

## Homogeneous catalysis by ruthenium carbonyl clusters

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MS received 10 October 1988; revised 18 January 1989

**Abstract.** The historical background of and the incentive for using ruthenium carbonyl clusters as homogeneous catalysts are outlined. Keeping in view the possible solutions the uncertainties arising from declusterification and metal colloid formation are discussed. All ruthenium cluster-catalysed reactions are broadly classified as reactions with or without carbon monoxide as one of the reactants and the basic differences between such reactions are highlighted. Some of the factors of special relevance to cluster-catalysed reaction systems are mentioned. The reactions involving carbon monoxide are then discussed. These include water-gas-shift reaction, carbon monoxide hydrogenation, hydroformylation, reductive carbonylation of nitrobenzene and other carbonylation reactions. Hydrogenation, transfer hydrogenation, isomerisation and a few other reactions are then discussed. For all these reactions, special emphasis is laid on well-characterised cluster complexes that have been proposed as catalytic intermediates. Finally an attempt has been made to identify the path that future research in cluster catalysis is likely to follow.

**Keywords.** Homogeneous catalysis; clusters; ruthenium; carbonyl.

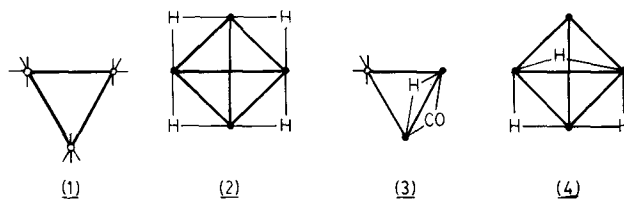
### 1. Introduction

Homogeneous catalysis by metal clusters is a promising though controversial (Collman and Hegedus 1980; Muetterties and Krause 1983) topic of current interest. This interest in evaluating the potential of carbonyl clusters as homogeneous or supported catalysts, primarily arises from the desire to use carbon monoxide or synthesis gas ( $\text{CO} + \text{H}_2$ ) for the industrial manufacture of large tonnage chemicals (Haggin 1982). However, in recent years, a number of other reactions that do not involve carbon monoxide as one of the reactants but are catalysed by carbonyl clusters have also been reported (Whyman 1980; Muetterties and Krause 1983; Marko 1986).

One of the simplest carbonyl clusters  $\text{Ru}_3(\text{CO})_{12}$  (1) has been known for more than fifty years (Manchot and Manchot 1936). However, it is only in the last ten years or so that the homogeneous catalytic applications of this and its other simple derivatives, such as  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  (2),  $[\text{HRu}_3(\text{CO})_{11}]^-$  (3),  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  (4), have been widely tested as homogeneous catalysts for a variety of reactions.

Uses of carbonyl clusters as homogeneous catalysts have been reviewed by Marko (1986). An earlier review by Whyman (1980) dealt with clusters as homogeneous catalysts and also as precursors for supported heterogeneous catalysts. Homogeneous catalysis by carbonyl and other molecular clusters has been reviewed by Muetterties and Krause (1983).

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In these and all subsequent pictures

$\times$  =  $\text{Ru}(\text{CO})_4$      $\bullet$  =  $\text{Ru}(\text{CO})_3$ . Only the  $C_{3v}$  isomer of (4) is shown.

Chart 1

## 2. Uncertainties in homogeneous catalysis by clusters

Two points of uncertainty are often associated with cluster-catalysed reactions. First of all, in most cases, it is very difficult to establish unequivocally that declusterifications leading to active mononuclear species do not take place (Collman and Hegedus 1980). Second, in catalytic systems where drastic conditions are used, the possibility of cluster breakdown leading to finely divided colloidal metal exists.

The suggestion originally made by Norton (1977) of using a chiral cluster as a catalyst for inducing asymmetry on a prochiral substrate, thereby establishing that fragmentation does not occur has been put into practice, but with inconclusive results (Pitman *et al* 1982). Other criteria including detailed kinetic analyses for identifying cluster catalysed reactions have also been proposed (Laine 1982). As will be seen for some of the recently reported catalytic systems, kinetic and other evidences do seem to suggest catalysis by intact clusters.

As far as the problem of cluster degradation to finely divided metal particles is concerned, methods other than light scattering and filtration have been proposed for distinguishing between homogeneous and heterogeneous catalysis (Collman *et al* 1984). It has been shown that polymeric substrates are hydrogenated in the presence of soluble mononuclear catalysts whereas heterogeneous catalysts are ineffective. These methods are yet to be applied to most of the cluster catalysed systems where involvement of colloidal metal is suspected.

