THE CATALYTIC ACTIVITY OF RHODIUM(I) COMPLEXES IN HYDROSILYLATION OF ALKENES*

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In hydrosilylation of 1-hexene with triethyl-, triethoxy-, and trichlorosilane the efficiency of the catalysts decreases in the order $[RhX\{P(C_6H_5)_3\}_3]$ (X = Cl > Br > I) > [RhCl(CO) . $\{P(C_6H_5)_3\}_2] \approx [RhH(CO)\{P(C_6H_5)_3\}_3]$ and L = $P(C_6H_{11})_3 > P(CH_3)_2(C_6H_5) > PCH_3$ . . $(C_6H_5)_2 \approx P(C_6H_5)_3 > P(OC_4H_9-n)_3 > P(OC_6H_5)_3 \gg (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. In the additions of trimethyl- and triethoxysilane to styrene the activity order is $[RhCl(CO)\{P(C_6H_5)_3\}_2]$ > $[RhH(CO)\{P(C_6H_5)_3\}_3] \approx [RhX\{P(C_6H_5)_3\}_3]$ (X = Cl $\gg$ I). The latter reaction produces two adducts, 1-silyl- and 2-silyl-substituted 1-phenylethane. Relative amounts of the latter adduct increase with increasing electronegativity of substituents at silicon ($CH_3 < C_2H_5O <$ < Cl). The activity order of rhodium complexes in hydrosilylation of both alkenes differs from that reported for homogeneous hydrogenation.

A variety of rhodium(I) complexes have been employed as hydrosilylation catalysts in this[1-6] and other laboratories (for review see[7,8]). However, reported data were obtained only rarely under comparable conditions, which makes it difficult to estimate the relation between the structure of these complexes and their activity or selectivity. In the present work we made comparative study of a series of rhodium(I) complexes of the type $RhXL_n$ as catalysts for hydrosilylation of 1-hexene and styrene. With respect to the frequently stressed similarity between the mechanism of hydrosilylation and hydrogenation[2], the choice of the alkenes and rhodium complexes was made with intention to compare the results obtained in this study with reported data on homogeneous hydrogenation of the same substrates.

EXPERIMENTAL

Compounds. Trimethyl-, triethoxy-, trichlorosilane[9-11] and rhodium(I) complexes, [RhX . . $\{P(C_6H_5)_3\}_3]$ (X = Cl ref.[7], Br (ref.[6]), I (ref.[6]), [*trans*-RhCl(CO)$\{P(C_6H_5)_3\}_2]$ (ref.[12-13]), [RhH(CO)$\{P(C_6H_5)_3\}_3]$ (ref.[14]), and [$\{Rh(1,5-C_8H_{12})Cl\}_2]$ (ref.[15]) were prepared by literature procedures as indicated. Tertiary phosphines and phosphites were commercial samples. Storage of and manipulation with all the above compounds were made under argon.

Hydrosilylation procedure. All experiments were carried out in sealed glass tubes under argon using degassed reactants and benzene as a solvent. The components were introduced into the tube in the order alkene, silicon hydride, and a solution of rhodium complex in benzene, except the reactions carried out in the presence of the *in situ* prepared rhodium catalyst. In that case the tube was charged with a solution of tertiary phosphine and $[\{Rh(1,5-C_8H_{12})Cl\}_2]$ in benzene, sealed and the mixture kept at 60°C for 1 h under shaking. Then the tube was cooled, unsealed and the reactants added. Reaction conditions are given in Tables I—IV. The temperature of the bath was kept constant within ± 0.1°C. As checked by separate measurements, the time in which the reaction mixture was warmed up to the desired temperature did not exceed 30 s. After completion of the reaction, the reaction mixture was cooled to and stored at a temperature of a dry ice–ethanol bath until analysed. The analysis was made by gas liquid chromatography under following conditions: Hydrosilylation with trichlorosilane — 18% Silicone FS-1265 (Fluid on Chromaton N, thermal conductivity detector, a 400×0.4 cm column, a 20 ml/min nitrogen flow rate, an oven temperature 130°C (1-hexene) and 170°C (styrene); hydrosilylation with trimethyl- and triethoxysilane — 14.6% E 302 silicon elastomer on Chromaton N, gas density balances, a 200×0.4 cm column, a 25 ml/min nitrogen flow rate, an oven temperature 105°C (1-hexene + trimethylsilane), 150°C (1-hexene + triethoxysilane), and 170°C (styrene). The yields of hydrosilylation products recorded in the tables are the average of at least three measurements. The results were reproducible within $\pm 5\%$ rel.

