Dinuclear Ruthenium Complexes as Active Catalyst Precursors for the Low Pressure Hydroformylation of Alkenes into Aldehydes

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Di-μ-acetato diruthenium complexes catalyse the low pressure hydroformylation of alkenes to give the corresponding aldehydes with high selectivities.

Many efforts have been devoted during the past decade to replace rhodium by the less expensive ruthenium metal in catalysis, provided that the catalytic activity, as well as the selectivities, are comparable. It has been shown in the literature[1,2,3] that ruthenium catalyses the hydroformylation reaction but leads also to hydrogenation products (alkanes from alkenes, alcohols from aldehydes), and that, even under high pressure (10—15 MPa), the rates remain low compared to the rhodium systems. More recently, a very selective conversion to linear aldehydes was reached with anionic hydridoruthenium complexes.[4] However, only a few turn-overs have been reached at 6 MPa. Due to our interest in the dinuclear catalyst precursors in the carbonylation reactions,[5,6] our attention was drawn to di-μ-acetato diruthenium carbonyl complexes which exhibit specific catalytic behaviour for the condensation of acetic acid and acetylene to give vinyl-acetate[7,8] and for the hydrogenation of carboxylic acids into alcohols.[9,10]

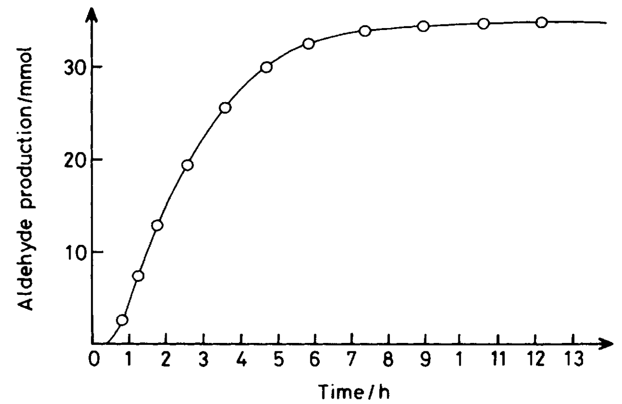

Figure 1. Hydroformylation of hex-1-ene with $Ru_2(\mu\text{-}OOCMe)_2(CO)_4(PPh_3)_2$; NEt_3 (50 μl) + H_2O (2ml); $P(H_2/CO\ 1/1) = 1.2$ MPa 25 ml toluene; $T = 80$ °C; 40 mmol hex-1-ene 0.1 mmol catalyst + 1 mmol PPh_3.

We report here that the di-μ-carboxylato diruthenium complexes substituted by tertiary phosphine or phosphite ligands can be active for hydroformylation at pressures as low as 1 MPa, provided that a small amount of a base (tertiary phosphine, amine or potassium hydroxide) is added to the mixture. $Ru_2(\mu\text{-}OOCR)_2(CO)_4L_2$ complexes catalyse the conversion of hex-1-ene into heptanal and 2-methyl hexanal, (Figure 1), under 1.2 MPa with an initial turn-over frequency of 0.9 mn^{-1}. We have observed that a minimal pressure of *ca.* 0.8 MPa of synthesis gas ($H_2/CO = 1/1$) is required. When the complexes are used alone, no catalysis occurs. However, when an extra ligand, such as NEt_3 or PPh_3, is added to the system, conversion of the alkene into aldehydes takes place. Better results were obtained by adding small amounts of aqueous triethylamine or potassium hydroxide. After each run the starting material was recovered as shown by its characteristic infrared pattern (for instance R = Me, L = PPh_3:ν_{CO} = 2025 s, 1981 m, 1953 vs cm^{-1} in toluene) showing a C_{2v} symmetry for the species.[11,12] We have established that hydrogen is necessary for the reaction. The water gas shift (WGS) reaction would produce hydrogen from water, but in this case, we have not observed CO_2 and moreover, carrying out the reaction with CO + KOH in water or CO + H_2O in the absence of alkene, no H_2 or CO_2 was detected in the gas phase. The rate of WGS can therefore be considered as negligible when compared to the rate of the hydroformylation reaction. Table 1 lists some of our results for the hydroformylation of oct-1-ene catalysed by various $Ru_2(\mu\text{-}OOCR)_2(CO)_4L_2$ complexes activated by three molar equivalents of NEt_3 in toluene/water (25 ml/2 ml). In most cases, a complete selectivity in aldehydes was achieved, with no hydrogenation products. Such a selectivity for ruthenium is striking and was observed only recently by Süss-Fink for the $HRu_3(CO)_{11}^-$ complex.[4] Good activities were observed; usually the initial turn-over frequencies are around 1 mn^{-1}. Moreover, Wilkin-

