

CATALYSIS BY METAL COMPLEXES. VII.*

HYDROSILYLATION CATALYSED BY TETRAKIS(ETHYLENE)-
DICHLORODIRHODIUM(I)

P.SVOBODA, M.ČAPKA and J.HETFLJEŠ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchbát*

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It was found that the competitive addition of couples of silicon hydrides of the type $(C_2H_5)_{3-n}SiHCl_n$ ($n = 0-3$) to 1-heptene catalysed by $[RhCl(C_2H_4)_2]_2$ yields usually only the products of the addition of the hydride containing the greater number of chlorine atoms, in contrast to preparative additions which afford individual hydrosilylation products in 40–65% yields. The reason of this discrepancy is discussed.

In connection with the study of the effect of structure of olefins¹ and silicon hydrides² on their reactivity in homogeneous catalysed hydrosilylation, in a previous work³ we made the attempt to determine relative reactivities of a series of the silicon hydrides $(C_2H_5)_{3-n}SiHCl_n$ ($n = 0-3$) in their addition to 1-heptene catalysed by $RhCl[P(C_6H_5)_3]_3$, using the method of competition reactions. We have observed that in the competition reaction of the couples of ethylchlorosilanes differing by one chlorine atom in their molecule, only the higher chlorine-substituted hydride underwent addition. This unexpected finding, which was in apparent discrepancy with the results of preparative experiments⁴ that indicated increasing reactivity of the hydrides with decreasing number of chlorine atoms in their molecule, has been attributed to a fast exchange of silyl ligands in the reaction intermediate, which is practically complete before its conversion to the reaction products.

These results did not allow us to ascertain whether this phenomenon is connected with a comparatively low activity of $RhCl[P(C_6H_5)_3]_3$ as hydrosilylation catalyst⁴⁻⁶, or whether, due to the high rate of the exchange of silyl ligands, relative to the rate of the conversion of the reaction intermediate to the products, has in the case of rhodium complexes more general character. In the present work we have therefore decided to perform an analogous study with the use of the more efficient catalyst, tetrakis(ethylene)dichlorodirhodium(I). Its high catalytic activity in the addition of ethyldichlorosilane to 1-hexene has recently been noted by Chalk and Harrod⁷ and its use as the catalyst for hydrosilylation of olefins by chloro-substituted silicon hydrides was protected by the same authors^{8,9}.

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EXPERIMENTAL AND RESULTS

Tetrakis(ethylene)dichlorodirrhodium(I) was prepared by the reaction of ethylene with $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ in methanol¹⁰ in 45% yield. The starting compounds, hydrosilylation products and the method of analysis of reaction mixtures were described in previous work^{2,3}. The competition and preparative additions were carried out in sealed ampoules under nitrogen, under the conditions specified in Table I. Relative rate constants were calculated in the usual manner¹¹.

The course of the hydrosilylation catalysed by $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ has not yet been studied in detail⁷. Our results, presented in Table I, show that it is very similar to the hydrosilylation catalysed by phosphine rhodium complexes¹²: the addition of trichlorosilane to internal olefins (*cis*- and *trans*-2-heptene) yielded *n*-alkyltrichlorosilane as the sole product; the *trans* isomer was less reactive than the *cis* isomer, both reacting at slower rate than the corresponding terminal olefins. We have further found that the ethylene complex is also effective in the addition of alkoxy-substituted hydrides to simple olefins. So for instance, the reaction of triethoxysilane with 1-hexene proceeded smoothly at mild conditions (24°C, 24 h), affording almost quantitative yield of *n*-hexyltriethoxysilane. An increased catalytic activity of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$, relative to $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$, exhibits itself especially in the addition of chloro-substituted silicon hydrides. While in the hydrosilylation catalysed by the phosphine complex the yields of the products were strongly dependent on the structure of silicon hydrides⁴, in the addition of the hydrides of type $(\text{C}_2\text{H}_5)_{3-n} \cdot \text{SiHCl}_n$ ($n = 0-3$) to 1-heptene catalysed by the ethylene complex, similar yields were obtained at the same experimental conditions with all the hydrides studied (46–60%), without distinct dependence on the structure of the substrates. When attempting to determine relative reactivities of these compounds by the competition

