

HOMOGENEOUS CATALYTIC HYDROGENATION, TRANSFER HYDROGENATION AND NITROBENZENE CARBONYLATION REACTIONS WITH $[\text{Ru}_3(\text{CO})_{12}]$ AS THE CATALYST*

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Use of $[\text{Ru}_3(\text{CO})_{12}]$ as a homogeneous catalyst precursor in hydrogenation, transfer hydrogenation and nitrobenzene carbonylation reactions are reported. In the nitrobenzene carbonylation reaction, on the basis of isolation and characterization of the complexes formed and their reactivity studies, participation of catalytically active cluster intermediates has been proposed. For the other two reactions although cluster intermediates have been isolated, their roles in the catalytic cycles, if any, remain uncertain.

Key Words : Catalysis; Cluster; Transfer Hydrogenation; Carbonylation

INTRODUCTION

HOMOGENEOUS catalysis with triruthenium dodecacarbonyl, $[\text{Ru}_3(\text{CO})_{12}]$ as the catalyst precursor, has attracted considerable attention in the last ten years.¹ This complex has been successfully used as a precatalyst in industrially important reactions such as Water Gas Shift Reaction, and in combination with other activators in Fischer-Tropsch reactions to give selective C_2 oxygenates.^{2,3} Other reactions that do not involve carbon monoxide as one of the reactants, but are catalysed by $[\text{Ru}_3(\text{CO})_{12}]$ or $[\text{Ru}_3(\text{CO})_{12}]$ derived complexes, such as hydrogenation, isomerisation, hydrosilylation etc., have also been reported.⁴ Two problems are however encountered in all cluster catalysed reactions, not just reactions involving $[\text{Ru}_3(\text{CO})_{12}]$ as the precatalyst. First, it is difficult to demonstrate that the catalytically active intermediates are in fact polynuclear rather than mononuclear species. Secondly, under drastic conditions the possibility of decomposition of the cluster to the metal exists. In this paper, we describe a summary of our results on the use of $[\text{Ru}_3(\text{CO})_{12}]$ and its derivatives in hydrogenation,⁵ transfer hydrogenation and nitrobenzene carbonylation reactions. Whenever possible, special attention has been paid to isolate and characterize the complexes formed in these reaction systems.

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RESULTS AND DISCUSSION

(a) *Hydrogenation Reactions*

Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with hydrogen to give $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ has been known for sometime. Use of $[\text{Ru}_3(\text{CO})_{12}]$ as a precatalyst in olefin or organic carbonyl functionality hydrogenation reactions therefore proceeds through the formation of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ as an intermediate. The catalytic activities of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ and its phosphine derivatives in hydrogenation reactions have been studied in detail by Bianchi *et al.*⁴ The desirability of phosphine-substituted clusters as precatalyst arises from the following considerations. First, the stabilities of the substituted derivatives are usually greater than that of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$; secondly, clusters substituted with chiral phosphines have been shown to be capable of influencing the enantiomeric distribution of the products. We have tested $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$, and its derivatives obtained from mild pyrolysis as precatalyst in olefin hydrogenation reactions.⁵ $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ shows low activity for the hydrogenation of cyclohexene (turnover $\sim 3 \text{ h}^{-1}$) and 2-cyclohexen-1-one (cyclohexanone $\sim 2 \text{ h}^{-1}$, cyclohexanol $\sim 1.3 \text{ h}^{-1}$) at 70°C under 25psi of hydrogen. At the end of the reactions the known hydridocarbonyls $[\text{H}_4\text{Ru}_4(\text{CO})_{12-x}(\text{PPh}_3)_x]$ ($X = 1$ to 4) could be isolated from the reaction mixture. An increase in temperature (100°C) results in significantly higher conversion in the hydrogenation of 2-cyclohexen-1-one. However, infrared spectroscopy during the reaction indicates that the catalytic intermediates in this case are not the tetraruthenium hydridocarbonyls. The carbonyl complex isolated at the end of the catalytic run is found to be $[\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)]$. While this complex shows higher catalytic activity than $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ for the hydrogenation of 2-cyclohexen-1-one, the activities for the hydrogenation of cyclohexene are comparable. An X-ray structure determination of this complex has recently been reported.⁷ Since it contains a benzyne ligand, its activity for ring hydrogenation reactions has also been tested. While it is inactive for benzene hydrogenation (100psi H_2 , 70°C), it shows low activity for the conversion of nitrobenzene to aniline (70°C , 25psi H_2 , turnover $\sim 2 \text{ h}^{-1}$). In all the catalytic reactions where $[\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)]$ has been used as the catalyst precursor, the solution i.r. spectra remain unchanged throughout the reaction, and by usual chromatographic technique the complex could be quantitatively recovered at the end of the reactions.

