Further Studies on the Homogeneous Hydroformylation of Alkenes by Use of Ruthenium Complex Catalysts †

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The use of several tertiary-phosphine–ruthenium complexes in the catalytic hydroformylation of alkenes is described. For mononuclear complexes the conversions into aldehyde, as well as the ratios of straight- to branched-chain aldehyde are essentially constant; the ruthenium complex recovered from the reactions is invariably tricarbonylbis(triphenylphosphine)ruthenium(0), $Ru(CO)_3(PPh_3)_2$. The dependence of conversion and aldehyde ratios on catalyst concentration, temperature, partial and total pressures, nature of the substrate, and addition of excess of triphenylphosphine and other ligands in hydroformylation with $Ru(CO)_3(PPh_3)_2$ is also described. Based on these results, a mechanism involving $Ru(H)_2(CO)_2(PPh_3)$ as the principal active catalytic species is suggested.

The compound $Ru(CO)_3(PPh_3)_2$ is also active for the hydrogenation of alkenes and aldehydes and mechanisms for these reactions are suggested.

Complexes formed by addition of various ligands to dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, are shown to be less active for hydroformylation than mononuclear complexes.

THE use of cobalt and rhodium carbonyl compounds in the homogeneous hydroformylation of alkenes has been the subject of several reviews.[1-6] Ruthenium compounds have received relatively little attention. Tricarbonylbis(triphenylphosphine)ruthenium was shown to be an effective hydroformylation catalyst;[7] reports on hydroformylation with dodecacarbonyltriruthenium[8] and catalysts of unspecified stoicheiometry[9,10] have also appeared.

We have now investigated the catalytic activity of a series of ruthenium compounds in hydroformylation. Under the conditions required for the reaction the same active species is produced from all the effective mononuclear complexes. After the reaction has been completed, the compound recovered is $Ru(CO)_3(PPh_3)_2$. This compound may be repeatedly used without any apparent loss in catalytic activity. A detailed study of the factors affecting the activity and selectivity of this complex in the hydroformylation of alkenes has been carried out. On this basis, and by analogy with known catalytic systems, a mechanism is suggested for the reaction. The activity of the complex for other reactions connected with hydroformylation such as isomerisation and hydrogenation of alkenes and reduction and decarbonylation of aldehydes has also been investigated, and mechanisms for the hydrogenation of aldehydes and alkenes are suggested. Catalysts derived from dodecacarbonyltriruthenium differ considerably from mononuclear complexes; the differences are explained by the presence of the metal cluster unit.

TABLE 1

Hydroformylation of hex-1-ene with ruthenium complexes. Hex-1-ene (1.2 ml, 10 mmol), catalyst (0.1 mmol), benzene (5 ml), 120 °C, 100 atm $H_2 + CO$ (1 : 1) for 20 h

Complex	% Conversion [a]	Selectivity for aldehydes [b] (%)	Ratio [c]
$Ru(CO)_3(PPh_3)_2$ [d]	83	100	2.4
$Ru(H)_2(CO)_2(PPh_3)_2$ [e]	86	99	2.4
$Ru(H)_2(CO)(PPh_3)_2$ [f]	87	97	2.4
$RuH(NO)(PPh_3)_3$ [g]	85	100	2.0
$Ru(H)_2(PPh_3)_4$ [f]	81	87	2.1
$Ru(H)_4(PPh_3)_3$ [f]	80	81	2.4
$Ru(CO_2CH_3)_2(PPh_3)_2$ [h]	85	100	2.0
$Ru(CO_2CF_3)_2(PPh_3)_2$	79	100	2.0
$Ru(CO_2CMe_3)_2(PPh_3)_2$ [i]	88	100	2.9
$Ru(CO)_3$(diphos) [j]	12	100	4.7
$Ru(CO)_2(C_6Cl_4O_2)(PPh_3)_2$ [k,l]	4	100	2.5
$(\eta\text{-}C_5H_5)RuH(PPh_3)_2$ [m]	5	100	1.2
$Ru(dmt)_2(PPh_3)_2$ [n,o]	0		

[a] Calc. from amount of unreacted hex-1-ene in reaction mixture. [b] As % of total product. [c] n-Heptanol : 2-methylhexanol. [d] Ref. 11. [e] Ref. 12. [f] Ref. 13. [g] Ref. 14. [h] Ref. 15. [i] Ref. 16. [j] diphos = 1,2-Bis(diphenylphosphino)ethane. [k] $C_6Cl_4O_2$ = Tetrachloro-*o*-benzoquinone. [l] Ref. 17. [m] Ref. 18. [n] dmt = Dimethyldithiocarbamate. [o] Ref. 19.

