HYDROSILYLATION OF 1,3-BUTADIENE CATALYSED WITH RHODIUM(I) COMPLEXES*

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The addition of trimethyl-, triethoxy-, and trichlorosilane to 1,3-butadiene catalysed with $[RhX\{P(C_6H_5)_3\}_3]$ (X = CH_3, Cl, Br, I), $[RhCl(CO)\{P(C_6H_5)_3\}_2]$, $[RhH(CO)\{P(C_6H_5)_3\}_3]$, and $[Rh(\eta\text{-}C_3H_5)\{P(C_6H_5)_3\}_2]$ was investigated. The reaction of trimethylsilane with 1,3-butadiene produced four products, 4-trimethylsilyl-1-butene, 1-trimethylsilyl-*cis*-2-butene, 1-trimethyl-silyl-*trans*-2-butene, and 1,4-bis(trimethylsilyl)-2-butene, while with triethoxy- and trichlorosilane corresponding 1-silyl-substituted *cis*-2-butenes were formed selectively. The reactivity of the silicon hydrides decreased in the sequence trimethyl-, triethoxy-, and trichlorosilane. The complexes $[RhX\{P(C_6H_5)_3\}_3]$ were more effective catalysts than the carbonyl–rhodium complexes in the addition of trimethylsilane and trichlorosilane, while the reverse activity order was observed for the triethoxysilane addition. The effect of reaction conditions and the catalyst structure on distribution of reaction products in the reaction of trimethylsilane is reported and mechanism of the reaction involving formation of η-allyl-rhodium intermediates is proposed.

Although being effective in the addition of organosilicon hydrides to alkenic and acetylenic compounds (for review see[1,2]), rhodium(I) complexes have been rarely employed as catalysts for hydrosilylation of conjugated dienes. In a recent study on the palladium- and nickel-catalysed hydrosilylation of 1,3-butadiene with trimethylsilane[3] it was noted that in the presence of $[RhCl\{P(C_6H_5)_3\}_3]$ the reaction proceeds smoothly at room temperature to give a mixture of 4-trimethylsilyl-1-butene and 1-trimethylsilyl-2-butene (of unknown isomerism) in the 1 : 2·1 molar ratio. No details concerning this reaction have been however reported.

In continuing our study of hydrosilylation of conjugated dienes catalysed with Group VIII transition metal complexes, $(cf.^{4,5}$ and references therein) in the present communication we report on the addition of trimethyl-, triethoxy-, and trichlorosilane to 1,3-butadiene catalysed with $[RhX\{P(C_6H_5)_3\}_3]$ (X = CH_3, Cl, Br, I), $[RhCl$ $.(CO)\{P(C_6H_5)_3\}_2]$, $[RhH(CO)\{P(C_6H_5)_3\}_3]$, and $[Rh(\eta\text{-}C_3H_5)\{P(C_6H_5)_3\}_2]$.

EXPERIMENTAL

Compounds Used

Trimethyl-, triethoxy-, and trichlorosilane were of the same provenience as in previous works. The pure compounds were degassed and stored under argon. 1,3-Butadiene (>98%, Kaučuk Kralupy n/Vlt.) was condensed, dried over a Nalsit 4 A molecular sieve and used as liquid (density 0·700 at −78°C). The following rhodium complexes were obtained pure by reported procedures: [RhCl{P($C_6H_5)_3$}$_3$] (ref.[7]), [trans-RhCl(CO) {P($C_6H_5)_3$}$_2$] (ref.[8]), [RhH(CO) {P($C_6H_5)_3$}$_3$] (ref.[9]), [Rh(η-C_3H_5) {P($C_6H_5)_3$}$_2$] (ref.[10]), [RhClH($SiCl_3$) {P($C_6H_5)_3$}$_2$] (ref.[11]), and [RhBrH($SiCl_3$) {P($C_6H_5)_3$}$_2$] (ref.[11]). [Rh(CH_3) {P($C_6H_5)_3$}$_3$] was prepared according to ref.[12] and the sample containing 12·5% inactive magnesium salts was further used (attempted removal of these salts by recrystallization of the complex led to its decomposition).