Hydrosilylation products. The addition of the above silanes to 1-hexene afforded corresponding 1-silylsubstituted hexanes as sole products. These were separated by fractional distillation and their IR spectra were compared with those of authentic samples. Their properties agreed with those reported. Hydrosilylation of styrene afforded a mixture of two isomers, 1-silyl-substituted and 2-silylsubstituted 1-phenylethane, which could be only partially separated by distillation. For that reason the presence of both isomers was detected gas chromatographically, by comparison of the retention times of the products with those of authentic samples prepared in the following way: 1-Trichlorosilyl-1-phenylethane by hydrosilylation of styrene with trichlorosilane catalysed by [Ni(CO)$_4$] (ref.[16]), and 2-trichlorosilyl-1-phenylethane by the hydrosilylation carried out in the presence of a $H_2PtCl_6–P(C_6H_5)_3$ system[16]. Respective trimethylsilyl derivatives were obtained by methylation of the above isomers with methylmagnesium bromide, and the triethoxysilyl derivatives by esterification of the chloro derivatives with ethanol in the presence of pyridine as hydrogen chloride acceptor.

Interaction of rhodium complexes with trimethylsilane. A mixture containing 1-hexene (1.18 ml, 9.4 mmol), trimethylsilane (1 ml, 9.4 mmol), [RhCl$\{P(C_6H_5)_3\}_3$] (0.1 g, 0.1 mmol), and benzene (10 ml) was heated in a sealed glass tube under argon at 80°C for 2 h. Then, the rhodium complex was isolated, washed with n-hexane and dried, For $C_{54}H_{45}Cl_1P_3Rh_1$ calculated: 3.8% Cl, 10.0% P, 11.1% Rh; found: 4.1% Cl, 9.9% P, 10.5% Rh. The distillate did not contain chlorine. This experiment was repeated with the exception that [RhH(CO)$\{P(C_6H_5)_3\}_3$] (0.1 g, 0.1 mmol) was used in place of the chloro(phosphine)rhodium complex. The complex was recovered unchanged, as shown by elemental analysis (for $C_{55}H_{46}O_1P_3Rh_1$ calculated: 10.1% P, 11.2% Rh; found: 10.3% P, 11.2% Rh) and IR spectroscopy; the spectrum was identical with that of the original sample, v(CO) 1924 cm^{-1}, v(Rh—H) 2007 cm^{-1} (KBr pellets).

Attempted hydrogenative desilylation of trimethylsilyl-1-phenylethanes. 1-Trimethylsilyl-1-phenylethane or 2-trimethylsilyl-1-phenylethane (2 ml, 9.8 mmol) was added to a solution of [RhCl . $\{P(C_6H_5)_3\}_3$] (1 . 10^{-3} mmol) in benzene (1 ml) and the mixture heated in the presence of trimethylsilane (9.8 mmol) in a sealed tube under argon at 120°C for 4 h. Gas chromatographic analysis did not reveal additional substances to the starting compounds.

RESULTS AND DISCUSSION

Hydrosilylation of 1-Hexene

In the presence of all the rhodium catalysts used in this study the addition of tri-methyl-, triethoxy-, and trichlorosilane to 1-hexene gave exclusively corresponding 1-silylsubstituted hexanes as products. It was reported[17] that in some cases the reaction is accompanied by extensive isomerisation of 1-hexene. The results obtained by Chalk[18] in the study of hydrosilylation of 1-pentene indicated, however, that relative importance of both processes might be a function of catalyst concentration. We have found that in our case the isomerisation is effectively suppressed when the catalyst is used in a c. 10^{-4} molar ratio with respect to the substrate. Suitable solvents for the additions turned out to be aromatic hydrocarbons. On using more polar (and coordinating) solvents such as dioxane or tetrahydrofuran, the addition of the organosilicon hydride proceeded at a drastically reduced rate. In examining the effect of anionic ligands using the complexes $\left[RhX\{P(C_6H_5)_3\}_3\right]$ ($X = Cl$, Br, I) it was confirmed that differences in their catalytic activity are not due to their decomposition during the addition or due to the cleavage of the Rh-X bonds. With trichloro-silane, it was observed also by other authors[19] that the rhodium complex isolated after the reaction of this silane with 1-hexene catalysed by $\left[RhCl\{P(C_6H_5)_3\}_3\right]$ contains the Rh—Cl bond.

