃) ₂		61.8 (60.8)	5.4 (5.6)		
RuH ₂ Cl(SiCl ₃)(PPh ₃) ₂	b	54.2 (54.1)	3.9 (4.0)	Cl 19.0 (17.8)	
	d	53.8	3.9	Cl 17.8	
RuH ₂ Cl[Si(OEt) ₃](PPh ₃) ₂ (DMF)		60.1	6.1	N 1.4	
		(60.0)	(6.0)	(1.6)	
				Cl 4.2 (4.0)	

^a Starting material: b, RuCl₂(PPh₃)₃; c, RuHCl(PPh₃)₃; d, RuH₂(PPh₃)₄.

Reactions of silyl complexes

(a) *With carbon monoxide.* The complex $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ (0.13 g, 0.12 mmol), dissolved in benzene (4 cm³), was stirred under carbon monoxide and the pressure monitored. Gas absorption was complete in 7 h, and three experiments gave an average uptake of 0.12 mmol. The mass spectrum of the residual gas showed that no hydrogen was present. The experiment was repeated using a stream of CO, and the IR and NMR spectra of the resulting solution showed resonances characteristic of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{HSi}(\text{OEt})_3$. Addition of hexane to the solution precipitated a white solid which was identified by analysis as $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (Found: C, 71.4; H, 5.1 calcd.: C, 71.9; H, 5.1%; $\nu(\text{Ru}-\text{H})$ 1960, 1900 cm⁻¹; $\nu(\text{C}-\text{O})$ 1940 cm⁻¹, (lit. [14] 1960, 1900, 1940 cm⁻¹)).

(b) *With hydrogen chloride.* The complex $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ ($\text{R}_3 = (\text{OEt})_3, \text{Cl}_2\text{Me}$) (0.25 mmol) was dissolved in benzene (3 cm³) and hydrogen chloride gas was bubbled through the solution. A brown solid was rapidly precipitated, filtered off, and identified by IR spectroscopy as $\text{RuCl}_2(\text{PPh}_3)_3$. The IR spectrum of the filtrate showed the presence of free HSiR_3 .

(c) *With trifluorosilane.* The complex $\text{RuH}_3(\text{SiR}_3)(\text{PPh}_3)_3$ ($\text{R}_3 = (\text{OEt})_3, \text{Cl}_2\text{Me}$) (0.25 mmol), benzene (0.3 cm³) and HSiF_3 (5.0 mmol) were sealed under vacuum and shaken for three days. The residual white solid was filtered off, washed with n-hexane and identified by analysis and IR spectroscopy as $\text{RuH}_3(\text{SiF}_3)(\text{PPh}_3)_3$. (C, 65.7; H, 4.7; F, 5.4. calcd.: C, 66.5; H, 4.8; F, 5.8%.)

(d) *With trichlorosilane.* The complex $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ (0.23 g, 0.22 mmol), benzene (0.3 cm³) and freshly distilled HSiCl_3 (5.0 mmol) were shaken until the white colour of the ruthenium complex disappeared (24 h). The yellow product was filtered off, washed with n-hexane and identified by analysis and IR spectroscopy as $\text{RuH}_2\text{Cl}(\text{SiCl}_3)(\text{PPh}_3)_2$ (C, 55.7; H, 4.0; Cl, 17.4. calcd.: C, 54.1; H, 4.0; Cl, 17.8%.)

(e) *With iodine.* The complex $\text{RuH}_3[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ (0.25 g, 0.24 mmol) in benzene (5 cm³) was treated with iodine (0.15 g, 0.12 mmol) and stirred for 30 min at room temperature. A gas was evolved and identified by mass spectrometry as hydrogen. A brown solid was also formed which, by analysis, IR and NMR spectroscopy, appeared to be $\text{RuH}_2\text{I}[\text{Si}(\text{OEt})_3](\text{PPh}_3)_3$ (C, 59.9; H, 4.3; I, 9.8. calcd.: C, 61.0; H, 5.2; I, 10.8%; $\nu(\text{Ru}-\text{H})$, 1965 cm⁻¹; $\text{Si}(\text{OCH}_2\text{CH}_3)_3$, τ 6.7, 9.3; $\text{Ru}-\text{H}$, τ 20.14 (CH_2Cl_2)).

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