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Journal of Molecular Catalysis A: Chemical 202 (2003) 87–95

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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A bimetallic hydroformylation catalyst: high regioselectivity through heterobimetallic cooperativity

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Received 11 October 2001; accepted 19 March 2003

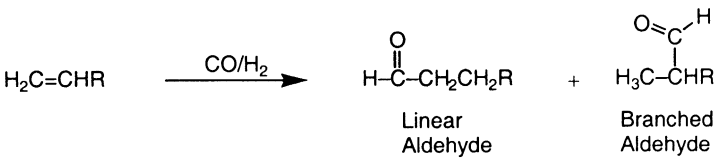
Abstract

The homogeneous hydroformylation of 1-octene using either of the heterobimetallic complexes $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^2\text{-}Ph_2P(CH_2)PPh_2\}RhCl_2]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^2\text{-}HC(PPh_2)_3\}RhCl_2]$ (**2**) as catalysts yields both *n*-nonanal and 2-methyloctanal. The best results were obtained with complex **2**, having the tripod $\{HC(PPh_2)_3\}$ bridging ligand, which showed the highest regioselectivity for linear aldehydes. Although the rate of reaction is slower for these heterobimetallic catalysts than for related monometallic species, the selectivity for terminal aldehydes is relatively greater. Two mechanisms involving bimetallic cooperativity between the Ru and the Rh metal centres, either in the form of an intramolecular hydride transfer, or in the form of the Ru centre acting as a labile ligand, are proposed.

Keywords: Hydroformylation; Bimetallic catalysis; Phosphine complexes; 1-Octene; Selectivity

1. Introduction

Hydroformylation is the world's largest industrial homogeneous catalytic process, producing more than six million tonnes of aldehydes each year [1]. In this process, alkenes react with hydrogen and carbon monoxide to give either linear or branched aldehydes (Eq. (1); R, alkyl).



(1)

Monometallic rhodium triphenylphosphine (Rh/PPh_3) catalysts dominate the hydroformylation industry, particularly for C_3 through C_6 1-alkenes, where regioselectivity in making the more valuable straight chain aldehyde products is critical.

The use of heterobimetallic complexes as catalysts in the hydroformylation reaction is of interest with regard to the possibilities of using the adjacent metal centres to increase catalytic activity and selectivity. A number of studies have provided evidence that such enhancements of activity and selectivity can be obtained in some cases [2–7]. An early example

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doi:10.1016/S1381-1169(03)00234-6

was provided by the $Co_2(CO)_8$–$RuCl_3$ system for the homologation of ethanol [2] and the $Co_2(CO)_8$–$Ru(CO)_{12}$ system for the hydroformylation of alkenes [3]. A more recent example from the Hidai group concerns the synergistic effects of Pd–Co bimetallic systems in the carbonylation of ArI with $CO/HSiEt_3$ and in the hydroformylation of internal alkynes [4]. It was suggested that the synergistic effects for the hydroformylation could be due to the promotion by the Co metal of CO insertion into the Pd–C bond and/or the acceleration of the hydrogenolysis of the acyl–Pd bond to produce the aldehyde. Indeed, it has been reported that CO insertion into the Pd–C bond in $(dppe)MePdCo(CO)_4$ is much faster than that in PdMeCl(dppe) [5]. Some insights into the cooperative effect in multimetallic catalysis have also been obtained through studies of complexes of the type $L_nRM\text{-}M'L_m$ (M = Pt, Pd, Ni, Au; M′ = Mo, W, Co, Fe, Re; L = cod, dppe, bpy, PPh_3; L′ = Cp, CO) as possible models of bimetallic catalysts [6]. For example, it has been shown that the β-hydrogen elimination process of the ethyl complex $(dppe)EtPt\text{-}Co(CO)_4$ is significantly facilitated by the electron-withdrawing $Co(CO)_4$ ligand, and that facile hydride transfer from Pt to Mo or W occurs on reaction of $(dppe)HPt\text{-}MCp(CO)_3$ (M = Mo, W) with dimethyl acetylenedicarboxylate or diphenylacetylene. A cooperative effect of two different metal ions in catalytic systems for hydroformylation is observed when a Zr(IV) complex of formula $Cp_2Zr(CH_2PPh_2)_2$ or $Cp_2Zr(H)(CH_2PPh_2)$ is added to Rh(I) catalyst precursors such as $HRhP_4$, $HRh(CO)P_3$ (P = PPh_3, $P(OPh)_3$) or $Rh(acac)(CO)_2$ [7].