Hydroformylation by Use of Various Ruthenium Complexes.—Mononuclear complexes. Results of hydroformylation experiments are collected in Table 1.[11-19]

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† No reprints available.

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For the first ten members of the series the conversions and aldehyde ratios are constant, within experimental error. Since $Ru(CO)_3(PPh_3)_2$ is recovered from all the reactions it is clear that the catalytically active species is the same in all cases; on the basis of evidence now presented this appears to be the compound $Ru(H_2)(CO)_2(PPh_3)$. Reduction to alkane and isomerisation of the olefin were not observed; only for $Ru(H)_2(PPh_3)_4$ and $Ru(H)_4(PPh_3)_3$ was a significant amount of alcohol produced along with the aldehyde.

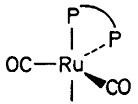
TABLE 2

Hydroformylation of hex-1-ene with $Ru_3(CO)_{12}$ in presence of various ligands. $Ru_3(CO)_{12}$ (63 mg, 0.1 mmol), hex-1-ene (1.2 ml, 10 mmol), benzene (5 ml), 120 °C, and 100 atm H_2 + CO (1 : 1) for 20 h

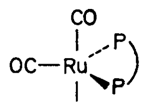
Catalyst	Ligand	P : Ru ratio	% Conversion [a]
(I)	None		24.2
(II)	PBu^n_3	1 : 1	10.4
(III)	$P(OEt)_3$	1 : 1	19.9
(IV)	PPh_3	1 : 1	88.2
(V)	$P(OPh)_3$	1 : 1	95.1
(VI)	$P(OR)_3$ [b]	1 : 1	97.6
(VII)	Diphos	2 : 3	10.6

[a] Calc. from amount of unchanged olefin in reaction mixture.
R = 2-Naphthyl.

The previously unreported compound $Ru(CO)_3$(diphos) [diphos = 1,2-bis(diphenylphosphino)ethane] is similar to $Ru(CO)_3(PPh_3)_2$ except that the phosphorus atoms necessarily occupy mutually *cis* positions. The complex is a monomer (see Experimental section) but we cannot distinguish between structures (*A*) and (*B*). From theoretical arguments,[20] the best π-acceptor ligand prefers to occupy an equatorial position whilst better π-donor ligands tend to occupy axial positions so that structure (*A*) seems most probable.



(*A*)



(*B*)

The ratio of linear to branched-chain aldehydes is improved with the chelate ligand but the rate is much lower than for $Ru(CO)_3(PPh_3)_2$; this is not unreasonable since a co-ordinatively unsaturated intermediate should be more readily formed from the latter. Similarly, the inactivity of the tetrachloro-*o*-benzoquinone, cyclopentadienyl, and dimethyldithiocarbamato-complexes can be ascribed to the formation of co-ordinatively saturated compounds under hydroformylation conditions; even the low conversions observed in some cases are due to formation of $Ru(CO)_3(PPh_3)_2$ during the reaction.

The complex $RuH(NO)(PPh_3)_3$ is isoelectronic with $RhH(CO)(PPh_3)_3$ and might have been expected to behave similarly, but it reacts with carbon monoxide to yield $Ru(CO)_3(PPh_3)_2$ and carbon dioxide (detected mass spectrometrically) as the only condensible gaseous product of the reaction. A plausible explanation seems to be the reduction of NO to N_2:

$$2NO + 2CO \longrightarrow 2CO_2 + N_2$$

in contrast with the known[21] reactions of transition-metal dinitrosyl complexes with carbon monoxide to produce CO_2 and N_2O.