Table 1. Hydroformylation of oct-1-ene by $Ru_2(\mu\text{-}OOCR)_2(CO)_4L_2$.

R	L	Time/ h	% Yield	Nonanal	2-Methyl-octanal	*n*%	Octane	Oct-2-ene
Me	PPh_3	20	96.0	72.4	23.5	75.4	0	0
Me	$P(OPh)_3$	17	95.9	65.2	25.2	72.1	5.5	0
Ph	PPh_3	16	81.7	63.2	18.5	77.4	0	0
CF_3	PPh_3	16	58.7	44.9	13.8	76.5	0	0
CMe_3	PPh_3	18	15.2	11.3	3.9	74.3	0	0
CMe_3	$P(OPh)_3$	22	100.0	64.0	18.3	77.8	16.0	1.7
Me	$P(OMe)_3$	20	97.1	73.3	23.8	75.5	0	0
Me	PBu_3	20	3.2	2.7	0.8	85.0	0	0
Ph[a]	PPh_3	20	99.5	69.1	28.6	71.0	1.8	0

Conditions: total pressure: 3 MPa ($H_2/CO = 1/1$); $T = 80$ °C, 10^{-4} mol of complex, 40 mmol oct-1-ene, 3×10^{-4} mol NEt_3, 2 ml H_2O, 25 ml toluene. [a] No water.

