CATALYTIC PROPERTIES OF RHODIUM HYDRIDOCARBONYL TRITHIENYLPHOSPHINE COMPLEXES IN THE HOMOGENEOUS HYDROGENATION AND ISOMERIZATION OF UNSATURATED COMPOUNDS

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UDC 541.128:547.732'128'718'197:543.422.25

Syntheses are reported for trithienylphosphine analogs of hydridocarbonyltris(triphenylphosphine)rhodium(I) and the catalytic activity of these analogs in the hydrogenation and isomerization of terminal olefins was demonstrated. The PMR chemical shifts and form of the signals of the hydride hydrogen atom of these rhodium hydridocarbonyl complexes correlate with their catalytic properties in homogeneous hydrogenation and isomerization.

In the case of the thiophene analog of the Wilkinson complex, we showed that the concept of isosterism may serve as a criterion in the search for new catalysts for the homogeneous hydrogenation of unsaturated compounds [1]. The term "isosterism" which was introduced by Langmuir [2] implies the analogy of benzene and thiophene in this specific case [3] and the steric and electronic analogy of triphenylphosphine and tri(thienyl-2)phosphine.

In the present work, we studied the catalytic properties of trithienylphosphine complexes, namely, hydridocarbonyltris[tri(thienyl-2)phosphine]rhodium(I) (K-I catalyst) and hydridocarbonyltris[tri(5-trimethylsilylthienyl-2)phosphine]rhodium(I) (I-II) which are isosteres of hydridocarbonyltris(triphenylphosphine)rhodium(I) (I-III) which is an efficient catalyst for the homogeneous hydrogenation of olefins [4]. In our subsequent communication, we used PMR spectroscopy to show the geometrical similarity of the structures of K-I and K-III [5]. The homogeneous hydrogenation of allylbenzene was taken as a model reaction.

Hydridocarbonyl complexes K-I, K-II, and K-III and hydridocarbonyltris[tri(5-tert-butylthienyl-2)phosphine]rhodium(I) (K-IV), which we specially synthesized for spectroscopic purposes, are highly soluble in benzene and chloroform but only moderately soluble in ether. The presence of a tert-butyl or trimethylsilyl group at $C_{(5)}$ of the thiophene ring markedly enhances the solubility of the complex. Light orange solutions are formed upon dissolving these complexes in benzene not containing oxygen; this color does not change upon the brief introduction of hydrogen and upon the addition of allylbenzene. Upon standing for 72 h, benzene solutions of K-I with concentration $\leqslant 1\cdot 10^{-2}$ mole/liter without access to atmospheric oxygen turn from light orange to dark red, which indirectly indicates the decomposition of catalyst K-I. Wilkinson et al. [6] have shown that the spontaneous decomposition

TABLE 1. Hydrogenation of Allylbenzene

Catalyst	Catalyst concentration, mole/liter	v_{sp} [ml $H_2\cdot min^{-1}\cdot mole^{-1}\cdot liter$]	v_h/v_{iso}*
K-I	$3{,}8\cdot 10^{-3}$	260	1,6
K-II	$3{,}6\cdot 10^{-3}$	320	2,3
K-III	$4{,}5\cdot 10^{-3}$	490	3,2

*v_h/v_{iso} is the ratio of the rates of hydrogenation and isomerization.

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*Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 787-792, June, 1986. Original article submitted October 29, 1985.

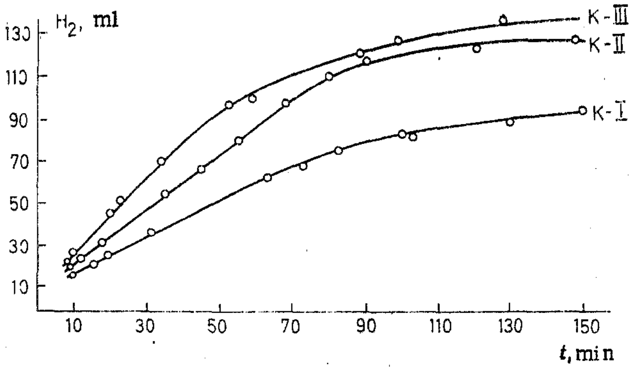


Fig. 1. Kinetic curves for the hydrogenation of allylbenzene in the presence of K-I, K-II, and K-III.