[RhBr{P($C_6H_5)_3$}$_3$]. As both procedures reported[7] for preparing this complex, using rhodium trichloride as starting compound, gave in our hands the products which had identical melting points with those reported but contained in addition to bromine also chlorine (the analysis was made by digestion of the sample with magnesium powder, its dissolving in water, followed by filtration of undissolved portion; halogens were determined by titration of the solution with silver nitrate using potentiometric indication), the pure complex was prepared in the following way. To a solution of triphenylphosphine (4 g, 17 mmol) in hot ethanol (100 ml) was added a solution of $RhBr_3$. 3 H_2O (1 g, 2·5 mmol) in ethanol (50 ml). The mixture was heated under reflux for 1·5 h. The red-brown crystals of the complex were collected and recrystallized from benzene containing an excess of triphenylphosphine to yield the red complex (3·2 g, 86%), m.p. 127—128°C (reported[7] m.p. 129—130°C). For $C_{54}H_{45}Br_1P_3Rh$ (969·1) calculated: 8·20% Br, 9·69% P, 10·62% Rh; found: 7·8% Br, 9·46% P, 10·36% Rh (0% Cl).

[RhI{P($C_6H_5)_3$}$_3$]. The original procedure[7] gave the product which was a mixture of the iodorhodium complex and the chlororhodium complex. The pure substance was obtained by the procedure reported[7] for preparing the bromorhodium complex. To a solution of $RhCl_3$. 3 H_2O (0·5 g, 2 mmol) in hot ethanol (30 ml) was added lithium iodide (2·5 g, 18·7 mmol) and the reaction mixture was refluxed for 5 min. Then a solution of triphenylphosphine (3 g, 12·9 mmol) in hot ethanol was added and the mixture heated under reflux for 45 min. Brown-red crystals of the complex were filtered off and dried in vacuo (1·5 g, 80%), m.p. 120—122°C (reported[7] m.p. 118 to 120°C). For $C_{54}H_{45}I_1P_3Rh$ (1016) calculated: 12·5% I, 9·10% P, 10·13% Rh; found: 12·0% I, 9·07% P, 10·10% Rh.

Hydrosilylation of 1,3-*butadiene*. All experiments were carried out in sealed tubes under argon using degassed reactants and the solvent benzene. The procedure and gas chromatographic analysis of reaction mixtures were the same as in previous works[4,5]. The yields of hydrosilylation products recorded in Table I are the average of at least three measurements (maximal deviation for individual products did not exceed 20% rel.). The reaction of trimethylsilane with 1,3-butadiene afforded four products, 4-trimethylsilyl-1-butene, 1-trimethylsilyl-cis-2-butene, 1-trimethylsilyl- -trans-2-butene, and 1,4-bis(trimethylsilyl)-2-butene. These compounds were isolated and characterized similarly as in a previous work[6]. Their physical properties were compared with those of authentic samples prepared independently, except 1-trimethylsilyl-trans-2-butene whose selective preparation has not yet been realized. In this case comparison was only made of the gas chromatographic retention time and IR spectrum of this adduct with the sample containing 81% mol of 1-trimethylsilyl-trans-2-butene and 19% of the cis isomer which was obtained earlier[13]. 1-Triethoxysilyl-cis-2-butene and 1-trichlorosilyl-cis-2-butene formed in reactions of 1,3-butadiene with triethoxy- and trichlorosilane, respectively, showed identical IR spectra and physico-chemical properties with authentic samples prepared and characterized elsewhere[5,14].

Dehydrogenation of 1,4-*bis(trimethylsilyl)butane.* A mixture of the title compound (1 ml, 3·8 mmol), 1 ml of benzene, and [RhCl{P(C₆H₅)₃}₃] (50 mg, 5·4 . 10⁻² mmol) was heated in a sealed glass tube at 80°C for 1 h. As found by gas chromatographic analysis, the dehydrogenation reaction did not occur under these conditions.

