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HYDROGENATION OF OLEFINS USING $CoH_3(PPh_3)_3$ AND $CoH(CO)(PPh_3)_3$

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In the previous communication (1), we have reported that the hydrido-complex of cobalt $CoH_3(PPh_3)_3$ is prepared by the reduction of cobalt(III) acetylacetonate with trialkylaluminium in the presence of triphenylphosphine under hydrogen atmosphere. This hydrido-complex reacts with carbon monoxide to give $CoH(CO)(PPh_3)_3$ (2). The analogous iridium and rhodium complexes $IrH_3(PPh_3)_3$ (3) and $RhH(CO)(PPh_3)_3$ (4) are known to be an effective catalyst for the homogeneous hydrogenation of olefins or aldehydes. We wish now to report on a comparative study of the above cobalt complexes and the analogous iridium and rhodium complexes as hydrogenation catalysts.

The reaction of $CoH_3(PPh_3)_3$ with aldehydes such as n-heptylaldehyde under argon occurred at room temperature with bubbling a small amount of H_2 and gave a cobalt carbonyl complex and a mixture of the corresponding alcohol and the decarbonylated product (2). The hydrogenation of aldehydes is not a catalytic reaction under hydrogen, although the analogous iridium complex $IrH_3(PPh_3)_3$ is a good catalyst for the homogeneous hydrogenation of aldehydes under mild conditions (3). However, a solution of $CoH_3(PPh_3)_3$ (1.32 mmole) in benzene (9.28 g) catalyzed the hydrogenation of cyclohexene (31.2 mmole) to cyclohexane at room temperature and 1 atm of H_2 at an initial rate of 1 mmole/hr. The rate of hydrogenation increased with an increase in the reaction temperature and hydrogen pressure. The hydrogenation of all-trans-1,5,9-cyclododecatriene at 80° and 50 atm of H_2 for 2 hr gave a mixture of cyclododecane (16%), cyclododecenes (41%), cyclododecadienes (27%), and cyclododecatrienes (16%).

The complex $CoH(CO)(PPh_3)_3$ showed a catalytic activity for the hydrogenation of olefins when the temperature and pressure were increased, for example to 150° and 50 atm of H_2. These conditions are much more vigorous than required for the rhodium analogue of the cobalt complex, namely $RhH(CO)(PPh_3)_3$. The latter complex dissociates in solution at room temperature extensively to the coordinatively unsaturated species $RhH(CO)(PPh_3)_2$, which coordinates an olefinic compound at the vacant site. This is why the rhodium complex is a good catalyst for the hydrogenation of olefins under mild conditions (4). Table I shows that the activity of the cobalt complex $CoH(CO)(PPh_3)_3$ for the hydrogenation is observed at lower temperatures when triethylaluminium is added. This is probably caused by the more ready removal of the coordinated triphenylphosphine with triethylaluminium, which gives the coordinatively unsaturated species $CoH(CO)(PPh_3)_2$ as an active intermediate.

TABLE I

Hydrogenation of Cyclohexene Using $CoH(CO)(PPh_3)_3$ as Catalyst (a)

Initial H_2 pressure at 25° (atm)	Temp., °C	Reaction time, hr	$AlEt_3$/Catalyst mole ratio	Cyclohexane % (b)
50	150	3.0	0	24
50	115	3.5	3.4	46
50	110	2.5	8.0	81 (c)
1	30	5.0	8.0	2 (d)

(a) $CoH(CO)(PPh_3)_3$/Cyclohexene (mole ratio): 1.3×10^{-3}; Solvent: benzene.

(b) % based on the cyclohexene initially introduced.

(c) Absorption of hydrogen was observed at ca. 30°.

(d) The hydrogen pressure was kept at 1 atm during the reaction.

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