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PHOSPHINE COMPLEXES OF SILYLRUTHENIUM HYDRIDES. INTERACTION OF SILICON HYDRIDE WITH $RuH_2(PPh_3)_4$, $RuCl_2(PPh_3)_3$, AND $RuHCl(PPh_3)_3$

HIROMICHI KONO *, NAOFUMI WAKAO, KAZUSHI ITO
Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara Kanagawa 229 (Japan)

and YOICHIRO NAGAI
Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

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Summary

The reaction of $RuH_2(PPh_3)_4$ with a variety of organosilicon hydrides, R_3SiH, gave the complexes $RuH_3(SiR_3)(PPh_3)_3$ where $R_3Si = Et_3Si$, $EtMe_2Si$, $PhMe_2Si$, Ph_3Si, $Ph(MeO)_2Si$, $(EtO)_3Si$, Et_2HSi, PhMeHSi, Ph_2HSi, cyclo-$C_6H_{11}H_2Si$, and PhH_2Si. Without solvent $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3 \cdot C_6H_6$ reacted with R_3SiH, where $R_3Si = Cl_3Si$, Cl_2MeSi, $ClMe_2Si$, $Ph(MeO)_2Si$, $(EtO)_3Si$, and $(MeO)_3Si$, to give $RuH(SiR_3)(PPh_3)_2$; in benzene solution, however, hydrides such as $ClMe_2SiH$, $Ph(MeO)_2SiH$, Et_2SiH_2, Ph_2SiH_2, and cyclo-$C_6H_{11}SiH_3$, afforded $RuH(SiR_3)(PPh_3)_3$. $RuCl_2(PPh_3)_3$ was reduced by Et_3SiH, $PhMe_2SiH$, and $EtMe_2SiH$ in organic solvents to give $RuHCl(PPh_3)_3 \cdot$ solvent. These silylruthenium hydride complexes were characterized by IR, NMR, and elemental analyses. The reactions of some silylruthenium hydride complexes were also investigated.

Introduction

A large number of silyl derivatives of transition metals has been prepared by the reaction of low valent metal complexes with silicon hydrides [1]. In particular, the oxidative addition of silicon hydrides to phosphine complexes of Group VIII elements such as cobalt [2], rhodium [3], iridium [4], nickel [5], palladium [6], and platinum [7] has been well studied in connection of hydrosilylation.

Previously we found that a silicon hydride reacts with $RuH_2(PPh_3)_4$ to give an apparently seven-coordinate silylruthenium hydride complex, $RuH_3(SiR_3)(PPh_3)_3$ [8]. It was therefore of interest to examine extensively the reaction of silicon hydrides with $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$. Quite recently, Svoboda, Řeřicha, and Hetflejš used ruthenium—phosphine complexes as catalysts for hydrosilylation without success and instead observed the formation of five-coordinate silylruthenium complexes such as $RuH(SiR_3)(PPh_3)_3$ and $Ru(SiR_3)_2(PPh_3)_3$ where R = EtO and Cl [9].

In this paper we present our observations on the interaction of silicon hydrides with phosphine complexes of ruthenium(II) including $RuH_2(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $RuHCl(PPh_3)_3$, and describe the preparation and properties of a series of silylruthenium hydride complexes.

Results and discussion

Although the phosphine complexes of silylruthenium hydrides here prepared were characterized by IR, NMR, and analytical data, the poor solubility and instability of some of the compounds in organic solvent made it impossible to obtain NMR data and to purify the complexes for accurate analytical data.

I. Interaction of silicon hydrides with $RuH_2(PPh_3)_4$

As described briefly in a previous paper [8], tetrakis(triphenylphosphine)-ruthenium dihydride, $RuH_2(PPh_3)_4$, reacted with silicon hydrides, such as Et_3SiH, $EtMe_2SiH$, $PhMe_2SiH$, $(EtO)_3SiH$, Ph_3SiH, Et_2SiH_2, $PhMeSiH_2$, cyclo-$C_6H_{11}SiH_3$, and $PhSiH_3$, to afford seven-coordinate silylruthenium compounds of general formula $RuH_3(SiR_3)(PPh_3)_3$.

$$RuH_2(PPh_3)_4 + R_3SiH \rightarrow RuH_3(SiR_3)(PPh_3)_3 + PPh_3 \qquad (1)$$

The complexes have been prepared at room temperature by the direct reaction of finely divided $RuH_2(PPh_3)_4$ with an excess of the silane in an evacuated tube or under an atmosphere of argon. Normally silicon hydrides reacted completely in 3—48 hours. Neither gas evolution nor exothermicity were observed during the course of reaction. Neat triethylsilane and triphenylsilane in degassed hexane reacted slowly and these reactions took several months for completion, as in the case of $RhCl(PPh_3)_3$, as reported by Haszeldine et al. [3]. Infrared and analytical data are summarized in Table 1.

The infrared spectra of the solid complexes indicated strong or medium bands due to ν(Ru—H) [9] at 1995—1880 cm^{-1}. The spectra of hydrosilylruthenium complexes showed two bands due to ν(Si—H) in a KBr disk spectrum, i.e., an absorption at 2135—2030 cm^{-1} which presumably depends on crystalline forms and was not detectable in a nujol mull spectrum, and one at 2060—1966 cm^{-1} (sharp). The assignment of Ru—H and Si—H stretching absorption bands was confirmed by infrared measurements of $RuH_2D(SiDPh_2)(PPh_3)_3$, which exhibited characteristic absorption bands at 1970 (br), (Ru—H), 1920 (br), (Ru—H), 1472 s, (Si—D), and 1418 s, (Ru—D) cm^{-1} in KBr disk. As typical examples, infrared spectra of $RuH_3(SiPh_3)(PPh_3)_3$, $RuH_3(SiHPh_2)(PPh_3)_3$, $RuH_2D(SiDPh_2)(PPh_3)_3$, and $RuH_3(SiH_2Ph)(PPh_3)_3$ (nujol mull) in the region 2100—1800 cm^{-1} are shown in Fig. 1.

