

CATALYTIC ACTIVITY OF RHODIUM(I) COMPLEXES CONTAINING
(ω -TRIMETHYLSILYLALKYL)DIPHENYLPHOSPHINES*

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Received January 18th, 1980

Kinetics of homogeneous hydrogenation of 1-heptene catalysed by rhodium(I) complexes prepared *in situ* from μ, μ' -dichloro-bis(cyclooctenerhodium) and phosphines of the type $\text{RP}(\text{C}_6\text{H}_5)_2$ ($\text{R} = -\text{CH}_3, -(\text{CH}_2)_n\text{Si}(\text{CH}_3)_3; n = 1-4$) have been studied. The substitution of the ligands by the trimethylsilyl group was found to increase significantly the catalytic activity of the complexes. The results are discussed in relation to the electron density on the phosphorus atom determined by ^{31}P NMR spectroscopy and to its proton acceptor ability determined by IR spectroscopy.

In our laboratory, a systematic study is made of the coordination bonding of transition metal complexes to supports¹⁻⁶. Within the framework of this investigation and with regard to the fact that silylsubstituted phosphines are frequently used to fix transition metal complexes to inorganic supports, we examined the mutual influencing of the phosphine and silyl groups⁷ by ^{13}C , ^{29}Si and ^{31}P -NMR spectroscopy, using a series of (ω -trimethylsilyl)alkyldiphenylphosphines of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$ ($n = 1-4$) as model compounds.

In this connection we were also interested in the use of these compounds as ligands of homogeneous catalysts. We found that corresponding rhodium(I) complexes are effective catalysts for hydrogenation of alkenes under mild conditions (normal hydrogen pressure, mildly increased temperature). In the present work we report on kinetics of this reaction and on comparison of the catalytic activity of these complexes with the electron density on the phosphorus of free ligands determined by NMR and IR measurements.

EXPERIMENTAL

Chemicals. (Trimethylsilyl)alkyldiphenylphosphines of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$ ($n = 1-4$) were the same as in a previous work⁷. μ, μ' -Dichloro-bis(cyclooctenerhodium) was prepared by reported procedure⁸. The catalysts were prepared *in situ* from the rhodium-cyclooctene complex and the trimethylsilylalkylphosphines in toluene, using both components in $\text{Rh} : \text{P}$ mol. ratio = 1 : 2. All manipulations were carried out under argon⁹.

* Part LXI in the series Catalysis by Metal Complexes; Part LX: Chem. Prům. in press.

Hydrogenations were measured on the apparatus described earlier¹⁰ under constant hydrogen pressure. The reaction order in the catalyst was determined by the differential method¹¹, that with respect to 1-heptene was found by comparison of kinetic data with the integral form of the first order reaction.

IR spectra of hydrogen bonding were recorded on a double-beam UR 20 spectrophotometer (Zeiss, Jena, GDR) in the region of $\nu(\text{C}-\text{D})$ stretching vibrations ($2300-2100\text{ cm}^{-1}$) and the $\nu(\text{O}-\text{H})$ stretching vibrations ($3700-3100\text{ cm}^{-1}$), using 0.01 and 0.1 cm thick KBr cells. Deuteriochloroform (2.5 mol/l conc.), phenol (0.02 mol/l conc.) and methanol (0.03 mol conc.) were used as proton donors and the studied silylalkylsubstituted phosphines and methyl-diphenylphosphines were used as proton acceptors. The ternary systems — proton donor / proton acceptor / solvent — were prepared under nitrogen by adding several drops of the proton acceptor to CCl_4 (spectrograde purity) or to heptane, followed by mixing with the proton donor. The spectra were recorded immediately after the preparation of ternary or binary (deuteriochloroform + P-base) systems.

RESULTS AND DISCUSSION

The interaction of (ω -trimethylsilyl)alkyldiphenylphosphines with μ, μ' -dichloro-bis(cyclooctenerhodium) results in the displacement of the cyclooctene ligand. The reaction proceeds easily and yields the complexes of Wilkinson type. The complexes are poorly soluble in toluene and are highly active in hydrogenation of alkenes under mild conditions (Table I).

Although the method used for determining the reaction order in the catalyst was less accurate, the results confirm that (at least in the concentration range used) the reaction is first order in the complex for all the phosphines studied, similarly

TABLE I

Reaction Order in the Catalyst and Rate Constants k ($\text{l mol}^{-1} \text{ min}^{-1}$) for Hydrogenation of 1-Heptene (1 ml, 7.1 mmol) Catalysed by the *in situ* Rhodium Complexes of the Type $[\text{RhCl}\{\text{RP}(\text{C}_6\text{H}_5)_2\}_2]$

Reaction temperature 37°C, 4 ml of toluene, hydrogen pressure 14 kPa.

R	The reaction order ^a	k^b	δ^c ppm
CH_3	0.96	1.5	-26 ^d
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	1.07	5.2	-30.7
$(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	1.12	5.2	-18.6
$(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	0.92	5.2	-26.1
$(\text{CH}_2)_4\text{Si}(\text{CH}_3)_3$	1.09	3.5	-24.9

^a Rh concn. range used = $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ mol/l. ^b $[\text{RhCl}\{\text{RP}(\text{C}_6\text{H}_5)_2\}_2]$ concn. = $6 \cdot 8 \cdot 10^{-3}$ mol/l. ^c ³¹P-NMR shift, ref.⁷. ^d Ref.¹⁵.

to the hydrogenation catalysed by other rhodium-phosphine complexes^{5,6,12,13}. In order to determine the order of the hydrogenation in the alkene, the first-order reaction was postulated and this assumption was verified by finding the excellent fit of the experimental rate data to the integral form of the first-order relation (Fig. 1), again in accordance with literature data^{5,6,13}.