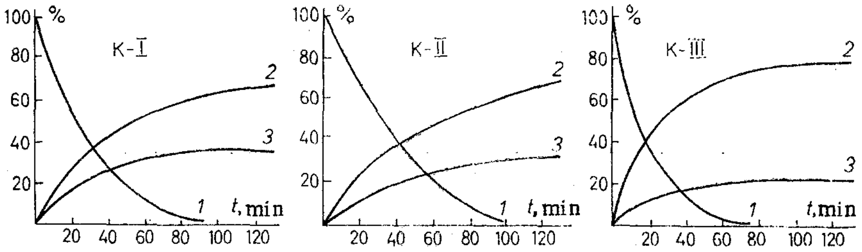


Fig. 2. Dependence of the change in the catalysate composition over time: 1) allylbenzene, 2) propylbenzene, and 3) cis- and trans-propenylbenzenes.

of complex K-III occurs in benzene solution with the formation of catalytically inactive compounds not containing hydridic hydrogen atoms. Upon storage of these complex in an argon atmosphere at about 4°C, their decomposition (darkening) is visible only after two weeks.

In their catalytic activity in the hydrogenation of allylbenzene and the nature of the corresponding kinetic curves, these new catalysts are comparable with the triphenylphosphine analog (see Fig. 1 and Table 1). The activity of the complexes increases in the series K-I < K-II < K-III. In all cases, the initial stage of the reaction (up to 20-40% allylbenzene conversion) proceeds with zero-order kinetics relative to the substrate. Then, the hydrogenation rate decreases and at allylbenzene conversion of $\geqslant$80% (for K-III) and $\geqslant$60-70% (for K-I and K-II), the reaction virtually is halted. The hydrogenation rate increases proportionally to the catalyst concentration.

Analysis of the catalysate composition showed that in addition to hydrogenation, there is also isomerization of the starting α-olefin to its β-isomer and cis- and trans-propenylbenzene accumulate in the catalysate (see Fig. 2). The rate of hydrogenation of the β-isomer is 1-1.5 times less than that of the starting olefin and this reaction is completed after 24 h. Similar results were obtained in the hydrogenation of 1-pentene [4]. The initial product of the isomerization is cis-2-pentene, which is converted to the thermodynamically more stable trans isomer.

Figure 2 shows that the extent of isomerization of allylbenzene in the case of trithienylphosphine complexes is 30-40%, while it is only 20% for the triphenylphosphine analog.

Thus, the new trithienylphosphine complexes differ from the triphenylphosphine analog in their activity both in the addition of hydrogen to olefins and in the catalysis of C=C bond migration. In our opinion, this difference should be attributed to the difference in the stability of these complexes (extent of dissociation) and different electronegativity of the hydride atoms of the hydridocarbonyl complexes.

In this regard, we studied the PMR spectra of the hydridic hydrogen atoms in K-1, K-II, K-III and specially prepared K-IV. In contrast to K-III, whose hydridic hydrogen atom appears at 25°C as a broad singlet at -9.67 ppm and at -30°C as a doublet of quartets, the hydridic hydrogen atoms of complexes K-I, K-II and K-IV appear even at 25°C as a well resolved doublet of quartets (see Fig. 3 and Table 2) with 1:3:3:1 ratio for the intensities of the quartet signals.

TABLE 2. Spectral Indices for Rhodium Hydridocarbonyl Complexes

Compound	IR spectrum, ν, cm^{-1}		PMR spectrum			
	CO	Rh—H	δ, ppm	J_{P-H}, Hz	J_{Rh-H}, Hz	J_{Rh-P}, Hz
K-I	1934	2014	−9,17	15,8±0,4	1,8±0,4	134
K-II	1938	2014	−8,92	15,6±0,3	1,5±0,3	164
K-III	1930	2004	−9,67	—	—	154
K-IV	1937	2012	−9,10	14,7±0,7	0,8±0,4	134

The finding of distinctly resolved signals for the hydridic hydrogen atoms indicates high configurational stability of the trithienylphosphine complexes K-I, K-II, and K-IV in comparison with K-III. Thus, broadening of the signal for the hydridic hydrogen atom (formation of a singlet) for complex K-I occurs in $CDCl_3$ and C_6D_6 at 52°C. The resolved signal reappears upon cooling of the sample to 25°C as a doublet of quartets.

