Olefin Isomerization over Tris(triphenylphosphine)chlororhodium

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Summary The isomerization of olefins over $[Rh(Ph_3P)_3Cl]$ has been shown to be dependent on the presence of oxygen in the system and on the solvent used.

IN the initial work on the homogeneous hydrogenation of olefins over tris(triphenylphosphine)chlororhodium(I) (**1**) Wilkinson reported[1] that no double bond isomerization was observed. Later, however, isomerization was shown to take place during this reaction.[2] Similar discrepancies have also appeared in reports on the homogeneous deuteriation of double bonds over (**1**). In one instance direct deuterium addition to a double bond with no exchange was reported[3] while, in another, extensive deuterium scrambling was observed.[4]

Because of these seemingly contradictory statements the various experimental procedures used were examined carefully. It was found that two factors were apparently responsible for the observed discrepancies: (i) the extent of the prehydrogenation of (**1**) prior to the introduction of the olefin, and (ii) the solvent system used. That work in which isomerization or deuterium scrambling was observed was run in benzene–ethanol while in benzene alone or benzene–hydrocarbon mixtures straightforward hydrogenation or deuteriation took place. Since these observations were merely circumstantial, the effect of these parameters on olefin isomerization over (**1**) was investigated more thoroughly.

TABLE 1.

Heptene hydrogenation over [Rh(Ph$_3$P)$_3$Cl]

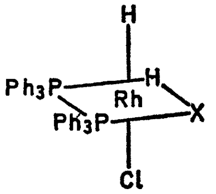
Olefin	Catalyst	Time (min.)	% Heptane	% Heptene -1-	cis-2-	trans-2-
Hept-1-ene	NPS[a]	15	13	56	12	19
		30	17	47	16	20
		70	22	32	17	29
	PS[b]	3	18	81	—	1
		7	29	70	—	1
		16	40	57	—	3
Hept-2-ene	NPS[a]	0	—	—	79	21
		15	12	—	41	47
		30	14	—	43	43
		90	18	9	11	42

[a] [Rh(Ph$_3$P)$_3$Cl] not presaturated with H_2.

[b] [Rh(Ph$_3$P)$_3$Cl] presaturated with H_2 for 60 min. prior to addition of olefin.

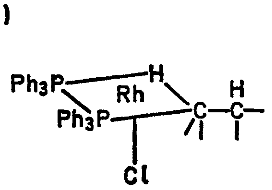
[Rh(Ph$_3$P)$_3$Cl]

(1)



(2) X = S

(3) X = >C=C<



(4)

The data shown in Table 1 for the hydrogenation of hept-1-ene and hept-2-ene in benzene–ethanol using both hydrogen presaturated and non-presaturated (**1**) bear out the necessity of pretreating (**1**) with hydrogen in order to avoid double bond isomerization. In benzene alone no isomerization occurred over either type of catalyst. It would appear, then, that on presaturation of (**1**) with hydrogen or during a hydrogenation run in the absence of alcohol the *cis*-dihydride, (**2**), initially described by Wilkinson is readily formed. Since the two hydrogens are both readily accessible for transfer to an adsorbed olefin, as in the olefin complex, (**3**), such transfer should occur readily. Thus, the metal-alkyl, (**4**), which is a necessary intermediate in isomerization, would either be not formed or very short lived depending on the time interval between the two hydrogen transfer steps.

In benzene–ethanol, however, treatment of (**1**) with the olefin before conversion into (**2**) leads to the formation of a different catalytic intermediate. The marked difference between (**2**) and this, as yet undefined, intermediate is further shown by the data given in Table 2 for the hydrogenation of 1-methylene-4-t-butylcyclohexane (**5**). Here it is shown that the hydrogenation of (**5**) over (**2**) is pressure independent but hydrogenation of (**5**) over non-presaturated (**1**) is not.

TABLE 2.

Hydrogenation of 1-*methylene*-4-*t-butylcyclohexane over* [Rh(Ph$_3$P)$_3$Cl]

Catalyst	Pressure (Atm.)	% 1-Methyl-4-t-butylcyclohex-1-ene	% 1-Methyl-4-t-butylcyclohexane *cis*	*trans*
NPS[a]	1	47	39	14
	20	7	77	16
	93	4	82	14
PS[b]	1	—	66	34
	90	—	67	33

[a,b] See footnotes to Table 1.

A clue to the nature of the isomerizing catalyst was found when it was discovered that the introduction of one mole of oxygen per mole of rhodium complex to the presaturated benzene–ethanol reaction mixture gave a catalyst which promoted extensive double-bond isomerization. Addition of oxygen to the complex dissolved in benzene alone did not result in any isomerization being observed. In both solvents the hydrogenation rate was increased by the addition of oxygen as previously reported.[5]

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