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REDUCTION OF CARBONYL COMPOUNDS VIA HYDROSILYLATION

I. HYDROSILYLATION OF CARBONYL COMPOUNDS CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM

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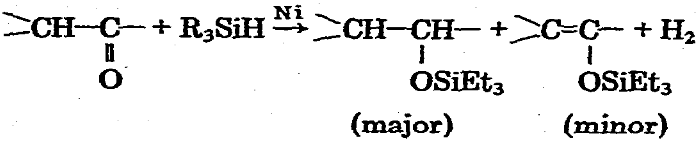
Summary

The hydrosilylation of various carbonyl compounds such as simple aldehydes, simple ketones, α,β-unsaturated carbonyl compounds, α-diketones, acyl cyanides and ketones having an electron-withdrawing group on the α-carbon using tris(triphenylphosphine)chlororhodium as a catalyst is described. Solvolysis of these silyl ethers and silyl enol ethers afforded the corresponding reduced products. The hydrosilylation of α,β-unsaturated carbonyl compounds was found to proceed by 1,4-addition. An oxidative adduct of triethylsilane to the rhodium-(I) complex was obtained as a reaction intermediate. The structure of the adduct was discussed on the basis of its IR and far-IR spectra.

Introduction

The hydrosilylation of olefins and acetylenes has been extensively studied in the last two decades [1]. However, hydrosilylation of carbon—hetero-atom mutiple bonds has received less attention. As a silicon—oxygen bond or a silicon—nitrogen bond can be easily hydrolyzed, the hydrosilylation of carbonyl compounds or imines is equivalent to hydrogenation. In this respect, we began our work on the hydrosilylation of these compounds in the hope of establishing a new reduction method.

It has been known that the hydrosilylation of carbonyl compounds can be effected by various catalytic systems such as UV light [5] and metal halides, e.g., $NiCl_2$ [2], $ZnCl_2$ [3] and H_2PtCl_6 [4]. The reaction of hydrosilane with simple ketones and aldehydes catalyzed by nickel [6] was reported to afford a mixture of the corresponding silyl ether, and silyl enol ether. The former was produced via hydrosilylation, while the latter was produced via dehydrogenative condensation (eqn. 1):

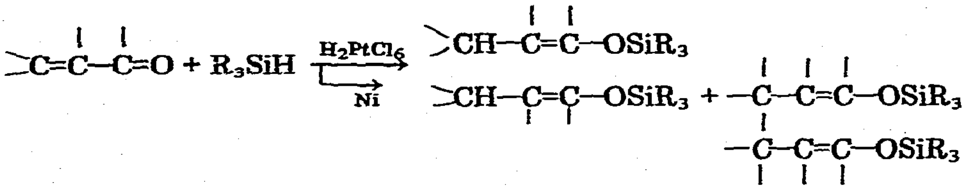


$$\gt CH{-}\underset{\substack{\|\\ O}}{C}{-} + R_3SiH \xrightarrow{Ni} \gt CH{-}\underset{\substack{|\\ OSiEt_3\\ (major)}}{CH}{-} + \gt C{=}\underset{\substack{|\\ OSiEt_3\\ (minor)}}{C}{-} + H_2 \qquad (1)$$

Calas, Frainnet and coworkers found that zinc chloride was a good catalyst for the hydrosilylation of carbonyl compounds [3]. However, the reaction proceeded under rather drastic conditions and disproportionation of the product often was observed in the case of aldehydes (eqn. 2):

$$RCHO + Et_3SiH \xrightarrow[ZnCl_2\text{ or }Ni]{} \left\{\begin{array}{l} RCH_2OSiEt_3 \\ RCH_2OCH_2R + Et_3SiOSiEt_3 \end{array}\right. \qquad (2)$$

Sadykh-Zade and Petrov reported that chloroplatinic acid was an effective catalyst for the hydrosilylation of α,β-unsaturated carbonyl compounds which proceeded by 1,4-addition [4]. When metallic nickel was used as catalyst, coupling reactions also were observed [6] (eqn. 3):



$$\gt C{=}\overset{|}{C}{-}\overset{|}{C}{=}O + R_3SiH \begin{array}{l} \xrightarrow{H_2PtCl_6} \gt CH{-}\overset{|}{C}{=}\overset{|}{C}{-}OSiR_3 \\ \xrightarrow{Ni} \gt CH{-}\underset{|}{C}{=}\underset{|}{C}{-}OSiR_3 + \begin{array}{l} -\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}OSiR_3 \\ \quad | \\ -\underset{|}{C}{-}\underset{|}{C}{=}\underset{|}{C}{-}OSiR_3 \end{array} \end{array} \qquad (3)$$

Moreover, the use of metal halide catalyst systems is restricted to application in reactions of monohydrosilanes, mainly due to the fact that disproportionation of polyhydrosilanes is also catalyzed by these substances [7].

We have found that tris(triphenylphosphine)chlororhodium, $(Ph_3P)_3RhCl$ is an extremely effective catalyst for the hydrosilylation of carbonyl compounds in comparison with other known catalysts, and already have reported briefly about the effective reduction of these compounds via hydrosilylation catalyzed by this rhodium(I) complex [8,9]. We give here a full account of our research on the high catalytic activity of this rhodium(I) complex for the hydrosilylation of carbonyl compounds and of the identification of an important intermediate, $(Ph_3P)_2RhH(SiEt_3)Cl$. We also discuss the stereochemistry of the rhodium(III) complex on the basis of IR and far-IR spectra.

Results and discussion

Hydrosilylation of simple ketones and aldehydes

The hydrosilylation of simple carbonyl compounds with monohydrosilanes was found to take place under very mild conditions to give the expected products. For example, a mixture of an equimolar amount of triethylsilane and cyclohexanone, and 0.5 mol% of $(Ph_3P)_3RhCl$ (I) was stirred at room temperature. An exothermic reaction took place and the hydrosilylation was complete within a few minutes. Work-up of the reaction mixture gave cyclohexyloxytriethylsilane in nearly quantitative yield.

