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Preliminary communication

Dinuclear rhodium complexes immobilized on functionalized diphenylphosphino-(styrene-divinylbenzene) resins giving high selectivities for linear aldehydes in hydroformylation reactions

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Abstract

A novel rhodium species grafted onto a polymer has been prepared by reacting the functionalized resin (Res-PPh_2) with $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ to afford $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(\text{Res-}PPh_2)_2]$. This complex catalyzes the hydroformylation of oct-1-ene under mild conditions with 99–100% selectivity in aldehydes and more than 90% selectivity in linear aldehyde. A peculiar inhibiting effect of dihydrogen has been shown.

The hydroformylation of alkenes requires the presence of cobalt or rhodium as catalysts, except for a few instances of catalysis with ruthenium and platinum compounds [1]. The aldehydes (or in some cases alcohols) thus obtained are raw materials for which high linearities are required. The reactions have generally been homogeneous, but many authors have tried to immobilize these complexes on various supports in order to separate very easily the organic products from the catalyst, and thus to avoid decomposition induced by distillation or other methods of recovery [2]. This communication reports the immobilization of dinuclear rhodium complexes on a polymeric organic support which allows high performance in hydroformylation with almost no loss of metal.

Organic polymers have usually been used successfully for grafting mononuclear complexes; Pittman, in particular, has shown that such catalytic systems transform alkenes into aldehydes efficiently with significantly improved selectivity in linear component [3,4]. It is even possible to support two different types of complexes so that successive multistep catalytic reactions can be carried out. However, it is generally recognized that the loss of precious metal to solution is far from negligible. Such processes, particularly using polystyrene-anchored rhodium sys-

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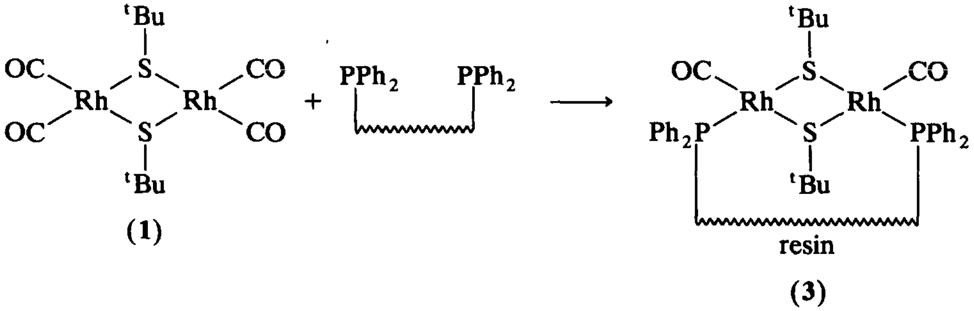
tems analogous to [HRh(CO)(PPh$_3$)$_3$], have yet to find an industrial application. Indeed, a phosphinated support may displace one or more triphenylphosphine ligands, but kinetic studies on the soluble species show that one or more phosphine ligands are eliminated during the catalytic cycle. The use of water-soluble ligands to maintain the active species in the aqueous phase is an elegant way to perform the catalytic reaction and to separate the organic products from the complex by a simple decantation [5]. Such a biphasic catalysis is extremely efficient for low-molecular-weight olefins, particularly propene. However, for heavier substrates the low solubility in water induces very slow rates.

We have recently shown that the dinuclear rhodium complex [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(PPh$_3$)$_2$] needs a slight excess of triphenylphosphine to be active in the low-pressure hydroformylation reaction and to reach high rates (up to 0.5 s^{-1} for the turnover frequency), full selectivities in aldehydes (99 to 100%) and linearities of about 75% [6]. In the absence of triphenylphosphine and under CO pressure, the complex gives [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_4$], which is inactive in catalysis. Our preliminary kinetic and mechanistic studies show that the catalytic cycle does not involve the elimination of a phosphine ligand [7], and so we explored the performance of [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(Res-PPh$_2$)$_2$] systems, obtained by reaction of [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_4$] with Res-PPh$_2$ particularly from the point of view of the selectivity in linear aldehyde and the loss of rhodium to solution.

