ENANTIOSELECTIVE HYDROSILYLATION
OF TERT-BUTYL PHENYL KETONE BY DIPHENYLSILANE CATALYSED
BY [Rh{(—)-DIOP}₂]⁺ClO₄⁻*

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Kinetics of the title reaction has been studied by the method of initial reaction rates. In the presence of free chiral ligand the hydrosilylation was found to be first order in the catalyst and in the ketone and fractional order in the organosilicon hydride. The rate data and the results of spectroscopic study of interaction of diphenylsilane with the rhodium complex have been interpreted in terms of a reaction model involving formation of the corresponding cationic silyl(hydrido)-rhodium complex followed by interaction of the ketone with this complex in the rate determining step. The results are confronted with those obtained for the analogous reaction catalysed by [Rh(1,5-COD)(—)-DIOP]⁺ClO₄⁻.

In the preceding communication of this series we reported[1] on the kinetics of enantioselective hydrosilylation of tert-butylphenyl ketone by diphenylsilane catalysed by [Rh(1,5-COD)(—)-DIOP]⁺ClO₄⁻. Some unexpected features of this reaction (*e.g.* formation of arene–rhodium complexes by interaction of the organosilicon hydride with the rhodium complex in the first stage of the reaction or efficient competition of the ketone with diphenylsilane for coordination site of these complexes) led us to investigate catalytic behaviour of related Rh–DIOP systems. The present work concerns with the addition catalysed by bis/(−)-2,3-O-cyclohexylidene-2,3-dihydroxy-1,4bis(diphenylphosphino)butane/rhodium perchlorate ([Rh{(−)-DIOP}₂]⁺.
.ClO₄⁻).

EXPERIMENTAL

Chemicals. Toluene (Lachema, Brno) was dried over sodium, distilled in the presence of calcium(II) hydride, degassed and stored under argon. Tert-butylphenyl ketone, diphenylsilane, 1-phenyl-1-diphenylsiloxy-2,3-dimethylpropane and 1-phenyl-2,2-dimethylpropanol were prepared by procedures described in the preceding work[1]. (—)-2,3-O-Cyclohexylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((—)-DIOP), m.p. 118·5 —120°C, $[\alpha]_D^{20} = -19.65°$ (*c* 0·6, benzene) was from laboratory stock and its preparation was reported earlier[2]. {[Rh(—)-DIOP)}₂]⁺.

.ClO_4^- was obtained in 70% yield by replacement of 1,5-COD from [Rh(1,5-COD)(—)-DIOP]$^+$. .ClO_4^- (for analysis and ^{1}H-NMR spectrum of this complex see ref.[1]) by (—)-DIOP according to reported procedure[3]. For $C_{68}H_{72}O_8P_4RhCl$ (1 278·9) calculated: 63·86% C, 5·63% H; found: 63·71% C, 6·12% H. ^{1}H-NMR spectrum (δ, ppm-hexamethyldisiloxane as internal reference, saturated CD_3COCD_3 or $CDCl_3$ solutions): 7·8—7·0 m (40 H, arom.); 3·83 m (4 H, CHO); 2·25 m (8 H, PCH_2); 1·40—1·25 m (20 H, cyclohexyl).

Hydrosilylation procedure. Experiments were carried out in 15 ml-Schlenk tubes topped with two-layer exchangable cover made of silicon rubber which was connected to the neck of the tube by means of a plastic screw. Temperature of the reaction mixture was maintained constant within 0·1°C by a thermostated bath. Prior to introducing reaction components and solvent the tubes were repeatedly evacuated to approx. 10 Pa and filled with argon *via* side tube provided with a three-way valve. Feeding of substances was made by hypodermic syringes in the following sequence: solvent, catalyst solution, diphenylsilane and ketone. In kinetic measurements the ketone was added after 30 min and this moment was regarded as the beginning of the reaction. The reaction course was followed by removing samples (50—100 μl) at fixed time intervals. The samples were immediately solvolysed by 0·5 mol/l ammonium fluoride solution in aqueous methanol and analysed gas chromatographically (for details see ref.[1]). The optical purity of the product, 1-phenyl-2,3-dimethylpropanol, was determined by the procedure reported elsewhere[1].

Spectroscopic measurements. Interaction of diphenylsilane with [Rh{(—)-DIOP}$_2$]$^+$ClO$_4^-$ was followed by electron absorption spectroscopy, using cells adapted from this purpose in the earlier reported way[1]. Prior to introducing into sealed cells, appropriate amount of diphenylsilane was added to the catalyst solution in toluene (prepared in Schlenk tube). This procedure ensured more accurate feeding of the silicon hydride, although the first recording of the spectrum could be made after *c.* 1 min after mixing the components.