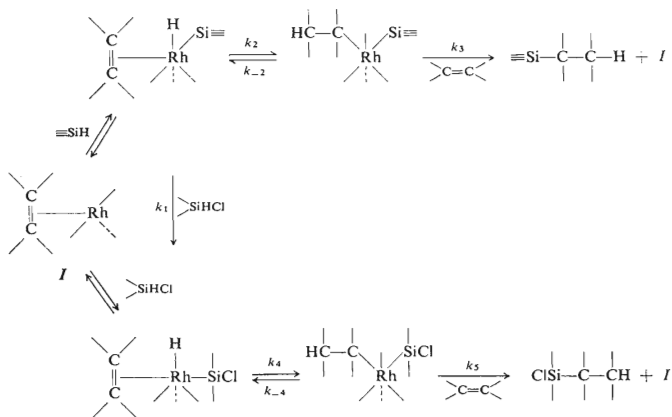
TABLE I

Hydrosilylation Catalysed by $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ Conditions: $4 \cdot 10^{-3}$ mmol of the catalyst, 2.25 mmol of benzene; temperature 85°C, time 2 h.

Silicon hydride (mmol)	Olefin (mmol)	Silane (%)
$\text{HSi}(\text{C}_2\text{H}_5)_3$ (2.6)	1-heptene (3.0)	<i>n</i> -heptyltriethyl (60)
$\text{HSi}(\text{C}_2\text{H}_5)_2\text{Cl}$ (3.0)	1-heptene (3.0)	<i>n</i> -heptyldiethylchloro (60)
$\text{HSi}(\text{C}_2\text{H}_5)\text{Cl}_2$ (3.5)	1-heptene (3.0)	<i>n</i> -heptylethyldichloro (46)
HSiCl_3 (4.2)	1-heptene (3.0)	<i>n</i> -heptyltrichloro (54)
HSiCl_3 (5.0)	<i>cis</i> -2-heptene (3.6)	<i>n</i> -heptyltrichloro (10)
HSiCl_3 (5.0)	<i>trans</i> -2-heptene (3.6)	<i>n</i> -heptyltrichloro (1)
$\text{Si}(\text{OC}_2\text{H}_5)_3$ (2.7)	1-hexene (4.0)	<i>n</i> -hexyltriethoxy (100)
$\text{Si}(\text{OC}_2\text{H}_5)_3^a$ (2.7)	1-hexene (4.0)	<i>n</i> -hexyltriethoxy (100)

^a 24°C, 24 h.

of the couples of silicon hydrides differing by one chlorine atom in their molecule, we have obtained different results, however. With the exception of the HSiCl_3 — $\text{C}_2\text{H}_5\text{SiHCl}_2$ couple, which yielded *n*-heptyltrichlorosilane and *n*-heptylethyl-dichlorosilane in the 9 : 1 ratio, in other cases the sole reaction product was *n*-alkylchlorosilane containing greater number of chlorine atoms, quite in harmony with the already mentioned results obtained with the phosphine complex³. It seems probable that this difference can again be ascribed to the possibility of the exchange of silyl ligands in the reaction intermediate. In analogy with the mechanism suggested by Chalk and Harrod⁷ for hydrosilylation catalysed by the olefinic complexes of platinum, the course of the competition addition studied in the present work can be depicted by Scheme 1.



SCHEME 1

The fact that the preparative addition affords hydrosilylation products in comparable yields indicates that transformation of the starting compounds to the products proceeds in both pathways by comparable rates. The occurrence of the only, higher chlorine-substituted product in the competition addition could be expected if the rate constant of silyl ligand exchange k_1 is at least by one order of magnitude greater than the rate constant k_2 . It cannot be ruled out, however, that this exchange proceeds simultaneously with the conversion of π -complex to σ -complex, since coordinatively unsaturated intermediate is formed in this process.

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