Immediate NMR measurement in C_6D_6 afforded legitimate support for the seven coordinate structure of the silylruthenium complexes, as inferred from an NMR spectrum of $RuH_3[Si(OEt)_3](PPh_3)_3$ (Fig. 2). Table 2 lists NMR signals due to RuH_3 of the silylruthenium complexes appearing in the high field (about τ 20)

TABLE 1

PHYSICAL PROPERTIES OF THE PHOSPHINE COMPLEXES OF SILYLRUTHENIUM TRIHYDRIDE

Compound	Decomp. point(°C)	IR (KBr disk) (cm^{-1})		Analyses: Found (calcd.) (%)	
		Ru—H	Si—H	C	H
$(Ph_3P)_3RuH_3(SiEt_3)$	101—104	1995 1975 1965		71.27 (71.62)	6.17 (6.31)
$(Ph_3P)_3RuH_3(SiEtMe_2)$	131—133	1993 1952		71.47 (71.57)	5.62 (6.01)
$(Ph_3P)_3RuH_3(SiPhMe_2)$	121—123	1982 1958 1948		72.32 (72.56)	5.99 (5.79)
$(Ph_3P)_3RuH_3(SiPh_3)$	130—132	1970 1948		75.31 (75.18)	5.58 (5.52)
$(Ph_3P)_3RuH_3[Si(OEt)_3]$	131—134	1975 1965		68.00 (68.36)	6.01 (6.02)
$(Ph_3P)_3RuH_3(SiHEt_2)$	103—105	1967 1942	2030 1996	69.94 (71.57)	5.92 (6.01)
$(Ph_3P)_3RuH_3(SiHMePh)$	110—112	1980 1948	2120 2000	72.09 (72.38)	5.82 (5.68)
$(Ph_3P)_3RuH_3(SiHPh_2)$	143—145	1975 1963 1918	2125 2010	72.66 (73.79)	5.49 (5.54)
$(Ph_3P)_3RuH_3(SiH_2C_6H_{11})$	119—121	1935	2120 2040 2010	70.96 (71.76)	6.42 (6.12)
$(Ph_3P)_3RuH_3(SiH_2Ph)$	131—133	1958 1934 1883	2135 2065	71.33 (72.20)	5.53 (5.55)

II. Interaction of silicon hydrides with $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ without solvent

The reactions of $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ with a variety of silicon hydrides were found to depend on the nature of the hydrides and also on the

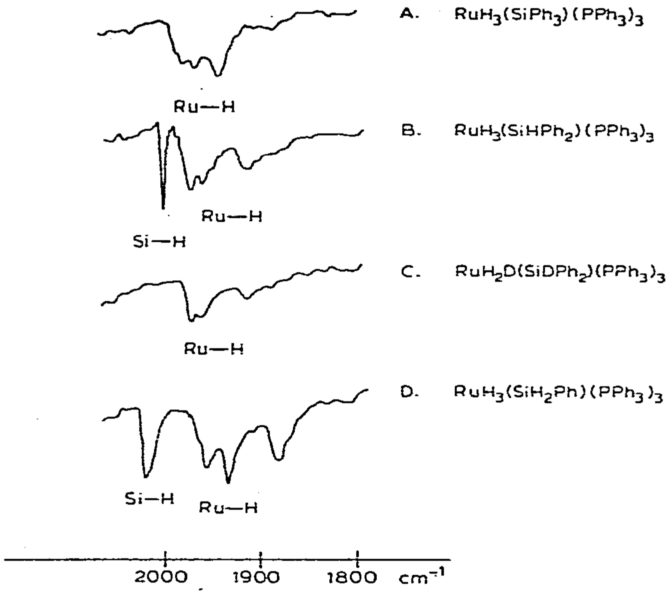

Fig. 1. Infrared spectrum (Nujol mull) in the region 2100—1800 cm^{-1} of the phosphine complexes of phenylsilylruthenium trihydride.

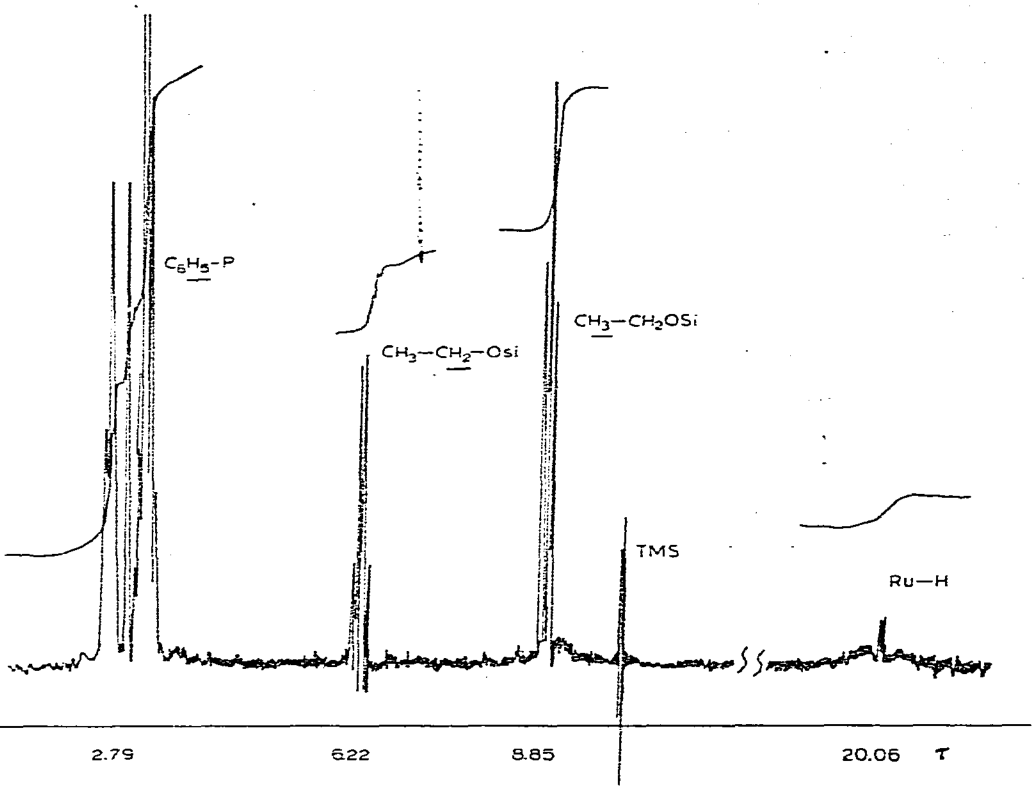

Fig. 2. NMR spectrum of $RuH_3[Si(OEt)_3](PPh_3)_3$ in C_6D_6.

solvent. In the absence of solvent, the ruthenium halides reacted with the chlorohydrosilanes, such as Cl_3SiH, Cl_2MeSiH, and $ClMe_2SiH$ and alkoxyhydrosilanes, such as $Ph(MeO)_2SiH$, $(EtO)_3SiH$, and $(MeO)_3SiH$, to give solid products which were formulated as $RuH(SiR_3)(PPh_3)_2$ on the basis of IR and analytical data (Table 3). The reaction was carried out with vigorous stirring at room temperature using excess silicon hydride under an atmosphere of argon or in an evacuated tube. Initial evolution of some gas was observed and the starting ruthenium compound gradually dissolved in the silicon hydride. Finally a pale brown solid was precipitated. The isolated complexes were sparingly soluble in organic sol-