The rate of the reaction was found to be slower in the case of aromatic ketones, and some heating was necessary to complete the reaction when a monohydrosilane was employed. For example, the reaction of acetophenone with triethylsilane in the presence of the rhodium(I) complex was complete in 15 min at 60°C and 1-phenylethoxytriethylsilane was obtained in 97% yield. The use of zinc chloride as a catalyst has been reported to require much more drastic conditions for the reaction [3], e.g., for cyclohexanone, 48 h at 95°C, 87% yield; for acetophenone, 150 h at 95°C, 40% yield. Thus, the hydrosilylation of these compounds proceeds under much milder conditions in high yield when the rhodium(I) complex I is used as a catalyst.

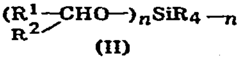
Further, the rate of the reaction was found to increase remarkably when a dihydrosilane or trihydrosilane was employed, e.g., the exothermic reaction of diethylsilane with acetophenone in the presence of 0.1 mol% of the rhodium(I) complex, which was complete within a few minutes, gave 1-phenylethoxydiethylsilane in 95% yield. Similarly, the hydrosilylation of cyclohexanone with phenylsilane in the presence of 0.1 mol% of the rhodium(I) complex I was accomplished within 10 min at ice-bath temperature and bis(cyclohexyloxy)phenylsilane was obtained in nearly quantitative yield.

When a metal halide such as $ZnCl_2$ or $NiCl_2$ was employed as catalyst in the hydrosilylation of benzaldehyde, it was reported that the silyl ether produced disproportionated immediately to dibenzyl ether and hexaethyldisiloxane under the reaction conditions. However, no disproportionation was observed in the case of the rhodium(I) complex I, and benzyloxysilanes were obtained in excellent yields. The results obtained by the use of various ketones, aldehydes and hydrosilanes are summarized in Table 1.

The silyl ethers thus obtained were smoothly solvolyzed by MeOH/KOH/

TABLE 1

SILYL ETHERS OBTAINED BY THE HYDROSILYLATION OF KETONES AND ALDEHYDES USING $(Ph_3P)_3RhCl$ (I) AS A CATALYST

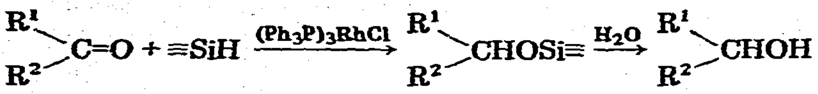


$(R^1R^2CHO—)_nSiR_{4-n}$

(II)

	Hydrosilane	Silyl ether R¹	R²	n	Amount of catalyst (mol%)	Conditions (temp, min)	Yield (%)
a	Et_3SiH	Ph	Me	1	1.0	60°C, 15	97
b	Et_3SiH	Me	Me	1	0.5	r.t., 10	95
c	Et_3SiH	$—(CH_2)_5—$		1	0.5	r.t., 5	98
d	Et_3SiH	Ph	H	1	0.1	r.t., 5	95
e	$PhMe_2SiH$	Ph	H	1	0.1	r.t., 5	94
f	$EtMe_2SiH$	Ph	t-Bu	1	0.1	40°C, 300	96
g	Ph_3SiH	Me	Me	1	1.0	reflux, 120	98
h	Et_2SiH_2	Ph	Ph	1	0.1	r.t., 5	95
i	$PhMeSiH_2$	n-Pr	H	1	0.1	r.t., 5	98
j	Ph_2SiH_2	t-Bu	Me	1	0.1	0°C, 10	97
k	Ph_2SiH_2	$—(CH_2)_5—$		1	0.1	0°C, 10	98
l	$PhSiH_3$	$—(CH_2)_5—$		2	0.1	0°C, 10	98
m	$PhSiH_3$	$—(CH_2)_5—$		3	0.1	70°C, 360	98

H_2O, MeONa/MeOH or *p*-toluenesulfonic acid/MeOH to afford the corresponding alcohols in quantitative yield:



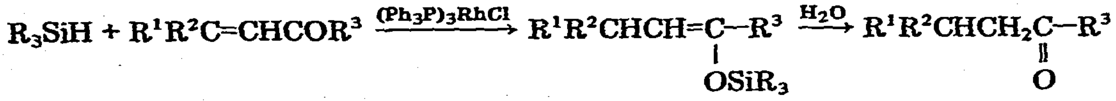
$$\begin{matrix}R^1\\ \\R^2\end{matrix}\!\!>\!C{=}O + {\equiv}SiH \xrightarrow{(Ph_3P)_3RhCl} \begin{matrix}R^1\\ \\R^2\end{matrix}\!\!>\!CHOSi{\equiv} \xrightarrow{H_2O} \begin{matrix}R^1\\ \\R^2\end{matrix}\!\!>\!CHOH \qquad \text{(II)}$$

Hydrosilylation of α,β-unsaturated ketones and aldehydes

The hydrosilylation of α,β-unsaturated ketones and aldehydes also proceeded smoothly under mild conditions to afford the adduct in excellent yield. In these cases, the reaction proceeded by 1,4-addition to afford silyl enol ethers. These were easily hydrolyzed to saturated ketones or aldehydes in quantitative yield. The silyl enol ethers were obtained as a mixture of *E* and *Z* (or *trans* and *cis*) isomers.

As for the selectivity of the 1,4-addition, monohydrosilanes were found to undergo 1,4-addition exclusively. However, a mixture of 1,4-addition and 1,2-addition was observed when dihydrosilanes were used. For instance, the hydrosilylation of benzalacetone with diethylsilane at ambient temperature gave a mixture of 1,4-adduct and 1,2-adduct. The ratio of 1,4-adduct to 1,2-adduct varied from 20/1 to 1/2 depending upon the reaction conditions. Higher temperatures favored the production of the 1,4-adduct.