Catalysts derived from dodecacarbonyltriruthenium. Tables 2 and 3 show the results of hydroformylating hex-1-ene with catalysts prepared by adding various ligands to $Ru_3(CO)_{12}$. Alkyl phosphines and phosphites decrease the conversions with respect to $Ru_3(CO)_{12}$ whilst aryl phosphines and phosphites increase the conversions considerably; this is clearly an electronic effect related to the basicity of the ligand. In the case of diphos, steric factors may be more important and when a 1 : 1 ratio of ruthenium to diphos is used, the cluster is broken down and converted into $Ru(CO)_3$(diphos). By use of $Ru_3(CO)_{12}$ the proportion of linear aldehyde is lowered by all the ligands used except diphos (see following Discussion). Mixtures of various ruthenium compounds are recovered from the reactions; the predominant species are probably the tetranuclear $H_4Ru_4(CO)_8L_4$ (L = phosphine or phosphite ligand); there is precedent for the formation of such species under similar conditions.[22]

TABLE 3

Product distribution in hydroformylation of hex-1-ene with $Ru_3(CO)_{12}$ in presence of various ligands. Hex-1-ene (1.2 ml, 10 mmol), $Ru_3(CO)_{12}$ (63 mg, 0.1 mmol), benzene (5 ml), 120 °C, and 100 atm H_2 + CO (1 : 1) for 20 h. Values as %

Catalyst	Alkanes	n-Heptanal	2-Methylhexanal	3-Methylhexanal	n-Heptanol	2-Methylhexanol	3-Methylhexanol	Other products
(I)	0.2	19.8	4.2					
(II)		8.0	2.4					
(III)	0.01	13.3	6.3					0.3
(IV)	0.1	51.5	36.3	0.3				
(V)	2.9	50.0	42.1					
(VI)	0.5	4.8	4.3	2.4	27.9	26.8	0.1	30.9
(VII)		8.8	1.6	0.2				

Factors Influencing Hydroformylation with $Ru(CO)_3(PPh_3)_2$.—*Effect of catalyst concentration.* Results in Figure 1 suggest a first-order dependence of the rate of hydroformylation of hex-1-ene on catalyst concentration but detailed kinetic measurements would be

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needed to reach a conclusive interpretation of these results. First-order dependence has also been reported for cobalt,[23] rhodium,[24] and ruthenium[10] catalysts. The ratio of linear to branched aldehyde does not vary appreciably with catalyst concentration.

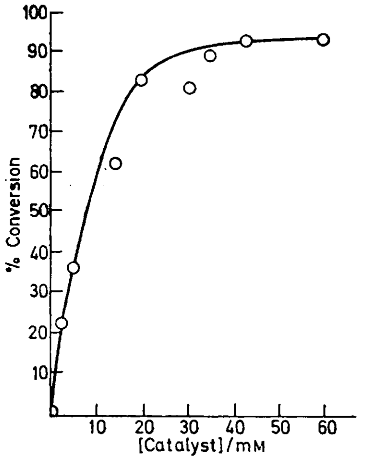


FIGURE 1 Effect of catalyst concentration on hydroformylation of hex-1-ene with Ru(CO)$_3$(PPh$_3$)$_2$. [Hex-1-ene] = 2M in benzene; 120 °C, 100 atm H$_2$/CO (1 : 1) for 20 h

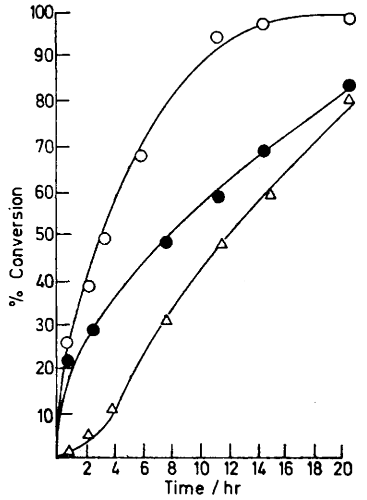


FIGURE 2 Comparison of rates of hydroformylation with Ru(CO)$_3$(PPh$_3$)$_2$ and Ru(H)$_2$(PPh$_3$)$_2$. [alkene] = 2M, [catalyst] = 0.02M in benzene. Open triangle: Hydroformylation with Ru(CO)$_3$(PPh$_3$)$_2$; 120 °C, 100 atm H$_2$/CO (1 : 1). Closed circle: hydroformylation with Ru(H)$_2$(CO)$_2$(PPh$_3$)$_2$, 120 °C, 100 atm H$_2$/CO (1 : 1); open circle: hydroformylation with Ru(H)$_2$(CO)$_2$(PPh$_3$)$_2$, 120 °C, 150 atm H$_2$/CO (2 : 1)