## 3. Classification of the reactions

As already mentioned, ruthenium clusters have been used to catalyse a variety of reactions that can be broadly divided into two categories: reactions with or without carbon monoxide as one of the reactants. Hereinafter these reactions are called CO-reactions and non-CO-reactions respectively. In the beginning, a few basic differences, particularly with respect to cluster fragmentation products, between these two types of reactions are worth mentioning.

To a first approximation cluster-catalysed CO-reactions may be rationalised on the basis of elementary well-established reactions of coordinated CO. Thus, investigations into the nucleophilic activations (Ford and Rokicki 1988) of CO, reactions of  $\pi$ -CO complexes (Horwitz and Shriver 1984), and reactivities of ketylidene complexes (Geoffroy and Bassner 1988) have proved to be of considerable use in proposing reasonable mechanistic pathways for the water gas shift reaction, Fischer-

Tropsch reaction etc. On the other hand, the role of the coordinated CO in non-CO-reactions is very often that of a labile ligand. In such reactions the parent cluster loses CO, often irreversibly, to generate coordinatively unsaturated, catalytically active intermediates. The original cluster is best described as a precatalyst in these cases.

The metal to carbon monoxide ratios of the active species or isolated complexes are expected to be different in non-CO and CO-reactions. In reactions where high pressures of CO are used this ratio will be low and species such as  $\text{Ru}(\text{CO})_5$  may be expected to be involved. This in fact has been observed in carbon monoxide hydrogenation reactions involving high  $\text{CO}/\text{H}_2$  pressures with (1) as the catalyst. The mononuclear species  $\text{Ru}(\text{CO})_5$  (5) has been shown to be formed almost quantitatively (Bradley 1979). On the other hand, the irreversible loss of CO in non-CO-reactions is expected to lead to the formation of species with low carbon monoxide to metal ratio.

#### 4. Factors of special importance to catalytic systems

Several factors are known to influence the reactivity and lability of coordinated CO and any attempt to discuss all of them is outside the scope of this article. However, a very brief outline of some of the major factors considered to be of special relevance to catalytic systems need to be discussed.

Lewis acids such as  $\text{AlCl}_3$ ,  $\text{BBr}_3$  and  $\text{BCl}_3$  have been used as promoters in CO hydrogenation reactions involving carbonyl clusters of iridium and osmium (Demitras and Muetterties 1977; Choi and Muetterties 1981; Wang *et al* 1981; Collmann *et al* 1983). The addition of base is known to generate anionic clusters through the abstraction of the hydrogen atom of the intermediate hydridocarbonyl species or through the nucleophilic attack on coordinated CO by  $\text{OH}^-$ , followed by decarboxylation (Ford and Rokicki 1988).

Organic salts with tetraalkyl ammonium, phosphonium or  $[\text{PPN}]^+$  as cations activate and/or labilise the coordinated CO groups through nucleophilic attack and have been found to have remarkable effects on the conversions and selectivities of a wide range of catalytic systems (Lavigne and Kaez 1984; Kampe *et al* 1984; Knifton 1981c).

Mixed metal or heterometallic cluster may be expected to exhibit unique catalytic properties (Gladfelter and Geoffroy 1980). In some catalytic systems combinations of (1) with carbonyl complexes of other transition metals have also been reported to show enhanced activities and *inter* molecular pathways have been proposed (Whyman 1983; Dombeck and Harrison 1983).

The ability of tridentate phosphines and similar ligands to impart extra stability to the metal framework have been known for some time (Huttner and Knoll 1987; Arduini *et al* 1980). In recent years efforts have been made to synthesise and evaluate the catalytic potentials of phosphine and phosphido substituted ruthenium clusters in a systematic manner (Bianchi *et al* 1980, 1982; Bruce *et al* 1983; Basu *et al* 1985; Mani and Vahrenkamp 1985; Bergounhov *et al* 1986; Bhaduri and Sharma 1988).

Finally a coordinating solvent such as acetonitrile when used in conjunction with (1) as the catalyst may generate the known (Foulds *et al* 1984) species  $\text{Ru}_3(\text{CO})_{11}(\text{MeCN})$  (6) and  $\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2$  (7) *in situ*, thereby playing an indirect role by labilising the coordinated CO groups.

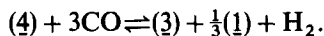
We now turn our attention to actual catalytic systems and discuss the CO-reactions first.