The results of the exclusive 1,4-addition of monohydrosilanes to α,β-unsaturated carbonyl compounds are listed in Table 2. $\Delta^{1,9}$-Octalone was also hydrosilylated to afford a cyclic silyl enol ether IIIg.

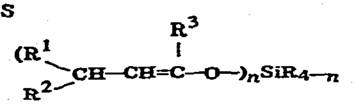


$$R_3SiH + R^1R^2C{=}CHCOR^3 \xrightarrow{(Ph_3P)_3RhCl} R^1R^2CHCH{=}\underset{\displaystyle OSiR_3}{\underset{|}{C}}{-}R^3 \xrightarrow{H_2O} R^1R^2CHCH_2\underset{\displaystyle O}{\underset{\|}{C}}{-}R^3$$

(III)

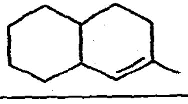
TABLE 2

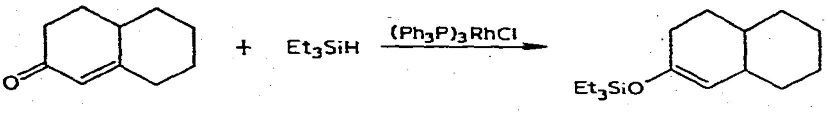
SILYL ENOL ETHERS OBTAINED BY THE HYDROSILYLATION OF α,β-UNSATURATED KETONES AND ALDEHYDES



$$(\begin{matrix}R^1\\ \\R^2\end{matrix}\!\!>\!CH{-}CH{=}\overset{\displaystyle R^3}{\overset{|}{C}}{-}O{-})_nSiR_{4-n}$$

(III)

Hydrosilane	Silyl enol ether				Amount of catalyst (mol %)	Conditions (°C, min)	Yield (%)
	R^1	R^2	R^3	*n*			
a Et_3SiH	*Me*	*Me*	*Me*	1	0.5	50, 15	94
b Et_3SiH	*Me*	H	*Ph*	1	0.5	60, 30	90
c Et_3SiH	*Me*	H	H	1	0.5	60, 15	95
d Et_3SiH	*Ph*	H	H	1	0.5	60, 15	96
e $PhMe_2SiH$	Me	Me	Me	1	0.5	50, 30	98
f Ph_3SiH	Me	H	H	1	0.5	60, 30	97
g Et_3SiH				1	0.5	50, 60	92

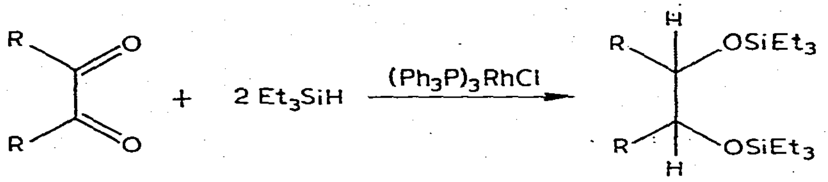


(IIIg)

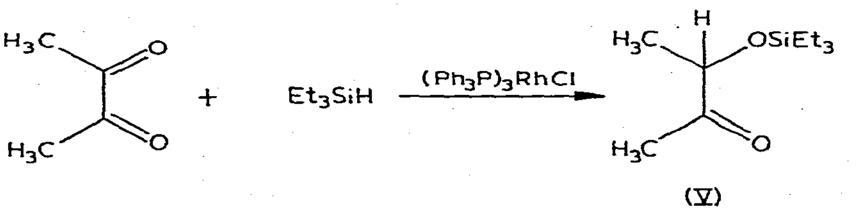
These findings clearly indicate that the reaction using monohydrosilane–rhodium(I) complex combinations with α,β-unsaturated carbonyl compounds may open a new route to selective hydrogenation of the carbon—carbon double bond in α,β-unsaturated carbonyl compounds, and also open an important route to the preparation of silyl enol ethers of potential interest as synthetic intermediates.

Hydrosilylation of other carbonyl compounds

The hydrosilylation of 2,3-butanedione using an equimolar amount of triethylsilane in benzene afforded a 1/1 adduct. When two equivalents of triethylsilane were used, a 1/2 adduct was produced as a mixture of the *d,l*- and *meso*-forms. In the case of benzil, a mixture of 1/1 adduct and 1/2 adduct was obtained even when equimolar amounts of benzil and triethylsilane were employed. When excess triethylsilane was used, only the 1/2 adduct was obtained as a mixture of the *d,l*- and *meso*-forms (37/63 on the basis of the NMR spectrum). The reaction of α-diketones with dihydrosilanes resulted in the formation of unidentified polymers.

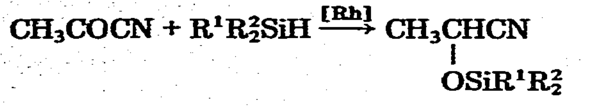


(IV) a R = CH$_3$
b R = Ph



(V)

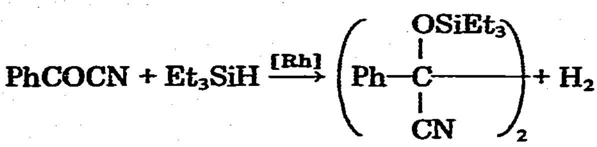
The hydrosilylation of acetyl cyanide using monohydrosilanes catalyzed by the rhodium(I) complex was accomplished smoothly at 80°C in 2-3 h to give α-silyloxypropionitriles (VI) in 75-85% yield. On the other hand, the reaction of benzoyl cyanide with triethylsilane proceeded in somewhat different fashion, giving 1,2-dicyano-1,2-diphenyl-1,2-bis(triethylsilyloxy)ethane (VII) as sole isolable product. However, when palladium chloride was employed as a catalyst for this reaction, the formation of the dimer was not observed, and the expected hydrosilylation product VIII was obtained.