Hydrosilylation of 4-*trimethylsilyl-*1-*butene with trimethylsilane.* A mixture of 4-trimethylsilyl-1-butene (1 ml, 5·7 mmol), trimethylsilane (0·61 ml, 5·7 mmol), and [RhCl{P(C₆H₅)₃}₃] (5·7 . . 10⁻³ mmol, benzene solution) was heated in a sealed glass tube under argon at 80°C for 2 h. By gas chromatographic and IR analysis it was found that the reaction gave 1,4-bis(trimethylsilyl)-butane in 42% yield (with respect to the starting butene). The addition was accompanied by isomerization of 4-trimethylsilyl-1-butene to 1-trimethylsilyl-*cis*-2-butene (the molar ratio of these compounds at the end of the reaction was 3 : 1). The experiment was repeated with the exception that the reaction was carried out in the absence of the solvent. The silyl-substituted butane was again formed as a sole hydrosilylation product (25% yield).

Hydrosilylation of monosilyl-substituted butenes with trimethylsilane. To a mixture (5·7 mmol) containing 1-trimethylsilyl-*cis*-2-butene (65 mol %), 1-trimethylsilyl-*trans*-2-butene (c. 10 mol %), and 4-trimethylsilyl-1-butene (c. 25 mol %) was added a solution of [RhCl{P(C₆H₅)₃}₃] (5·7 . . 10⁻³ mmol) in benzene (1 ml) and the mixture was then heated under argon at 80°C for 2·5 h. The reaction gave 1,4-bis(trimethylsilyl)-butane in c. 3% mol yield (by gas chromatography). Isomerization of the starting compounds did not essentially occur (relative amounts of the silyl--substituted butenes in the resultant mixture agreed within experimental errors with the initial composition).

Isomerization of 4-*trimethylsilyl-*1-*butene.* A solution of 4-trimethylsilyl-1-butene (1 ml, 5·7 mmol) and [RhCl{P(C₆H₅)₃}₃] (5·7 . 10⁻³ mmol) in benzene (1 ml) was heated under argon at 80°C for 2·5 h. Only trace amounts of 1-trimethylsilyl-*cis*-2-butene were formed .
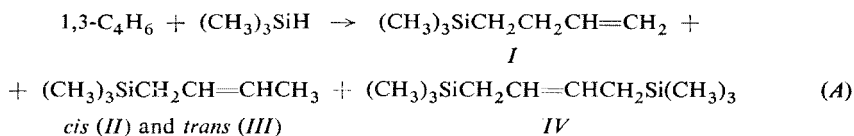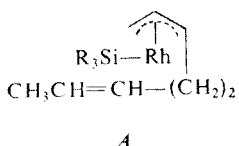

RESULTS AND DISCUSSION

With regard to the fact that the addition of silicon hydrides to 1,3-butadiene catalysed with rhodium(I) complexes has not yet been systematically studied we first examined the effect of reaction conditions on the course of the addition of trimethylsilane catalysed with $[RhCl\{P(C_6H_5)_3\}_3]$. As it was already mentioned in the introduction, this complex was to be efficient catalyst for this addition (*cf.*[3]). The results of our experiments do not fully corroborate this statement. At room temperature, a catalyst to butadiene ratio of 1 . 10⁻⁴, and with the use of equimolar amounts of the reactants, the reaction proceeded in both the absence and presence of the solvent benzene (30% solution), at a relatively slow rate (the 1,3-butadiene conversion 25% and 14%, respectively). Good yields of hydrosilylation products were obtained only at elevated temperatures, as demonstrated by following data (12·9 mmol 1,3-butadiene, 12·9 mmol trimethylsilane, 1 ml benzene, the catalyst to butadiene molar ratio = 1 : 10⁴, reaction time 15 min):

t, °C	50	60	70	80
Conversion, %	6	20	34	75

With the catalyst concentrations by one order of magnitude lower, the reaction was ill reproducible.