Treatment of kinetic data. Kinetic analysis was made by the method of initial reaction rates. Because of the complexity of the system under study, kinetic equations were analysed in their differential forms. These equations which were derived on the basis of some simplifying assumptions were applied to experimental reaction rates, using the same procedure as in the preceding work[1].

RESULTS AND DISCUSSION

In a previous work we found[1] that one of the steps of the catalytic cycle for hydrosilylation ketones of in the presence of [Rh(1,5-COD)(—)-DIOP]$^+$ClO$_4^-$ is formation of the organosilyl((hydrido)(—)-DIOP-rhodium complex. As a similar situation can be expected to occur also in the case of [Rh{(—)-DIOP}$_2$]$^+$ClO$_4^-$, we first examined the course of the reaction of diphenylsilane with this complex in benzene by electron absorption spectroscopy.

As shown in Fig. 1, the spectrum of the dissolved complex exhibits an absorption band with maximum at 438 nm ($\varepsilon_{438} = 4.30 \cdot 10^3$ mol^{-1} cm^2) whose position and intensity are not sensitive to oxygen, analogously to the solid complex. The addition of diphenylsilane leads immediately to colour changes of the solution from orange to pale yellow. Time changes of the spectrum are illustrated in Figs 1 and 2 and show two distinct phases of the reaction. The first one is characterized by a decrease in the intensity of 438 nm band which is not accompanied by formation of another ab-

sorption maximum in the wavelength region recorded (measurements in the near ultraviolet region were not possible due to the strong absorption of benzene and phenyl groups of the chiral diphosphine). The second stage (Fig. 2) is documented by appearance of a new absorption maximum at 380 nm. Increasing diphenyl-silane concentration increases the rate of these changes without influencing the resulting absorbance at 380 nm, while on increasing temperature from 30 to 50°C the first stage of the reaction becomes immeasurable and the resulting absorption band has intensity which is approximately one third of that at 30°C. The addition of free chiral diphosphine ($(-)$-DIOP) does not affect both the pattern of the spectrum, the rate of discussed processes and the resulting intensity of the 380 nm band.

The above facts can be ascribed to formation of corresponding organosilyl(hydrido)rhodium complexes of the type $[\mathrm{Rh}/\mathrm{SiH}(C_6H_5)_2)/H/(-)\text{-DIOP}]_n]^+ClO_4^-$ as the products of oxidative addition of diphenylsilane. This assumption is supported also by the successful isolation of a pale yellow rhodium complex formed in the first stage of the reaction whose IR spectrum (KBr pellets) exhibits two broad bands at $2048\ cm^{-1}$ and $2132\ cm^{-1}$. The first one can be assigned to the Rh-H stretching
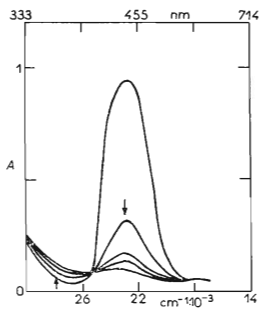

Fig. 1

Time Changes of the Electron Absorption Spectrum of $[\mathrm{Rh}\{(-)\text{-DIOP}\}_2]^+ClO_4^-$ after Addition of Diphenylsilane ($c_{Rh}^0 = 4 \cdot 10^{-4}$ mol l^{-1}, $c_{Si}^0 = 0\cdot20$ mol l^{-1}, 0·5 cm cell, benzene, 30°C, time intervals of recordings approx. 30 s)
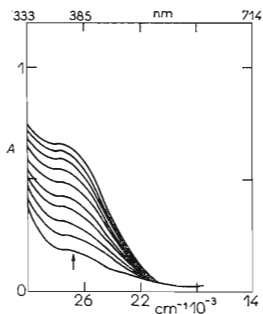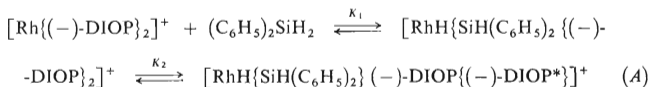

Fig. 2

Interaction of Diphenylsilane with [Rh. .$\{(-)\text{-DIOP}\}_2]^+ClO_4^-$ (Fig. 1 contd)