## 5. CO-reactions

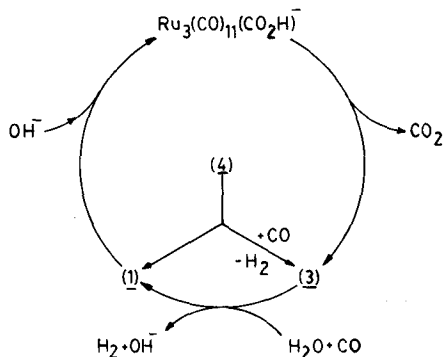
### 5.1 Water-gas shift reaction

The homogeneous catalysis of the water-gas shift reaction (WGSR) has been exhaustively reviewed recently (Ford and Rokicki 1988; Laine and Crawford 1988). A few of the well-established reactions of (1) to (4) and their relation to the WGSR systems will be discussed here. The reactions (shown in scheme 1) have all been established and are considered to be the essential steps in the catalytic cycle.

Equilibration between (3) and (4) under CO/H<sub>2</sub> (1 atm) has been shown (Bricker *et al* 1985) to exist in aprotic media as,



In accordance with this equilibrium in basic catalytic systems with (1) or (2) as the catalyst, catalytic activity decreases with accumulation of H<sub>2</sub>, and the equilibrium is shifted towards the formation of (4).



Scheme 1

In contrast, when H<sub>2</sub> is continuously removed from the system, an increase in the concentration of (3) with concomitant increase in catalytic activity is observed. The fact that under protic and WGSR conditions the mononuclear species [HRu(CO)<sub>4</sub>]<sup>-</sup> (8) is rapidly converted to (3) suggests that under the operating conditions (3) does not undergo fragmentation (Bricker *et al* 1984).

The formation of (3) from (1) is thought to involve nucleophilic attack of OH<sup>-</sup> on the coordinated CO molecule followed by decarboxylation. Recently a detailed quantitative study on these and related reactions has been reported (Gross and Ford 1985). The cluster [Ru<sub>3</sub>(CO)<sub>11</sub>(CO<sub>2</sub>Me)]<sup>-</sup> is stable under CO and has been characterised by spectroscopic methods (Anstock *et al* 1984; Taube *et al* 1987). The hydroxy carbonyl cluster [Ru<sub>3</sub>(CO)<sub>11</sub>(CO<sub>2</sub>H)]<sup>-</sup> is unstable with respect to conversion to (3) and has been characterised on the basis of its electronic spectrum which is similar to the methoxy carbonyl analogue. As already mentioned both (3) and (4)

have been characterised by single crystal X-ray diffraction studies (Churchill *et al* 1977; Jackson *et al* 1978; Johnson *et al* 1979).

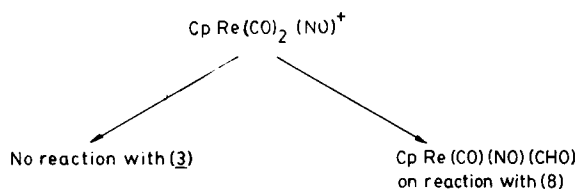
The decarboxylation reaction has been found to follow a base-independent pathway which may be interpreted as  $\beta$ -elimination with concerted transfer of the hydrogen to a metal centre. It seems fairly certain now that for WGSR system in alkaline media, ruthenium clusters rather than mononuclear catalytic intermediates are involved in the catalytic cycle.

WGSR catalysis has also been studied using group VIII mixed metal carbonyls and mixtures of group VIII metal carbonyls in pyridine solution. The clusters,  $\text{FeRu}_2(\text{CO})_{12}$  and  $\text{Fe}_2\text{Ru}(\text{CO})_{12}$  were found to be more active catalyst precursors than homonuclear clusters  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_{12}$  (Venalainen *et al* 1986). Only monosubstitution on  $\text{Fe}_2\text{Ru}(\text{CO})_{12}$  by phosphane  $\text{PPh}_3$  and phosphite  $\text{P}(\text{OMe})_3$  was found to have an enhancing effect on catalytic activity.

## 5.2 Carbon monoxide hydrogenation

The mechanistic features of CO hydrogenation reactions have been reviewed by Muetterties and Stein (1979). Though the catalytic activities of clusters in such reactions have been tested extensively, very little is known about the nature of the cluster-derived active intermediates, the bonding modes of the moieties arising from the reduction of the coordinated CO groups, or the mechanistic details of the carbon-carbon bond-forming reactions. However, owing to the enormous practical importance of CO hydrogenation reactions, empirical observations on ruthenium cluster-based catalytic systems that have been reported in the recent years are summarized in table 1.