Effect of temperature. The temperature range 50—200 °C has been investigated (Table 4). Below 80 °C hydroformylation is very slow and above 150 °C conversions decrease and mixtures of ruthenium complexes are recovered from the reaction; the optimum temperature for the reaction is *ca.* 120 °C. The ratio of n-heptanal to 2-methylhexanal is fairly constant within this temperature range.

TABLE 4

Effect of temperature in hydroformylation of hex-1-ene with Ru(CO)$_3$(PPh$_3$)$_2$ in benzene; [Ru] : [alkene] = 0.01, 100 atm H$_2$ + CO (1 : 1) for 20 h

T/°C	% Conversion [a]	Ratio [b]
50	0	
80	5	2.5
110	83	2.4
150	79	2.9
200	65	2.7

[a] Calc. from amount of unreacted hex-1-ene in reaction mixture. [b] Ratio n-heptanol : 2-methylhexanol.

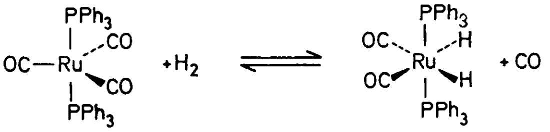
TABLE 5

Effect of partial pressures on hydroformylation of hex-1-ene with Ru(CO)$_3$(PPh$_3$)$_2$. Hex-1-ene (1.2 ml, 10 mmol), catalyst (91 mg, 0.1 mmol), benzene (5 ml), 120 °C, and 100 atm total pressure for 20 h

H$_2$/CO	% Conversion	Ratio [a]
11 : 1	82	2.5
2 : 1	96	2.1
1 : 2	2	2.2

[a] Ratio straight to branched chain.

Effect of pressure. (*a*) *Effect of partial pressures.* It was found that high partial pressures of hydrogen increase the rate of hydroformylation of hex-1-ene whilst high partial pressures of carbon monoxide drastically inhibit the reaction (Table 5 and Figure 2). This agrees well with the first step of the reaction being the oxidative addition of molecular hydrogen to tricarbonylbis(triphenylphosphine)ruthenium, with simultaneous loss of a CO ligand, *viz.*:



This is a known reaction[12] which we have reproduced in our solvent system, and it is reasonable to assume that it is the rate-determining step of the hydroformylation cycle.

(*b*) *Effect of total pressure.* Data collected in Table 6 indicate that the rate of hydroformylation increases with the total pressure whilst aldehyde ratios remain fairly constant. By combining this effect with the effect of high partial pressures of hydrogen already

TABLE 6

Effect of total gas pressure on hydroformylation of hex-1-ene with Ru(CO)$_3$(PPh$_3$)$_2$ in benzene. [Ru] : [Hex-1-ene] = 0.01, 120 °C for 20 h

Total Pressure [a]/ atm	% Conversion	Ratio [b]
60	79	2.2
100	83	2.4
140	95	2.0

[a] Values at room temperature; at 120 °C calc. values are 80, 135, and 190 atm; $p_{H_2} : p_{CO} = 1$. [b] Ratio n-heptanol : 2-methylhexanol.

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[23] G. Natta, R. Ercoli, and S. Castellano, *Chimica e Industria*, 1955, **37**, 6.

[24] C. K. Brown and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, **2753**.

described, faster reactions are achieved; thus at 150 atm of 2 : 1 hydrogen–carbon monoxide reaction of hex-1-ene in benzene at 120 °C was virtually complete in *ca.* 15 h. However, g.l.c. analysis of the products showed that the mixture consisted of 35% hexane and only 65% aldehydes.

Variation of substrate. Table 7 shows the results of hydroformylating various alkenes with $Ru(CO)_3(PPh_3)_2$. The catalyst is fairly selective for terminal olefins as compared to internal or cyclic ones. Increasing steric hindrance at the terminal double-bond is accompanied by a decrease in olefin conversion; conjugation of the double bond stops the reaction completely. This is probably due to formation of a ruthenium–diene complex, but attempts to isolate such a complex have failed.