For reaction conditions see Fig. 1. Time intervals of recordings c. 10 min.

frequency, the other to the Si—H stretching frequency of the diphenyl(hydrido)silyl ligand (v(Si—H) for diphenylsilane ≈ 2142 cm^{-1}) in agreement with the values reported for other organosilyl(hydrido)rhodium-phosphine complexes[4,5]. On the basis of elemental analysis, the compound was assigned the structure of $[$RhH$.$ $.\{$SiH(C$_6$H$_5$)$_2\}\{(-)$-DIOP$\}_2]^+$ClO$_4^-$. In benzene solution and in absence of excess diphenylsilane, the complex undergoes dissociation, yielding the starting $[$Rh$.$ $.\{(-)$-DIOP$\}_2]^+$ClO$_4^-$, as demonstrated by the electron absorption spectrum identical with that shown in Fig. 1.

These findings indicate that we deal here with a series of equilibria which are visualized by equation (A) (for simplicity the perchlorate anion is omitted), where

$$[\text{Rh}\{(-)\text{-DIOP}\}_2]^+ + (\text{C}_6\text{H}_5)_2\text{SiH}_2 \overset{K_1}{\rightleftharpoons} [\text{RhH}\{\text{SiH}(\text{C}_6\text{H}_5)_2\{(-)\text{-}$$

$$\text{-DIOP}\}_2]^+ \overset{K_2}{\rightleftharpoons} [\text{RhH}\{\text{SiH}(\text{C}_6\text{H}_5)_2\}\ (-)\text{-DIOP}\{(-)\text{-DIOP*}\}]^+ \quad (A)$$

$(-)$-DIOP and $(-)$-DIOP* denote the chiral phosphine coordinated as bidentate and monodentate ligand, respectively.

In the presence of excess diphenylsilane the first equilibrium is shifted strongly to the right hand side. Although the evidence for formation of the Rh–DIOP complex with one monodentate DIOP ligand is not conclusive, the following facts can be taken as a support for this assumption: the observed, already discussed, absorption band with maximum at 380 nm, which excludes the possibility that the oxidative addition of organosilicon hydride leads immediately to $[$RhH$\{$SiH(C$_6$H$_5$)$_2\}$ $(-)$-DIOP$]^+$ClO$_4^-$ which was found by us[1] to be the product of analogous reaction of $[$Rh(1,5-COD)$(-)$-DIOP$]^+$ClO$_4^-$. This complex exhibits absorption maximum at different wavelength ($\lambda = 395$ nm). Furthermore, in such a case, the excess of the free ligand has to affect the equilibrium, which was not observed.
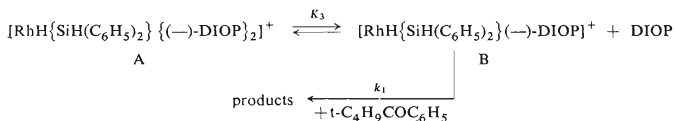
In this connection it should be mentioned that the above results have been obtained at 30°C, *i.e.* the temperature at which the rhodium complex studied is rather poor hydrosilylation catalyst. It catalyses efficiently the addition at 50°C, where the absorption spectra indicate decreasing concentration of the organosilyl(hydrido)bis-(DIOP)Rh complex, predominantly due to its further dissociation to the species containing one DIOP ligand. The presence of this step in the catalytic cycle is demonstrated also by the results obtained on following the dependence of the initial reaction rate of the hydrosilylation on catalyst concentration as well as by the effect of free DIOP on the reaction rate.

Kinetic measurements were first centered on the determination of the reaction order in the catalyst. The results are presented in Table II. The linear regression of these data according to Eq. (1) showed that the slope of the dependence has a value of 0·58, indicating that in the absence of excess free DIOP ligand, the reaction

is one half order in the catalyst.

$$\log r^0 = \text{const.} + c \log c_{Rh}^0 . \qquad (1)$$

This finding is consistent with the assumption that in addition to the above mentioned equilibria, the catalytic cycle involves dissociation of $[RhH\{SiH(C_6H_5)_2\}\{(-)\text{-}DIOP\}_2]^+$ species to give $[RhH\{SiH(C_6H_5)_2\}(-)\text{-}DIOP]^+$. Interaction of the ketone with the latter species leads to the reaction products. This situation is illustrated in Scheme 1.

