

## CATALYSIS BY METAL COMPLEXES. IX.\*

CATALYTIC PROPERTIES  
OF TRIS(DIPHENYLPHOSPHINE)CHLORORHODIUM(I)

P.SVOBODA, M.ČAPKA and J.HETFLÉŠ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

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Catalytic activity of tris(diphenylphosphine)chlororhodium(I) in hydrosilylation, hydrogenation, and hydroformylation was studied and compared with the activity of its analogue, tris(triphenylphosphine)chlororhodium(I). The diphenylphosphine rhodium complex was found to be effective hydrosilylation catalyst, but relatively poor hydrogenation catalyst. In its presence hydroformylation proceeds under comparatively mild conditions.

In connection with the study of hydrosilylation of alkenes catalysed with soluble rhodium complexes<sup>1,2</sup> we were also interested in the effect of the structure of a complex on its catalytic activity in this and some other reactions which proceed by a similar mechanism. In the present work we deal with the catalytic properties of tris(diphenylphosphine)chlororhodium(I) as the analogue of tris(triphenylphosphine)chlororhodium(I), the well-known hydrogenation catalyst<sup>3</sup> which has recently been shown to be also effective hydrosilylation catalyst<sup>4</sup>. In addition to hydrosilylation and hydrogenation, we have also tested the activity of tris(diphenylphosphine)chlororhodium(I) in hydroformylation.

## EXPERIMENTAL

Temperature data are uncorrected. The preparation of and all operations with the compounds were carried out under argon. The alkenes, supplied by Fluka AG (Buchs, Switzerland), were thoroughly degassed and used without further purification. The preparation and physical properties of the silicon hydrides and hydrosilylation products were described elsewhere<sup>2,6</sup>.

Tris(diphenylphosphine)chlororhodium(I) was prepared<sup>5</sup> by the reaction of  $[(C_2H_5)_2RhCl]_2$  with  $(C_6H_5)_2HP$  in 58% yield (m.p. 172.5–174°C, lit.<sup>5</sup> 173–175°C).

*Hydrosilylations* were carried out in sealed ampoules under the conditions given in Table I. Reaction products were analysed on Griffin G 6 gas chromatograph on a 2 m column (0.4 cm i.d.) filled with 5% Silicone Elastomer E 301 on ground unglazed tiles.

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*Hydrogenations* were carried out in unsealed glass ampoules placed in a 100 ml steel autoclave. The ampoule was charged under argon with 1 ml of heptene and 0.1 ml of 0.01M solution of  $[\text{PH}(\text{C}_6\text{H}_5)_2]_3\text{RhCl}$  in methylene chloride, and the autoclave was flushed out with hydrogen and after its sealing the hydrogen pressure was raised to 35 atm. The reaction was carried out at 85°C over a period of 17 h. The cooled reaction mixture was analysed on Chrom 3 instrument (Laboratorní přístroje, Prague) provided with flame-ionization detector on a 50 m capillary column filled with tricresyl phosphate at 30°C.

*Hydroformylation* experiments were performed in a similar fashion as were hydrogenations. An appropriate amount of an alkene and the dichloromethane solution of the catalyst were charged into 5 ml glass ampoule, this was placed in the autoclave, which, after flushing with hydrogen, was pressured by the gas to the required pressure. Then carbon monoxide was added and the autoclave was heated with rocking to the desired temperature for appropriate time. The reaction mixture was allowed to cool to the ambient temperature and then analysed by g.l.c. The proportion of the aldehydes and the mixture of alkanes and alkenes was determined on Chrom 3 instrument with the use of Apiezon E as stationary phase, the composition of the mixture of alkanes and alkenes was determined with the same instrument with the use of the capillary column filled with tricresyl phosphate.

A mixture of alkenes formed by isomerization during hydrogenation and hydrosilylation was analysed in a similar fashion. The analyses were made with the heptane–heptene fraction obtained by distillation of the reaction mixture.

## RESULTS AND DISCUSSION

We were first interested in some properties of tris(diphenylphosphine)chlororhodium(I). When determining its molecular weight osmotically, we have found that in the methylene chloride solution at 25°C on exposure to air, the molecular weight of the complex mildly increases with increasing concentration; it is, however, always substantially lower than theoretical value (697). The molecular weight was for the concentration of the complex 5.45 g/l 433, for 8.15 g/l 441, and for 12.30 g/l 468. This speaks for extensive dissociation of the complex in this solvent. Similar behaviour was already observed with analogous triphenylphosphine derivative<sup>3</sup>,  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}$ , both in chloroform and in benzene solutions. By contrast, Hayter<sup>5</sup> found that the diphenylphosphine complex is practically undissociated in benzene (m.w. 680). Unfortunately, the method and conditions used were not reported. We therefore attempted to determine the molecular weight of the complex cryoscopically with the exclusion of air. This attempt has failed, however, since in the absence of air the complex was very poorly soluble in the solvent.