TABLE 7

Hydroformylation of various alkenes with $Ru(CO)_3(PPh_3)_2$. Alkene (10 mmol), catalyst (0.1 mmol), benzene (5 ml), 120 °C and 100 atm $H_2 + CO$ (1 : 1) for 20 h

Alkene	% Conversion
Ethylene	100
Hex-1-ene	82
Styrene	15
cis-Pent-2-ene	22
Cyclohexene	0
Buta-1,3-diene	0

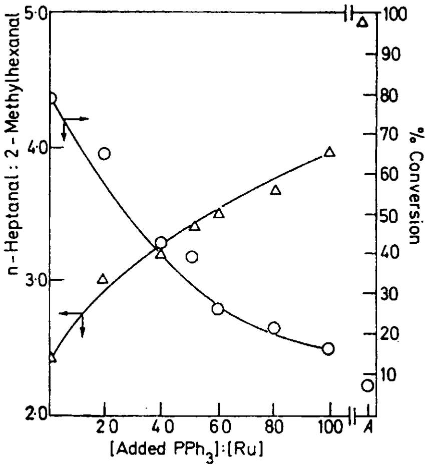

FIGURE 3 Effect of adding excess of triphenylphosphine on the hydroformylation of hex-1-ene with $Ru(CO)_3(PPh_3)_2$ in benzene. [Ru] : [alkene] = 0.01, 120 °C, and 100 atm H_2/CO (1 : 1) for 20 h. *A* is value with molten PPh_3 as solvent

Effect of excess triphenylphosphine. Addition of an excess of triphenylphosphine to rhodium catalysts gives a large increase in the proportion of linear aldehyde without an appreciable sacrifice in rate.[24] While for $Ru(CO)_3(PPh_3)_2$ the addition of excess of triphenylphosphine also improves the linear to branched aldehyde ratio there is a marked decrease in the rate of reaction (Figure 3). In molten triphenylphosphine, hydroformylation of hex-1-ene gives a ratio of *ca.* 5 : 1 but conversions after 20 h were <10%. These results show that dissociation of triphenylphosphine is an important feature of the reaction (see Discussion).

Effect of other ligands. Results are shown in Table 8. All the ligands used inhibited the reaction, probably by effectively competing with the alkene for vacant co-ordination sites on the metal. Only triphenylphosphine has a favourable effect on the aldehyde ratio.

Comparison of Hydroformylation with $Ru(CO)_3(PPh_3)_2$ *and* $Ru(H)_2(CO)_2(PPh_3)_2$.—Approximate rate measurements in terms of alkene conversion as a function of time have been carried out for $Ru(CO)_3(PPh_3)_2$ and $Ru(H)_2(CO)_2(PPh_3)_2$ (Figure 2). When the former is used, hydroformylation of hex-1-ene is very slow for the first 1—2 h and then becomes fairly rapid. The induction period can be removed by pretreatment of the catalyst solution with hydrogen until i.r. spectra show virtually complete conversion into $Ru(H)_2(CO)_2(PPh_3)_2$. This induction period clearly corresponds to the time required for the formation of the dihydrido-species in sufficient concentration to sustain the catalytic cycle. If this reaction mixture is allowed to cool under CO pressure, $Ru(CO)_3(PPh_3)_2$ is regenerated and it is essentially the only compound recovered. The effect of excess of hydrogen has been noted earlier and is included in Figure 2 for comparison.

TABLE 8

Effect of adding various ligands to $Ru(CO)_3(PPh_3)_2$ in the hydroformylation of hex-1-ene in benzene. [Catalyst] = 0.02M, [alkene] = 2M, [ligand] = 0.1M, 120 °C, and 100 atm H_2 = $H_2 + CO$ (1 : 1) for 20 h

Ligand	% Conversion	Ratio[a]
PPh_3	35	3.4
$P(OPh)_3$	39	2.3
PBu^n_3	0	
Diphos	0	
Pyridine	0	
Benzoic acid	0	

[a] Ratio straight to branched chain.