$$CH_3COCN + R^1R^2_2SiH \xrightarrow{[Rh]} \underset{\displaystyle OSiR^1R^2_2}{CH_3\underset{|}{C}HCN}$$

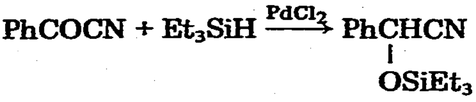
(VI)

a $R^1 = R^2 = Et$
b $R^1 = Et, R^2 = Me$
c $R^1 = Ph, R^2 = Me$



$$PhCOCN + Et_3SiH \xrightarrow{[Rh]} \left(Ph-\overset{\displaystyle OSiEt_3}{\underset{\displaystyle CN}{C}}- \right)_2 + H_2$$

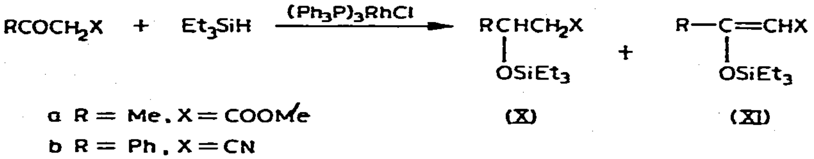
(VII)

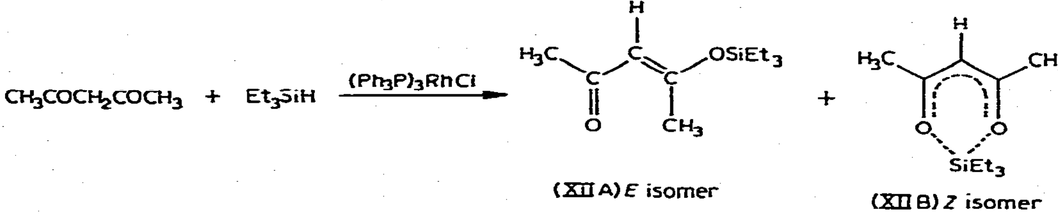


$$PhCOCN + Et_3SiH \xrightarrow{PdCl_2} \underset{\displaystyle OSiEt_3}{PhCHCN}$$

(VIII)

The reaction of triethylsilane with methyl acetoacetate in the presence of the rhodium(I) complex afforded a mixture of hydrosilylated and dehydrogenative condensation products Xa/XIa in the ratio of 81/19 in 80% yield [10]. A mixture of hydrosilylated and dehydrogenative condensation products Xb and XIb was also obtained in 90% yield by the reaction of triethylsilane with benzoylacetonitrile [10]. When acetylacetone was chosen as substrate, the hydrosilylation was strongly suppressed and the dehydrogenative condensation predominated, affording the corresponding silyl enol ether (XII) [10]. The silyl enol ethers obtained in this reaction may be a mixture of *Z* and *E* isomers, but a determination of the ratio of the two isomers was unclear for XIa and XIb on the basis of their NMR spectra only. In the case of XII, however, the determination of the product ratio was possible on the basis of the NMR spectrum since the *Z* isomer of XII (XIIB) has an absorption at δ 2.11 ppm due to methyl group as a singlet because of chelation, while the *E* isomer of XII (XIIA) has two singlets at δ 2.11 and δ 2.29 ppm due to the non-equivalent methyls [11].



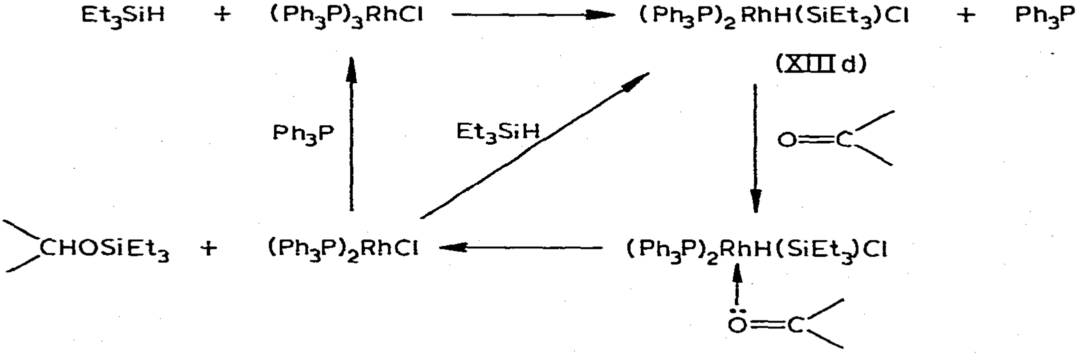


Oxidative adducts of hydrosilanes to tris(triphenylphosphine)chlororhodium and their far-infrared spectra

In the course of the investigation on the hydrosilylation of ketones using triethylsilane catalyzed by the rhodium(I) complex, it was found that all the red complex disappeared and a yellow solid was precipitated when the reaction was relatively slow, e.g., hydrosilylation of acetophenone, mesityl oxide, etc. The precipitate redissolved as the reaction temperature rose which suggested the yellow complex may be an intermediate of the reaction. The yellow complex was precipitated by the addition of n-hexane and identified as hydridochloro(triethylsilyl)bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH(SiEt_3)Cl$ (XIIId), which resulted from the oxidative addition of triethylsilane to the rhodium(I) complex.

Accordingly, a plausible mechanism which accomodates our results for the hydrosilylation of carbonyl compounds catalyzed by the rhodium(I) complex can be proposed (Scheme 1).