By comparison with  $[(\text{C}_6\text{H}_5)_3]_3\text{RhCl}$ , the diphenylphosphine complex turned out to be much more stable, both in solid state and in solution. So, for example, while the former decomposed in solution on standing under inert atmosphere in an ice-box after 3 days and became inactive in hydrosilylation, the latter could be allowed to stand in air for several weeks without losing its catalytic activity (Table I).

*Hydrosilylation.* As evident from Table I, tris(triphenylphosphine)chlororhodium(I) is efficient catalyst for hydrosilylation of simple alkenes by alkyl- and alkoxy-

TABLE I  
Hydrosilylation Catalysed by  $[(C_6H_5)_2PH]_3RhCl$   
0.01M Solution of the catalyst in dichloromethane, 85°C, 2 h.

Silicon hydride (mmol)	Alkene (mmol)	Catalyst ml	Product (yield, %)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2.6)	1-hexene (4.0)	0.1	n-C <sub>6</sub> H <sub>13</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (95)
HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (2.4)	1-hexene (4.0)	0.1	n-C <sub>6</sub> H <sub>13</sub> Si(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (78)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (1.6)	1-hexene (2.4)	0.05 <sup>a</sup>	n-C <sub>6</sub> H <sub>13</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (87)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2.6)	1-hexene (4.0)	0.1 <sup>b</sup>	n-C <sub>6</sub> H <sub>13</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (50)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (1.6)	3,3-dimethyl-1-butene (2.3)	0.1	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (90)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2.6)	<i>cis</i> -2-heptene (3.6)	0.1	n-C <sub>7</sub> H <sub>15</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (60)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2.6)	<i>trans</i> -2-heptene (3.6)	0.1	n-C <sub>7</sub> H <sub>15</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (5)
HSiCl <sub>3</sub> (4.9)	1-heptene (3.6)	0.05	n-C <sub>7</sub> H <sub>15</sub> SiCl <sub>3</sub> (10)
HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (9.6)	allyl chloride (36.8)	0.2	(n-C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> SiCl, CH <sub>2</sub> =CH-CH <sub>3</sub> (85)
HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (9.6)	allyl chloride (36.8)	0.2	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> SiCl, CH <sub>2</sub> =CH-CH <sub>3</sub> (85)

<sup>a</sup> 20°C, 20 h; <sup>b</sup> the solution of the catalyst was allowed to stand in air for 3 days.

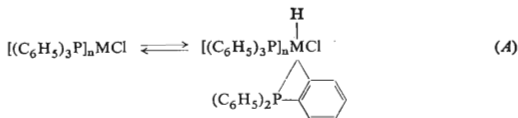
substituted silicon hydrides. The reaction with chloro-substituted hydrides afforded only poor yields of hydrosilylation products<sup>1,2</sup>. With allyl chloride, instead of hydrosilylation, the replacement of the labile chlorine atom by the hydrogen of the Si—H bond is taking place, giving rise to propene; this reaction proceeds here almost as readily as does the addition of silicon hydrides to simple alkenes. The products of hydrosilylation reaction are n-alkylsilanes. The higher reactivity of the *cis*-isomer, relative to the *trans* one, indicates that the reaction proceeds *via* the *cis* addition, similarly as with other transition metal hydrosilylation catalysts. The reaction is further accompanied by isomerization of the starting alkene (Table II), the *cis*-2-alkene being preferentially formed. This is also indirectly indicated by the data given in the

TABLE II  
Isomerization and Hydrogenation in Hydrosilylation Catalysed with  $[(C_6H_5)_2PH]_3RhCl$

