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The Formation of the Rhodium Carbonyl Complexes from Chlorotris[triphenylphosphine]rhodium with Alcohols in the Presence of Diene and Olefin

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Synopsis. The decarbonylation of alcohols using chlorotris[triphenylphosphine]rhodium in the presence of diene or olefin occurs with the formation of the rhodium carbonyl complex and a hydrocarbon originating from the alcohol. The most suitable reaction system is rhodium compound/methanol/butadiene. The results suggest catalysis by a rhodium species.

It is well known that the decarbonylation of acyl halides and aldehydes by chlorotris[triphenylphosphine]rhodium ($RhCl(PPh_3)_3$: W-complex) yields chlorocarbonylbis[triphenylphosphine]rhodium ($RhCl(CO)(PPh_3)_2$: CO-complex) *via* an acyl complex as an intermediate.[1–3] A similar reaction of allylic alcohols by means of the W-complex occurs easily,[4–6] while the reaction of the common alcohols does not thus occur, though it does occur by means of another complex, $RhCl_3(PPh_3)_3$, with an alkaline base.[7] This note will briefly describe the successful abstraction of carbon monoxide from an alcohol molecule by means of the W-complex in the presence of diene or olefin.

When an alcoholic solution of the W-complex and diene or olefin was heated, the crystalline CO-complex[8] was formed quantitatively with the saturated hydrocarbon originating from the alcohol used. Only hydrogen gas instead of the hydrocarbon evolves from methanol. The reactions with other alcohols proceed at very low rates. These results are summarized in Table 1.

The title reaction requires a satisfactory dissolution of the W-complex into the reaction mixture at 80 °C. If one uses less of either alcohol or diene, the completion of the reaction requires a very long time. The reaction is insensitive to air and humidity. Olefin is also effective for the reaction, but shows a lower rate than diene. The presence of diene or olefin is essential to achieve the reaction, as is supported by Experiment No. 13 in Table 1. The reaction of allyl alcohol proceeds even in the absence of diene, as has previously been reported.[4–6]

The clarification of the reaction mechanism can be

TABLE 1. FORMATION OF $RhCl(CO)(PPh_3)_2$ BY REACTION OF $RhCl(PPh_3)_3$ (100 mg) WITH ALCOHOLS IN THE PRESENCE OF DIENE OR OLEFIN AT 80 °C

No.	Alcohol	ml	Diene or Olefin	ml	Reaction Time hr	Yield %	Observed by-products
1	Methyl	3.3	1,3-Butadiene	3.3	12	96	C_4H_8, hydrogen[a]
2	Methyl	5	Isoprene	1	24	83	2-Methyl-1-butene 2-Methyl-2-butene
3[b]	Methyl	5	Isoprene	1	60	89	3-Methyl-1-butene Hydrogen[a]
4[c]	Methyl	5	Isoprene	5	30	92	
5	Methyl	1	Isoprene	1.3	48	17	
6	Methyl	3.3	1,3-Pentadiene[d]	2	11	63	
7[e]	Methyl	2	Styrene	1.3	72	61	Ethylbenzene
8	Methyl	3	2-Methyl-2-butene	1	76	73	Isopentane
9[e]	Methyl	3	2-Methyl-2-butene	1	15	53	
10	Ethyl	5	Isoprene	1	72	5	Methane[a]
11	*n*-Propyl	5	Isoprene	1	115	20	Ethane[a]
12	Isopropyl	5	Isoprene	1	115	5	
13	Methyl	5	None	—	24	trace	
14[f]	Allyl	4	None	—	0.5	91	

a) Originated from alcohol. b) At 60 °C. c) Air and humidity were removed by a high vacuum line technique. d) Purity: 38.6%. e) Used 3 ml of methylene chloride as a solvent. f) *cf.* Ref. 4.

TABLE 2. COMPOSITION (%) OF HYDROGENATED PRODUCTS OF ISOPRENE

Reactions	2-Methyl-2-butene	3-Methyl-1-butene	2-Methyl-1-butene	Isopentane
$RhCl(PPh_3)_3$/methanol/isoprene[a]	42	12	46	(0)
$RhCl(CO)(PPh_3)_2$/methanol/isoprene[b]	55	2.2	43	(0)
$RhCl(PPh_3)_3$/hydrogen/isoprene[c]	63	6	13	17

a) Experimental No. 2 in Table 1. b) Same conditions as a). c) Atm. Press., at 25 °C.

made by an analysis of the by-products. When the W-complex/methanol/isoprene system was used, the hydrogenated products of isoprene could be observed as the main products, the total amount was found by gas chromatography to be 10 times as much as the yield of the CO-complex. Their compositions, shown on Table 2, resemble those of the reaction products from CO-complex/methanol/isoprene, but not those from W-complex/hydrogen/isoprene. It is noticeable that the products lack isopentane.

The above results indicate the following two conclusions: [1] on an identical rhodium atom, two hydrogen atoms of the methanol molecule migrate to isoprene and two others evolve as hydrogen gas, and [2] the CO-complex also induces the decarbonylation of the alcohol, suggesting a ligand-exchange reaction between carbonyl and isoprene. Consequently, the title reaction involves a catalytic scheme.

Experimental

In a glass autoclave, 100 mg of $RhCl(PPh_3)_3$ prepared according to the literature,[9] 5 ml of purified methanol, and 1 ml of distilled isoprene were placed. After evacuation, the reaction was carried out for 24 hr at 80 °C. The resultant yellow prism crystalline was isolated and washed with dry diethyl ether. The elemental-analytical results and IR spectrum of the product were identical with those of *trans*-$RhCl(CO)(PPh_3)_2$[8] prepared from $RhCl(PPh_3)_3$ and carbon monoxide. The crude product obtained in a lower yield was purified by recrystallization from methylene chloride-methanol. The hydrogenated products of diene and olefin and the evolved gas were analyzed by gas chromatography, using "benzyl cyanide-$AgNO_3$" and "Carbocieve" columns.

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