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Preliminary communication

Low pressure catalytic hydroformylation of 1-hexene by the carbonylhydrido-tris(triphenylphosphine)rhodium(I), $RhH(CO)(PPh_3)_3$, in association with phosphinomethylzirconium complexes

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Abstract

Low pressure catalytic hydroformylation of 1-hexene was performed in the presence of $RhH(CO)(PPh_3)_3$ in association with diphenylphosphinomethylzirconium complexes such as $Cp_2Zr(CH_2PPh_2)_2$ and $[Cp_2Zr(CH_2PPh_2)]_2O$ or in the presence of bis(diphenylphosphine)butane. An isolated rhodium–zirconium complex, formulated as $[Cp_2Zr(CH_2PPh_2)_2RhH(CO)PPh_3]$, was found to be catalytically active.

In recent publications, we have demonstrated the efficiency of bimetallic systems in catalytic hydroformylation of olefins, enhancement of both activity and selectivity being observed when the zirconium diphosphine $Cp_2Zr(CH_2PPh_2)_2$ was incorporated into rhodium complexes [1,2]. In continuation of these studies we have investigated the influence of addition of $Cp_2Zr(CH_2PPh_2)_2$ (I) [3] or $[Cp_2Zr(CH_2PPh_2)]_2O$ (II) [4] to $RhH(CO)(PPh_3)_3$ (III) and compared the activity of these new precursors to that of the rhodium complex III alone or in presence of conventional diphosphine such as bis(diphenylphosphino)butane (dppb).

Hydroformylation of 1-hexene was carried out under mild conditions of pressure p 5 bar; $H_2/CO = 1/1$) and temperature (80 °C). The reaction was monitored by GPC and by the decrease in the pressure in the gas tank connected to the autoclave [1b].

Table 1

Hydroformylation of 1-hexene in the presence of $RhH(CO)(PPh_3)_3$ (III) and $Cp_2Zr(CH_2PPh_2)_2$ (I) or $(Cp_2Zr(CH_2PPh_2))_2O$ (II) and related systems [a]

Experiment	Catalyst	Time [b] (h)	[Heptanal]/ [Methylhexanal]
a	III	11	3.0
b	[III + dppb]	10	1.8
c	[I + III]	1	2.6
d	[II + III]	0.5	2.7
e	[2/3 II + III]	5	2.3
f	isolated complex IV	0.5	2.6

[a] Reaction conditons: $H_2/CO = 1/1$; p 5 bar; 80 °C. [1-hexene]/[catalyst] = 400/1; solvent: toluene.
[b] Time required for 95% conversion.

Representative catalytic data for the various catalyst mixtures denoted by ["diphosphine" + $RhH(CO)(PPh_3)_3$], are included in Table 1. The curves in Fig. 1 show a plot of the degree of conversion of the alkene against time. In all cases the reaction was found to be fully selective toward aldehyde formation.

There are no significant differences in the initial rates in experiments a–d, but improved overall performance was observed for the zirconium–rhodium mixtures [I + III] or [II + III].

Some deactivation of the catalytic system occurs with complex III alone or in the presence of dppb, so that nearly 10 h are needed for conversion of 95% of the