In this paper, we report our studies on the hydroformylation of 1-octene catalysed by two heterobimetallic complexes $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}Ph_2P(CH_2)PPh_2\}RhCl_2]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_3\}RhCl_2]$ (**2**).

Other monometallic complexes each having a chemical structure representing a single metal environment of **1** or **2** have been tested under the same catalytic conditions, and their catalytic activities and selectivities were compared to those of **1** and **2**. This comparison allowed us to demonstrate the catalytic cooperativity of metal centres in the bimetallic complexes. The mechanism is proposed to either involve bimetallic cooperativity between the Ru and the Rh metal centres in the form of an intramolecular hydride transfer or the cooperativity arises through a mechanism involving the Ru centre acting as a labile ligand.

2. Experimental

2.1. Catalysis

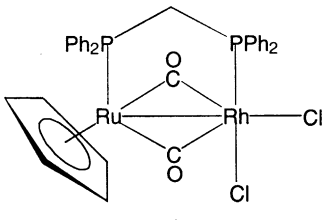
All the catalytic runs were performed under the same reaction conditions.

2.1.1. Materials

All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of argon or CO/H_2. 1-Octene (substrate), toluene (solvent) and decane (GC internal standard for quantitative analysis) were all purchased from Aldrich, dried by standard procedures and freshly distilled before use. All organic compounds were checked for purity by gas chromatography. Syngas (CO/H_2, 1:1) was supplied by "Air Liquide" (purity >99%) and used directly from cylinders without further purification.

2.1.2. Experimental setup

All catalytic runs were performed in a 85 ml stainless-steel autoclave equipped with gas and liquid inlets, a speed-controlled magnetic stirrer, a high precision pressure-regulator gauge, and a safety rupture



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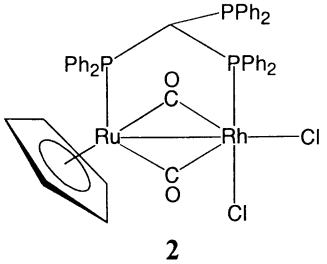

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valve (maximum pressure of 150 atm). The reactor and feed vessel were equipped with certified Omega thermocouples, automatically controlling the temperature within ±1 °C. The reactor was designed for a working pressure of 200 atm and a temperature up to 250 °C. For safety reasons, all the catalytic runs were carried out under a hood equipped with a special CO detector.

The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor.

Reaction products and starting materials were analyzed by gas chromatographic methods on a Hewlet Packard 6890 chromatograph equipped with a HP1 30 m column, film thickness 320 μm, and FID detector. The carrier gas was He, and the temperature programme was from 40 °C (15 min) to 200 °C (30 °C min^{-1}).

2.1.3. Catalytic runs

For the kinetic measurements, catalyst solutions of each complex were prepared by using the appropriate solvents. These solutions were prepared by weighing the different components of the catalytic system, then combining them at room temperature in a 100 ml Schlenk vessel. The quantities of the various components were as follows: 1.7 cm^3 (1.215 g) 1-octene, 21.6×10^{-3} mmol of the catalyst (relative to rhodium), 0.6 cm^3 (0.438 g) decane and 22.9 cm^3 (16.373 g) toluene to bring the total volume to 25.2 cm^3. This allowed us to have a ratio of catalyst to substrate of 1:500.

The autoclave was closed and degassed through four vacuum-argon cycles, then the catalytic solution was introduced into the autoclave and syngas was added up to the desired pressure (60 atm). In all reactions the stirring rate was kept at the same value. The reactor temperature was then raised and automatically controlled at 115 °C.