TABLE 2

^{1}H NMR DATA OF THE PHOSPHINE COMPLEXES OF SILYLRUTHENIUM TRIHYDRIDE

Compound	Ru—H (τ in C_6D_6)
$(Ph_3P)_3RuH_3(SiEtMe_2)$	19.4
$(Ph_3P)_3RuH_3(SiPhMe_2)$	19.7
$(Ph_3P)_3RuH_3[Si(OEt)_3]$	20.1
$(Ph_3P)_3RuH_3(SiHEt_2)$	19.9
$(Ph_3P)_3RuH_3(SiHPhMe)$	19.9
$(Ph_3P)_3RuH_3(SiHPh_2)$	19.9
$(Ph_3P)_3RuH_3(SiH_2C_6H_{11})$	19.7
$(Ph_3P)_3RuH_3(SiH_2Ph)$	19.5

TABLE 3

PHYSICAL PROPERTIES OF THE BIS-PHOSPHINE COMPLEXES OF SILYLRUTHENIUM HYDRIDE

Compound	Decomp. point (°C)	IR (KBr disk) (cm^{-1}) Ru—H	Analyses Found (calcd.) (%)		
			C	H	Cl
$(Ph_3P)_2RuH(SiCl_3)$	165—167	1978	56.52 (56.81)	4.58 (4.11)	
$(Ph_3P)_2RuH(SiMeCl_2)$	145—147	1945	59.02 (60.00)	4.82 (4.63)	9.87 (9.57)
$(Ph_3P)_2RuH(SiMe_2Cl)$	130—132	1955	63.61 (63.37)	5.23 (5.18)	4.96 (4.92)
$(Ph_3P)_2RuH[SiPh(OMe)_2]$	140—142	1967	66.59 (66.57)	5.05 (5.33)	
$(Ph_3P)_2RuH[Si(OEt)_3]$	128—132	1969	64.18 (63.86)	5.58 (5.87)	
$(Ph_3P)_2RuH[Si(OMe)_3]$	124—127	1970	63.05 (62.47)	5.59 (5.39)	

vents including $CHCl_3$, CCl_4, and benzene, and stable in air in the solid phase. The infrared spectra of $RuH(SiR_3)(PPh_3)_2$ exhibited a medium broad band due to ν(Ru—H) at 1980—1945 cm^{-1} (Table 3), but the far-infrared spectra of the compounds showed no absorption band assignable to ν(Ru—Cl).

Triorganomonohydrosilanes such as Et_3SiH, $EtMe_2SiH$, and $PhMe_2SiH$ did not react with the ruthenium complexes even at elevated temperature.

$$RuCl_2(PPh_3)_3 + R_3SiH \xrightarrow{-Cl_2} RuH(SiR_2)(PPh_3)_2 + PPh_3 \qquad (2)$$

$$RuHCl(PPh_3)_3 + R_3SiH \xrightarrow{-HCl} RuH(SiR_3)(PPh_3)_2 + PPh_3 \qquad (3)$$

$R_3 = Cl_3, Cl_2Me, ClMe_2, Ph(OMe)_2, (OEt)_3, (OMe)_3$

With silicon di- and tri-hydrides, such as Et_2SiH_2, $PhMeSiH_2$, Ph_2SiH_2, cyclo-$C_6H_{11}SiH_3$, and $PhSiH_3$ *, solid products which are very sensitive to air were also readily obtained. The IR spectrum of each showed all the characteristic absorptions due to the triphenylphosphine complex of a silylruthenium hydride. However, at the present time, characterization of the products remains incomplete.

III. Interaction with $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ in benzene

Recently we used Et_3SiH and Et_2SiH_2 as reducing agents for the reduction of $RuCl_2(PPh_3)_3$, $RuBr_2(PPh_3)_3$, and $RhCl(PPh_3)_3$ in the presence of triethylamine in benzene [10]. In this respect, the observation of Hetflejš and his colleagues is worthy of note: they reported that by the action of Et_3SiH in benzene $RuCl_2(PPh_3)_3$ was converted to $RuHCl(PPh_3)_3 \cdot C_6H_6$ (eq. 4), and that the reaction with $(EtO)_3SiH$ gave a mixture of $RuHCl(PPh_3)_3$ and $RuH[Si(OEt)_3](PPh_3)_3$. However, in the case of Cl_3SiH, $RuH(SiCl_3)(PPh_3)_3$ and $Ru(SiCl_3)_2(PPh_3)_3$ (eq. 5) were obtained [9].

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* We observed that in the presence of $RuCl_2(PPh_3)_3$ or $RuHCl(PPh_3)_3$ the trihydride $PhSiH_3$ spontaneously disproportionated to Ph_2SiH_2 and SiH_4.

$$RuCl_2(PPh_3)_3 + Et_3SiH \xrightarrow{C_6H_6} RuHCl(PPh_3)_3 \cdot C_6H_6 + Et_3SiCl \quad (4)$$

$$RuCl_2(PPh_3)_3 + Cl_3SiH \xrightarrow{C_6H_6} RuH(SiCl_3)(PPh_3)_3 + Ru(SiCl_3)_2(PPh_3)_3 \quad (5)$$

In accordance with their observations, we found that $EtMe_2SiH$ and $PhMe_2SiH$ also reacted with the ruthenium compound to give $RuHCl(PPh_3)_3 \cdot C_6H_6$, whereas $Ph(MeO)_2SiH$ and $ClMe_2SiH$ afforded $RuH[SiPh(OMe)_2](PPh_3)_3$ and $RuH(SiMe_2Cl)(PPh_3)_3$, respectively. The reaction of $RuHCl(PPh_3)_3$ with Et_3SiH, $EtMe_2SiH$, and $PhMe_2SiH$, even at elevated temperature, gave only recovered $RuHCl(PPh_3)_3$, but with $Ph(MeO)_2SiH$ and $ClMe_2SiH$ afforded the silyl complex, $RuH(SiR_3)(PPh_3)_3$, as in the case of $RuCl_2(PPh_3)_3$.

Analogous reactions of $RuCl_2(PPh_3)_3$ in benzene with the di- and tri-hydrides, such as Et_2SiH_2, Ph_2SiH_2, and cyclo-$C_6H_{11}SiH_3$ gave an unexpected product, $RuH(SiR_2Cl)(PPh_3)_3$, which was characterized on the basis of the presence of a Ru—H band and absence of Ru—Cl absorption in the infrared spectrum, as well as elemental analyses. The physical data are summarized in Table 4.

$$RuCl_2(PPh_3)_3 + R_2SiH_2 \xrightarrow{C_6H_6} RuH(SiR_2Cl)(PPh_3)_3 \quad (6)$$