SCHEME 1



Silyl—rhodium(III) complexes have been described by previous workers [12,13]. Hydridochloro(triethylsilyl)bis(triphenylphosphine)rhodium(III) (XIIId) obtained as a reaction intermediate just mentioned above displays two Rh—H stretching bands at 2100 and 2080 cm^{-1} and also shows two Rh—Cl stretching bands at 286 and 278 cm^{-1}. Thus, the rhodium(III) complex which we isolated may be a mixture of stereoisomers having a different configuration from that obtained by Haszeldine and his coworkers [12], who reported only one band for the rhodium(III) complex in the Rh—H region at 2020 cm^{-1}. Attempts to prepare the rhodium(III) complex, $(Ph_3P)_2RhH(SiEt_3)Cl$, showing an Rh—H stretching band at 2020 cm^{-1} have not been successful though the procedure reported by Haszeldine and coworkers was employed. The rhodium(III) complex obtained by this method also displays two Rh—H and two Rh—Cl stretching bands in the same frequencies as those observed for the complex obtained as the intermediate described above.

A similar result was reported by Wilkinson and coworkers [13] for the rhodium(III) complex, $(Ph_3P)_2RhH(SiMe_3)Cl$ which showed two Rh—H stretching bands of approximately equal intensity at 2065 and 2107 cm^{-1}.

In order to establish the stereochemistry of the rhodium(III) complex XIIId, the *trans* influence of silyl groups upon Rh—Cl stretching frequencies was investigated. Although a series of rhodium(III)—silyl complexes has been synthesized by oxidative addition of hydrosilanes to the rhodium(I) complex, $(Ph_3P)_3RhX$, and IR and NMR spectra were measured [12,13], nothing is known

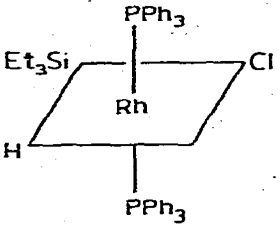
TABLE 3

FAR-INFRARED SPECTRA OF RHODIUM(III)—SILYL COMPOUNDS

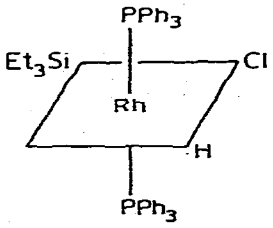
Complex		νRh—Cl	νRh—H	
XIIIa	$(Ph_3P)_2RhH(SiCl_3)Cl$	294	2042	(lit. [12], 2040)
XIIIb	$(Ph_3P)_2RhH(SiMeCl_2)Cl$	288	2054	(lit. [12], 2050)
XIIIc	$(Ph_3P)_2RhH(SiMe_2Cl)Cl$	286	2058	(lit. [12], 2060)
XIIId	$(Ph_3P)_2RhH(SiEt_3)Cl$	286, 278	2100, 2080	(lit. [12], 2020)
XIV	*trans*-$(Ph_3P)_2Rh(CO)Cl$	310		
I	$(Ph_3P)_3RhCl$	296		

about their far-IR spectra. We have carried out such studies the results of which are listed in Table 3.

As is shown from Table 3, the sensitivity of the Rh—Cl stretching frequency to changes in the structures of the silyl group suggests that these two ligands are mutually *cis*, not *trans*. Namely, the variation in the metal—Cl stretching frequency observed for these rhodium(III) complexes is markedly smaller compared with that reported for the iridium(III) complexes [14]. Our results correspond well to the reported data of X-ray analysis for a rhodium(III) complex, $(Ph_3P)_2RhH(SiCl_3)Cl \cdot xHSiCl_3$, which may adopt a distorted trigonal bipyramidal or a distorted octahedral structure, where the silyl group and chlorine are mutually *cis*. Accordingly, our results may provide supporting evidence for the proposed structures of these rhodium(III) complexes, the structures of which have not yet been determined by X-ray analysis. The structures of the two isomers are postulated to be as follows:



(A)



(B)

Experimental

Measurements

The melting points and boiling points were uncorrected. The infrared spectra were recorded on a Hitachi EPI-G3 spectrophotometer, using samples as neat liquid, KBr disks, or Nujol mulls. Far-infrared spectra were measured on a Hitachi FIS-3 spectrophotometer using samples as Nujol mulls. The nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or a Varian T-60 spectrometer, using TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimazu GC-3BT or GC-3BF using a column packed with 3% or 20% SE-30, 10% QF-1 and 3% OV-17.

Materials

Hydrosilanes were prepared by known methods. Tris(triphenylphosphine)-chlororhodium was prepared from rhodium trichloride trihydrate and triphenylphosphine. Carbonyl compounds are commercially available and were purified by distillation or recrystallization.

Hydrosilylation of simple ketones and aldehydes in the presence of tris(triphenylphosphine)chlororhodium

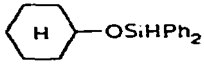
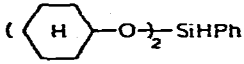
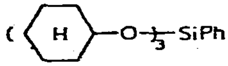
A typical procedure is described for the hydrosilylation of cyclohexanone by diphenylsilane.

To a mixture of 2.94 g (30 mmol) of cyclohexanone and 5.52 g (30 mmol) of diphenylsilane, 19 mg (0.07 mol%) of $(Ph_3P)_3RhCl$ was added, and the mixture was stirred at ice-bath temperature. The hydrosilylation was complete within 10 min. n-Hexane (100 ml) was added to the reaction mixture, the resulting precipitate filtered off, the solvent evaporated and the residual solution distilled under reduced pressure to give 8.34 g (98%) of cyclohexyloxydiphenylsilane.

The silyl ether thus obtained was smoothly hydrolyzed by $MeOH/KOH/H_2O$, or p-$CH_3C_6H_4SO_3H/MeOH$ solution at ambient temperature for 1 h to afford cyclohexanol quantitatively. Results are summarized in Table 1. The data on the identification of the new silyl ethers are listed in Table 4.