2.1.4. Sampling procedure

Each time that a sample of the reaction solution was taken, the stirrer was switched off and the solution allowed to stand briefly to ensure no bubbles of the CO/H_2 gas mixture would pass through the sampling valve. Then, a very small portion of the solution was left to cool and discarded; this represents a residual volume in the valve and sampling tube left from the preceding sample. Then, the desired sample which had a constant volume of 0.1 ml was used to obtain qualitative and quantitative information about the evolution of products during the reaction (using gas chromatography).

2.2. Synthesis

2.2.1. Materials

The compound $(\eta^5\text{-}C_5H_5)RuCl(\eta^4\text{-}C_8H_{12})$ [8] was prepared by the literature method. 1,1,1-tris(Diphenylphosphino)methane $HC(PPh_2)_3$ and $[RhCl(CO)_2]_2$ were purchased from Aldrich and used without further purification. Nuclear magnetic resonance spectra were obtained on a Bruker AC-300 spectrometer operating at 300 MHz for ^1H, 75 MHz for ^{13}C and 121 MHz for ^{31}P. Chemical Shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed at the CNRS Central Analysis Service, Solaize. FAB mass spectra were recorded on a ZAB2 SEQ VG instrument using 3-nitrobenzyl alcohol as matrix. Infrared spectra were recorded on a Nicolet 550 spectrophotometer using CH_2Cl_2 solutions in 0.3 cm KBr cells.

Complexes **1** [9] and **2** [10] were prepared by literature methods.

3. Results and discussion

The hydroformylation of 1-octene was studied at 115 °C using **1** and **2** as catalysts, 1-octene concentration of 9.55×10^{-3} mol cm^{-3}, catalyst concentration of 1.9×10^{-5} mol cm^{-3} and a total pressure ($P_{CO} + P_{H_2}$) of 60 atm (at ambient temperature; CO/H_2, 1:1).

3.1. Hydroformylation catalysed by $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}Ph_2P(CH_2)PPh_2\}RhCl_2]$ (1)

It was observed from the initial stages of the reaction (where conversion of 1-octene is low) that the straight chain and the branched aldehydes were formed, and these were the only reaction products (Fig. 1). About 50% of the 1-octene is converted after 40 h. The *n*-nonanal was the major product with a relatively constant *n*/*iso* ratio of 2.8.

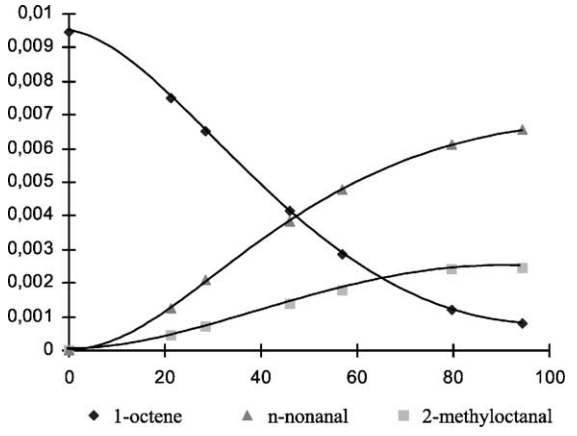

Fig. 1. Plot of amount of reactant/product (mol) vs. time (h) for complex **1** as catalyst.

3.2. Hydroformylation catalysed by [(η^5-C_5H_5)$Ru(\mu$-CO)$_2\{\mu$-η^1:η^1-$HC(PPh_2)_3\}RhCl_2$] (**2**)

The mole number–time profile of 1-octene and reaction products for the hydroformylation reaction catalysed by complex **2** is shown in Fig. 2. With this bridging tripod complex the activity is about the same as that of dppm complex **1** (50% conversion after 40 h); however, the *n*/*iso* ratio is much higher, between 8 and 9.