$R_2 = Et_2, Ph_2$, cyclo-C_6H_{11} H

The infrared spectrum of $RuH(SiR_2Cl)(PPh_3)_3$, which was prepared by the reaction of $RuCl_2(PPh_3)_3$ with Et_2SiH_2 and Ph_2SiH_2, showed strong or medium broad absorption bands at 1980—1910 cm^{-1} due to ν(Ru—H), but no band in the region of 2200—2000 cm^{-1} assignable to ν(Si—H). The spectrum of $RuH(SiHCl \cdot C_6H_{11})(PPh_3)_3$ showed a broad band at 1980 cm^{-1} due to ν(Ru—H) and a medium sharp band at 2045 cm^{-1} due to ν(Si—H). The assignment of Ru—H stretching absorption bands was confirmed by an infrared study of $RuD(SiPh_2Cl)(PPh_3)_3$. The spectrum exhibited three characteristic bands which might be assignable to ν(Ru—D) at 1420, 1415, and 1373 cm^{-1}, in place of three due to ν(Ru—H) at 1980, 1968, and 1910 cm^{-1}, which were observed in the spectrum of $RuH(SiPh_2Cl)(PPh_3)_3$. The infrared spectra (KBr disk) of RuD-

TABLE 4

PHYSICAL PROPERTIES OF THE TRIS-PHOSPHINE COMPLEXES OF SILYLRUTHENIUM HYDRIDE

Compound	Decomp. point(°C)	IR (KBr disk) (cm^{-1}) Ru—H			Analyses Found (calcd.) (%)		
					C	H	Cl
$(Ph_3P)_3RuH[SiPh(OMe)_2]$	134—135	1972	1955		70.18 (70.52)	5.90 (5.44)	
$(Ph_3P)_3RuH(SiMe_2Cl)$	137—139	1998	1917	1940	67.73 (68.46)	5.33 (5.33)	4.32 (3.61)
$(Ph_3P)_3RuH(SiEt_2Cl)$	107—108	1963(br)			69.40 (68.93)	6.11 (5.59)	3.00 (3.51)
$(Ph_3P)_3RuH(SiPh_2Cl)$	161—163	1980	1968	1910	71.16 (71.63)	5.33 (5.10)	2.78 (3.20)
$(Ph_3P)_3RuH(SiHClC_6H_{11})$ [a]	127—129	1980(br)			68.75 (69.54)	5.89 (5.64)	4.51 (3.36)

[a] ν(Si—H) 2048 cm^{-1}.

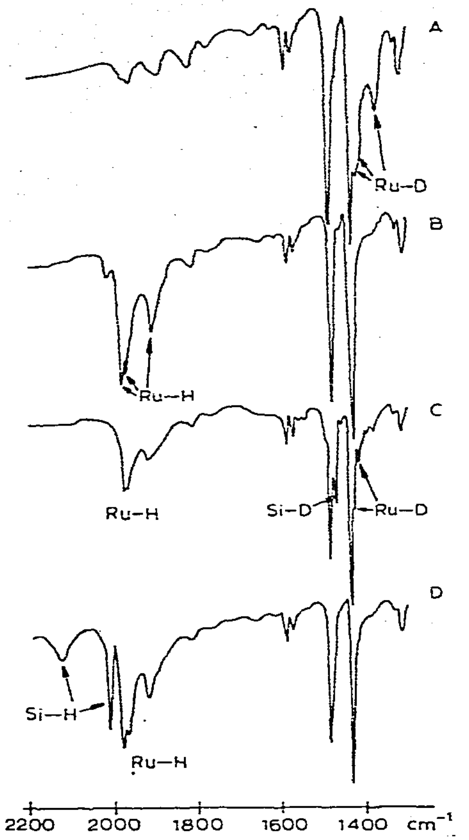


Fig. 3. Infrared spectrum (KBr disk) in the region 2200—1300 cm^{-1} of the phosphine complexes of phenylsilylruthenium hydride: A; RuD(SiClPh$_2$)(PPh$_3$)$_3$, B; RuH(SiClPh$_2$)(PPh$_3$)$_3$, C; RuH$_2$D(SiDPh$_2$)(PPh$_3$)$_3$, D; RuH$_3$(SiHPh$_2$)(PPh$_3$)$_3$.

(SiPh$_2$Cl)(PPh$_3$)$_3$ and RuH(SiPh$_2$Cl)(PPh$_3$)$_3$, together with those of RuH$_2$D(SiPh$_2$D)(PPh$_3$)$_3$ and RuH$_3$(SiPh$_2$H)(PPh$_3$)$_3$, are shown in Fig. 3.

The NMR spectrum of RuH(SiEt$_2$Cl)(PPh$_3$)$_3$ showed multiplet signals at τ 2.5—3.3 (phenyl protons of triphenylphosphine, 45 H), multiplets at τ 8.9—9.6 (ethyl protons of triethylsilyl, 10 H) and in the high field, multiplets centered at τ 22.1 ppm (Ru—H, 1 H).

The reaction of RuHCl(PPh$_3$)$_3$ with Et$_2$SiH$_2$ also afforded a brown solid product. The IR spectrum of the compound was very similar to that of RuH(SiEt$_2$Cl)(PPh$_3$)$_3$, but halogen analyses showed less than the theoretical content of halogen.

IV. Reduction of RuCl$_2$(PPh$_3$)$_3$ with Et$_3$SiH in a variety of solvents

To examine the solvent dependence of the reaction of RuCl$_2$(PPh$_3$)$_3$ with Et$_3$SiH, we carried out this reaction in C$_6$H$_5$Me, C$_6$H$_5$OMe, C$_6$H$_5$NO$_2$, C$_6$H$_5$NMe$_2$, C$_6$H$_5$CN, and CH$_2$Cl$_2$ at room temperature. The reduction product, RuHCl(PPh$_3$)$_3$, was obtained as the solvated complex except for the reaction in C$_6$H$_5$CN. The physical properties of RuHCl(PPh$_3$) · solvent are summarized in Table 5. In C$_6$H$_5$NMe$_2$, an additional unknown ruthenium complex was isolated as a by-product. In C$_6$H$_5$CN, RuCl$_2$(PPh$_3$)$_3$ was not reduced, but instead gave a ligand-

TABLE 5

PHYSICAL PROPERTIES OF $RuHCl(PPh_3)_3 \cdot$ solvent

Product	Decomp. point(°C)	IR (in KBr disk) (cm^{-1})		Analyses Found (calcd.) (%)			
		Ru—H	Others	C	H	N	Cl
$RuHCl(PPh_3)_3 \cdot C_6H_5CH_3$	102—104	2020	1598 1490	71.61 (72.07)	5.40 (5.35)	—	3.68 (3.40)
$RuHCl(PPh_3)_3 \cdot C_6H_5NO_2$	108—110	2020	1525 1349 848 790	68.26 (68.80)	4.89 (4.91)	1.19 (1.34)	3.33 (3.36)
$RuHCl(PPh_3)_3 \cdot C_6H_5OMe$	109—112	2020	1598 1495 1247	70.90 (70.96)	5.49 (5.27)	— —	3.61 (3.43)
$RuHCl(PPh_3)_3 \cdot C_6H_5NMe_2$	106—108	2020	1600 1503 1340	70.51 (71.22)	5.49 (5.49)	1.35 (1.34)	3.67 (3.39)

exchange product, $RuCl_2(C_6H_5CN)_3(PPh_3)_2$ *.

$$RuCl_2(PPh_3)_3 + Et_3SiH \xrightarrow{\text{solvent}} RuHCl(PPh_3)_3 \cdot \text{solvent} + Et_3SiCl \qquad (7)$$

$$RuCl_2(PPh_3)_3 + 3\ C_6H_5CN \rightarrow RuCl_2(C_6H_5CN)_3(PPh_3)_2 + 2\ PPh_3 \qquad (8)$$

V. *The reactions of silylruthenium hydride complexes*

$RuH_3(SiMe_2Ph)(PPh_3)_3$ reacted with carbon disulfide at room temperature to give a red-orange crystalline solid, m.p. 178—181°C, which was identified as $Ru(S_2CH)_2(PPh_3)_2$ by its IR spectrum which was in accordance with the one reported [12] and also by elemental analysis.