Irrespective of the reaction conditions (temperature, catalyst concentration, molar ratios of the reactants), the reaction produced four products, 4-trimethylsilyl-1-butene (I), 1-trimethylsilyl-*cis*-2-butene (II), 1-trimethylsilyl-*trans*-2-butene (III), and 1,4-bis(trimethylsilyl)-2-butene (IV) (equation (A)). These compounds have all the trimethylsilyl group bonded to the terminal carbon atom. Formation of isomers with the internal silyl group has not been detected. In addition to IR analysis of the compounds, the absence of 2-silylsubstituted adducts was also confirmed by hydrogenation of the mixtures of monosilyl-substituted butenes in acetic acid with platinum black which always gave only one product, butyltrimethylsilane.

$$R_3Si \!-\! Rh$$
$$CH_3CH \!=\! CH \!-\! (CH_2)_2$$

$$A$$

$$1,3\text{-}C_4H_6 + (CH_3)_3SiH \rightarrow (CH_3)_3SiCH_2CH_2CH\!=\!CH_2 +$$
$$I$$
$$+ (CH_3)_3SiCH_2CH\!=\!CHCH_3 + (CH_3)_3SiCH_2CH\!=\!CHCH_2Si(CH_3)_3 \qquad (A)$$
$$cis\ (II)\ \text{and}\ trans\ (III) \qquad\qquad\qquad IV$$

As some of the above products could be formed by consecutive reactions, we investigated the factors influencing the relative ratio of $I-III$ to IV. It was found that IV is formed already in the initial stage of the addition and its relative amount does not significantly change during the reaction (*e.g.* in the hydrosilylation carried out at 50°C with equimolar amounts of the reactants and the catalyst to butadiene ratio $= 1 : 1 . 10^4$, the $(I-III)/IV$ ratio equaled to 6 at 18% butadiene conversion and to 5·8 at 76% conversion). This ratio was further only slightly affected by the reaction temperature. Thus, for example, on increasing the temperature from 50°C to 120°C, the $(I-III)/IV$ ratio increased from 6 to 7. As expected, distribution of the products was influenced by the butadiene to trimethylsilane ratio chosen; however, even on using butadiene in relatively great excess, formation of IV was not fully supressed; as it is seen from the following results obtained at 80°C:

| $1,3\text{-}C_4H_6/(CH_3)_3SiH$ mol. ratio	1 : 3	1 : 1	2 : 1	5 : 1
$(I-III)/IV$	4·8	6·6	8·0	8·8

The same hydrosilylation products as with $[RhCl\{P(C_6H_5)_3\}_3]$ were also obtained in the presence of the other rhodium(I) complexes studied. Of these, only the carbonyl–

–rhodium complexes, $[RhCl(CO)\{P(C_6H_5)_3\}_2]$ and $[RhH(CO)\{P(C_6H_5)_3\}_3]$, were more "selective" than the chlororhodium complex. In their presence and under identical reaction conditions with those used in the previous case, *IV* was formed in relative amounts which were about one half of those obtained with Wilkinson catalyst.