$$[RhH\{SiH(C_6H_5)_2\}\{(-)\text{-}DIOP\}_2]^+ \quad \underset{}{\overset{K_3}{\rightleftharpoons}} \quad [RhH\{SiH(C_6H_5)_2\}(-)\text{-}DIOP]^+ + DIOP$$

$$\text{A} \hspace{9cm} \text{B}$$

$$\text{products} \quad \overset{k_1}{\underset{+\,t\text{-}C_4H_9COC_6H_5}{\longleftarrow}}$$

SCHEME I

In such a case, the reaction rate is expressed by Eq. (2).

$$r = -dc_{Kt}/dt = k_1 c_{Kt}[B] \qquad (2)$$

TABLE I

Dependence of Initial Reaction Rate r^0 ($1\,mol^{-1}\,s^{-1}$) on Catalyst Concentration c_{Rh}^0 ($mol\,l^{-1}$) for Hydrosilylation Catalysed by $[Rh\{(-)\text{-}DIOP\}_2]^+ClO_4^-$ in Toluene at 50°C

Diphenylsilane conc. (c_{Si}^0) = 0·33 mol l^{-1}, t-C$_4$H$_9$COC$_6$H$_5$ conc. (c_{Kt}^0) = 0·12 mol l^{-1}.

$c_{Rh}^0 \cdot 10^4$	2·6	4·2	6·8	10·0	15·2	22·3
$r^0 \cdot 10^6$	2·2	3·1	4·7	5·6	6·6	7·5

TABLE II

The Effect of Free DIOP (c_L, mol l^{-1}) on Initial Rate r^0 ($1\,mol^{-1}\,s^{-1}$) of Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane Catalysed by $[Rh\{(-)\text{-}DIOP\}_2]^+ClO_4^-$ in Toluene at 50°C

$c_{Rh}^0 = 2·58 \cdot 10^{-3}$ mol l^{-1}, $c_{Si}^0 = 0·33$ mol l^{-1}, $c_{Kt}^0 = 0·15$ mol l^{-1}.

$c_L \cdot 10^4$	3·57	7·14	8·33	10·50	14·70	25·00
$r^0 \cdot 10^6$	9·15	6·48	5·52	3·93	3·24	1·93

As $K_3 = [B][DIOP]/[A]$ and in the absence of excess free ligand $[B] = [DIOP]$, the equation can be rewritten to the expression (3), which accounts for the observed one half order of the reaction in the catalyst

$$r = k_1 c_{K_1} K_3^{1/2}[A]^{1/2}. \tag{3}$$

The presence of the mentioned dissociation step is supported also by the observed rate-retarding effect of free DIOP (Table II). Dependence of the initial reaction rate on reciprocal free ligand concentration is represented graphically in Fig. 3. It is seen that for $c_L > 10^{-3}$ mol l^{-1} the reaction rate is nearly inversely proportional to the concentration of the added ligand. In order to derive kinetic law for this case, we examined the effect of individual components of the reaction system on hydrosilylation rate. Treatment of data on the effect of catalyst concentration (Table III) with the use of Eq. (1) yielded the linear r^0 vs c_{Rh}^0 plot with the slope having a value of 1·036. This proves the first order of the reaction in the catalyst. This change of the reaction order can be expected on the basis of the proposed reaction scheme when concentra-
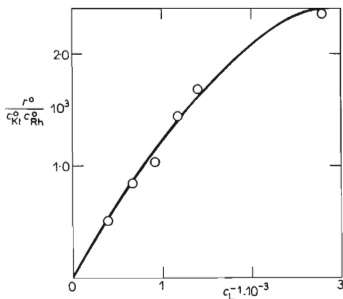

FIG. 3

Dependence of Initial Reaction Rate on Concentration of Free Chiral Ligand (c_L in mol . . l^{-1}) for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane Catalysed by [Rh{(—)-DIOP}$_2$]$^+$ClO$_4^-$ in Toluene at 50°C ($c_{Rh}^0 = 2·58 . 10^{-3}$ mol l^{-1}, $c_{Si}^0 = 0·33$ mol l^{-1}, $c_{K_1}^0 = 0·15$ mol l^{-1})
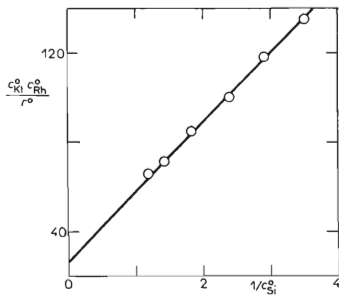
FIG. 4

Dependence of Initial Reaction Rate on Diphenylsilane Concentration c_{Si}^0 (mol l^{-1}) for Hydrosilylation of Tert-Butyl Phenyl Ketone Catalysed by [Rh{(—)-DIOP}$_2$]$^+$ClO$_4^-$ in the Presence of Added Chiral Ligand

For reaction conditions see Table V.

tion of added ligand is by more than one order of magnitude greater compared to the concentration of the ligand released by dissociation (Scheme 1 and Eq. (22)).