Intermolecular hydride-transfer to coordinated CO leading to a metal formyl species has been proposed as a plausible first step for CO hydrogenation reactions. It has been shown (Dombeck and Harrison 1983) that  $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$ , a complex known to form stable formyl complexes upon reduction with boron hydrides, can react with  $[\text{HRu}(\text{CO})_4]^-$  (8) to give a formyl species (scheme 2) Cp = cyclopentadiene.



Scheme 2

On the other hand (3), a species often isolated from CO hydrogenation catalytic systems, does not have the ability to reduce the coordinated CO group of  $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$ . The mononuclear species (8) is expected to be formed from the fragmentation of (3) under high hydrogen and CO pressures. In view of this and the fact that in several of the catalytic systems  $\text{Ru}(\text{CO})_5$  has been clearly identified as the major species, it seems likely that mononuclear complexes rather than clusters are the active intermediates in most of the above described systems.

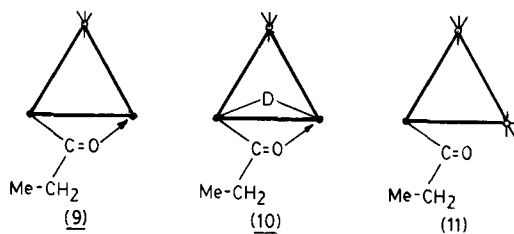


Chart 2

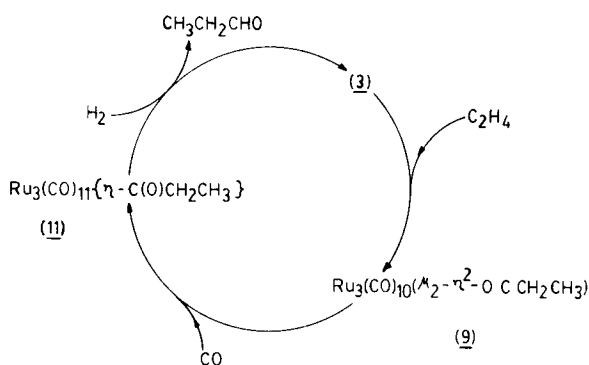
Table 1. Carbon monoxide hydrogenation reactions.

Catalytic system	Major reactants and products	Comments
<p>The precatalyst (1) in conjunction with the following acid/or halide promoters:</p> <p>(i) Onium halides and acids (Kiso and Saeki 1986; Kiso <i>et al</i> 1986; Yoshida <i>et al</i> 1987);</p> <p>(ii) Halide salts, acids and phosphine oxide (Dombeck 1980, 1981, 1983; Knifton 1981, 1983). (iii) Molten quaternary phosphonium or ammonium salts (Knifton 1981) (iv) Imidazole derivatives (Kiso and Saeki 1986; Kiso <i>et al</i> 1986, 1987; Murata <i>et al</i> 1987; Chen <i>et al</i> 1982) and amines.</p>	<p>From synthesis gas in acidic media, esters are formed. Also synthesis gas plus carboxylic acids are converted to higher homologues.</p>	<p>Catalytic species considered to be ion-pairs (Yoshida <i>et al</i> 1987). Species such as <math>[\text{Ru}(\text{CO})_3\text{I}_3]^-</math> (with <math>\text{I}^-</math> as the promoter), <math>\text{Ru}(\text{CO})_4</math> (1-alkylimidazole (with imidazole promoters), (3) and (5) have been identified in the systems (Dombeck 1980, 1981, 1983; Warren and Dombeck 1983; Kiso <i>et al</i> 1987) Note that <math>\text{Ru}(\text{CO})_5</math> has been identified as the major species in promoter-free systems also</p>
<p>In 2-methoxy ethanol, (1) as the precatalyst (Daroda <i>et al</i> 1980).</p>	<p>Hydrogenation of CO to methanol and acetone</p>	<p>Deuterium-labelling studies indicate reduction of CO is accompanied by considerable solvent reaction</p>
<p>Bimetallic systems involving the following components: (i) (1), <math>\text{Re}_2(\text{CO})_{10}</math> and halides (Kiso <i>et al</i> 1987).</p> <p>(ii) Mononuclear Ru and Rh precursors which generate carbonyl species under the reaction conditions. Molten phosphonium salts or acetic acid are used as reaction media (Knifton 1983; Whyman 1983; Pursiainen <i>et al</i> 1986).</p> <p>(iii) (1) and <math>\text{CO}_2(\text{CO})_8</math> or mixed clusters such as <math>\text{RuCO}_3(\text{CO})_{12}^-</math>, <math>\text{HRuCO}_3(\text{CO})_{12}^-</math> with halides (Dno <i>et al</i> 1987; Knifton <i>et al</i> 1984; Hidai <i>et al</i> 1983; Andrianary <i>et al</i> 1987; Jenner and Andrianary 1986).</p>	<p>Hydrogenation of CO to ethylene glycol, its ester derivatives</p> <p>Hydrogenation of CO to acetic acid and/or methanol, ethanol and their acetate esters. Also homologation of methanol of propanol</p>	<p>Both rhodium and rhenium have beneficial effects with respect to ethylene glycol selectivity. There are conflicting reports (Knifton 1983; Whyman 1983) regarding evidence for the presence of mixed Ru-Rh species during or after the reaction. Isotope-labelling studies using <math>^{14}\text{C}</math> establish that products are not solvent-derived (Whyman 1983) Species such as <math>\text{Ru}(\text{CO})_3\text{X}_3^-</math> (X = halide), <math>\text{Co}(\text{CO})_4^-</math> and (3) have been identified</p>