Formation of the 1,4-bis(trimethylsilyl) derivative *IV* in relatively large amounts in the course of this addition reaction was not expected, since the higher silyl-sub-stituted compound which would be produced by reaction of two molecules of tri-methylsilane with butadiene should be the saturated substance, bis(trimethylsilyl)-butane. However, in none of the experiments performed was this compound present in the reaction mixture in the amounts detectable by gas chromatography ($> 1\%$). With respect to the ease with which trimethylsilane adds to 1-hexene in the presence of Wilkinson catalyst[15] this fact seemed surprising, since among the monosilyl-substituted butenes formed by reaction of trimethylsilane with 1,3-butadiene at least 4-trimethylsilyl-1-butene having terminal C=C bond could be reactive enough to compete with the alkadiene for the silicon hydride. Hydrosilylation experiments made with *I* showed, however, that this substance adds trimethylsilane relatively reluctantly. Thus, for example, at a temperature of 80°C and under the conditions used in the butadiene + trimethylsilane reaction (see p. 7, reaction time 2 h) *I* reacted to give 1,4-bis(trimethylsilyl)butane in 42% yield, while in the hydrosilylation of buta-diene overall yield of the reaction products *I*−*IV* was about twice as high (94% mol). Furthermore, in competition experiments carried out with the use of 100% mol excess of *I* and 1,3-butadiene (1 : 1 mol ratio) with respect to trimethylsilane, bis(tri-methylsilyl)butane has been formed only in c. 2% yield, the overall yield with respect to trimethylsilane being 92%. This shows that in the presence of 1,3-butadiene hydro-silylation of *I* is effectively suppressed. It is worthy of note that the low reactivity of *I* toward trimethylsilane observed in the hydrosilylation of this compound catalysed with Wilkinson catalyst is undoubtly also due to the fact that during the reaction *I* is isomerized to the *cis*-isomer *II*. As established by gas chromatography, the *II* to *I* ratio after the reaction was approximately 0·3. In accordance with the generally lower reactivity of internal alkenes compared to terminal ones, which was observed by a number of authors and also in this laboratory[16], hydrosilylation of 1-trimethyl-silyl-*cis*-2-butene (*II*) afforded under the above reaction conditions only very low yield of the bis(trimethylsilyl)butane ($< 2\%$). Similarly low yields of this adduct were also obtained in the hydrosilylation of a mixture of isomers *I*−*III* (4%). These results all indicate that 1,4-bis(trimethylsilyl)butane is not the compound which will be the precursor of the unsaturated derivative *IV*. This assumption is supported also by the fact that under the conditions analogous to those used in hydrosilylations, none of the rhodium complexes tested in the present study dehydrogenated the bis(trimethylsilyl)butene to *IV*. Indeed, such a reaction is little probable from thermo-dynamic reasons.

Formation of *IV* has until now been observed to occur in the presence of some

palladium(II) compounds such as $[Pd(C_6H_5CN)_2Cl_2]$ and $[Pd_2(\eta\text{-}C_3H_5)_2Cl_2]$ (ref.[6]). With these catalysts the yield of IV did not exceed several per cent. The reaction produced also 1-trimethylsilyl-1,3-butadiene which was shown by separate experiments to interact with trimethylsilane to give IV (Equation (B)).

$$(CH_3)_3SiCH=CHCH=CH_2 + (CH_3)_3SiH \rightarrow IV \qquad (B)$$
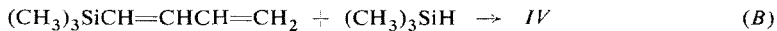
This path was then assumed to be responsible for formation of IV in the course of hydrosilylation of the alkadiene. It seems likely that in our case IV is not formed by this way, since the silylbutadiene was not found among hydrosilylation products. In this connection it is worth mentioning that in the study of ligand effects in the nickel catalysed hydrosilylation of 1,3-butadiene with trichlorosilane[14] it was observed that the reaction produces the bis-silylsubstituted butene of analogous structure, 1,4-bis-(trichlorosilyl)-2-butene, only when 4-trichlorosilyl-1-butene is also formed. In case that formation of the latter compound was supressed, also the former substance was absent. It was further confirmed that 1,4-bis(trichlorosilyl)-2-butene did not arise from 4-trichlorosilyl-1-butene. This led to conclusion that both derivatives are formed *via* intermediates of similar structure. The results discussed in the present work do not contradict this assumption.