Since the regioselectivity (expressed as *n*/*iso* ratio) to linear aldehyde using the tripod bridging complex **2** is higher than that of the analogous bridging dppm

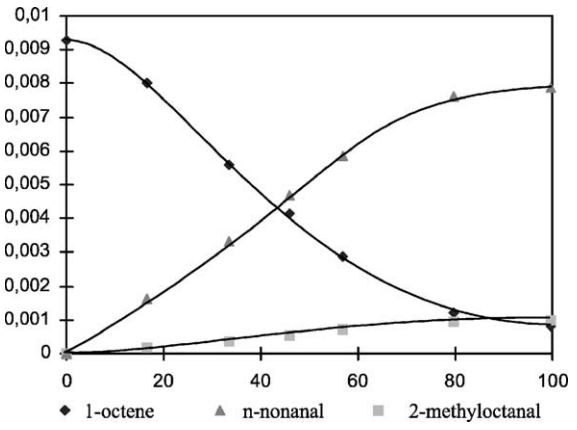

Fig. 2. Plot of amount of reactant/product (mol) vs. time (h) for complex **2** as catalyst.

complex **1**, it is clear that the presence of the free diphenylphosphine group on the central carbon atom in **2** has a strong effect in controlling the selectivity of the reaction. This may be explained essentially by steric effects.

This result is in accordance with virtually all other phosphine- or phosphite-coordinated Rh hydroformylation catalysts, where excess phosphine ligand (for example, PPh_3) is needed to maintain good selectivity or stability. The need for excess PPh_3 in monometallic Rh catalysts arises from the relatively weak Rh–PPh_3 bonding. In order to maintain the coordination of two PPh_3 ligands, which are required for good regioselectivity, a large excess of PPh_3 is required to force the dissociation equilibrium to favour $HRh(CO)(PPh_3)_2$ [11]. In our case, the free dangling phosphine of the tripod seems to play an analogous role.

It is important to note that complexes **1** and **2** are recovered unchanged from the reaction mixture following catalysis, and ^{31}P NMR spectroscopy of the product solution showed no other phosphorus-containing species present.

We explored the hydroformylation reaction for monometallic model complexes that represent one "half" of the bimetallic catalysts **1** or **2**. These tests give us an idea about whether each metal centre is functioning as a conventional monometallic catalyst or whether there is some cooperativity. Thus, the catalytic activity and selectivity of the complexes (η^5-C_5H_5)$RuCl(\eta^2$-$Ph_2PCH_2PPh_2$), (η^5-C_5H_5)$RuCl\{\eta^2$-$HC(PPh_2)_3\}$ and $[RhCl(CO)_2]_2$ were studied under the same conditions as described above.

The complexes (η^5-C_5H_5)$RuCl(\eta^2$-$Ph_2PCH_2PPh_2$) and (η^5-C_5H_5)$RuCl\{\eta^2$-$HC(PPh_2)_3\}$ are extremely poor hydroformylation catalysts. They showed less than 0.5% conversion of alkene to aldehyde product after 30 h, low linear to branched ratios of one or less, and undesirable amounts of alkene isomerisation and hydrogenation products.

The complex $[RhCl(CO)_2]_2$ is a much more active catalyst with a relatively high turnover frequency of 156 mol product (mol catalyst h)$^{-1}$ (at 50% conversion) (compared to a turnover frequency of 5 for **1** and 4 for **2**), and 97% conversion of 1-octene after 3 h, under our conditions. The products are exclusively the straight chain and the branched aldehydes with an *n*/*iso* ratio of approximately 1. No alkene isomerisation or hydrogenation products were observed (Fig. 3).

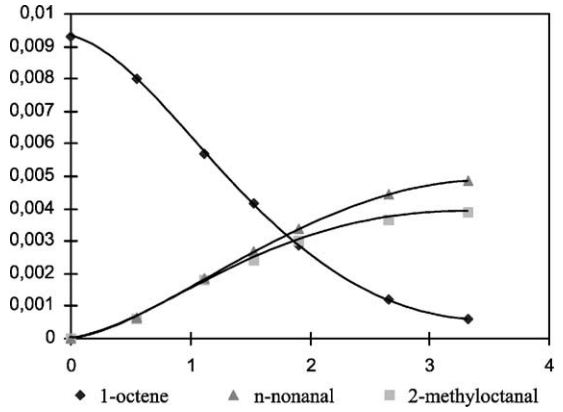

Fig. 3. Plot of amount of reactant/product (mol) vs. time (h) using the complex $[RhCl(CO)_2]_2$ as catalyst.