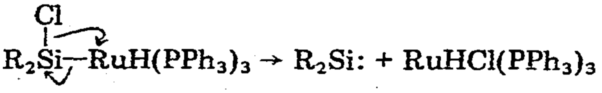
$$RuH_3(SiR_3)(PPh_3)_3 + 2\ CS_2 \xrightarrow{-R_3SiH,\ -PPh_3} Ru(S_2CH)_2(PPh_3)_2 \qquad (9)$$

No reaction occurred between $RuH[Si(OMe)_3](PPh_3)_2$ and carbon disulfide at room temperature, and the silylruthenium hydride was recovered quantitatively.

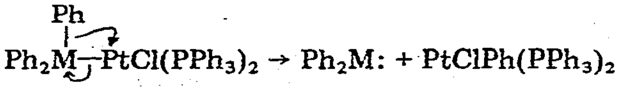
With acyl chlorides, such as MeCOCl and PhCOCl, $RuH[Si(OMe)_3](PPh_3)_2$ reacted readily to give brown products. The IR spectrum of each showed ν(Ru—H), (R = Me; 1955 cm^{-1}, R = Ph; 1970 cm^{-1}) and ν(C=O) (R = Me; 1810 cm^{-1}, R = Ph; 1773 cm^{-1}) bands together with the characteristic bands of triphenylphosphine and the methoxysilyl ligands. On the basis of these results and the elemental analyses obtained, the products may be formulated as $RuH[SiCl(OMe)_2](COR)Cl(PPh_3)_2$. The formation of the acyl(silylruthenium(IV)) complexes can be rationalized in terms of the following equation:

$$RuH[Si(OMe)_3](PPh_3)_2 + RCOCl \xrightarrow{-RCOOMe} RuH[SiCl(OMe)_2](PPh_3)_2$$
$$\xrightarrow{RCOCl} RuH[SiCl(OMe)_2](COR)Cl(PPh_3)_2 \qquad (10)$$

Chlorosilylruthenium hydrides such as $RuH(SiClMe_2)(PPh_3)_3$, $RuH(SiClEt_2)(PPh_3)_3$, and $RuH(SiClPh_2)(PPh_3)_3$ decomposed easily in excess benzene to give $RuHCl(PPh_3)_3 \cdot C_6H_6$. The formation of $RuHCl(PPh_3)_3$ possibly can be accounted for in terms of the migration of a chlorine atom from the silyl ligand to the ruthenium, followed by fission of the Si—Ru bond which resembles the disproportionation of $PtCl(MPh_3)(PPh_3)_2$ (M = Sn, Pb) to $PtClPh(PPh_3)_2$ [13] (eq. 12).



$$R_2\overset{Cl}{Si}-RuH(PPh_3)_3 \rightarrow R_2Si: + RuHCl(PPh_3)_3 \qquad (11)$$



$$Ph_2\overset{Ph}{M}-PtCl(PPh_3)_2 \rightarrow Ph_2M: + PtClPh(PPh_3)_2 \qquad (12)$$

Thus, this reaction strongly suggests the elimination of a silylene (or silenoid) species from $RuH(SiR_2Cl)(PPh_3)_3$. However, when $RuH(SiClMe_2)(PPh_3)_3$ was treated with excess $MeOSiMe_2SiMe_2OMe$ [14] or Et_3SiH [15] in benzene, the reaction mixture was found by GLC analysis to contain a number of products, so that the effort to isolate each product was abandoned for the present.

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* Gilbert and Wilkinson obtained $RuCl_2(C_6H_5CN)_2(PPh_3)_2$ by the reaction of $RuCl_2(PPh_3)_3$ with C_6H_5CN in acetone [11].

Conclusions

Our investigation finds the following notable features:

1. Tetrakis(triphenylphosphine)ruthenium(II) dihydride, $RuH_2(PPh_3)_4$, reacts oxidatively with a silicon hydride to give a series of seven-coordinate silylruthenium(IV) complexes, $RuH_3(SiR_3)(PPh_3)_3$ (eq. 1).
2. Without solvent, ruthenium(II) halide complexes, $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$, react with a silicon hydride to afford a variety of four-coordinate silylruthenium(II) complexes, $RuH(SiR_3)(PPh_3)_2$, (eq. 2 and 3).
3. In benzene solution, the ruthenium(II) halide complexes react with Cl_3SiH, Me_2ClSiH, and $Ph(MeO)_2SiH$ to give five-coordinate silylruthenium(II) complexes, $RuH(SiR_3)(PPh_3)_3$ (eq. 5).
4. In benzene solution, tris(triphenylphosphine)ruthenium(II) dihalides, $RuX_2(PPh_3)_3$, react with Et_3SiH, $EtMe_2SiH$, and $PhMe_2SiH$, respectively, to give the reductive product, $RuHX(PPh_3)_3 \cdot C_6H_6$ (eq. 4).
5. In benzene solution, ruthenium(II) halide complexes, $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$, react with silicon di- and tri-hydrides to afford five-coordinate chlorosilylruthenium(II) complexes, $RuH(SiClR_2)(PPh_3)_3$ (eq. 6).
6. The Ru—Si bond in $RuH_3(SiR_3)(PPh_3)_3$ is readily reactive toward carbon disulfide (eq. 9).
7. The complexes, $RuH(SiClR_2)(PPh_3)_3$, easily lose R_2Si upon treatment with benzene to give $RuHCl(PPh_3)_3 \cdot C_6H_6$, (eq. 11).
8. $RuH[Si(OMe)_3](PPh_3)_2$ is stable in carbon disulfide and oxidatively reacts with acyl chlorides to afford six-coordinate acyl(silylruthenium(IV)) complexes, $RuH[SiCl(OMe)_2](COR)Cl(PPh_3)_2$ (eq. 10).

