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RHODIUM AND COBALT CATALYSIS OF THE HYDROFORMYLATION AND HYDROGENATION OF 1,1-DIPHENYLETHYLENE

YASUSHI MATSUI and MILTON ORCHIN

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)

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Summary

Rhodium and cobalt catalyzed reactions of 1,1-diphenylethylene are compared under catalytic hydroformylation conditions (120–180°C, 1500–3000 psi H_2/CO). With $[RhCl(CO)_2]_2$ an 85% yield of aldehyde (hydroformylation) and a 11% yield of 1,1-diphenylethane (hydrogenation) resulted. With cobalt on the other hand a maximum of 5% aldehyde and a 95% yield of hydrocarbon was obtained. The cobalt reaction is very likely free radical in nature while the rhodium reaction involves the conventional olefin insertion into a metal–hydride bond.

Introduction

A recent review [1] discusses the analogies and dissimilarities between rhodium and cobalt catalysis of the hydroformylation of alkenes. Despite the fact that the mechanism of the hydroformylation of alkenes with both catalysts is assumed to be similar, it was pointed out that isomerization of the alkene is usually greater with rhodium and that the partial pressure of CO has a greater effect on the catalytic activity of cobalt than it does with rhodium.

We have shown recently that the reaction of 1,1-diphenylethylene with stoichiometric quantities of $HCo(CO)_4$ leads exclusively to 1,1-diphenylethane (hydrogenation) and that the reaction with this terminal olefin proceeds by a mechanism which is completely different from that which operates in the hydroformylation reaction of 1-alkenes with $HCo(CO)_4$ [2]. The reaction of olefins such as 1,1-diphenylethylene, in which the double bond is conjugated to an aromatic system, with stoichiometric quantities of $HCo(CO)_4$ is radical in character as shown by the CIDNP effect observed in the ^1H NMR spectrum [3] and by other evidence. There is no evidence to suggest that either the hydroformylation or the hydrogenation catalyzed by rhodium complexes proceeds by an analogous mechanism. We now wish to report on a comparative study of the behavior of 1,1-diphenylethylene with rhodium and with cobalt catalysts under catalytic hydroformylation conditions.

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TABLE 1

REACTIONS WITH 1,1-DIPHENYLETHYLENE (DPE)

Experiment	DPE (mmol)	Catalyst		Solvent[c]	CO/H_2[d] (psi)	Temperature (°C)	Time (h)	Products (mol %)		
		Type[a]	%[b]					Ph_2CHCH_3	Ph_2CHCH_2CHO	$Ph_2CH(CH_2)_2OH$
1	10	none	none	B	3000	150	3	0	0	0
2	1	Rh-1	1	T	1600	140	1	0	0	0
3	1	Rh-1	1	B	1500[e]	120	1	100	0	0
4	1	Rh-2	1	B	1500[e]	120	1	40	0	0
5	1	Rh-2	1	B	3000	150	4	87.6	12.4	0
6	1	Rh-3[f]	1	T	2000	150	2	11.3	84.7	3.9
7	10	Rh-3	1	B	3000	150	3	22.5	74.1	3.4
8	10	Rh-3[f]	1	B	3000	150	2	21.9	74.2	3.9
9	100	Rh-3[g]	1	B[h]	3000	150	7	50.0	1.3	48.7
10	1	Rh-3[i]	2	B	2600	180	2	100	0	0
11	10	(Co)	.6	C	3000	150	2.5	95.1	4.9	0
12	10	(Co)	6	C	3000	150	2.5	95.8	3.1	1.1
13	10	(Co)	60	C	3000	150	2.5	100	0	0
14	1	(Co)[j]	2	B	2600	180	2	100	0	0
15	10	(Co)	1	B	3000	150	3	95.4	4.6	0

[a] Rh-1 is $RhCl(PPh_3)_3$; Rh-2 is $RhCl(CO)(PPh_3)_2$; Rh-3 is $[RHCl(CO)_2]_2$; (Co) is $Co_2(CO)_8$. [b] g atoms of metal over moles DPE times 100. [c] 10 ml (unless otherwise noted), B is benzene, T is toluene and C is cyclohexane. [d] 1/1 mixture, initial psi. [e] H_2 only. [f] 0.2 g NaOAc added. [g] 2 g NaOAc added. [h] 50 ml. [i] 0.1 g Ph_3P added. [j] 0.1 g n-Bu_3P added.