TABLE 4

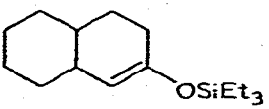
IDENTIFICATION OF NEW SILYL ETHERS

	Silyl ether	b.p. (°C/Torr)	Elemental analysis found (calcd.) (%)		NMR (δ) (ppm)	
			C	H	methyne (methylene)	Si—H
IIe	$PhCH_2OSiMe_2Ph$	126/2	74.42 (74.33)	7.38 (7.48)	4.65(s)	
IIf	Ph-t-$BuCHOSiMe_2Et$	132/26	72.02 (71.93)	10.22 (10.46)	4.58(s)	
IIg	$Me_2CHOSiPh_3$	89-90[a]	79.19 (79.20)	6.81 (6.96)	4.19(quin, J = 6Hz)	
IIh	$Ph_2CHOSiHEt_2$	132/0.4	75.27 (75.50)	8.11 (8.20)	5.58(s)	4.61(quin, J = 2Hz)
IIi	n-$PrCH_2OSiHMePh$	74/3	67.90 (67.98)	9.34 (9.34)	3.65(m)	5.00 (J = 3Hz)
IIj	t-$BuMeCHOSiHPh_2$	105/0.45	75.73 (76.00)	8.20 (8.50)	3.82(q, J = 7Hz)	5.76(s)
IIk		147/0.4	76.37 (76.54)	7.87 (7.85)	3.73(m)	5.17(s)
IIl		147/1.1	71.21 (71.00)	9.28 (9.27)	3.83(m)	5.10(s)
IIm		178/0.7	71.46 (71.59)	9.25 (9.51)	3.87(m)	

[a] m.p.

TABLE 5

INDNTIFICATION OF SILYL ENOL ETHER

	Silyl enol ether	B.p. (°C/ Torr)	Elemental analysis found (calcd.) (%)		NMR (δ) (ppm) Olefinic Proton(s)	Isomer ratio Z/E (cis/trans)
			C	H		
IIIa	$Me_2CHCH{=}CMeOSiEt_3$	98/18	67.45 (67.22)	12.10 (12.22)	4.15(d, J = 7Hz) (Z) 4.39(d, J = 7Hz) (E)	64/36
IIIb	$EtCH{=}CPhOSiEt_3$	89/0.2	72.95 (73.21)	9.78 (9.99)	4.92(t, J = 7Hz) (Z) 5.02(t, J = 7Hz) (E)	50/50
IIIc	$EtCH{=}CHOSiEt_3$	79/18	64.27 (64.44)	11.61 (11.90)	4.36(sex, J = 7, 5Hz) (*cis*) 4.91(sex, J = 7, 12Hz) (*trans*)	59/41
IIId	$PhCH_2CH{=}CHOSiEt_3$	155/20	72.36 (72.52)	9.46 (9.74)	4.53(sex, J = 7, 6Hz) (*cis*) 5.01(sex, J = 7, 12Hz) (*trans*)	75/25
IIIe	$Me_2CHCH{=}CMeOSiMe_2Ph$	125/20	71.49 (71.73)	9.17 (9.46)	4.15(d, J = 9Hz) (Z) 4.35(d, J = 9Hz) (E)	64/36
IIIf	$EtCH{=}CHOSiPh_3$	175/0.7	79.95 (79.95)	6.65 (6.71)	4.54(sex, J = 7, 6Hz) (*cis*) 5.20(sex, J = 7, 12Hz) (*trans*)	50/50
IIIg		116/0.9	72.19 (72.11)	11.10 (11.35)	4.69(d, J = 4Hz)	

Hydrosilylation of α,β-unsaturated ketones and aldehydes

α,β-Unsaturated carbonyl compounds were hydrosilylated in a similar manner to that used with simple ketones and aldehydes. The silyl enol ethers obtained were smoothly hydrolyzed by the action of $K_2CO_3/MeOH/H_2O$ to afford α,β-saturated carbonyl compounds. Results are listed in Table 2. The data on the identification of the products are listed in Table 5.

Hydrosilylation of 2,3-Butanedione

To a mixture of 2,3-butanedione (860 mg, 10 mmol) and triethylsilane (1.16 g, 10 mmol) was added 50 mg of $(Ph_3P)_3RhCl$ (0.5 mol%) and the mixture was stirred at 70°C for 2 h. Distillation of the reaction mixture afforded a mixture of 1/2 adduct IV (main product) and 1/1 adduct V (minor product).

Two equivalents of triethylsilane employed. A mixture of 2,3-butanedione (860 mg, 10 mmol), triethylsilane (2.90 g, 25 mmol) and $(Ph_3P)_3RhCl$ (50 mg) was stirred at 70°C for 3h. Distillation of the reaction mixture provided 2,3-bis(triethylsilyloxy)butane (IV) (2.70 g) in 85% yield. IVa b.p. 120°C/1.8 Torr, NMR($CDCl_3$): δ 0.35-1.20 (m, 36H) and 3.65 (m, 2H). (Found: C, 60.06; H, 11.81. $C_{16}H_{38}O_2Si_2$ calcd.: C, 60.31; H, 12.02 %.)

When benzene was used as solvent, 3-triethylsilyloxybutan-2-one (V) was obtained as the sole product. 2,3-Butanedione (1.72 g, 20 mmol), triethylsilane (2.32 g, 20 mmol) and $(Ph_3P)_3RhCl$ (50 mg) were dissolved in 50 ml of benzene and stirred at 60 °C for 2 h. GLC analysis revealed that only the 1/1 adduct (V) had been produced and that 1/2 adduct (IV) had not been formed. After the solvent was evaporated, the residual solution was distilled under reduced pressure to afford 3.23 g (80% yield) of 3-triethylsilyloxybutan-2-one (V). Va: b.p. 100°C/485 Torr, NMR($CDCl_3$): δ 0.35-1.20 (m, 15H), 1.29 (d, $J = 7$ Hz, 3H), 2.21 (s, 3H) and 4.17 (q, $J = 7$ Hz, 1H). (Found: C, 59.45; H, 10.69. $C_{10}H_{22}O_2Si$ calcd.: C, 59.35; H, 10.96%.)