Experimental

The melting and decomposition points are uncorrected. The infrared spectra were recorded as KBr disks or Nujol mulls on a Hitachi EPI-G3 spectrometer. The nuclear magnetic resonance spectra were obtained by use of a Varian HA-100 or a Varian T-60 spectrometer, using TMS as the internal standard.

Hydrosilanes were prepared by known methods. Dihydridotetrakis(triphenylphosphine)ruthenium was prepared by the reaction of $RuCl_3$, triphenylphosphine, and Et_3Al in THF [16], or the reaction of $RuCl_3 \cdot n\ H_2O$, triphenylphosphine, and sodium borohydride in ethanol [17]. Dichlorotris(triphenylphosphine)ruthenium was prepared by the reaction of $RuCl_3 \cdot n\ H_2O$ and triphenylphosphine in methanol [18]. Hydridochlorotris(triphenylphosphine)ruthenium was obtained by the reduction of $RuCl_2(PPh_3)_3$ with hydrogen in the presence of triethylamine [19] or with triethylsilane as described in previous papers [9,10].

All the reactions were carried out under argon or in an evacuated tube. Solvents were dried and distilled before use under argon.

The reaction of silicon hydrides with dihydridotetrakis(triphenylphosphine)ruthenium(II)

A typical procedure is described for the reaction of ethyldimethylsilane with $RuH_2(PPh_3)_4$.

$RuH_2(PPh_3)_4$ (0.5 g) was sealed in an evaculated tube with $EtMe_2SiH$ (2 ml) and the tube was kept at room temperature for 24 hours. Hexane (10 ml) was added to the resulting reaction mixture, and white powdery crystals of trihydrido(ethyldimethylsilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiMe_2Et)(PPh_3)_3$, were filtered, washed with hexane and dried in vacuo, yield 87%, IR (KBr disk): 3040, 3000, 2990, 2925, 2870, 1993, 1952 s, 1484, 1435, 1245, 1236, 1090, 918, 845, 757, 748, 700, 522 cm^{-1}.

By a procedure similar to that described above, the following trihydrido(silyl)tris(triphenylphosphine)ruthenium complexes were obtained in reactions of $RuH_2(PPh_3)_4$ with the corresponding silicon hydride.

Trihydrido(phenyldimethylsilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiPhMe_2)(PPh_3)_3$. White powder, yield 94%, IR (KBr disk): 3045, 2940, 2875, 1982, 1958, 1948, 1480, 1430, 1242, 1234, 1084, 822, 803, 739, 694, 514 cm^{-1}. NMR (C_6D_6): τ 2.1—3.4 (50 H), 8.5—9.5 (multiplet 6 H), 19.7 (Ru—H, 3 H).

Trihydrido(triethoxysilyl)tris(triphenylphosphine)ruthenium, $RuH_3[Si(OEt)_3](PPh_3)_3$. White powder, yield 91%, IR (KBr disk): 3035, 2945, 2900, 2850, 1975, 1965, 1480, 1433, 1100, 1085, 1068, 940, 744, 695, 510 cm^{-1}. NMR (C_6D_6): τ 2.4—3.7 (45 H), 6.2 (quartet 6 H), 8.9 (triplet 9 H), 20.1 (Ru—H, 3 H).

Trihydrido (diethylhydrosilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiHEt_2)(PPh_3)_3$. White powder, yield 70%, IR (KBr disk): 3025, 2910, 2840, 2030, 1996, 1967, 1942 s, 1478, 1429, 1087, 966, 885, 845, 746, 697, 515 cm^{-1}. NMR (C_6D_6): τ 2.2—3.2 (45 H), 4.6 (Si—H, 1 H), 8.2—9.6 (multiplet 10 H), 19.9 (Ru—H, 3 H).

Trihydrido(phenylmethylhydrosilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiHPhMe)(PPh_3)_3$. White powder, yield 80%, IR (KBr disk): 3020, 2960, 2020, 2000, 1980, 1948, 1478, 1430, 1238, 987, 890, 747, 695, 515 cm^{-1}. NMR (C_6D_6): τ 2.4—3.4 (50 H), 4.9 (Si—H, singlet 1 H), 9.3—9.7 (multiplet 3 H) 19.9 (Ru—H, 3 H).

Trihydrido(diphenylhydrosilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiHPh_2)(PPh_3)_3$. White powder, yield 82%, IR (KBr disk): 3040, 2980, 2120, 2010, 1975, 1963, 1918, 1485, 1432, 1090, 885, 847, 747, 703, 523, 515 cm^{-1}. NMR (C_6D_6): τ 2.8—3.4 (55 H), 4.4 (Si—H, 1 H), 19.9 (Ru—H, 3 H).

Trihydrido(cyclohexyldihydrosilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiH_2C_6H_{11})(PPh_3)_3$. White powder, yield 61%, IR KBr disk): 3025, 2890, 2820, 2120, 2040, 2010, 1935 (br), 1477, 1432, 1085, 974, 920, 748, 697, 518 cm^{-1}. NMR (C_6D_6): τ 2.5—3.4 (45 H), 4.9 (Si—H, 2 H), 7.8—9.4 (11 H), 19.7 (Ru—H, 3 H).

Trihydrido(phenyldihydrosilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiH_2Ph)(PPh_3)_3$. White powder, yield 77%, IR (KBr disk): 3030, 2975, 2135, 2065, 1958, 1934, 1883, 1478, 1430, 1090, 952, 922, 746, 697, 518 cm^{-1}. NMR (C_6D_6): τ 2.3 (5 H), 2.6—3.4 (45 H), 4.3 (Si—H, doublet 2 H), 19.5 (Ru—H, 3 H).

Trihydrido(triethylsilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiEt_3)(PPh_3)_3$. $RuH_2(PPh_3)_4$ (0.5 g) was sealed in an evacuated tube with triethylsilane (3 ml) and maintained at room temperature for 6 months. The pale yellow solid product was filtered, washed with hexane and dried in vacuo, yield 69%, IR (KBr disk): 3050, 2945, 2860, 1995, 1975, 1965, 1480, 1433, 1087, 748, 700, 515 cm^{-1}.

Trihydrido(triphenylsilyl)tris(triphenylphosphine)ruthenium, $RuH_3(SiPh_3)(PPh_3)_3$. A mixture of $RuH_2(PPh_3)_4$ (0.3 g) and triphenylsilane (0.65 g) in 5 ml of hexane was sealed in an evacuated tube and maintained at room temperature for 6 months. The pale brown solid product was filtered, washed with hexane and ether, and dried in vacuo, yield 98%, IR (KBr disk): 3048, 3010, 2947, 1970, 1948, 1478, 1431, 1115, 1085, 800, 743, 695, 513, 502 cm^{-1}.