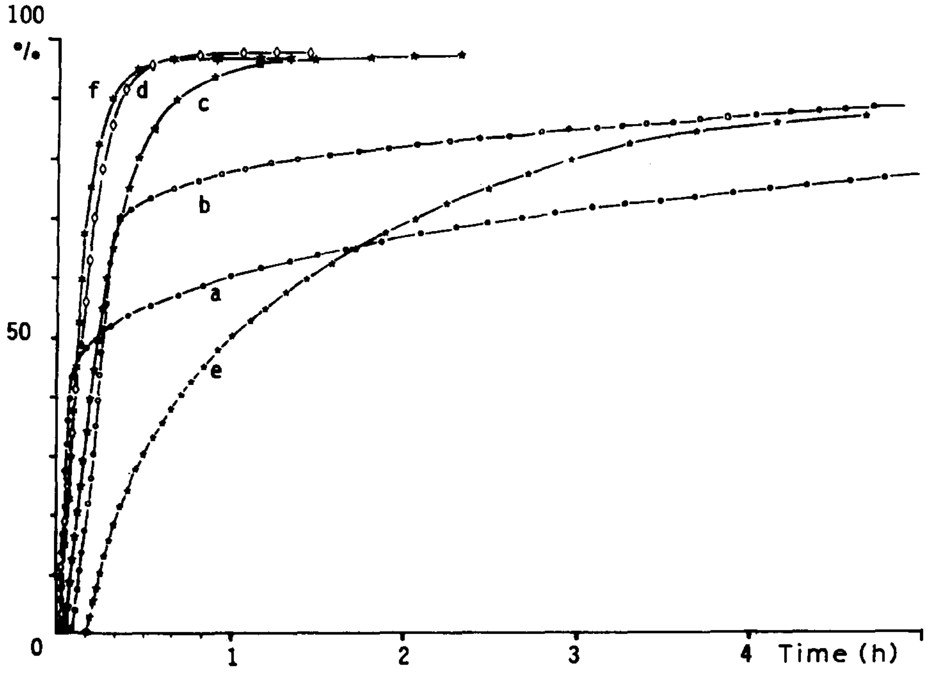


Fig. 1. Conversion of 1-hexene against time. Experimental conditions as in Table 1.

substrate (experiments a and b). Addition of the zirconium-containing diphosphines prevents this deactivation, and nearly complete conversion is obtained in a shorter time (experiments c and d). In addition, the selectivity for linear aldehyde is enhanced compared with that for [III + dppb] (see Table 1) (linear/branched ratio of 2.6–2.7, compared with 1.8 for [III + dppb]), although rather similar to that observed with the isolated complex III (experiment a).

As shown in experiment e, increase in the amount of I decreases the linear/branched ratio, and the initial rate of reaction. Such an influence of an excess of a diphosphine with III was previously noticed in hydroformylation of 1-hexene [5].

The effectiveness of the catalyst mixture [I + III] and [II + III] prompted us to attempt to isolate an active catalytic species.

The $^{31}P\{^1H\}$ NMR spectrum of the stoichiometric amount of [I + III] shows at room temperature an intense doublet (δ 10.5 ppm; J(Rh–P) 123 Hz) and two small broad resonances (at 23.5 and 3.5 ppm), together with signals from free PPh_3. Lowering the temperature to −80 °C changes the spectrum, which mainly shows a AB_2X pattern [*] and a minor AB_2X system [**], probably owing to the presence of two conformers. The same spectra (except for the signals from free PPh_3) were observed from the isolated product (obtained by adding pentane to a toluene solution of the mixture).

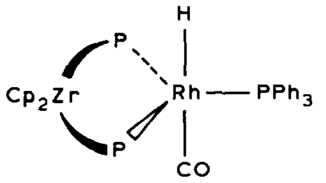
By analogy with findings on $RhH(PPh_3)_4$ associated with $Cp_2Zr(CH_2PPh_2)_2$, which gives the bimetallic complex $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$ [2] (fully characterized by spectroscopic data and crystal structure), the reaction-equation for the present system may be written:

$$\underset{\text{(I)}}{Cp_2Zr(CH_2PPh_2)_2} + \underset{\text{(III)}}{RhH(CO)(PPh_3)_3} \rightarrow$$

$$\underset{\text{(IV)}}{Cp_2Zr(CH_2PPh_2)_2RhH(CO)(PPh_3)} + 2PPh_3$$

The ^1H NMR spectrum at low temperature (−80 °C) shows the presence of a pseudoquintet for the hydride proton resonance centered at −12.1 ppm (^1J(Rh–H) 16 Hz; ^2J(P–H) 18 Hz). This low J(P–H) coupling value is consistent with a hydrogen atom in *cis* to the phosphorus atoms [6] (compare $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$ [2], where the hydrogen atom is *trans* to the PPh_3, with $J(P_{trans}\text{–}H)$ 85.5 Hz and $J(P_{cis}\text{–}H)$ 24.6 Hz).

A proposed structure consistent with the $^{31}P\{^1H\}$ spectroscopic data for IV is:



The isolated complex was also tested in catalytic hydroformylation of 1-hexene and found to be very active, with no induction period and a high rate of conversion

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[*] [$\delta(P_B)$ 9.72 ppm, $J(R\text{–}P_B)$ 125.5 Hz; $\delta(P_A)$ 26.35 ppm, $J(Rh\text{–}P_A)$ 116.2 Hz; $^2J(P_A\text{–}P_B)$ 38.6 Hz].

[**] [$\delta(P_B)$ 10.60 ppm, $J(Rh\text{–}P_B)$ 128.6 Hz; $\delta(P_A)$ 4.78 ppm, $J(Rh\text{–}P_A)$ 117.1 Hz; $^2J(P_A\text{–}P_B)$ 41.2 Hz].

(experiment f), but the ratio of normal to branched product is not greater than with the mixture [I + III].

Since a strong interaction of the zirconium atom with a ligand bonded to the rhodium atom has been demonstrated in previously reported comparable systems [1c,2b], and structural investigations are under way to reveal the exact role of the zirconium centre on the course of the catalysed reaction.

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