Other Reactions.—We have investigated the catalytic properties of $Ru(CO)_3(PPh_3)_2$ for other reactions connected with hydroformylation. The complex is inactive for the decarbonylation of heptaldehyde heated under reflux in benzene or decalin. However, propionaldehyde is reduced to propan-1-ol under 20 atm of hydrogen at 120 °C; at 150 °C and 50 atm of hydrogen, reduction is complete in 3 h. Hex-1-ene is also hydrogenated under the same conditions (Table 9). Isomerisation of hex-1-ene was not observed during hydrogenation. The compound recovered from hydrogenation reactions is $Ru(H)_2(CO)_2(PPh_3)_2$.

DISCUSSION

The mechanism of alkene hydroformylation with cobalt [25] and rhodium [7,24] catalysts has been discussed in terms of equilibria involving steps such as oxidative addition of hydrogen to low-valent complexes, dissociation of phosphine ligands to form co-ordinatively unsaturated intermediates, hydride transfer to co-

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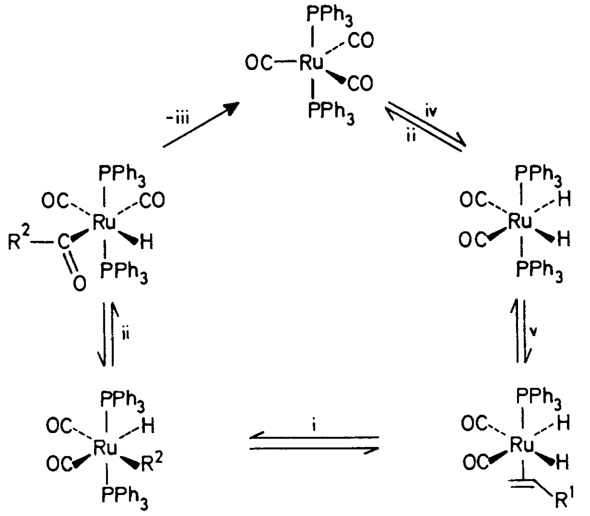
[25] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023.

ordinated alkenes to form alkyl intermediates, alkyl migrations or ' carbon monoxide insertion ' to form acyl intermediates, and reductive elimination of aldehydes which completes the cycle. All these steps with appropriate intermediate complexes can be accommodated for $Ru(CO)_3(PPh_3)_2$ as in Scheme 1. The oxidative addition of hydrogen appears to be the rate-determining step of the reaction and it must be preceded or followed by dissociation of a phosphine ligand to produce the active unsaturated species $Ru(H)_2(CO)_2(PPh_3)$, which is capable of co-ordinating the alkene. It is impossible to know whether dissociation occurs before or after addition of hydrogen; however, the importance of the dissociation is shown by the marked decrease in rates on addition of excess of triphenylphosphine. The fact that no isomerisation or hydrogenation takes place concurrently with hydroformylation is a good indication that the formation of the alkyl and acyl intermediates is very fast. This also suggests that the formation of branched aldehydes is not due to hydroformylation of isomerised alkene.

TABLE 9

$Ru(CO)_3(PPh_3)_2$ as catalyst for other reactions

Substrate	Conditions	Products	% Conversion	Cpd. recovered
n-Heptanal	[Ru] : [heptanal] = 0.01 Reflux in benzene or decalin Up to 24 h, under N_2	None		$Ru(CO)_3(PPh_3)_2$
Propionaldehyde	[Ru] : [propionaldehyde] = 0.01 20 atm H_2, 120 °C, 20 h	Propan-1-ol	60	$Ru(H)_2(CO)_2(PPh_3)_2$
Propionaldehyde	[Ru] : [propionaldehyde] = 0.01 50 atm H_2, 150 °C, 3 h	Propan-1-ol	99	$Ru(H)_2(CO)_2(PPh_3)_2$
Hex-1-ene	[Ru] : [hexene] = 0.01 50 atm H_2, 150 °C, 3 h	Hexane	65	$Ru(H)_2(CO)_2(PPh_3)_2$