As demonstrated by data presented in Table IV, under these conditions the reaction is also first order in the ketone, while increase in the initial reaction rate due to increasing diphenylsilane concentration (Table V) does not obey first order dependence.

TABLE III

Dependence of Initial Reaction Rate r^0 ($1 \text{ mol}^{-1} \text{ s}^{-1}$) on Catalyst Concentration c_{Rh}^0 ($\text{mol} 1^{-1}$) for Hydrosilylation Catalysed by $[Rh\{(-)\text{-DIOP}\}_2]^+ClO_4^-$ in the Presence of Excess Free Ligand (c_L).

$c_L = 1 \cdot 5 \cdot 10^{-3} \text{ mol} 1^{-1}$, $c_{Si}^0 = 0 \cdot 29 \text{ mol} 1^{-1}$, $c_{Kt}^0 = 0 \cdot 15 \text{ mol} 1^{-1}$, toluene, 50°C.

$c_{Rh}^0 \cdot 10^3$	1·11	1·76	2·22	2·77	3·33	4·44
$r^0 \cdot 10^6$	1·06	1·84	2·23	3·02	3·45	4·50

TABLE IV

Dependence of Initial Hydrosilylation Rate r^0 ($1 \text{ mol}^{-1} \text{ s}^{-1}$) on Tert-Butyl Phenyl Ketone Concentration c_{Kt}^0 ($\text{mol} 1^{-1}$

$c_{Rh}^0 = 3 \cdot 20 \cdot 10^{-3} \text{ mol} 1^{-1}$, $c_L = 1 \cdot 50 \cdot 10^{-3} \text{ mol} 1^{-1}$, $c_{Si}^0 = 0 \cdot 55 \text{ mol} 1^{-1}$, toluene, 50°C.

c_{Kt}^0	0·30	0·50	0·80	1·00
$r^0 \cdot 10^5$	1·14	1·90	3·00	3·80

TABLE V

Dependence of Initial Hydrosilylation Rate r^0 ($1 \text{ mol}^{-1} \text{ s}^{-1}$) on Diphenylsilane Concentration c_{Si}^0 ($\text{mol} 1^{-1}$)

$c_{Rh}^0 = 3 \cdot 25 \cdot 10^{-3} \text{ mol} 1^{-1}$, $c_L = 1 \cdot 46 \cdot 10^{-3} \text{ mol} 1^{-1}$, $c_{Kt}^0 = 0 \cdot 25 \text{ mol} 1^{-1}$, toluene, 50°C.

c_{Si}^0	0·29	0·34	0·42	0·54	0·68	0·84
$r^0 \cdot 10^5$	0·60	0·69	0·81	0·85	1·12	2·10

$$[Rh\{(\!-\!)\text{-DIOP}\}_2]^+ + R_2SiH_2 \underset{}{\overset{K_1}{\rightleftharpoons}} [RhH(SiHR_2)\{(\!-\!)\text{-DIOP}\}_2]^+$$

$$A \qquad\qquad\qquad\qquad B \;\updownarrow\, K_2$$

$$[RhH(SiHR_2)(\!-\!)\text{-DIOP}\{(\!-\!)\text{-DIOP*}\}]^+$$

$$C \;\updownarrow\, K_3$$

$$[RhH(SiHR_2)(R^1COR^2)(\!-\!)\text{-DIOP}]^+ \underset{R^1COR^2}{\overset{k_1}{\rightleftharpoons}} [RhH(SiHR_2)(\!-\!)\text{-DIOP}]^+ + DIOP$$

$$E \qquad\qquad\qquad\qquad\qquad D$$

$$\downarrow\, \text{fast}$$

$$\text{product}$$

$$R_2SiH_2 = (C_6H_5)_2SiH_2, \quad R^1COR^2 = t\text{-}C_4H_9COC_6H_5$$
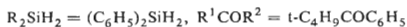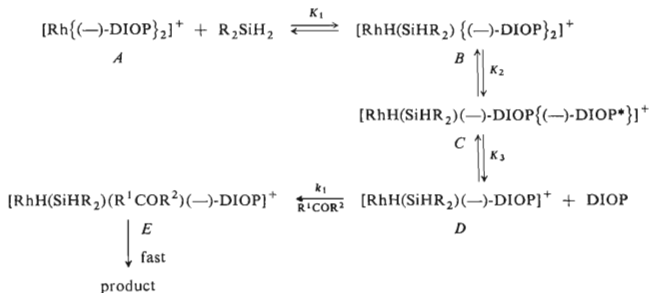
SCHEME 2