We assume that the decrease in catalyst activity in going from K-III to K-I and K-II is related to the configurational stability of the two latter complexes and, as a consequence, a decrease in the concentration of $L_2Rh(CO)H$ species which are active intermediates in the hydrogenation reaction and are formed upon the dissociation of $L_3Rh(CO)H$ according to the equation:

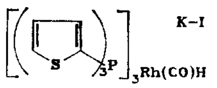
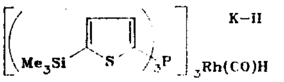
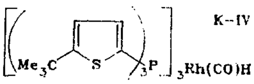
$$L_3Rh(CO)H \underset{+L}{\overset{-L}{\rightleftarrows}} L_2Rh(CO)H + L$$

(L=ligand)

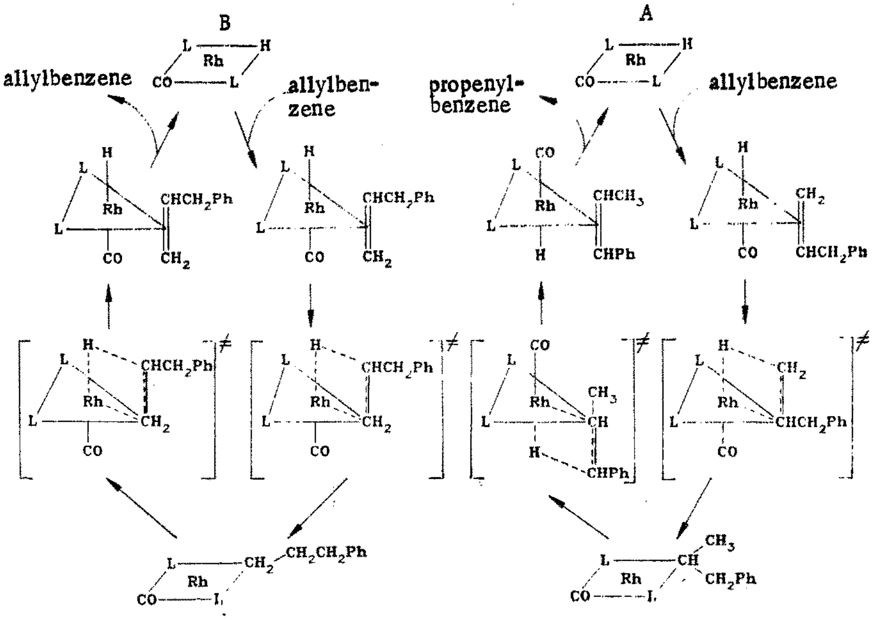
Hence, the specific hydrogenation activity in the case of complex K-III should be greatest as found in our experiments (Table 1).

In the catalytic cycle for isomerization, the hydridic hydrogen atom of the intermediate may add to the substrate both in accord and counter to the Markovnikov rule. Addition according to the Markovnikov rule leads to the formation of the isomerization products while anti-Markovnikov addition does not lead to the formation of isomerization products since the starting allylbenzene is obtained upon reductive β-elimination ("empty cycle"). The direction of the addition depends on the charge on the hydrogen atom [7]. An increase in the negative charge on the hydrogen atom facilitates anti-Markovnikov addition. Comparison of the chemical shifts of the hydridic hydrogen atoms of K-I, K-II, K-III and K-IV shows that greatest shielding is found for the hydrogen atom in K-III (see Table 2). Hence, anti-Markovnikov addition is most favored in the case of complex K-III, i.e., the extent of isomerization in this case should be minimal. In light of the isosteric nature of the trithienylphosphines and triphenylphosphine (the volumes of the thienyl and phenyl groups are virtually the same [8, 9], while the steric effect of the thiophene ring substituents should not have an effect due to their considerable distance from the reaction site), the "electronegativity" of the hydrogen atom of the hydridocarbonyl complex is the factor determining the extent of isomerization of the unsaturated compound. Of course, this only holds for the isomerization of the same alkene and for sterically

TABLE 3. Rhodium Hydridocarbonyl Trithienylphosphine Complexes

Compound	Dec. T, °C	Found, %				
		C	H	P	Rh	S (Si)
 K-I	>119	45,7	3,3	9,0	10,0	—
 K-II	>165	47,5	6,3	5,4	5,9	17,6 (14,6)
 K-IV	>150	59,8	7,0	6,1	6,7	19,4

unhindered hydridocarbonyl complexes.