Of other products, we studied in more detail formation of 1-trimethylsilyl-*cis*--2-butene (II). As already mentioned, this compound is isomerized to II during its hydrosilylation. We found that the isomerization does not proceed in the absence of the silicon hydride. This shows that the double bond migration proceeds *via* η-alkene (equation (C)) rather than η-allyl mechanism[17] (equation (D)).
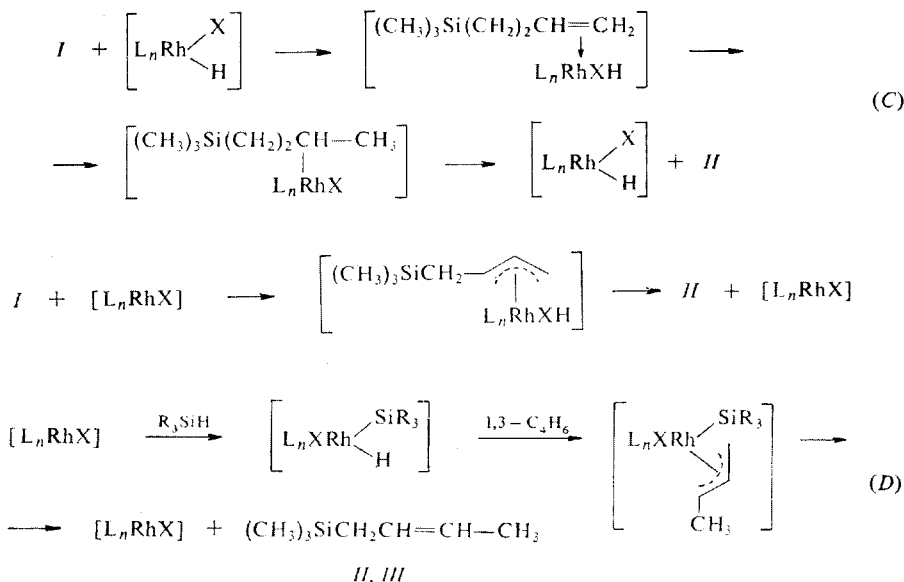
The fact that I undergoes isomerization under conditions similar to those used in hydrosilylation of 1,3-butadiene could indicate that this compound is in fact the primary product of the hydrosilylation and the isomers II and III are produced by its subsequent transformations. The following results speak, however, against this assumption. From comparison of the values of the II/I ratio found for hydrosilylation of I and the addition of trimethylsilane to 1,3-butadiene (1 : 3 and 2 : 1 respectively) it follows that the *cis*-isomer prevails in the latter case. Furthermore, in hydrosilylation of 1,3-butadiene II is formed in the relative amounts (with respect to I) comparable to those found at the end of the reaction already in the initial stage of the reaction (*e.g.* for 17% conversion of the diene the ratio equaled to 2·5 : 1), *i.e.* in the time when the reaction of I is accompanied only by negligible isomerization of this compound ($<5\%$).

In addition, hydrosilylation of 1,3-butadiene with triethoxysilane and trichloro-silane gave selectively only one product, the corresponding 1-silylsubstituted *cis*--2-butene.

Formation of the adducts with internal double bond II and III can be visualized by the reaction scheme involving η-allyl complexes as reaction intermediates (Scheme 1), similar to the related palladium-[3,6] and nickel-catalysed[13] addition. The assump-

tion that the first step involves oxidative addition of organosilicon hydride to the rhodium complex seems justified especially in the case of triethoxy- and trichlorosilane. This is supported by the fact that on standing the reaction mixtures containing the reactants and $[RhCl\{P(C_6H_5)_3\}_2]$ at a temperature at which hydrosilylation reaction does not essentially take place the organosilicon hydride (triethoxysilane, trichloro-silane) interacts with the catalyst to give the known complex $[RhCl(SiR_3)\{P.\ .(C_6H_5)_3\}_2]$ (R = CH$_3$ (ref.[11]), C$_2$H$_5$O (ref.[18]). Insertion of 1,3-butadiene to the rhodium–hydrogen bond to form a η-crotylrhodium complex has in some cases been established[10,19]. The course of the addition of trimethylsilane is more complex. However, formation of *I*, *i.e.* 1,2-addition product, is not unexpected, since the in-sertion of butadiene molecule to the rhodium–hydrogen bond is undoubtly preceeded by π-coordination of the diene to the complex. Coordination of butadiene as a mono-dentate ligand followed by essentially concerted addition of both fragments (the silyl group and hydrogen) would result in the 1,2-addition.