### 5.3 Hydroformylation

It has been shown that (3) is an active catalyst for hydroformylation of ethylene, propylene etc (Suss-Fink and Herrmann 1985; Suss-Fink and Schmidt 1987; Knifton 1987). Isotope-labelling studies on the hydroformylation of ethylene are consistent with a mechanism that involves intermediacy of intact ruthenium clusters (Suss-Fink and Herrmann 1985). Further support for such a mechanism comes from deuterium-labelling, followed by spectral characterisation of the cluster intermediate (10).

The proposed catalytic cycle for the hydroformylation of ethylene is shown in scheme 3. Species (9) can be trapped by deuteration to give (10), while (11) has been proposed as a transient intermediate (Suss-Fink and Herrmann 1985).



Scheme 3

The chemo- and regio-selectivity of the hydroformylation of propylene by (3) have also been studied as functions of solvent, temperature and pressure (Suss-Fink and Schmidt 1987). The catalyst was found to be chemospecific and independent of the reaction conditions; aldehydes were formed exclusively, no alcohols were detected in the mixture. In every case the catalyst remained unchanged in solution. Hydroformylation of the internal olefin substrate to give predominantly linear 'oxo' alcohols has been catalysed by (1) dispersed in low melting quaternary phosphonium salts as reaction media (Knifton 1987). Here again (3) is the predominant metal carbonyl species in the reaction media. These observations are consistent with the hypothetical reaction cycles as shown in scheme 3.

### 5.4 Reductive carbonylation of nitrobenzene

A number of reports have appeared on the reductive carbonylation of  $\text{PhNO}_2$  with (1) as the catalyst (Eplattenier *et al* 1970; Des Abayes and Alper 1977; Alper and Paik 1978; Alper and Amaratunga 1980; Alper and Hashem 1981; Cenini *et al* 1984, 1988; Basu *et al* 1987a). Various systems differing in detail have been described for the syntheses of  $\text{PhNH}_2$ ,  $\text{PhNHCHO}$ ,  $\text{PhNHCO}_2\text{Me}$  and  $\text{PhNCO}$  with high selectivities. It has been shown that anions such as halides, hydroxides or alkoxides have remarkable effects on the activities and selectivities of the catalytic systems (Des Abayes and Alper 1977; Alper and Paik 1978; Alper and Amaratunga 1980; Alper and Hashem 1981; Cenini *et al* 1984, 1988). Halide ions in alcoholic solvents have been shown to favour the formation of carbamate esters. However, hydroxide and

methoxide ions are known to promote the formation of  $\text{PhNH}_2$  and  $\text{PhNHCHO}$  respectively. Finally the use of a coordinating solvent such as acetonitrile has been found to give moderate yields of  $\text{PhNCO}$ .

Studies of the reactivity of metal clusters containing  $\mu_3\text{-NPh}$  ligands and of their relevance in some of these catalytic systems have recently been reported (Williams *et al* 1985, 1987; Han and Geoffroy 1986; Smieja *et al* 1986, 1987; Han *et al* 1987). Such modelling studies using fully characterised clusters to test the feasibility of proposed reaction steps, have proved to be a useful approach for rationalising hypothetical catalytic cycles.