Of the silicon hydrides studied, only trimethylsilane reacts with 1-hexene at room temperature. The reaction proceeds, however, at a slow rate and only with the rhodium complexes $\left[RhX\{PC_6H_5)_3\}_3\right]$ as catalysts (the yield of 1-trimethylsilylhexene after 24 h for $X = Cl$ 50%, $X = Br$ 30%, $I = 17\%$; for other conditions see Table I). Triethoxy- and trichlorosilane did not essentially react. The low reactivity of tri-chlorosilane under similar conditions was already reported[19] ($3°C$, 50 h, benzene, the catalyst to 1-hexene mol. ratio $5 . 10^{-4}$: the yield of 1-trichlorosilylhexane for $\left[RhCl\{P(C_6H_5)_3\}_3\right] \sim 5\%$ $\left[RhCl(CO)\{P(C_6H_5)_3\}\right] < 5\%$). All the additions proceed smoothly at elevated temperatures. As follows from the results presented in Table I, the yields of the corresponding adducts decrease in dependence on anionic ligand in the order $Cl > Br > I$, the carbonyl(phosphine)rhodium complexes being less efficient than $\left[RhCl\{P(C_6H_5)_3\}_3\right]$ and comparable in their activity, contrary to homogeneous hydrogenation[20]. The effect of neutral ligands is shown in Table II in which these are arbitrarily listed in the order of their decreasing π-acceptor ability[21]. The observed dependences seem contradictory. It has been postulated by several authors[2] that hydrosilylation proceeds through formation of hydrido(silyl)rhodium(III) complexes of the type $\left[RhXH(SiR_3)\{P(C_6H_5)_3\}_2\right]$, some of which are known (see[17,18]). For a given substrate and catalyst the ease with which addition of a given silicon hydride takes place can be related to the stability of the respective hydrido(silyl)rhodium complex formed. Thus it was found that the reactivity of the silicon hydrides decreases with increasing stability of the rhodium(III) complexes which are formed by oxidative

addition of silicon hydrides to the rhodium(I) compounds[18]. The reactivity order observed in this work (($CH_3)_3SiH$ > $(C_2H_5O)_3SiH$ > $HSiCl_3$, Table I) is in harmony with this trend. Also the established effect of anionic ligands on catalytic activity of the rhodium complexes does not contradict this assumption, since the stability of the hydrido(silyl)rhodium complexes can be expected[22] to increase with decreasing electronegativity of the ligand, *i.e.* in the order Cl < Br < I. On the other

TABLE I

Yields (%) of 1-Silylsubstituted Hexanes in the Additions of Silicon Hydrides (9·3 mmol) to 1-Hexene (9·4 mmol) Catalysed with Rhodium(I) Complexes in Benzene (1 ml)
 The catalyst to 1-hexene ratio $1 . 10^{-4}$.

Complex	$(CH_3)_3SiH^a$	$HSi(OC_2H_5)_3^b$	$HSiCl_3^c$
[RhCl{P($C_6H_5)_3$}$_3$] (*I*)	82	64	68
[RhBr{P($C_6H_5)_3$}$_3$] (*II*)	71	52	52
[RhI{P($C_6H_5)_3$}$_3$] (*III*)	34	36	44
[RhCl(CO){P($C_6H_5)_3$}$_2$] (*IV*)	29	55	41
[RhH(CO){P($C_6H_5)_3$}$_3$] (*V*)	21	54	39

^{a} 50°C, 15 min, ^{b} 100°C, 2 h; ^{c} 120°C, 2 h.