The reactivity of $[RhCl(CO)_2]_2$ in the presence of various amounts of added tripod ligand was also investigated. It was found that the presence of excess tripod ligand had very little effect on the *n*/*iso* ratio of the aldehydes, with the maximum not exceeding 1.5 even with a Rh/tripod ratio of 1:4 (Table 1).

The activity and regioselectivity of **1** and **2** therefore contrasts to that of monometallic Rh or Ru complexes, and the regioselectivity of complex **2** is particularly noteworthy. These results indicate that the active species uses some sort of bimetallic cooperativity to effect high regioselectivities.

Any discussion of bimetallic mechanisms should take into account the early work on cobalt-catalysed hydroformylation [12]. A monometallic mechanism was proposed that has become the generally accepted pathway [13] for both Co and Rh catalysts. A more speculative bimetallic mechanism was also suggested involving an intermolecular hydride transfer from $HCo(CO)_4$ to $Co(acyl)(CO)_4$. Elimination of the aldehyde product then produces $Co_2(CO)_8$, which reacts with H_2 to break the Co–Co bond to reform two $HCo(CO)_4$ molecules. This suggests an interesting mechanistic possibility for our catalyst.

Table 1
n/*iso* ratio at 40% conversion of 1-octene for various catalytic systems

Catalyst	*n*/*iso* ratio
1	2.8
2	8.9
$[RhCl(CO)_2]_2$	1.0
$[RhCl(CO)_2]_2$ + 1 tripod	1.23
$[RhCl(CO)_2]_2$ + 2 tripod	1.38
$[RhCl(CO)_2]_2$ + 4 tripod	1.45

The constrained proximity of the two metal centres, held together by the tripod ligand, should dramatically increase the probability of an intramolecular hydride transfer. We propose just such a mechanism (Fig. 4) in which bimetallic cooperativity, via an intramolecular hydride transfer, facilitates the elimination of aldehyde from the acyl intermediate **8**. This mechanism uses proximity for catalytic power just as many bioorganic models of enzyme catalysts do [14].

The first several steps in the proposed mechanism are essentially the same as those established for monometallic Rh/PPh_3 catalysts, except that the proposed oxidative addition of H_2 is bimetallic: (i) addition of H_2 to **2** produces **3**; (ii) coordination of alkene (1-octene) to **3** produces **4**; (iii) alkene insertion into the Rh–H bond gives the linear (or branched) alkyl species **5**; (iv) **6** is formed by the coordination of CO to the Rh centre and (v) CO insertion into the Rh–alkyl bond yields the acyl complex **7**. In monometallic systems, the next step is addition of H_2 to a Rh(I) to produce a Rh(III) dihydride species that can then eliminate aldehyde product. Compound **7** avoids this problem by having a proximate Ru−H moiety, which intramolecularly transfers a hydride to facilitate the aldehyde elimination (***7*** → ***8*** → ***2***). Thus, the final steps of the mechanism are: (i) H and CO bridge formation between the Ru and the Rh atoms and (ii) elimination of the aldehyde and reformation of **2**.

A similar mechanism can be proposed for complex **1**.

An additional factor supporting the bimetallic mechanism is that the bimetallic acyl intermediate, **7**, can readily form a doubly bridged intermediate species, **8**. The hydride thus bridges to the acyl-bound Rh, while the CO ligand on the acyl Rh can bridge to the hydrido-bound Ru (Fig. 4). We believe that the second bridging interaction present in complex **8**, favours the intramolecular hydride transfer by stabilising the Ru–H bond-breaking step.

The bimetallic cooperativity in the proposed mechanism represents a very effective way of performing hydroformylation. The fundamental concept of a hydride transfer between two metal centres has been studied and shown to occur in stoichiometric