Comparison of rate constants (Table I, the first order rate constant was divided by the catalyst concentration) shows that the substitution of hydrogen in methyl-diphenylphosphine for the trimethylsilyl group increases the catalytic activity more than three times. This agrees with our earlier conclusions⁷ about the higher electron density on the phosphorus in (ω -trimethylsilyl)alkyldiphenylphosphines compared to alkyldiphenylphosphines which was made on the basis of ³¹P-NMR chemical shifts. This should enhance also the catalytic activity of the corresponding rhodium-phosphine complexes.

TABLE II

Relative Proton Acceptor Ability $\Delta\nu$ (cm^{-1}) of Phosphines $\text{PR}(\text{C}_6\text{H}_5)_2$ in Binary Mixture with 2.5 mol/l CDCl_3 and in Ternary Mixture with 0.03 mol/l CH_3OH and CCl_4

R	CDCl_3			CD_3OH		
	ν_{free}^a	ν_{assoc}^a	$\Delta\nu_{(\text{C}-\text{D})}^b$	ν_{free}^b	ν_{assoc}^c	$\Delta\nu_{(\text{OH})}^d$
CH_3	2 251	2 228	23	3 635	3 405	230
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	2 251	2 222	29	3 638	3 376	262
$(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	2 251	2 226	25	3 638	3 395	243
$(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	2 252	2 226	26	3 638	3 391	247
$(\text{CH}_2)_4\text{Si}(\text{CH}_3)_3$	2 251	2 226	25	3 638	3 388	250

Accuracy^a $\pm 1 \text{ cm}^{-1}$; ^b $\pm 2 \text{ cm}^{-1}$; ^c $\pm 5 \text{ cm}^{-1}$; ^d $\pm 7 \text{ cm}^{-1}$.

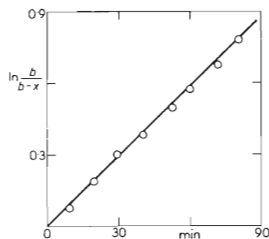


FIG. 1

$\ln b/(b-x)$ vs Time Plot for Hydrogenation of 1-Heptene (7.1 mmol)

$[\text{RhCl}\{\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2\}_2]$ 0.034 mmol, total volume of the reaction mixture 5 ml, hydrogen pressure 114 kPa; b is the initial 1-heptene concn., $(b-x)$ corresponds to the heptene concn. in time t .

Experimental data demonstrate, however, that the trend in the catalytic activity and ^{31}P -NMR chemical shifts observed for the free ligands is not too close. Thus, whereas the chemical shift attains the usual minimal value¹⁴⁻¹⁷ for the β -derivative, the catalytic activity of the complexes containing α -, β - and γ -silylsubstituted alkyl-diphenylphosphines is nearly identical and only the use of the δ -derivative leads to the catalyst which is substantially less active (Table II). As this disagreement would result from the fact that in addition to the electronegativity also other factors influence the magnitude of the chemical shift (such as steric demands, bond angles, etc.), we used an independent method for determining the electron density on the phosphorus, the IR measurements of hydrogen bonding due to interaction of the ligand with proton donors.

The relative basicities were determined from differences in the wavenumbers of the free and associated form of donor-acceptor interaction (Table II). The accuracy of this determination is very good for deuteriochloroform as proton donor. In this case, the bands are sharp and their shape is not time dependent. By contrast to this, the basicities determined with the use of methanol should be considered as semi-quantitative. The absorption bands corresponding to hydrogen bonding between methanol and the phosphines change with time, the intensity of the $\nu(\text{OH})_{\text{free}}$ absorption band being decreased and the $\nu(\text{OH})_{\text{assoc.}}$ band being shifted to the shorter wavenumbers. A similar situation has also been observed on using heptane in place of tetrachloromethane. The values presented in Table II were obtained immediately after preparing the solutions. Phenol could not be used as the proton donor since the instability of the spectrum was even more pronounced. Moreover, the $\nu(\text{OH})_{\text{assoc.}}$ band reached partially to the region of C—H bond vibrations.

Data given in Table II further show that the acceptor ability of the alkyl-diphenylphosphines in their interaction with deuteriochloroform or methanol mildly increases on introducing the trimethylsilyl group to the α -position of the alkyl substituent. On the other hand, the phosphines having the trimethylsilyl group more remote exhibit smaller proton acceptor ability which is within experimental error comparable to that of methyl-diphenylphosphine.

It can be therefore stated that only the electron density increase due to the δ -substitution by the trimethylsilyl group, manifested also in the corresponding ^{31}P chemical shift⁷, agrees qualitatively with the increased catalytic activity. The findings discussed above set limits to the considerations of electron structure changes of the uncoordinated ligand in relation to the behaviour of the corresponding complex. For instance, the lower reactivity of the rhodium complex containing (4-trimethylsilylbutyl)diphenylphosphine might be caused by the flexibility of the 1,4-butylene group and its lengths allowing the trimethylsilyl group to approach the rhodium atom or to weakly interact with it. This problem is further investigated in our laboratory.

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Translated by J. Hetflejš.