TABLE II

The Effect of Neutral Ligands L in Hydrosilylation of 1-Hexene (8 mmol) by Trimethyl- and Triethoxysilane (8 mmol) Catalysed with a [{Rh(1,5-C_6H_{12})Cl}$_2$] + L System (Rh : P = 1 : 2) in Benzene (1 ml)
 The catalyst to 1-hexene ratio $1 . 10^{-4}$.

L	Yield, %	
	$(CH_3)_3SiH^a$	$HSi(OC_2H_5)_3^b$
P(OC$_6$H$_5$)$_3$	17	31
P(OC$_4$H$_9$-n)$_3$	22	39
P(C$_6$H$_5$)$_3$	24^c	37^d
P(CH$_3$)(C$_6$H$_5$)$_2$	31^e	42^e
P(CH$_3$)$_2$(C$_6$H$_5$)	52	62
P(cyclo-C$_6$H$_{11}$)$_3$	62	67

^{a} 80°C, 2 h; ^{b} 100°C, 1 h; ^{c} Rh : P 1 : 4, 5%; ^{d} Rh : P = 1 : 6, 35%; ^{e} (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P. .(C$_6$H$_5$)$_2$ inactive.

hand, the increase in the yields of silylsubstituted hexanes with decreasing π-acceptor and increasing σ-donor ability of neutral ligands (Table II) cannot be rationalized in this way (both effects would lead to stabilization of the oxidation–addition products), indicating thus that here also steric effects of the ligands should be considered. After this work had been completed[23], a study on the stability of chlorohydridobis-(phosphine) (silyl)rhodium(III) complexes has been published[24] which gives some support for this assumption. The authors found that the stability to dissociation of the complexes decreases in the order $P(C_6H_5)_3 > P(C_6H_{11})_3$, and $P(C_6H_5)_3 > P(CH_3)(C_6H_5)_2$, i.e. in the sequence of increasing efficiency of the catalysts (Table II). The increase in catalytic activity along the series of neutral ligands in accordance with their π-acceptor and σ-donor strength is thus fortituous in that it is in fact the result of the two competing effects. It should be noted that the different order of catalytic activity was found in the above mentioned work for hydrosilylation of 1-hexene with triethylsilane.

As it is seen from Table I, the increase of the P : Rh molar ratio leads in the case of hydrosilylation by trimethylsilane to supression of the addition (Rh : P = 1 : 4, 5% yield, see footnote ^{c}), while on using triethoxysilane the yield of 1-triethoxysilylhexane is not practically affected even by increasing this ratio to 1 : 6. The deactivation by excess ligand was established also in homogeneous hydrogenation[25] and was ascribed to its effect on one or both of the equilibria (A) and (B).

$$RhClL_2 + L \;\rightleftarrows\; RhClL_3, \qquad\qquad (A)$$

$$RhH_2ClL_2 + L \;\rightleftarrows\; RhH_2ClL_3. \qquad\qquad (B)$$
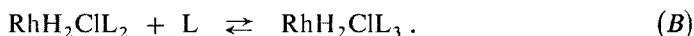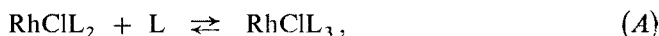
We observed that even in those cases where hydrosilylation by trimethylsilane was supressed by excess free ligand the trimethylsilylrhodium(III) complex was formed, as indicated by the colour change of the solution to yellow on heating the mixture to reaction temperature. This indicates that the effect of free ligand on reassociation equilibrium (B) could be here more important, precluding thus coordination of the alkene.

Hydrosilylation of Styrene

With the aim of examining the effect of the structure of rhodium(I) complexes on their selectivity we chose hydrosilylation of styrene as model reaction. The reaction affords in general a mixture of two isomers, 1-silylsubstituted (A) and 2-silylsubstituted 1-phenylethane (B). The results presented in Table III show that this is the case also in the hydrosilylation by trimethylsilane catalysed with the two groups of rhodium complexes for which distinct changes in their relative activity were observed in the addition to 1-hexene. In the presence of these catalysts the isomer A is formed in a

small excess which depends only slightly on the catalyst. The addition is accompanied by formation of relatively great amounts of ethylbenzene. Data in the table indicate that the relative amount of this substance does not essentially depend on the rhodium catalyst (see values of $C/(A + B)$ and data in footnote[a], Table III). Although hydrogenation of styrene to ethylbenzene proceeds in the expense of trimethylsilane (comparison of the styrene conversions given in footnote[b] of Table III with the amount

TABLE III

The Addition of Trimethylsilane (8·7 mmol) to Styrene (8·7 mmol) Catalysed with Rhodium(I) Complexes at 80°C (2 h)

The catalyst to styrene ratio 1 . 10^{-4}.