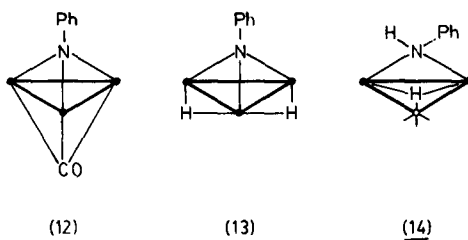
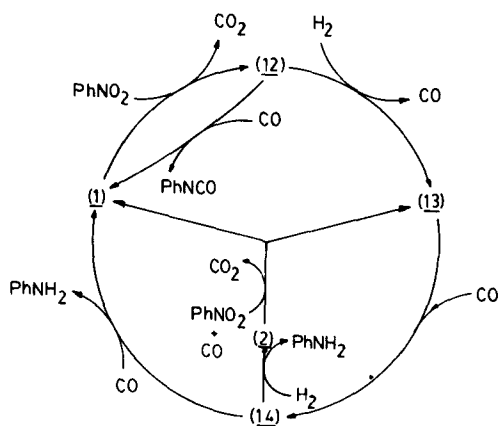


Chart 3



Scheme 4

The formation of phenyl isocyanate with  $\text{CO}$ , and aniline with a mixture of  $\text{CO}$  and  $\text{H}_2$ , may be explained by the reactions shown in scheme 4. The cluster species (2), (12), (13) and (14) are fully characterised (Sappa and Milone 1973; Wilson *et al* 1978; Bhaduri *et al* 1983).

Most of the individual reactions shown in scheme 4 have been established and as an integrated whole rationalise the formation of aniline and phenyl isocyanate in promoter-free systems (Basu *et al* 1989).

In the presence of  $\text{OH}^-$  under one atom of  $\text{CO}$ , a ' $\text{PhNCO}$ '-containing cluster  $\text{HRu}_3(\text{CO})_9(\text{PhNCO})^-$  (15), rather than the  $\mu_3\text{-NPh}$ -containing cluster  $\text{HRu}_3(\text{CO})_9(\text{PhN})^-$  (16), is considered to be the important catalytic intermediate (Bhaduri *et al* 1988; Basu *et al* 1989).

The hypothetical catalytic cycle with  $\text{OH}^-$  as the promoter is shown in scheme 5. Formation of (15) through the reaction of (3) with  $\text{PhNO}_2$  and regeneration of (1)



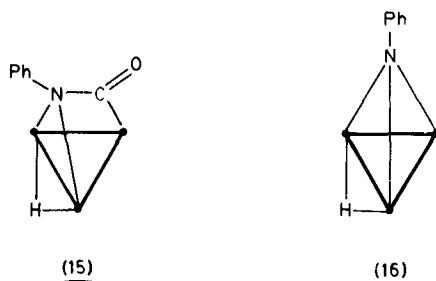
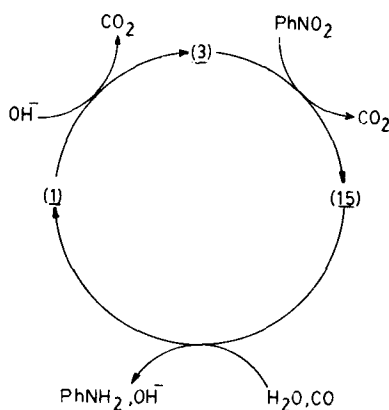


Chart 4

in the reaction between (15), water and CO are low-yield processes (Basu *et al* 1989). The pathway through which (15) is converted to a formamido cluster is not shown in scheme 5.



Scheme 5

### 5.5 Other carbonylation reactions

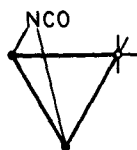
Ketones and esters have been synthesised from CO and olefins with alcohols as a source of hydrogen, using (1) and other ruthenium complexes as catalysts (Isnard *et al* 1982; Hidai *et al* 1987). Carbonylation of alcohols to acids and esters by (1)-based catalytic systems has also been reported (Bitsi and Jenner 1987; Darensbourg *et al* 1987). Carbonylation of amines, hydroamidation of olefins and some related reactions have been achieved using (1) as the catalyst (Tsuiji *et al* 1986, 1987; Bitsi and Jenner 1987; Sasaki and Dixneuf 1986). The fate of (1), and the identities of the catalytic intermediates are unknown in these catalytic systems.

## 6. Non-CO-reactions

### 6.1 Hydrogenation, transfer-hydrogenation and isomerisation reactions

Recently it has been shown that selected olefins can be rapidly hydrogenated under mild conditions (1 atm  $H_2$ ,  $25^\circ C$ ) using anion-promoted ruthenium clusters (Zuffa *et al* 1986). The anionic isocyanate derivative  $[Ru_3(CO)_{10}(\mu_2-NCO)]^-$  (17), generated

*in situ* and characterised on the basis of spectroscopic data (Fjare *et al* 1983), has been found to be the most effective catalyst.