The reaction of trimethyl- and triethoxysilane catalysed with rhodium complexes differs in its course from the analogous hydrosilylation catalysed with palladium and nickel complexes in that it does not produce the coupled addition products, silyl-substituted octadienes. In this respect all the rhodium complexes studied are also more "selective" compared to their behaviour in the additions of other compounds contain-ing active hydrogen, *e.g.* amines, that were shown to produce complex mixture of

$$I \;+\; \left[L_nRh\!\!\begin{array}{c}X\\H\end{array}\right] \longrightarrow \left[\begin{array}{c}(CH_3)_3Si(CH_2)_2CH\!\!=\!\!CH_2\\ \downarrow\\ L_nRhXH\end{array}\right] \longrightarrow$$

$$\longrightarrow \left[\begin{array}{c}(CH_3)_3Si(CH_2)_2CH\!-\!CH_3\\ |\\ L_nRhX\end{array}\right] \longrightarrow \left[L_nRh\!\!\begin{array}{c}X\\H\end{array}\right] \;+\; II \qquad (C)$$

$$I \;+\; [L_nRhX] \longrightarrow \left[\begin{array}{c}(CH_3)_3SiCH_2\!\!-\!\!\overbrace{\qquad}\\ |\\ L_nRhXH\end{array}\right] \longrightarrow II \;+\; [L_nRhX]$$

$$[L_nRhX] \xrightarrow{R_3SiH} \left[L_nXRh\!\!\begin{array}{c}SiR_3\\H\end{array}\right] \xrightarrow{1,3-C_4H_6} \left[\begin{array}{c}L_nXRh\!\!\begin{array}{c}SiR_3\\ \searrow\\ \vdots\\ CH_3\end{array}\end{array}\right] \longrightarrow$$

$$\longrightarrow [L_nRhX] \;+\; (CH_3)_3SiCH_2CH\!\!=\!\!CH\!-\!CH_3 \qquad (D)$$

II, III

SCHEME 1

C_4- and C_8-adducts in the presence of $[RhCl\{P(C_6H_5)_3\}_3]$ (ref.[20]), $[RhCl(CO) \cdot \{P(C_6H_5)_3\}_2]$ (ref. [20]), $[RhCH_3\{P(C_6H_5)_3\}_3]$ (ref.[21]), and $[Rh(\eta\text{-}C_3H_5)\{P(C_6H_5)_3\}_2]$ (ref.[21]). Within the framework of the mechanism proposed, the absence of C_8-adducts indicates that the η-allyl intermediate has a lifetime which is not long enough to enable coordination of another butadiene molecule to give C_8-intermediate of the type A.

As already mentioned, the rhodium catalysts studied do not affect significantly the type of the products formed and differ only in their activity. The results presented in Table I show that both carbonyl–rhodium complexes are very efficient catalysts for the addition of triethoxysilane. The activity of the halogenorhodium complexes $[RhX\{P(C_6H_5)_3\}_3]$ (X = Cl, Br, I) falls with the electronegativity of anionic ligand. This trend is most pronounced in the case of trichlorosilane addition. Because of lack of data concerning ligand effects in individual reaction steps, it is at present ambiguous to discuss this order in more detail. It is of interest, however, that the same activity as the starting complexes $[RhCl\{P(C_6H_5)_3\}_3]$ and $[RhBr\{P(C_6H_5)_3\}_3]$ showed also the related hydrido(silyl)rhodium complexes $[RhXH(SiCl_3)\{P(C_6H_5)_3\}_2]$ (100°C, 30 min; X = Cl, conversion 78%, X = Br, conversion 2%). All of these catalysts were inactive when milder conditions were employed (80°C, 8 h). In that case the above silylrhodium complexes were recovered from the reaction mixture intact. This could indicate that the supression of the addition in the presence of the bromorhodium complex is not due to prevention of oxidative addition of the silicon hydride but rather due to insufficient activation of 1,3-butadiene. The marked

TABLE I

Catalytic Activity of Rhodium Complexes in Additions of Trimethyl-, Triethoxy-, and Trichlorosilane to 1,3-Butadiene (19·2 mmol of Each Reactant, Catalyst to Butadiene Mol. Ratio = = 1 . 10^{-4}, Benzene (1 ml))