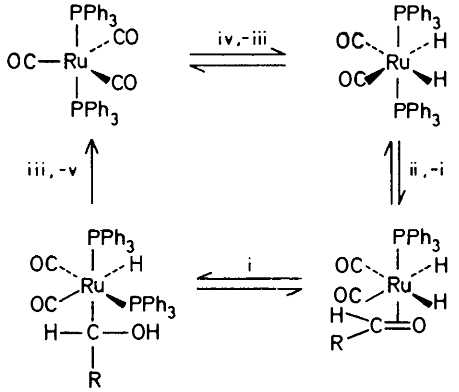


SCHEME 1 Suggested mechanism of hydroformylation with $Ru(CO)_3(PPh_3)_2$. Reagents i, PPh_3; ii, CO; iii, R^2CHO; iv, H_2; v, $R^1CH{=}CH_2$

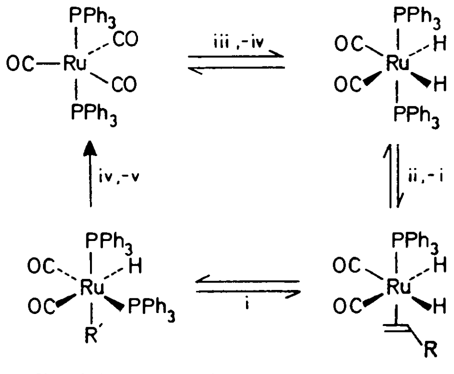
The low ratios of linear to branched aldehyde produced by this catalyst as compared to rhodium systems can be accounted for by comparing the intermediate species formed in both cases after alkene co-ordination. In the case of rhodium this species is either $RhH(alkene)(CO)(PPh_3)_2$ or $RhH(alkene)(CO)_2(PPh_3)_2$, whilst in the case of ruthenium it is probably $Ru(H)_2(CO)_2(alkene)(PPh_3)$. The presence of the phosphine ligands tends to make the hydrogen atoms less hydridic and thus promotes anti-Markownikov addition whilst the steric effects of bulky ligands also favour formation of linear alkyls. Clearly, in the case of ruthenium the situation is not as advantageous as for rhodium, since there are two hydrogens and one phosphine attached to the metal as opposed to one hydrogen and two phosphines for rhodium; the desired effects, probably mainly steric, are therefore smaller for the ruthenium catalyst. At high phosphine concentrations, a species like $Ru(H)_2(alkene)(CO)(PPh_3)_2$ may well be formed, which would account for the higher ratios obtained under those conditions; however, carbon monoxide would be competing with the alkene for the vacant co-ordination site, or even displacing it from the metal and thus lowering the rate of hydroformylation. Attempts to use other ruthenium complexes with different electronic and steric properties have been unsuccessful due to either their being converted into $Ru(H)_2(CO)_2(PPh_3)_2$ under the reaction conditions or else to the impossibility of forming co-ordinatively unsaturated intermediates.

In the hydrogenation of aldehydes and alkenes by $Ru(CO)_3(PPh_3)_2$, the predominant species under hydrogen in absence of carbon monoxide is $Ru(H)_2(CO)_2(PPh_3)_2$ and again the rate-determining step in these reactions is probably the oxidative addition of hydrogen to a ruthenium(0) species. The presence of carbon monoxide promotes rapid formation of the acyl intermediates under hydroformylation conditions and thus hydrogenation of the alkene is not an important competitive reaction. These acyl intermediates are probably more stable than the hydroxy-alkyl species formed in the reduction of aldehydes and therefore aldehyde formation prevails over alcohol formation. The fact that no isomerised alkene is produced under hydrogen pressure, indicates that transfer of a second hydrogen atom to the co-ordinated alkyl is faster than elimination to regenerate the olefin. Possible mechanisms of hydrogenation of aldehydes and alkenes are shown in Schemes 2 and 3.

For the polynuclear complexes the mechanism of hydroformylation appears to be somewhat different. Although conversions are increased by adding aryl phosphines or phosphites to $Ru_3(CO)_{12}$, the ratios are invariably lowered; this would seem to indicate that the alkene interacts simultaneously with more than one metal centre to produce fairly high ratios of linear to branched chain aldehyde. The presence of ligands other than hydrogen or carbon monoxide may be preventing the olefin from interacting with the metal cluster in this way and thus decreasing the proportion of linear products.