Complex[a]	Yield[b], %			A/B	$C/(A + B)$
	A	B	C		
I	16·5	10	5·5	1·6	0·3
III	14	9	5	1·5	0·2
IV	23·5	19	11	1·2	0·3
V	16·5	13	8	1·3	0·3

[a] For denotation of the complexes see Table I. [b] A 1-Trimethylsilyl-1-phenylethane, B 2-trimethylsilyl-1-phenylethane, C ethylbenzene. The yields listed are the average of three measurements. After 6 h, the overall conversion of styrene was successively 88, 90, 89, and 86% and the yield of ethylbenzene 20, 19, 20, and 22%.

TABLE IV

The Addition of Triethoxysilane (8·7 mmol) to Styrene (8·17 mmol) Catalysed with Rhodium(I) Complexes in Benzene (1 ml) at 100°C (2 h)

The catalyst to styrene ratio 1 . 10^{-4}.

Complex[a]	Yield[b] %, of		C/D
	C	D	
I	7	46	0·17
III	5	40	0·13
IV	13	62	0·20
V	12	41	0·30

[a] For denotation of the complexes see Table I. [b] C 1-Triethoxysilyl-1-phenylethane, D 2-triethoxysilyl-1-phenylethane.

of ethylbenzene shows that these conversions are maximum ones which can be expected providing that trimethylsilane quantitatively reacted), the mode of hydrogen transfer from the silicon hydride can at present be only postulated. Experiments made thus far rule out the possibility that ethylbenzene arises by consecutive hydrogenative desilylation of the adducts A and B. Direct hydrogenation of styrene *via* a dihydridorhodium species seems thus the most probable process.

While in the addition of trimethylsilane both adducts are formed in comparable amounts, hydrosilylation by triethoxysilane produces isomer B as major product (Table IV). By contrast to the previous case, ethylbenzene is not present in the amounts detectable by gas liquid chromatography $(>1\%)$. A similar difference in the extent of hydrogenation reaction between alkyl- and alkoxysilanes was already observed by us[4] in the study of hydrosilylation of 1-heptene catalysed by some rhodium complexes. In both the additions to styrene mentioned above rhodium complexes show similar activity order, $[RhCl(CO)\{P(C_6H_5)_3\}_2]$ being the most efficient catalyst.

The results further indicate that the relative amount of isomer B increases with increasing electronegativity of substituents at silicon. In accordance with this, the addition of trichlorosilane produces essentially exclusively the 2-silylsubstituted product, irrespective of the rhodium complex used as a catalyst (*e.g.* $[RhCl\{P.(C_6H_5)_3\}_3]$, 120°C, 2 h, other conditions see Table IV; $A \approx 1\%$, B 33%). In this case, however, oligomerization of styrene could not be avoided, which has made estimation of the catalytic activity of individual rhodium complexes unwarranted.

Summarizing, the mode of the addition of organosilicon hydrides across the C—C double bond of styrene is affected only slightly by changes in the structure of the catalyst. These changes exert effect on the ease of the addition in the way which, similarly to hydrosilylation of 1-hexene, differs from that observed for homogeneous hydrogenation of the same substrate. While in the hydrosilylation by trimethyl- and triethoxysilane the catalytic activity of rhodium(I) complexes decreases in the sequence $[RhCl(CO)\{P(C_6H_5)_3\}_2] > [RhH(CO)PC_6H_5)_3\}_3] \approx [RhCl\{P(C_6H_5)_3\}_3]$, the following activity order was reported[20] for analogous hydrogenation: $[RhCl.P(C_6H_5)_3\}_3] > [RhH(CO)\{P(C_6H_5)_3\}_3] > [RhCl(CO)\{P(C_6H_5)_3\}_2]$.

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Translated by the author (J. H.).