Hydrosilylation of benzil

The hydrosilylation of benzil with the use of an equimolar amount of triethylsilane catalyzed by $(Ph_3P)_3RhCl$ afforded a mixture of 1/1 adduct (Vb) (minor) and 1/2 adduct (IVb) (predominant) using various reaction conditions. Benzil (2.10 g, 10 mmol) and triethylsilane (2.32 g, 20 mmol) were dissolved in 50 ml of n-hexane. To this solution was added 50 mg of $(Ph_3P)_3RhCl$ and the mixture was stirred under reflux for 4 h. After the solvent was evaporated, the residual solution was distilled under reduced pressure to afford 1,2-bis(triethylsilyloxy)-1,2-diphenylethane (IVb) (3.67g) in 83% yield. This product was found to be a mixture of *d,l*- and *meso*-isomers on the basis of its NMR spectrum. IVb: b.p. 154°C/0.48 Torr, NMR($CDCl_3$): δ 0.05-1.10 (m, 30H), 4.54 (s, 0.74H, *d, l*), 4.74 (s, 1.26H, *meso*) and 6.90-7.40 (m, 10H). (Found: C, 70.27; H, 9.42. $C_{26}H_{42}O_2Si_2$ calcd.: C, 70.53; H, 9.56%.)

Hydrosilylation of acetyl cyanide

A mixture of acetyl cyanide (3.45 g, 50 mmol), triethylsilane (5.80 g, 50 mmol) as $(Ph_3P)_3RhCl$ (100 mg) was stirred at 80 °C for 2 h. The rhodium(I) complex catalyst was converted to pale yellow crystals. After the precipitated complex was filtered and washed with n-hexane, the filtrate was distilled under reduced pressure to afford α-triethylsilyloxypropionitrile (VIa) (8.14 g) in 88% yield. In a similar manner, α-dimethylethylsilyloxypropionitrile (VIb) and α-dimethylphenylsilyloxypropionitrile (VIc) were obtained in 90 and 87% yields, respectively. VIa: b.p. 99°C/17.5 Torr, NMR (CCl_4): δ 0.40-1.30 (m, 15H), 1.47 (d, $J = 7$ Hz, 3H) and 4.50 (q, $J = 7$ Hz, 1H). (Found: C, 58.22; H, 10.10; N, 7.43. $C_9H_{19}NOSi$ calcd.: C, 58.32; H, 10.33; N, 7.56%.) VIb: b.p. 79°C/30 Torr, NMR (CCl_4): δ 0.20 (s, 6H), 0.40-1.30 (m, 5H), 1.50 (d, $J = 7$ Hz, 3H) and 4.47 (q, $J = 7$ Hz, 1H). (Found: C, 53.65; H, 9.36; N, 8.97. $C_7H_{15}NOSi$ calcd.: C, 53.45; H, 9.61; N, 8.91%.) VIc: b.p. 145°C/18 Torr, NMR (CCl_4): δ 0.43 (s, 3H), 0.49 (s, 3H), 1.42 (d, $J = 7$ Hz, 3H), 4.39 (q, $J = 7$ Hz, 1H) and 7.10-7.70 (m, 5H). (Found: C, 64.29; H, 7.52; N, 6.78. $C_{11}H_{15}ONSi$ calcd.: C, 64.35; H, 7.36; N, 6.82%.)

Hydrosilylation of benzoyl cyanide

A mixture of benzoyl cyanide (2.62 g, 20 mmol), triethylsilane (2.32 g, 20 mmol) and $(Ph_3P)_3RhCl$ (50 mg) was stirred at 110°C for 18 h. The reaction mixture solidified after cooling at ambient temperature. The solidified product was recrystallized from n-hexane to afford 1,2-dicyano-1,2-diphenyl-1,2-bis(triethylsilyloxy)ethane (VII) (2.45 g) in 50% yield. VII: m.p. 157-159°C, IR (KBr disc): 2225 cm^{-1} ($\nu C{\equiv}N$), NMR ($CDCl_3$): δ 0.10-1.00 (m, 30H) and 7.35-8.05 (m, 10H). (Found: C, 68.23; H, 8.29; N, 5.71. $C_{28}H_{40}NO_2Si_2$ calcd.: C, 68.24; H, 8.18; N, 5.68%.)

When $PdCl_2$ was employed as catalyst instead of $(Ph_3P)_3RhCl$, a usual hydrosilylation product was obtained. Twenty mmol each of benzoyl cyanide and triethylsilane were allowed to react in the presence of 40 mg of $PdCl_2$ in similar manner. After the catalyst was filtered and washed with n-hexane, the filtrate was distilled under reduced pressure to afford 1-phenyl-1-triethylsilyloxyacetonitrile (VIII) in 45% yield. VIII: b.p. 158-160°C/13 Torr, NMR ($CDCl_3$): δ 0.30-1.30 (m, 15H), 5.42 (s, 1H) and 7.35 (s, 5H). (Found: C, 67.76; H, 8.27; N, 5.77. $C_{14}H_{21}NOSi$ calcd.: C, 67.96; H, 8.56; N, 5.66%.)