Alkene (mmol)	Silicon hydride (mmol)	°C/h	Composition of heptene–heptane fraction, %				Conversion of the hydride %
			heptane	1-heptene	<i>cis</i> -2-heptene <i>trans</i> -2-heptene	<i>cis</i> -3-heptene <i>trans</i> -3-heptene	
<i>cis</i> -2-Heptene (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2-6)	85	5	4	13	7	60
		2		40	31		
<i>trans</i> -2-Heptene (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2-6)	85	6	2	11	7	5
		2		43	30		
1-Heptene (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (5-3)	85	5	14	16	5	95
		1-5		43	16		
1-Heptene (36)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (26-5)	80	3	42	25	3	97
		1		27	0		
1-Heptene (36)	HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (14-3)	80	3	43	24	4	97
		7		26	0		
1-Heptene (36)	HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (14-3)	80	17	10	23	5	85
		1		35	10		
1-Heptene <sup>a</sup> (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2-6)	80	16	4	19	9	87
		7		35	17		
1-Heptene <sup>b</sup> (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2-6)	85	4	20	23	5	80
		2		38	11		
1-Heptene <sup>a</sup> (3-6)	HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (2-6)	85	6	2	13	9	85
		2		42	30		
1-Heptene <sup>a</sup> (3-6)	HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (2-4)	85	9	15	24	4	50
		2		34	14		
1-Heptene <sup>b</sup> (3-6)	HSi(C <sub>3</sub> H <sub>7-n</sub> ) <sub>3</sub> (2-4)	85	48	1	7	7	60
		2		19	20		

<sup>a</sup> The catalyst was  $[(C_6H_5)_2PH]_3RhCl$ ; <sup>b</sup> the catalyst was  $[(C_2H_4)_2RhCl]_2$ .

line 5 of the table, in all the cases studied the rate of isomerization is higher than the rate of hydrosilylation. A similar situation has also been found with tris(triphenylphosphine)chlororhodium(I) and tetrakis(ethylene)dichlorodirhodium(I) (see lines 4 and 5 in Table II). The course of the isomerization is strongly dependent on the concentration of the silane. After the silane had almost completely reacted, the distribution of isomers has not changed on prolonged heating the reaction mixture (compare lines 4 and 5 in Table II). As confirmed by separate experiment, under the reaction conditions used in hydrosilylation experiments, in the absence of silicon hydride the rhodium complex studied does not catalyse isomerization. On the other hand, if the reaction mixture is heated in the presence of a silicon hydride for a sufficiently long time, the distribution of isomers is very near to the equilibrium distribution (see lines 1 and 2 in Table II). Although these phenomena have not yet been reported for hydrosilylation catalysed with rhodium complexes, analogous situation is known to arise in the hydrosilylation catalysed by Pt(II) complexes. This dependence was explained by Chalk and Harrod<sup>7</sup> in terms of a given catalyst to be isomerization catalyst, it must be activated by formation of the metal-hydrogen bond, in this case by the reaction of the complexes with silicon hydride. We believe that our results can be explained similarly. As shown in Table II, also alkanes are formed in the course of hydrosilylation. Although hydrogenation proceeds to a relatively very small extent and the results are thus laden with greater experimental errors, they do allow to conclude that the amount of the formed alkane depends on the structure of silicon hydride and parallels its reducing ability (compare data for tripropylsilane and triethoxysilane). Of the three catalysts compared, the tendency to effect hydrogenation is most distinct in the case of the ethylene complex (lines 9 and 10, Table II). Although these results indicate that the hydrogen comes from the organosilicon hydride, the mechanism of its transfer to the alkene is still unclear. One of the possibilities could be, at least in part, also the hydrogenation due to the metalation reaction (A) which



is known to occur with a number of group VIII metal complexes (for review see<sup>8</sup>). We have therefore carried out the reaction of 1-heptene with the stoichiometric amount of  $[(C_6H_5)_2PH]_3RhCl$  in the absence of a silicon hydride. No hydrogenation has however been observed under the conditions used in hydrosilylation experiments; the starting alkene was only slightly isomerized (to about 2%).

**Hydrogenation.** Contrarily to tris(triphenylphosphine)rhodium chloride, which is very effective hydrogenation catalyst<sup>3</sup>, the diphenylphosphine analogue catalyses

TABLE III

Composition of Reaction Mixture in Hydrogenation Catalysed by  $[(C_6H_5)_2PH]_3RhCl$ 

Initial hydrogen pressure 35 atm, 0.05 ml of 0.1M dichloromethane solution of the catalyst, 85°C, 17 h.

Alkene (3.6 mmol)	Heptane 1-Heptene		2-Heptene		3-Heptene	
			<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
1-Heptene	96	1	0	1	0	2
<i>cis</i> -2-Heptene	69	1	4	14	3	9
<i>trans</i> -2-Heptene	2	3	91	0	2	2
<i>trans</i> -3-Heptene	2	2	2	2	0	93

TABLE IV

Hydroformylation of Heptenes Catalysed with  $[(C_6H_5)_2PH]_3RhCl$ 3.6 mmol Alkene,  $1 \cdot 10^{-3}$  mmol of the catalyst added as its 0.01M or 0.005M solution in dichloromethane.