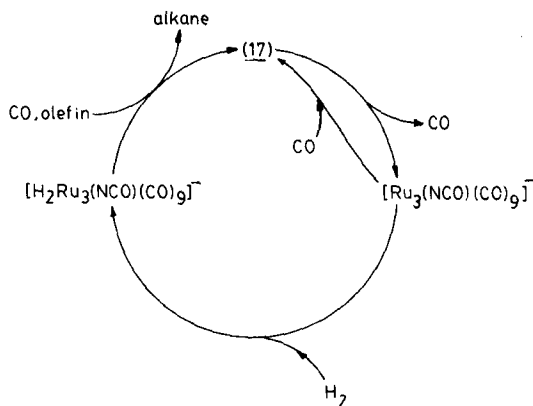
(17)

Chart 5

Spectroscopic evidence indicates that (17) is the only species that could be correlated to catalytic activity. The experimentally derived rate law for the catalysis is given by

$$\text{Rate} = k_{\text{obs}}[(17)]^{\frac{1}{2}}[\text{H}_2].$$

The observed rate law, the solvent effect, the inhibiting effect of a very small quantity of CO, and a deuterium-isotope effect of 1.7 suggest the catalytic cycle shown in scheme 6 with the oxidative addition of dihydrogen being the rate-determining step.



Scheme 6

Ruthenium clusters with doubly or triply bridging phosphido or imido ligands have been tested as hydrogenation catalysts. Thus (18)–(21) have been used as catalysts in model olefin hydrogenation reactions and recovered quantitatively. As mentioned earlier, the bridging groups are considered to impart extra stabilities to the metal framework (Bruce *et al* 1983; Basu *et al* 1985; Mani and Vahrenkamp 1985; Bergounhou *et al* 1986; Smieja *et al* 1986; Castiglioni *et al* 1988).

Unusual chemo- or regio-selectivity may be considered to be an indication of multimetal activation of the substrates. This however has not been observed for any of these reactions. However, one example has been reported (Evans and Jingxing 1985) for pent-1-ene isomerisation using ruthenium and gold mixed clusters obtained by substitution of one or two hydrogen atoms in (2) by Au(PPh<sub>3</sub>).

Unusual chemoselectivity has also been observed in the transfer hydrogenation reactions of  $\alpha$ ,  $\beta$ -unsaturated aldehydes catalysed by  $\text{H}_4\text{Ru}_4(\text{CO})_8\text{L}_4$  ( $\text{L} = \text{PR}_3$ ). In these reactions  $\alpha$ ,  $\beta$ -unsaturated alcohols are formed with high selectivities (Bhaduri

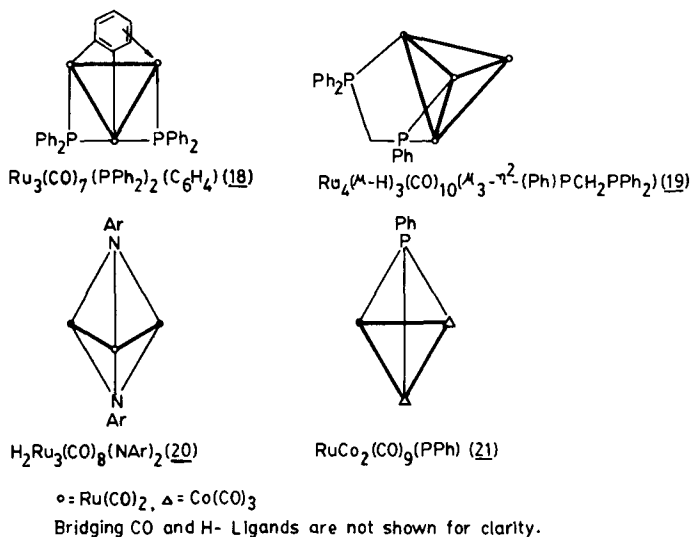


Chart 6

and Sharma 1988). Quantitative recovery of the cluster and evidences based on kinetic and deuterium-labelling studies indicate that reversible cluster fragmentation leading to active species of different nuclearities do not take place during the reactions.

Transfer hydrogenation reactions involving a wide range of acceptor and donor pairs have been reported (Bianchi *et al* 1980, 1982; Shvo *et al* 1982; Blum and Shvo 1984) to be catalysed by clusters (1)–(4) and phosphine derivatives of (2). Thus ketones, aldehydes, their  $\alpha$ ,  $\beta$ -unsaturated analogues, acetylenes, imines and nitrobenzene can be reduced using alcohols preferably isopropanol, as donors. Conversions of alcohols to esters or the coupling of diols to give polyesters and lactones have also been reported (Shvo *et al* 1982; Blum and Shvo 1984) to be catalysed by (1). In most of these systems (1) behave as precatalysts. Attempts have also been made (Bianchi *et al* 1982) to achieve enantioselective catalytic systems, by using chiral phosphine-substituted (2).