Among various styrene/divinylbenzene polymers functionalized with diphenylphosphino-groups, the microporous resins commercialized by STREM and cross-linked with 2% divinylbenzene [8–11] gave satisfactory and reproducible results. We found that a good route to immobilize effectively the rhodium complex was to swell the resin (3 g) with the minimum amount of toluene in such a way that no extra solvent was seen on the beads. This took about 1 h. Then, according to equation 1, the tetracarbonyldirhodium complex **1**, [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_4$], was added in the solid state and 5 ml of toluene were introduced. Two or three vacuum/nitrogen atmosphere cycles were done while gentle stirring was maintained. The colour of the solution disappeared completely within 15 min. The resin was washed five times with 10 ml toluene, then dried under vacuum at room temperature. Two ν(CO) bands, at 1966 (s) and 1952 (s) cm^{-1} in KBr dispersions, compare quite well with those of [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(PPh$_3$)$_2$] (**2**) (1965, 1948 cm^{-1} in KBr) and, in the absence of other ν(CO) bands, they can be assigned to the dinuclear species **3** represented in equation 1. This representation means that two phosphorus ligands, wherever they are bonded to the polymer, are coordinated to the dinuclear framework. This species forms our resin-anchored catalyst in the presence of an excess of diphenylphosphino-groups.



(1)

Table 1

Effect of the ratio of the P/Rh concentrations on reaction products

Run no.	Reaction time (h)	$\frac{[\text{oct-1-ene}]}{[\text{cat}]}$	$\frac{pH_2}{pCO}$	P/Rh	Conv. in aldehydes (%)	n/n+iso (%)	TOF [a] (min^{-1})	Internal octenes (%)
1	4	94	1	1	72	84	0.32	3
2	17	400	1	5	87	87	1.13	5
3	15	740	1.64	10	85	91	1.73	4
recycle	15	740	1.64	10	77	89	1.67	5
5	15	740	1	20	62	93	0.70	5

[a] TOF = turnover frequency = rate/[cat.].

These resins were used for the hydroformylation of oct-1-ene at 80°C and 0.37 MPa for 15 h with a $H_2/CO = 1/1$ (syngas) mixture. A 90% conversion was achieved, giving 84% aldehydes and 4% internal octenes (*Z* and *E* isomers); in this case linearity reached 90%. It is emphasized that no hydrogenation was detected in all these experiments, and that, except for some isomerization of the alkene, the conversion is fully selective in aldehydes. About 730 turnovers were obtained and the turnover frequency value of 1.55 min^{-1} means that the reaction proceeds dramatically slower than with complex **2** (30 min^{-1}). Table 1 shows the results observed for various molar phosphorus-to-rhodium ratios. A good compromise between the conversion in aldehydes and linearity appears for P/Rh ratios near 10. For P/Rh = 1 the turn-over frequency and the selectivity were 0.32 min^{-1} and 84% respectively; for P/Rh = 5 we obtained 1.13 min^{-1} and 87% and for P/Rh = 20, 0.7 min^{-1} and 93%. In addition we checked that recycling the resin-anchored catalyst maintained its performances within the experimental error.

Since we observed for complex **2** in homogeneous phase that the rate-determining step is certainly the activation of dihydrogen [7], we introduced in the autoclave unbalanced H_2/CO mixtures before admitting a 1/1 H_2/CO mixture in the usual way. As shown on Table 2, carbon monoxide appears to have an inhibiting effect, as previously described for all cobalt and rhodium catalysts [1]. Examination of the results in Table 2 shows that an increase in the pH_2/pCO ratio induces higher selectivities in linear aldehyde. For instance, for a ratio 2.27, the selectivity was 97%. The only side reaction was the isomerization of substrate into internal octenes, which was slightly favoured when the hydrogen pressure was increased.

However, Table 2 shows also that the higher is the hydrogen partial pressure, the slower is the reaction rate. This phenomenon, which is quite unexpected, prompted us to examine in more detail the effects of dihydrogen on the kinetics. The results of our preliminary kinetic investigations are summarized in Fig. 1. Reaction rates were calculated from the kinetic curves for a 20% conversion (similar curves and conclusions can be obtained for 30, 40% conversions). For a constant carbon monoxide partial pressure (0.185 MPa in Fig. 1) the rates are linearly proportional to the pH_2 value until 0.3 MPa, as observed classically. Above a pH_2/pCO ratio of 1.7 the rates decrease dramatically.