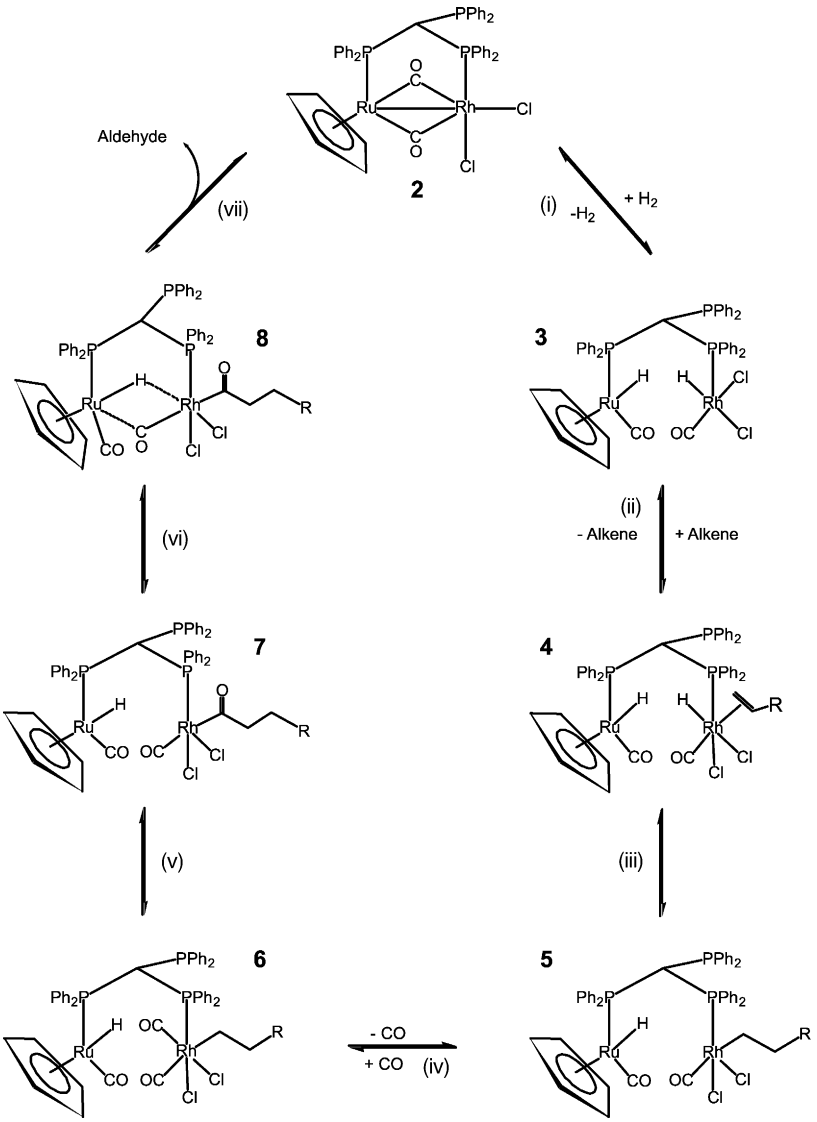

Fig. 4. Proposed mechanism for hydroformylation via bimetallic hydrogen addition.

model reactions by numerous groups [15]. Hidai and Matsuzaka [16] attributed the synergistic effect observed in the hydroformylation of olefins by the $Co_2(CO)_8$–$Ru_3(CO)_{12}$ bimetallic system to a "dinuclear reductive elimination of aldehydes from cobalt acyls and ruthenium hydride(s)". $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(PPh_3)_2$ is another hydroformylation catalyst for which bimetallic cooperativity has been proposed [17]. However, the reaction rates and regioselectivities of $Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(PPh_3)_2$ very closely resemble those of Rh/PR_3 monometallic catalysts, indicating that the active catalyst may be monometallic in nature [18], quite unlike **3**.

Dinuclear oxidative additions, and reductive eliminations, are formally forbidden for 18-electron or 16-electron complexes if the least-motion pathway is followed, although the energy barrier can be reduced by the presence of π-acceptor ligands. Importantly, the

presence of π-donor ligands such as Cl^- make dinuclear reductive elimination unfavourable, but make dinuclear oxidative addition more favourable [19]. The dinuclear oxidative addition reaction, while formally forbidden, is suggested to be thermodynamically more favourable than the reverse, reductive elimination reaction [19].