Thus, the PMR spectral data, specifically, the chemical shift of the hydridic hydrogen atom and its lineshape, may be used to predict the catalytic properties of rhodium hydridocarbonyl complexes. Thus, the complexes with highest shielding $\delta_{Hr} \geqslant -9.6$ ppm of the hydridic hydrogen atom with broad line shape (at room temperature) will probably have enhanced activity in hydrogenation (with minimal isomerization), while complexes with relatively low chemical shifts $\delta_{Hr} \leqslant -8.8$ ppm for the hydridic hydrogen atom should be more active in the C=C bond migration.

EXPERIMENTAL

The PMR spectra were taken on Bruker WM-250 and Bruker AM-300 spectrometers in $CDCl_3$ and C_6D_6 with TMS as the internal standard. The IR spectra were taken on a Perkin–Elmer 577 spectrometer for CsI pellets and a UR-20 spectrometer for KBr pellets. The gas–liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a flame ionization detector and nitrogen gas carrier using a 100 × 0.3 cm column packed with 10% PEGS on Chromatone N-AW. The temperature for the onset of decomposition of the complexes was determined on a Boetius microscopic block.

A sample of tri(thienyl-2)phosphine was obtained according to Issleib and Brack [10], mp of the sublimed product was 34-35°C. Samples of tri(5-tert-butylthienyl-2)phosphine with mp 138.5-140.0°C (from ethanol) and tri(5-trimethylsilylthienyl-2)phosphine with mp 55-57°C (from ethanol) were prepared according to our previous procedures [5]. Compelxes K-I, K-II, and K-III were obtained by analogy to the method of Wilkinson et al. [11] while complex K-IV was obtained by analogy to the method of Ahmad et al. [12]. The characteristics of complexes K-I,

Chemical formula	Calculated, %				
	C	H	P	Rh	S (Si)
$C_{37}H_{28}OP_3RhS_9$	45,7	2,9	9,6	10,6	
$C_{66}H_{100}OP_3RhS_9Si_9$	47,4	6,2	5,7	6,3	17,8 (15,6)
$C_{73}H_{100}OP_3RhS_9$	59,3	6,8	6,3	7,0	19,5

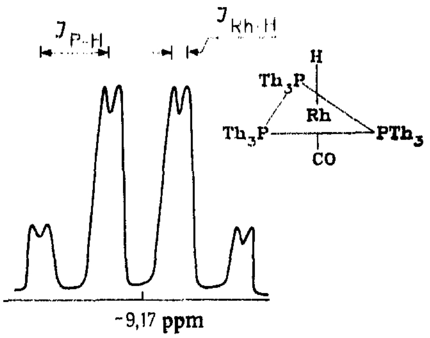


Fig. 3. PMR spectrum of hydridocarbonyltris[tri(thienyl-2)phosphine]rhodium(I) (hydridic region) in $CDCl_3$ at 25°C.

K-II and K-IV are given in Table 3.

Samples of allylbenzene and benzene were thoroughly dried, distilled in an argon stream over metallic sodium, and stored in an argon atmosphere. The hydrogenation was carried out using hydrogen purified to remove traces of oxygen.

Hydrogenation Procedure. A sample of the catalyst was introduced into a long-necked hydrogenation flask and argon was flushed through. A sample of 20-30 ml benzene flushed previously with argon was introduced by means of a syringe. After the catalyst was completely dissolved, the argon was replaced by hydrogen, maintained for 2-4 min and 1 ml allylbenzene was introduced by means of a syringe. The hydrogenation was carried out at 20°C with vigorous rocking (700 cycles per minute).

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