The reaction of silicon hydrides with dichlorotris(triphenylphosphine)ruthenium or hydridochlorotris(triphenylphosphine)ruthenium without solvent

Silicon hydrides reacted with $RuCl_2(PPh_3)_3$ or $RuHCl(PPh_3)_3$ without solvent to give hydrido(silyl)bis(triphenylphosphine)ruthenium complexes in high yield (90—96%).

In a typical procedure, $RuCl_2(PPh_3)_3$ (250 mg, 0.27 mmol) was treated with stirring under argon with an excess of dimethylchlorosilane (2 ml). A gas was evolved as the ruthenium complex dissolved to give a brown solution. After stirring for 2 hours at room temperature, hexane (5 ml) was added and the white solid was filtered, washed with more hexane (3 × 5 ml) and dried in vacuo to give hydrido(dimethylchlorosilyl)bis(triphenylphosphine)ruthenium, $RuH(SiClMe_2)(PPh_3)_2$, yield 96%. The complex was prepared similarly from $RuHCl(PPh_3)_3$, yield 92%, IR (KBr disk): 3030, 2930, 1955, 1483, 1436, 1264, 1090, 810, 748, 700, 520 cm^{-1}.

The other hydrido(silyl)bis(triphenylphosphine)ruthenium complexes were prepared similarly, but with minor variations in the reaction time in the cases of Cl_3SiH (2 days), $(MeO)_3SiH$ (1 week), and $(EtO)_3SiH$ (1 week).

Hydrido(trichlorosilyl)bis(triphenylphosphine)ruthenium, $RuH(SiCl_3)(PPh_3)_2$. Pale brown powder, IR (KBr disk): 3060, 1978, 1485, 1437, 1115, 1095, 745, 696, 572, 520, 497 cm^{-1}.

Hydrido(methyldichlorosilyl)bis(triphenylphosphine)ruthenium, $RuH(SiCl_2Me)(PPh_3)_2$, pale brown powder, IR (KBr disk): 3025, 2935, 1945, 1482, 1435, 1275, 1250, 1125, 1090, 796, 748, 700, 520 cm^{-1}.

Hydrido(trimethoxysilyl)bis(triphenylphosphine)ruthenium, $RuH[Si(OMe)_3](PPh_3)_2$. White powder, IR (KBr disk): 3030, 2920, 2820, 1960, 1482, 1431, 1082, 890, 750, 704, 525, 480 cm^{-1}.

Hydrido(triethoxysilyl)bis(triphenylphosphine)ruthenium, $RuH[Si(OEt)_3](PPh_3)_2$. White powder, IR (KBr disk): 3030, 2910, 2810, 1969, 1484, 1435, 1090, 753, 704, 523, 514 cm^{-1}.

Hydrido(phenyldimethoxysilyl)bis(triphenylphosphine)ruthenium, $RuH[Si(OMe)_2Ph](PPh_3]_2$. White powder, IR (KBr disk): 3025, 2900, 2800, 1967, 1481, 1433, 1188, 987, 845, 750, 700, 520, 510 cm^{-1}.

The reaction of silicon hydrides with dichlorotris(triphenylphosphine)ruthenium in benzene

In benzene solution, silicon hydrides reacted with $RuCl_2(PPh_3)_3$ to afford hydrido(silyl)tris(triphenylphosphine)ruthenium complexes.

Hydrido(phenyldimethoxysilyl)tris(triphenylphosphine)ruthenium, $RuH[Si(OMe)_2Ph](PPh_3)_3$. $RuCl_2(PPh_3)_3$ (500 mg, 0.52 mmol) was treated with $Ph(MeO)_2SiH$ (1 ml) in benzene (3 ml) under argon at room temperature. After stirring for 5 hours, 10 ml of hexane was added to the homogeneous reaction mixture and the pale brown solid was filtered off. It was washed with hexane (2 × 10 ml) and dried in vacuo to give $RuH[Si(OMe)_2Ph](PPh_3)_3$ as white powder, yield 70%, IR (KBr disk): 3030, 2920, 2905, 1972, 1955, 1479, 1432, 1173, 1087, 1070, 748, 697, 680, 514 cm^{-1}. NMR ($CDCl_3$): τ 2.7—3.4 (50 H), 6.9 (singlet 6 H).

Hydrido(dimethylchlorosilyl)tris(triphenylphosphine)ruthenium, $RuH(SiClMe_2)(PPh_3)_3$. As described above, $RuCl_2(PPh_3)_3$ (2.35 g, 2.45 mmol) was treated with Me_2ClSiH (4 ml) in benzene (5 ml) for 4 hours to give $RuH(SiClMe_2)(PPh_3)_3$, white powder, yield 98%, IR (KBr disk): 3040, 2945, 2880, 1998, 1957, 1940, 1480, 1433, 1246, 1084, 837, 806, 743, 697, 516 cm^{-1}.

Hydrido(diethylchlorosilyl)tris(triphenylphosphine)ruthenium, $RuH(SiClEt_2)(PPh_3)_3$. Et_2SiH_2 (2 ml) was added to $RuCl_2(PPh_3)_3$ (2.0 g, 2.09 mmol) suspended in benzene (10 ml), with stirring. The complex dissolved and the initial dark brown solution became light brown with concomitant evolution of a gas. After stirring for 5 hours at room temperature, hexane (10 ml) was added and the complex, $RuH(SiClEt_2)(PPh_3)_3$, was collected as pale brown needles, washed with hexane, and dried in vacuo, yield 52%, IR (KBr disk): 3040, 2945, 2860, 1963, 1480, 1432, 1087, 845, 747, 696, 516 cm^{-1}. NMR($CDCl_3$): τ 2.66—3.25 (45 H), 8.92—9.64 (10 H), 20.26 (Ru—H, 1 H).

Hydrido(diphenylchlorosilyl)tris(triphenylphosphine)ruthenium, $RuH(SiClPh_2)(PPh_3)_3$. The complex, $RuH(SiClPh_2)(PPh_3)_3$, was prepared by the reaction of $RuCl_2(PPh_3)_3$ (500 mg, 0.52 mmol) and Ph_2SiH_2 (5 ml) in benzene (2 ml), tan powder, yield 97%. IR (KBr disk): 3040, 2000, 1980, 1968, 1910, 1480, 1432, 1087, 743, 697, 506 cm^{-1}.

Hydrido(cyclohexylchlorohydrosilyl)tris(triphenylphosphine)ruthenium, $RuH(SiHClC_6H_{11})(PPh_3)_3$. By a similar procedure to that described above, the complex $RuH(SiHClC_6H_{11})(PPh_3)_3$ was obtained by the reaction of $RuCl_2(PPh_3)_3$ (500 mg, 0.52 mmol) and cyclo-$C_6H_{11}SiH_3$ (1 ml) in benzene (5 ml), white powder, yield 39%, IR (KBr disk): 3040, 2910, 2840, 2045, 1980, 1478, 1431, 1084, 745, 696, 515 cm^{-1}. NMR ($CDCl_3$): τ 2.75—3.26 (45 H); 8.10—9.43 (11 H), 20.04 (Ru—H, 1 H).