We believe that the high linear aldehyde regioselectivity arises from the shape of **2** and **3**. The crystal structure of **2** has not been determined, but the structure of the AuCl derivative, $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_2(PPh_2AuCl)\}RhCl_2]$ provides evidence for the steric hindrance due to the μ-tripod ligand (Fig. 5) [4]. When the rhodium alkyl complex **5** is formed from the rhodium alkene complex **4**, the steric effect of the tripod ligand will cause preferential formation of the linear alkyl group, which goes on to form the linear aldehyde.

An alternative mechanism is one in which the oxidative addition of hydrogen occurs at the Rh centre only, with the Ru centre acting as a labile ligand. This mechanism is shown in Fig. 6.

In this proposed mechanism, after the monometallic addition of H_2 to the Rh centre, alkene substi-

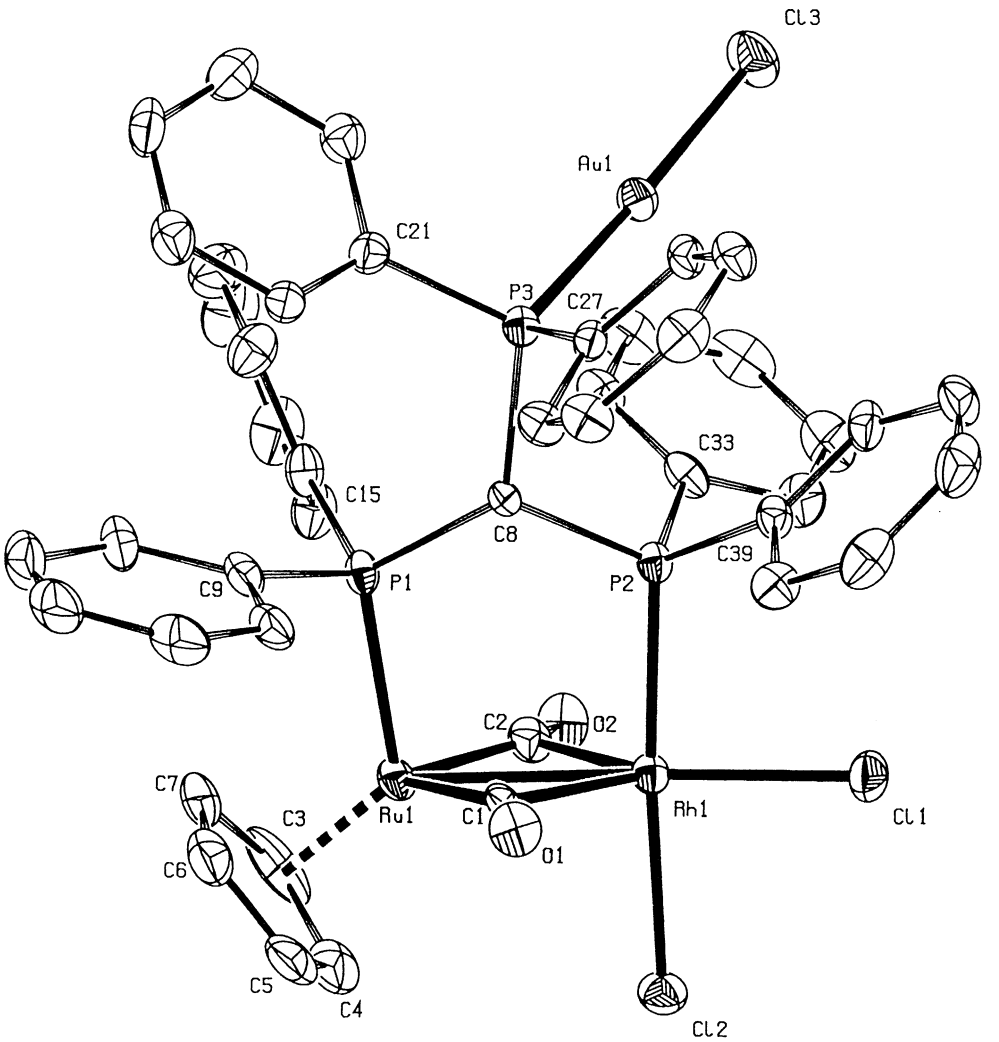

Fig. 5. The molecular structure of $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_2(PPh_2AuCl)\}RhCl_2]$.