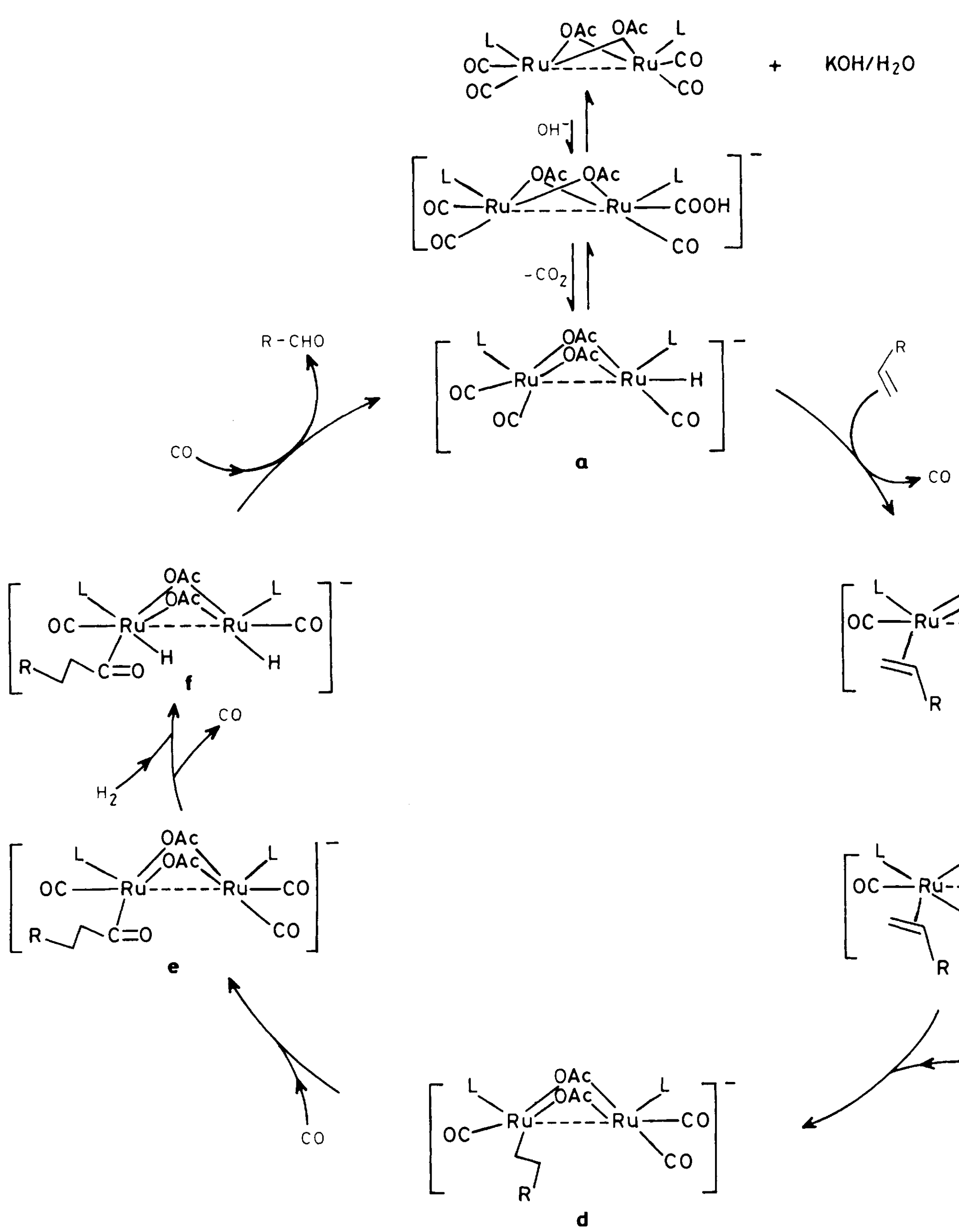

Figure 2

son *et al.*[3] have shown that many starting complexes are active under higher pressures (10—15 MPa), leading to the active species $Ru(CO)_3L_2$. In our case, the recycling of the dimeric catalysts gives the same activity and selectivity, confirming that the dimeric starting complex is not converted to other species. The effect of the basicity of the phosphorus ligand was examined (Table 1): tributylphosphine presents a low level activity, tris(dimethylamino)phosphine completely inactivates the reaction; however triphenylphosphine or the less basic trimethyl- or triphenylphosphites gave good conversion rates. In the latter case the steric hindrance of the ligand as well as of the bridges allowed some hydrogenation of oct-1-ene into octane and, even with the pivalic bridges, some isomerization of the carbon–carbon double bond. Concerning the selectivity in linear aldehydes, we observed almost no variation in the experiments, approaching *ca.* 75%, as generally observed for the ruthenium systems. In order to see if this chemistry parallels the rhodium performances in hydroformylation we have added an excess of triphenylphosphine: with a P/Ru ratio of 50, the regioselectivity in nonanal peaks at 86%, which remains lower than the 92% reached with $HRh(CO)(PPh_3)_3$.[2]

The question arises for the activation of the diruthenium complexes by NEt_3 or KOH in water. In our opinion, the $[HNEt_3]OH$ or KOH molecules activate the precursor through a nucleophilic attack of the OH^- species to generate a hydroxycarbonyl anionic complex which loses a CO_2 molecule to form the active species, $L(CO)_2Ru(\mu\text{-}OOCR)_2Ru(H)(CO)L^-$. Attempts to characterize this anionic complex or the presence of a hydride species by n.m.r. have been unsuccessful. However we propose a catalytic cycle (Figure 2) in which the co-ordination of the alkene molecule, the hydride transfer on the alkene, and then the CO insertion lead to the $L(CO)_2Ru(\mu\text{-}OOCR)_2Ru(acyl)(CO)L^-$ intermediate complex. The activation of dihydrogen should occur on the ruthenium centres to form a $L(CO)_2(H)Ru^{II}(\mu\text{-}OOCR)_2Ru^{II}(H)(acyl)(CO)L^-$ complex, which gives the aldehyde and regenerates the active species by reductive elimination.

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