Reaction of triethylsilane with methyl acetoacetate and benzoylacetonitrile catalyzed by $(Ph_3P)_3RhCl$

A mixture of methyl acetoacetate (2.32 g, 20 mmol), triethylsilane (2.32 g, 20 mmol) and $(Ph_3P)_3RhCl$ (50 mg) was stirred at 60°C for 12 h. Distillation of the reaction mixture afforded 3.71 g of a mixture of methyl 3-triethylsilyloxybutyrate (Xa) and methyl 3-triethylsilyloxybut-2-enoate (XIa) (b.p. 60-62°C/0.7 Torr) (Xa/XI a = 81/19). Pure samples of Xa and XIa were isolated by preparative GLC. Xa: NMR ($CDCl_3$): δ 0.30-1.20 (m, 15H), 1.19 (d, J = 7Hz, 3H), 2.41 (octet, J = 7Hz, 14Hz, 2H), 3.67 (s, 3H) and 4.44 (sex, J = 7Hz, 1H). (Found: C, 57.09; H, 10.16. $C_{11}H_{24}O_3Si$ calcd.: C, 56.85; H, 10.41%.) XIa: NMR ($CDCl_3$): δ 0.30-1.20 (m, 15H), 2.29 (s, 3H), 3.37 (s, 3H) and 4.86 (s, 1H). (Found: C, 57.08; H, 9.51. $C_{11}H_{22}O_3Si$ calcd: C, 57.35; H, 9.63%.)

Similarly, a mixture of β-phenyl-β-triethylsilyloxypropionitrile (Xb) and β-triethylsilyloxycinnamonitrile (XIb) was obtained in 90% total yield by the reaction of benzoylacetonitrile with triethylsilane catalyzed by $(Ph_3P)_3RhCl$. (b.p. 110-117°C/0.25 Torr) (Xb/XIb = 53/47). Pure samples of Xb and XIb were isolated by preparative GLC. Xb: NMR ($CDCl_3$): δ 0.30-1.20 (m, 15H), 2.65 (d, J = 6Hz, 2H), 4.96 (t, J = 6Hz, 1H) and 7.34 (s, 5H). IR (neat): 2230 cm^{-1} ($\nu C{\equiv}N$). (Found: C, 68.77; H, 8.69; N. 5.44. $C_{15}H_{23}NOSi$ calcd.: C, 68.91; H, 8.87; N, 5.36%.) XIb: m.p. 80.5-81.5°C (colorless needles from n-hexane). NMR ($CDCl_3$): δ 0.50-1.30 (m, 15H), 4.79 (s, 0.27H), 5.10 (s, 0.73H) and 7.20-8.00 (m, 5H). (Found: C, 69.34; H, 7.95. $C_{15}H_{21}NOSi$ calcd.: C, 69.45; H, 8.16%.)

Reaction of triethylsilane with acetylacetone catalyzed by $(Ph_3P)_3RhCl$

Acetylacetone (3.00 g, 30 mmol) was allowed to react with triethylsilane (3.48 g, 30 mmol) in the presence of 50 mg of $(Ph_3P)_3RhCl$ at 75°C for 5 h. Distillation of the reaction mixture afforded 4-triethylsilyloxypent-3-en-2-one (XII) (5.96 g) exclusively in 92% yield. XII: b.p. 76°C/1.0 Torr, NMR ($CDCl_3$): (A) δ 0.50-1.30 (m, 15H), 2.11 (s, 3H), 2.29 (s, 3H) and 5.60 (s, 1H); (B) δ 0.50-1.30 (m, 15H), 2.11 (s, 6H) and 5.24 (s, 1H). (Found: C, 61.43; H, 10.13. $C_{11}H_{22}O_2Si$ calcd.: C, 61.63; H, 10.34%.)

Oxidative adducts of hydrosilanes to $(Ph_3P)_3RhCl$

The rhodium(III)—silyl complexes (XIIIa-c) were prepared in accordance with the procedure reported by Haszeldine et al. [12].

The rhodium(III) complex, $(Ph_3P)_2RhH(SiEt_3)Cl$ (XIIId) was isolated from the reaction mixture of triethylsilane (2.32 g) with acetophenone (10 ml) in the presence of $(Ph_3P)_3RhCl$ (500 mg) at 35 °C by adding 50 ml of n-hexane. XIIId: yellow prisms, m.p. 103-107°C (dec.). (Found: C, 64.01; H, 5.92; Cl, 4.59. $C_{42}H_{46}ClP_2SiRh$ calcd.: C, 64.41; H, 5.92; Cl, 4.55%.)

References

1 C. Eaborn and R.W. Bott in A.G. Diarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 1. Marcel Dekker, 1968, pp. 213-279 and refs. therein.
2 N.E. Glushkova and N.P. Kharitorov, Izv. Akad. Nauk SSSR Ser Khim., (1967) 88.
3 R. Calas, E. Frainnet and J. Bonastre, C.R. Acad. Sci. Paris, 251 (1960) 2987.
4 S.I. Sadykh-Zade and A.D. Petrov, Zh. Obshch. Khim., 29 (1959) 3194; idem, Dok. Acad. Nauk SSSR 121 (1958) 119.
5 R. Calas and N. Duffaut, C.R. Acad. Sci. Paris, 245 (1957) 906; C. Eaborn, Organosilicon Compounds Butterworth, London, 1960, p. 213.
6 E. Frainnet, Pure Appl. Chem., 19 (1965) 489.
7 M. Gilman and D.H. Miles, J. Org. Chem., 23 (1958) 326.
8 I. Ojima, M. Nihonyanagi and Y. Nagai, Chem. Commun., (1972) 938.
9 I. Ojima, T. Kogure, M. Nihonyanagi and Y. Nagai, Bull Chem. Soc. Japan, 45 (1972) 3506.
10 I. Ojima and Y. Nagai, J. Organometal. Chem., 57 (1973) C42.
11 I.K. Kusnezowa, K. Rühlmann and E. Gründemann, J. Organometal. Chem., 47 (1973) 53.
12 R.N. Haszeldine, R.V. Parish and D.J. Parry, J. Chem. Soc. A, (1969) 683.
13 F. de Charenteray, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 787.
14 R.N. Haszeldine, R.V. Parish and J.H. Setchfield, J. Organometal. Chem., 57 (1973) 279.