This inhibiting effect parallels that observed for complex **2** in homogeneous phase [7], also shown in Fig. 2. This effect can be considered as indirect evidence that dinuclear species still exist on the polymer. Two hypotheses were proposed to

Table 2

Effect of the ratio pH_2/pCO on catalytic activity

pCO (MPa)	pH_2 (MPa)	pH_2/pCO	Conversion in aldehydes (%)	n/n+iso (%)	TOF [a] (min^{-1})	Internal octenes (%)
0.278	0.185	0.66	60	90	1.0	3
0.185	0.152	0.82	67	90	1.2	2
0.185	0.185	1.00	84	90	1.5	4
0.140	0.185	1.32	87	92	2.1	5
0.185	0.285	1.54	87	92	2.4	4
0.176	0.290	1.65	81	94	1.7	5
0.140	0.240	1.71	80	94	1.5	5
0.160	0.308	1.92	79	94	1.0	5
0.140	0.280	2.00	74	94	1.0	5
0.140	0.318	2.27	55	97	0.5	4
0.116	0.345	3.00	30	98	0.4	6

Range of conditions studied for the kinetics of hydroformylation of oct-1-ene: [cat.] = 3.4×10^{-7} mol/cm^3; P/Rh = 10; [oct-1-ene] = 2.5×10^{-4} mol/cm^3; T = 80°C; toluene: 150 cm^3; reaction time = 15 h. The reaction rate is determined at 20% conversion. [a] TOF = turnover frequency = rate/[cat.].

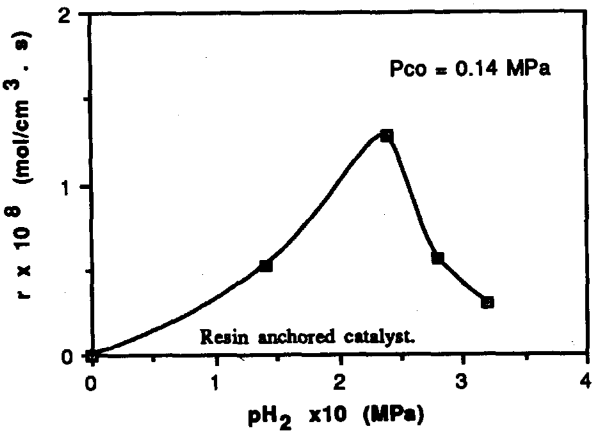


Fig. 1. Effect of pH_2 on the rate of hydroformylation.

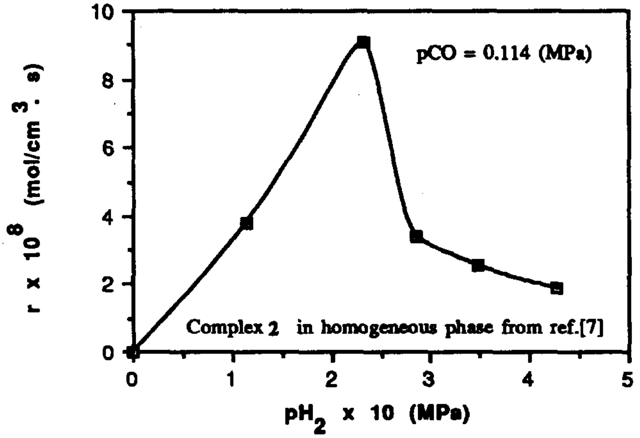


Fig. 2. Effect of pH_2 on the rate of hydroformylation.

explain the anomalous effect of high hydrogen pressure. The first one is that the precursor is transformed in a tetrahydrido-species which coordinates alkene very hardly. In the second hypothesis, the fastest "alkene route" is handicapped owing to the formation of the complex $[(H)_2(CO)(Res\text{-}PPh_2)Rh(\mu\text{-}S^tBu)_2(CO)(Res\ PPh_2)]$.

At the present time, the kinetic curves, particularly in homogeneous solution, appear very difficult to model satisfactorily. Work is in progress to rationalize the effect of dihydrogen.

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