These results can be explained in terms of the following reaction scheme (Scheme 2). Providing that the concentration of species E is very small compared to that of species A−D and can be thus neglected and further that all equilibria are established fast, then under the steady state condition the reaction rate can be expressed by Eq. (4).

$$r^0 = -\frac{dc_{Kt}}{dt} = \frac{k_1 K_1 K_2 K_3 c_{Kt}^0 c_{Si}^0 c_{Rh}^0}{1 + K_1(1 + K_2 + K_2 K_3/c_L) c_{Si}^0} \; (1/c_L). \tag{4}$$

This relation describes reasonably well the behaviour of the catalyst system studied. Thus, for example, it accounts for the observed rate retarding effect of excess free ligand (Fig. 3). At higher ligand concentrations ($c_L > 10^{-3}$ mol l^{-1}) the reaction rate is nearly inversely proportional to c_L since the term $K_1 K_2 K_3/c_L$ in the denominator can be neglected. At lower concentrations its value is significant, which leads to the stronger rate retarding effect of the ligand on the reaction rate, as observed. For $c_L > 10^{-3}$ mol l^{-1} the relation (4) can be transformed into the following form (Eq. (5)).

$$r^0 = \frac{k_1 K_1 K_2 K_3 c_{Si}^0 c_{Kt}^0 c_{Rh}^0}{1 + (K_1 + K_1 K_2) c_{Si}^0} \; (1/c_L). \tag{5}$$

In order to express the effect of diphenylsilane concentration, this expression has been linearised (Eq. (6)).

$$\frac{c_{Rh}^0 c_{Kt}^0}{r^0} = \frac{c_L}{k_1 K_1 K_2 K_3 c_{Si}^0} + \frac{c_L(K_1 + K_1 K_2)}{k_1 K_1 K_2 K_3}. \tag{6}$$

As it is shown in Fig. 4 experimental data fit this relation (Table V).

Treatment of experimental data by linear regression yields the expression (7) which describes well the behaviour of the catalyst system under given conditions.

$$\frac{r^0}{c_{Rh}^0 c_{Kt}^0} = \frac{4 \cdot 85 \cdot 10^{-5} c_{Si}^0}{1 + 0 \cdot 92 c_{Si}^0} \frac{1}{c_L}. \tag{7}$$

In conclusion it can be said that both the so far obtained spectroscopic evidence and kinetic data comport with the proposed reaction scheme. The course of the hydrosilylation catalysed by $[Rh\{(-)\text{-DIOP}\}_2]^+ClO_4^-$ involves several steps which are analogous to those found for the addition catalysed by $[Rh(1,5\text{-COD})(-)\text{-DIOP}]^+ClO_4^-$: the oxidative addition of organosilicon hydride to give the corresponding organosilyl(hydrido)rhodium species is an equilibrium reaction which precedes the rate-determining interaction of ketone. In both cases ketone interacts with the rhodium species containing one coordinated DIOP ligand. By contrast to the latter complex, formation of such a species in the former case requires dissociation of the chiral ligand from the rather stable $[RhH\{SiH(C_6H_5)_2\}\{(-)\text{-DIOP}\}_2]^+ClO_4^-$. The small extent of this dissociation is likely the main reason for the lower catalytic effectiveness of $[Rh\{(-)\text{-DIOP}\}_2]^+ClO_4^-$ compared to the cyclooctadiene(DIOP)-rhodium complex. The participation of the catalytically active species of the same structure is indicated also by similar stereospecifty of both additions, as demonstrated by the optical bias of the hydrosilylations carried out under identical reaction conditions (23·2% optical yield of (R)-(+)-tert-butylphenylcarbinol with $[Rh(1,5\text{-COD}) \cdot (-)\text{-DIOP}]^+ClO_4^-$ *vs* 24·6% optical yield obtained with the use of $[Rh\{(-)\text{-DIOP}\}_2]^+ClO_4^-$). This finding provide thus additional support for the validity of the reaction scheme proposed.

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