Alkene	H <sub>2</sub> : CO °C	Atm/h	Octanal	2-Methyl- heptanal	<i>cis</i> -2-Heptene <i>trans</i> - 2-heptene	<i>cis</i> -3-Heptene <i>trans</i> - 3-heptene
1-Heptene	1 : 1.75	50	45	30	6	3
	75	7			12	4
1-Heptene	1 : 1.75	65	52	27	4	1
	90	5.5			13	3
<i>cis</i> -2-Heptene	1 : 1.75	60	12	35	10	7
	75	5			19	17
<i>trans</i> -2-Heptene	1 : 1.75	60	15	51	3	3
	75	5			9	9
<i>trans</i> -3-Heptene	1 : 1.75	65	17	41	6	5
	90	5.5			14	17
1-Heptene	2 : 1	70	41	34	3	8
	90	6			8	9
1-Heptene	1 : 4.4	70	65	28	1	1
	90	6			4	1
1-Heptene	1 : 2	70	28	19	9	8
	145	4			19	7
1-Heptene	1 : 2 <sup>a</sup>	65	56	32	2	2
	95	6			4	4

<sup>a</sup> The gases were added in the reverse order (CO first, than H<sub>2</sub>).

this reaction only at elevated temperatures and pressures (Table III). Similarly as hydrosilylation, hydrogenation is also accompanied by isomerization of starting alkenes, which proceeds however to much lesser extent. The relation between the structure of alkenes and their reactivity is similar for both phosphinerhodium complexes. As expected, also here hydrogenation proceeds as the *cis* addition<sup>3</sup>.

**Hydroformylation.** The catalytic activity of the studied complex is illustrated by the results summarized in Table IV. Under the conditions used for hydroformylation of *trans*-3-heptene also several other alkenes were reacted. So, for example, 1-decene gave 4% aldehydes, vinyl ethyl ether afforded 17% yield of aldehydes, and cyclohexene reacted to give aldehydes in 30% yield. The alkenes with the lower electron density on the double bond, such as allyl chloride, croton aldehyde, vinyl acetate, and diethyl maleate, did not react. Ethylene and propene reacted only reluctantly, which under the condition used, could be due to their low concentration in the liquid phase. From the table it is further obvious that the higher alkenes can be hydroformylated under relatively mild conditions. The reaction is always accompanied by the isomerization of the unreacted alkene; the absence of 1-heptene in the reaction mixture indicates that it is preferentially consumed by the reaction, while the isomers with internal double bond are less reactive. Reasoning by analogy with tris(triphenylphosphine)chlororhodium<sup>9</sup>, it can be assumed that also here the proper catalyst is an intermediate containing carbonyl group as the ligand. The attempts to isolate this complex have so far been unsuccessful. Low yields of hydroformylation products obtained at 145°C could be indicative of the instability of this intermediate under these conditions. Apart from 1-heptene, also internal alkenes undergo hydroformylation to give preferentially branched aldehydes. The fact that on hydroformylation of 3-heptene, only 1-heptanal and 2-methylheptanal are formed, and not 3-ethylhexanal, indicates that the insertion of coordinated carbonyl is preceded by isomerization of the starting alkene.

#### REFERENCES

1. Svoboda P., Čapka M., Hetflejš J.: This Journal 37, 3059 (1972).
2. Svoboda P., Čapka M., Hetflejš J., Chvalovský V.: This Journal 37, 1581 (1972).
3. Osborn J. A., Jardine I. H., Young J. F., Wilkinson G.: J. Chem. Soc. (A) 1966, 1711.
4. Chalk A. J.: J. Organometal. Chem. 21, 207 (1970).
5. Hayter R. G.: Inorg. Chem. 3, 301 (1964).
6. Čapka M., Svoboda P., Bažant V., Chvalovský V.: This Journal 36, 2785 (1971).
7. Chalk A. J., Harrod J. F.: J. Am. Chem. Soc. 87, 16 (1965).
8. Parshall Q. W.: Accounts Chem. Res. 3, 139 (1970).
9. Baird M. C., Mague J. T., Osborn J. A., Wilkinson G.: J. Chem. Soc. (A) 1967, 1347.

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