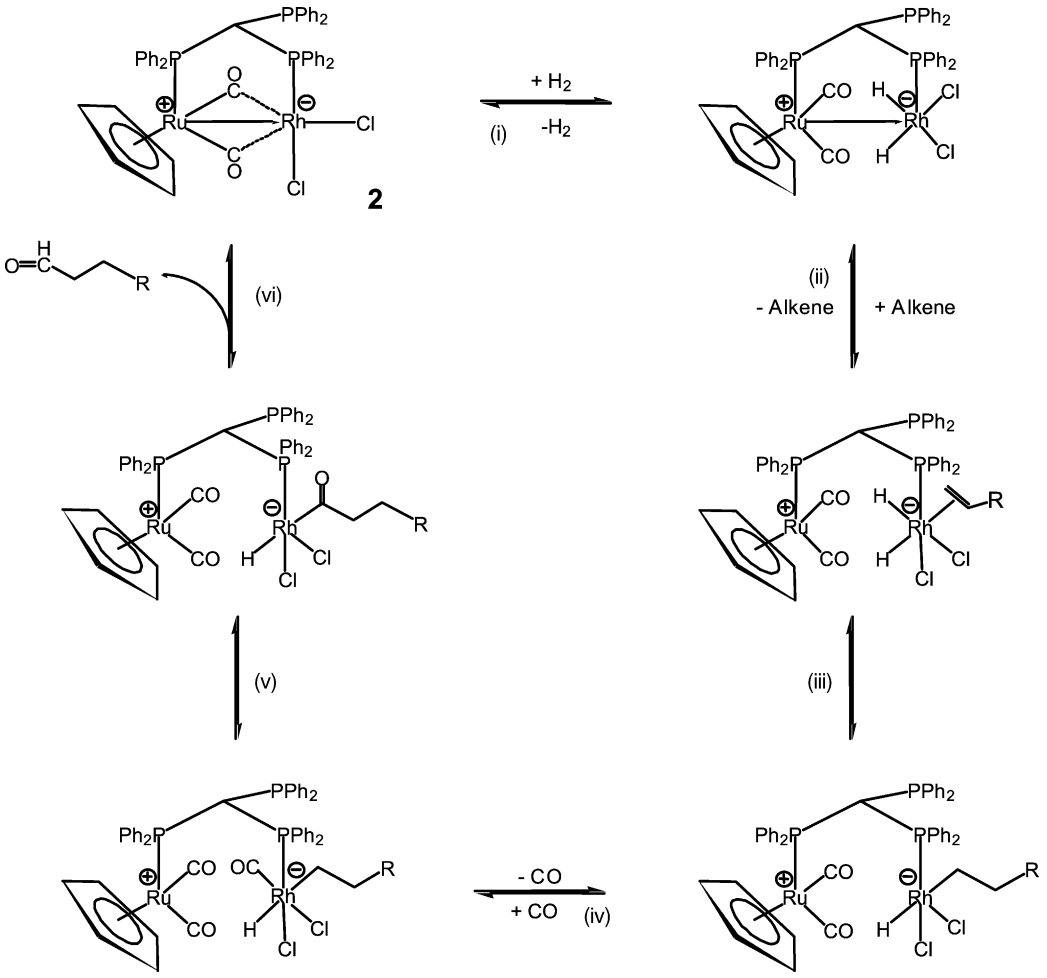

Fig. 6. Proposed mechanism for hydroformylation with the Ru centre acting as a labile ligand.

tution at the Rh centre occurs with the loss of the Ru centre as a ligand on Rh. The Rh–Ru bond is re-formed at the end of the cycle when the aldehyde is reductively eliminated. During the cycle, the two metal centres are maintained in the same complex by the bridging phosphine ligand. The same stereochemical arguments invoked for the previous mechanism to explain the *n*/*iso* ratio may be used, requiring that the coordination of the bridging phosphine ligand is maintained.

Thus, both the possible mechanisms proposed demonstrate a cooperative effect between the two metal centres.

Acknowledgements

We thank Dr. C. Copéret for his help and useful discussions during the course of this work.

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