SCHEME 2 Possible mechanism for the hydrogenation of aldehydes with $Ru(CO)_3(PPh_3)_2$. Reagents: i, PPh_3; ii, RCHO; iii, CO; iv, H_2; v, RCH_2OH



SCHEME 3 Possible mechanism for the hydrogenation of alkenes with $Ru(CO)_3(PPh_3)_2$. Reagents: i, PPh_3; ii, $RCH=CH_2$; iii, H_2; iv, CO; v, alkane

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College. I.r. spectra were recorded by use of a Perkin-Elmer 457 spectrometer, n.m.r. spectra by use of a Perkin-Elmer R 12A spectrometer. G.l.c. measurements were carried out by use of Perkin-Elmer F 11 and F 33 chromatographs fitted with flame ionisation detectors and carbowax and squalene columns. Peak areas were obtained with an Infotronic electronic integrator. High-pressure reactions were performed using 25 or 100 ml stainless steel autoclaves (Baskerville and Lindsay Limited).

Materials.—Ruthenium trichloride trihydrate (Johnson, Matthey Ltd.); triphenylphosphine (Albright and Wilson) was recrystallised from benzene–ethanol before use. Hex-1-ene (Emmanuel), *cis*-pent-2-ene (Koch-Light), cyclohexene (Hopkin and Williams), and styrene (Koch-Light) were purified as described previously.[26] Ethylene, hydrogen, and carbon monoxide (British Oxygen Company) were used without further purification. Other phosphine and phosphite ligands were used as obtained. Ruthenium complexes were prepared by published methods (see Table 1) and identified spectroscopically.

Bis(triphenylphosphine)bis(trifluoroacetato)ruthenium.—This complex was prepared by a method essentially analogous to that for the acetato-complex,[15] by use of trifluoroacetic acid and sodium hydrogencarbonate (Found: C, 56.9; H, 3.8; F, 10.6; P, 7.4%. $C_{40}H_{30}F_6O_4P_2$-Ru requires C, 56.4; H, 3.5; F, 13.4; P, 7.3%); m.p. 197—202 °C (decomp.); ν_{CO} 1 667 cm^{-1}, ν_{CF} 1 200, 1 152 cm^{-1} (Nujol mull).

[1,2-*Bis(diphenylphosphino)ethane*]*tricarbonylruthenium*.—Dodecacarbonyltriruthenium (160 mg, 0.25 mmol), 1,2 bis(diphenylphosphino)ethane (275 mg, 0.75 mmol), and benzene (5 ml) were charged into a 25 ml stainless steel autoclave. The vessel was flushed with carbon monoxide twice and then pressurised with 100 atm of CO and heated at 100 °C for 4—5 h. After cooling at room temperature the excess pressure was released and the pale yellow solution kept below 0 °C for 4—5 h to give long pale-yellow needles of the *complex*, which was washed with cold benzene (2 × 1 ml) and light petroleum (2 × 1 ml) and dried *in vacuo*. Yields are essentially quantitative [Found: C, 60.0; H, 4.4; P, 10.1%; *M* (benzene), 560. $C_{29}H_{24}O_3P_2$-Ru requires C, 59.7; H, 4.1; P, 10.6%; *M*, 583]; m.p. 150—152 °C (uncorr.); ν_{CO} 1 997, 1 942, and 1 885 cm^{-1}.

Hydroformylation Experiments.—The autoclave containing the catalyst, solvent, and alkene was flushed twice with carbon monoxide and then compressed to the required pressure of CO + H_2; the values of pressures reported throughout refer therefore to room temperature and not to the actual reaction temperature. The autoclaves were heated in an electric oven without agitation and after the reaction they were cooled in water and the products analysed immediately by g.l.c. Rate measurements were made by the same procedure; several autoclaves were prepared and heated simultaneously and the reactions quenched at different times. Reactions were carried out at least twice in different vessels to avoid spurious results.

Other Reactions.—Hydrogenation experiments were essentially similar to hydroformylation, using only hydrogen. Decarbonylation experiments were performed by heating under reflux a mixture of tricarbonylbis(triphenylphosphine)ruthenium (0.1 mmol) and n-heptaldehyde (10 mmol) in benzene or decalin for 2 to 24 h. Reaction mixtures were analysed by g.l.c.

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