Catalyst	Conversion, % mol.[a]		
	$(CH_3)_3SiH^b$	$HSi(OC_2H_5)_3{}^c$	$HSiCl_3{}^d$
$[RhCl\{P(C_6H_5)_3\}_3]$	80(7)^c	36	80
$[RhBr\{P(C_6H_5)_3\}_3]$	76(7)	17	5
$[RhI\{P(C_6H_5)_3\}_3]$	71(7)	0	2
$[RhCl(CO)\{P(C_6H_5)_3\}_2]$	10(12)	92	2
$[RhH(CO)\{P(C_6H_5)_3\}_3]$	6(12)	96	2
$[Rh(\eta\text{-}C_3H_5)\{P(C_6H_5)_3\}_2]$	77(7)	55	0
$[RhCH_3\{P(C_6H_5)_3\}_3]$	88(8)	52	0

[a] To reaction products I—IV, V, or VI, respectively. [b] 80°C, 15 min; the I—III to IV mol. ratio is given in parentheses. [c] 100°C, 30 min. [d] 100°C, 6 h. [e] A high conversion (91%) was also achieved with the dimer $[Rh_2Cl_2\{P(C_6H_5)_3\}_4]$.

difference between the catalytic activity of the chloro- and bromorhodium complexes (which does not arise from inactivation of the latter *via* its decomposition) gives support for the assumption that the anionic ligand remains coordinated to the catalytically active rhodium species, as depicted in Scheme 1.

REFERENCES

1. Pomerantseva M. G., Belyakova Z. V., Golubtsova S. A., Shvarts N. S.: *Poluchenye Karbofunktsionalnykh Organosilanov po Reaktsii Prisoedinenya.* NIITEKCHIM, Moscow 1971.
2. Cundy C. S., Kingston B. M., Lappert M. F.: Advan. Organometal. Chem. *11*, 253 (1973).
3. Takahashi S., Shibano T., Kojima H., Hagishara N.: Organometal. Chem. Syn. *1*, 193 (1970/ 1972).
4. Langová J., Hetflejš J.: This Journal *40*, 420 (1975).
5. Čapka M., Hetflejš J.: This Journal, in press.
6. Langová J., Hetflejš J.: This Journal *40*, 432 (1975).
7. Osborn J. A., Jardine F. H., Young J. F., Willkinson G.: J. Chem. Soc., A, *1966*, 1711.
8. Evans D., Yagupsky G., Wilkinson G.: J. Chem. Soc., A, *1968*, 2660.
9. Ahmad N., Robinson S. D., Uttley M. F.: J. Chem. Soc., Dalton Trans. 1, *1972*, 843.
10. Reilly C. A., Thyret H.: J. Amer. Chem. Soc. *89*, 5144 (1967).
11. Charenteney F., Osborn J. A., Wilkinson G.: J. Chem. Soc., A, *1968*, 787.
12. Keim W.: J. Organometal. Chem. *8*, P 25 (1967).
13. Čapka M., Hetflejš J.: This Journal, in press.
14. Vaisarová V., Čapka M., Hetflejš J.: Syn. Inorg. Metal-Org. Chem. *2*, 289 (1972).
15. Rejhon J., Hetflejš J.: Unpublished results.
16. Čapka M., Svoboda P., Bažant V., Chvalovský V.: Chem. Prům. *21*, 46 (1971).
17. Keim W. in the book: *Transition Metals in Homogeneous Catalysis* (G. N. Schrauzer, Ed.), Chapter 3. Dekker, New York 1971.
18. Haszeldine R. N., Parish R. V., Parry D. J.: J. Chem. Soc., A, *1969*, 683.
19. Cramer R.: J. Amer. Chem. Soc. *89*, 1635 (1967).
20. Baker R., Holliday D. E.: Tetrahedron Lett. *1972*, 2773.
21. Dewhirst K. C., Keim W., Thyret H. E.: U.S. 3 502 725.

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