The reaction of $RuCl_2(PPh_3)_3$ with Et_3SiH in a variety of solvents

$RuCl_2(PPh_3)_3$ (400 mg, 0.41 mmol) was treated with Et_3SiH in a solvent such as toluene, nitrobenzene, anisole, or *N*-dimethylaniline with stirring at room temperature for 20 hours to afford the corresponding solvated $RuHCl(PPh_3)_3$ as a violet powder which is listed in Table 5. Respective yields were 75% ($C_6H_5CH_3$), 45% ($C_6H_5NO_2$), 69% ($C_6H_5OCH_3$), and 71% ($C_6H_5NMe_2$).

(a) In CH_2Cl_2. $RuCl_2(PPh_3)_3$ was reduced in CH_2Cl_2 to give less pure $RuHCl(PPh_3)_3 \cdot CH_2Cl_2$ in a yield 36%, IR (KBr disk): 3040, 2020, 1480, 1423, 1265, 1180, 1118, 1090, 850, 748, 695, 540, 520 cm^{-1}. (Found: C, 64,17; H, 4.88; Cl, 8.23. $C_{55}H_{48}P_3Cl_3Ru$ calcd.: C, 65.47; H, 4.79; Cl, 10.54%).

(b) In $C_6H_5N(CH_3)_2$. $RuCl_2(PPh_3)_3$ (400 mg, 0.41 mol) was treated with Et_3SiH (0.2 ml) in $C_6H_5N(CH_3)_2$ (4 ml) for 20 hours at room temperature. $RuHCl(PPh_3)_3 \cdot C_6H_5N(CH_3)_2$ was filtered and the filtrate gave an unknown orange crystalline product (30 mg) m.p. 166—168°C, IR (KBr disk): 3040, 2990, 2940, 2870, 1480, 1450, 1430, 1187, 1090, 740, 695, 515, 498 cm^{-1}. (Found: C, 58.84; H, 4.85%).

(c) In C_6H_5CN. A mixture of $RuCl_2(PPh_3)_3$ (400 mg, 0.41 mmol) and Et_3SiH (0.2 ml) in C_6H_5CN (4 ml) was stirred for 5 hours at room temperature. To the reaction mixture was added 15 ml of hexane and the yellow solution was cooled to give an orange crystalline product (180 mg) which was characterized by IR and elemental analysis as $RuCl_2(C_6H_5CN)_3(PPh_3)_2$, m.p. 163—165°C (decomp.), IR (KBr disk): 3040, 2210, 1483, 1443, 1432, 1088, 744, 695, 515 cm^{-1}. (Found: C, 68.09; H, 4.91; N, 4.52; Cl, 6.38. $C_{57}H_{45}N_3P_2Cl_2Ru$ calcd.: C, 68.06; H, 4.51; N, 4.18; Cl, 7.01%).

The reaction of trihydrido(phenyldimethylsilyl)tris(triphenylphosphine)-ruthenium with carbon disulfide.

A mixture of $RuH_3(SiMe_2Ph)(PPh_3)_3$ (100 mg) and carbon disulfide (2 ml) was cooled in liquid nitrogen, degassed, and stirred under an atmosphere of nitrogen at room temperature for 3 hours. To the reaction mixture was added hexane (5 ml) and it was cooled to give a red-orange crystalline product which was collected, washed with hexane, and dried in vacuo. The compound decomposed above its melting point (178—181°C) with evolution of CS_2 and was identified as $Ru(S_2CH)_2(PPh_3)_2$ on the basis of the complete accordance of its infrared spectrum with that in the literature [12] and its elemental analysis. (Found: C, 58.13; H, 3.94; S, 16.77. $C_{38}H_{32}S_4P_2Ru$ calcd.: C, 58.52; H, 4.14; S, 16.44%).

The reaction of hydrido(trimethoxysilyl)bis(triphenylphosphine)ruthenium with acetyl chloride.

A mixture of $RuH[Si(OMe)_3](PPh_3)_2$ (250 mg) and acetyl chloride (2 ml) was stirred at room temperature for 20 hours. Filtration of the reaction mixture gave a pale brown powder (210 mg) which was characterized as $RuH[SiCl(OMe)_2](COMe)Cl(PPh_3)_2$ by its IR spectrum and elemental analysis, m.p. 121—122°C (decomp.), IR (KBr disk): 3030, 2960, 2810, 1955, 1810, 1710, 1482, 1434, 1088, 746, 697, 520 cm^{-1}. (Found: C, 58.49; H, 4.92; Cl, 7.71. $C_{40}H_{40}O_3Cl_2P_2SiRu$ calcd.: C, 57.83; H, 4.85; Cl, 8.53%).

The reaction with benzoyl chloride.

By a similar procedure to that described above, the treatment of $RuH[Si(OMe)_3](PPh_3)_2$ (250 mg) with benzoyl chloride (1 ml) afforded $RuH[SiCl(OMe)_2](COPh)(PPh_3)_2$ (180 mg) as an orange-brown powder, m.p. 126—127°C (decomp.), IR (KBr disk): 3040, 2940, 2850, 1970, 1773, 1482, 1436, 1295, 1090, 850, 744, 694, 542, 524, 500 cm^{-1}. (Found: C, 61.94; H, 5.07; Cl, 9.61. $C_{45}H_{42}O_3Cl_2P_2SiRu$ calcd.: C, 60.54; H, 4.74; Cl, 7.95%).

The formation of $RuHCl(PPh_3)_3$ from $RuH(SiClMe_2)(PPh_3)_3$

(a) In benzene. $RuH(SiClMe_2)(PPh_3)_3$ (150 mg), suspended in benzene (3 ml), was stirred at room temperature for 20 hours. An insoluble violet precipitate was filtered, washed with hexane, and dried in vacuo to give $RuHCl(PPh_3)_3 \cdot C_6H_6$ (80 mg) (which was identified by its IR spectrum).

In the presence of $MeOSiMe_2SiMe_2OMe$ (1 ml), $RuH(SiClMe_2)(PPh_3)_3$ (500 mg) was treated with benzene (2 ml) at 60°C for 4 hours to give $RuHCl(PPh_3)_3 \cdot C_6H_6$ (330 mg). GLC analysis indicated the residue was a complex mixture.

Also, in the presence of Et_3SiH (2 ml), the treatment of $RuH(SiClMe_2)(PPh_3)_3$ (2 g) in benzene afforded $RuHCl(PPh_3)_3 \cdot C_6H_6$ (1.2 g) and a complex mixture.

(b) In toluene. $RuH(SiClMe_2)(PPh_3)_3$ (300 mg) in toluene (2 ml) was stirred at room temperature for 20 hours to give $RuHCl(PPh_3)_3 \cdot C_6H_5CH_3$ (260 mg) [20].

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