Results and discussion

Three different complexes of rhodium(I) were employed as catalyst precursors. The results obtained with these catalysts are shown in the experiments 1 through 10 of Table 1. Although $[RhCl(PPh_3)_3]$ readily hydrogenates 1,1-diphenylethylene in the absence of CO (experiment 3), neither hydroformylation nor hydrogenation occurs under similar conditions in the presence of H_2/CO (experiment 2). In the presence of CO, $[RhCl(PPh_3)_3]$ is converted to $[RhCl(CO)(PPh_3)_2]$ which is a poorer hydrogenation catalyst than its precursor (experiment 4). Although the rhodium carbonyl is an effective hydroformylation catalyst with alkenes the hydroformylation of the relatively hindered ethylene, $Ph_2C{=}CH_2$, proceeds much more slowly (experiments 4 and 5). The dimeric complex $[RhCl(CO)_2]_2$ is a much better catalyst precursor for hydroformylation than the phosphine-containing complexes; the maximum hydroformylation (85%) in the series of experiments was achieved with this catalyst precursor (experiment 6). The aldehyde produced in all experiments with $Ph_2C{=}CH_2$ was exclusively the straight chain aldehyde. When the concentrations of both catalyst and substrate were increased, hydrogenation at the expense of hydroformylation occurred (compare 6 experiments with 7 and 8). We believe that this result can be explained by the lower dissolved CO/substrate ratio [4] when larger quantities of substrate were used even though the ratio of Rh/substrate was kept constant. At long reaction times the aldehyde is reduced to alcohol (experiment 9); the high proportion of hydrocarbon in this experiment may be due to slow decarbonylation of the aldehyde.

Although high yields of aldehyde (hydroformylation) from 1,1-diphenylethylene can be obtained with a rhodium catalyst, the cobalt catalyst gave 1,1-diphenylethane (hydrogenation) almost exclusively. A small amount of hydroformylation was obtained (experiments 11, 12) at low catalyst concentrations. Perhaps the most valid direct comparison between the rhodium and cobalt catalysts involves the results of experiment 7 and 15 where conditions are most similar. Such a comparison shows that rhodium catalysis is much more favorable for the hydroformylation and much less favorable for the hydrogenation of 1,1-diphenylethylene than is cobalt catalysis. The effect of triphenylphosphine in the presence of a rhodium catalyst that is an otherwise good hydroformylation catalyst is shown in experiment 10. Unlike alkenes which readily undergo hydroformylation in the presence of phosphines [5], hydrogenation occurs exclusively with diphenylethylene.

The above results are consistent with the probable radical character of the cobalt-catalyzed reaction of aromatic olefins with cobalt hydride species [3,6] and the olefin insertion (into a rhodium carbonyl hydride species) mechanism that characterizes rhodium hydroformylation [7].

Experimental

All high pressure reactions were carried out in small (70 ml) shaking autoclaves equipped with a glass liner. The catalysts $[RhCl(PPh_3)_3]$, $[RhCl(CO)(PPh_3)_2]$, $[RhCl(CO)_2]_2$, and $Co_2(CO)_8$ were all prepared, respectively, according to the literature directions [8–11]. Analyses were carried out by GLC, using a 1/4″ × 7′ column packed with 15% PEG-6000 on chromosorb W operating at 200°C under helium. All chemicals and solvents were reagent grade and were not further purified.

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References

1 P. Pino, J. Organometal. Chem., 200 (1980) 223.

2 J.A. Roth and M. Orchin, J. Organometal. Chem., 182 (1979) 229; T.E. Nalesnik and M. Orchin, J. Organometal. Chem., 199 (1980) 265; T.E. Nalesnik, J.H. Freudenberger and M. Orchin, J. Mol. Cat., 16 (1982) 43.

3 T.E. Nalesnik and M. Orchin, Organometallics, 1 (1982) 222.

4 F. Ungváry and L. Markó, J. Organometal. Chem., 219 (1981) 397.

5 R.L. Pruett and J.A. Smith, J. Org. Chem., 34 (1969) 327; J.H. Craddock, A. Hershman, F.E. Paulik and J.F. Roth, Ind. Eng. Chem. Prod. Res. Develop., 8 (1969) 291; L.H. Slaugh and R.D. Mullineaux, U.S. 3,239,566, 1966.

6 H.M. Feder and J. Halpern, J. Am. Chem. Soc., 97 (1975) 7186.

7 F.E. Paulik in H. Heineman (Ed.), Catalysis Reviews, Vol. 6, Dekker, Inc. New York, 1972, p. 63.

8 J.A. Osborn and G. Wilkinson, Inorg. Syn., 10 (1967) 67.

9 J.A. McCleverty and G. Wilkinson, Inorg. Syn., 8 (1965) 214.

10 J.A. McCleverty and G. Wilkinson, Inorg. Syn., 8 (1965) 211.

11 I. Wender, H. Sternberg, S. Metlin and M. Orchin., Inorg. Syn., 5 (1957) 190.