So far very few mechanistic or modelling studies have been carried out on these systems. For the reductions of benzanilide and its derivatives with isopropanol, (22) has been proposed as the active intermediate (Basu *et al* 1987b, c). From the reaction of cyclohex-1-en-2-one with (1),  $\text{Ru}_4(\text{CO})_{12}(\text{C}_6\text{H}_6\text{O})$  (23) has been obtained (Basu *et al* 1987) and found to be an active precatalyst.

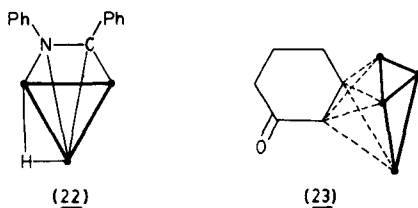


Chart 7

## 6.2 Other reactions

A number of other reactions where CO is not one of the reactants have been reported to be catalysed by ruthenium clusters. These are listed in table 2.

Table 2. Other non-CO-reactions.

Reaction	Catalyst	Reference
Transalkylation of tertiary amines	(1)	Laine (1982); Wilson and Laine (1985)
Oligomerisation of silazanes	(1), (2)	Blum and Laine (1986)
Addition of carboxylic acids to substituted acetylenes	(1)	Rotem and Shvo (1983)
Isocyanates to N-formyl ureas	(4)	Suss-Fink and Herrmann (1986)
Spirocyclization of $[\text{HRu}_3(\text{CO})_{10}(\text{SiR})_2]^-$ alkyl isocyanates	(24)	Suss-Fink <i>et al</i> (1983)
Hydrocondensation of $\text{CO}_2$ , $\text{H}_2$ in methanol to give methyl formate	(3) or (4)	Darensbourg <i>et al</i> (1982, 1987)
Hydrosilylation and silacarbonylation	(24)	Suss-Fink and Reiner (1981, 1982)
Isomerisation of vegetable oil	(1)	Basu and Sharma (1986)

The cluster anion (24) has been made from the reaction of (3) with trialkylsilanes (Suss-Fink 1982). It has been characterised on the basis of spectroscopic data and shown to have the following reversible relationship with (3).

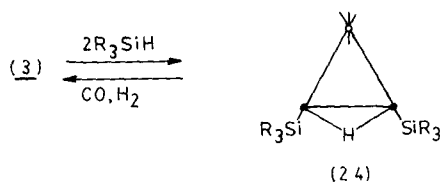


Chart 8

The mechanistic details of transalkylation reactions of tertiary amines have been probed through detailed kinetic analysis. The mechanism involves a metal cluster of at least two, and most probably three, atoms interacting with the amine through insertion into an  $\alpha$ -C-H bond to give a metallazacyclopropane or metal iminium complex. Though modelling studies on ruthenium clusters have not been carried out, interesting results have been reported on osmium clusters (Adams *et al* 1985, 1987).

## 7. Summary and outlook

It would appear from the above results and discussion that our understanding of ruthenium cluster-catalysed reactions has improved considerably in the last few years. This progress has been possible through the combined use of kinetic, modelling and other supportive studies carried out on fully-characterised cluster species. Whether or not declusterification occurs for a given cluster has been found to be dependent on the nature of and the conditions used for the particular reaction. While there is good evidence for the participation of cluster intermediates in reactions such as WGS, hydroformylation, reductive carbonylation of nitrobenzene etc., in carbon monoxide hydrogenation reactions, involvement of mononuclear species is more than likely.

In the future, progress is expected in three areas. First, novel methods of cluster activation e.g. photoactivation (Graft and Wrighton 1980; Doi *et al* 1983), use of selective reagents to generate unsaturated or reactive clusters *in situ* (Lavigne and

Kaesz 1984; Bruce *et al* 1982), will receive more attention. Second, so far most of the studies have been limited to homonuclear ruthenium clusters. It is expected that in future the use of heteronuclear ruthenium clusters in catalytic systems will increase. Finally, for complex reactions where detailed kinetic analyses are virtually impossible, modelling studies based on fully characterised cluster complexes will emerge as a viable and fruitful approach.

### Acknowledgement

The authors wish to thank IEL Limited for financial support.

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