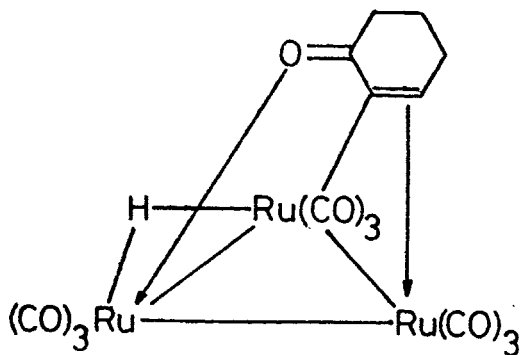
(b) *Transfer Hydrogenation Reactions*

Recently $[\text{Ru}_3(\text{CO})_{12}]$ has been reported as an active catalyst precursor for the conversion of alcohols to esters ($2 \text{ RCH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_2\text{R}$) at 145°C in the presence of a suitable acceptor such as diphenylacetylene, activated olefin or some ketones.⁸ Formation of esters proceeds through the formation of aldehydes as intermediates. Both $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ as precatalysts generate catalytic systems of equal activities and i.r. spectral studies indicate a number of carbonyl complexes to be present in both the cases. When ketonic acceptor such as cyclohexanone or acetone are used metal formation takes place. Although with Ph_2C_2 as the acceptor a catalytically active complex $[\text{Ru}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)]$ could be

isolated, the identities of all the other intermediates and the mechanism(s) of the reactions in any significant detail remain unknown.

Our preliminary results on transfer hydrogenation reactions with $[\text{Ru}_3(\text{CO})_{12}]$ as the precatalyst at a considerably lower temperature (80°C) are somewhat different. We find that ketones from secondary alcohols, and aldehydes rather than esters from primary alcohols, are formed in the presence of activated olefins as the substrate. In fact at this temperature the transfer hydrogenation works best with a secondary alcohol as the hydrogen donor and a ketone or an activated ketone e.g. 2-cyclohexen-1-one as the acceptor. In the later case stepwise formations of cyclohexanone and cyclohexanol are observed.

Reaction between $[\text{Ru}_3(\text{CO})_{12}]$ and 2-cyclohexen-1-one in cyclohexane gives tri and tetra ruthenium clusters $[\text{H Ru}_3(\text{CO})_9 (\text{C}_6\text{H}_7\text{O})]$ and $[\text{Ru}_4(\text{CO})_{12} (\text{C}_6\text{H}_8\text{O})]$. The formulations are made on the basis of analytical, mass spectroscopic and H^1 nmr data. The osmium analogue of the triruthenium species is known⁹ based on which a tentative structural formulation for this complex can be made :



The tetraruthenium species does not have any metal hydride signal in its H^1 nmr spectrum in the region of 10 to -60ppm making any definite structural assignment difficult. The reaction of this complex with isopropyl alcohol gives $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ and other uncharacterised carbonyl complexes. $[\text{Ru}_4(\text{CO})_{12}(\text{C}_6\text{H}_7\text{O})]$ acts as an active catalyst precursor while $[\text{H Ru}_3(\text{CO})_9 (\text{C}_6\text{H}_7\text{O})]$ does not. $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ or $[\text{Ru}_3(\text{CO})_{12} (\text{C}_6\text{H}_8\text{O})]$ when used as catalysts undergo conversions to mixtures containing these and other uncharacterised carbonyl species.

Addition of sodium or potassium hydroxide remarkably increases the activities of $[\text{Ru}_3(\text{CO})_{12}]$ based catalytic systems. In reactions with cyclohexanone as the acceptor and isopropyl alcohol as the donor on addition of base the turnover number for the formation of cyclohexanol goes up from $\sim 5\text{h}^{-1}$ to 50h^{-1} . Since base treatment of $[\text{Ru}_3(\text{CO})_{12}]$ is known to lead among other carbonyl complexes the formation of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{H Ru}_3(\text{CO})_{11}]^-$ the catalytic activities of these two anions have been separately tested. Both of them have been found to be highly active catalysts, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ on i.r. spectroscopic evidence is considered to remain unchanged during the reaction.

(c) *Carbonylation of Nitrobenzene*

Use of $[\text{Ru}_3(\text{CO})_{12}]$ as the precatalyst in the conversion of nitrobenzene to aniline and various other reduced products with CO as one of the reactants has recently been reported.¹⁰ We have isolated and characterised some of the intermediates that are involved in the catalytic cycles, from the reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with nitrobenzene and further reacting the derivatives thus obtained with hydrogen.¹¹

$[\text{Ru}_3(\text{CO})_{12}]$ when used as a precatalyst in the reaction between PhNO_2 and CO (160 °C, 700psi) shows moderate reactivity for the conversion of PhNO_2 to PhNCO (Turnover $\sim 5\text{h}^{-1}$). The presence of trace quantities of water gives mainly PhNH_2 and small quantities of $(\text{PhNH})_2\text{CO}$. In a dry non-protic solvent using a mixture of CO and H_2 (1 : 1) complete conversion of PhNO_2 to aniline could be effected (Turnover $\sim 20\text{h}^{-1}$).

In these reactions as long as the CO pressure is $\geq 700\text{psi}$, $[\text{Ru}_3(\text{CO})_{12}]$ is quantitatively recovered back from the reaction mixture. At lower pressures however, $[\text{Ru}_3(\text{CO})_{12}]$ is converted to a mixture of carbonyl species from which $[\text{Ru}_3(\text{CO})_{10}(\text{NPh})]$ and $[\text{Ru}_3(\text{CO})_9(\text{NPh})_2]$ could be isolated in low yields (together ~ 10 per cent). Another species which on the basis of analytical and i.r. spectral data appear to be mononuclear is formed under these conditions. $[\text{Ru}_3(\text{CO})_{10}(\text{NPh})]$ on prolonged heating at 100 °C disproportionates into $[\text{Ru}_3(\text{CO})_9(\text{NPh})_2]$, $[\text{Ru}_3(\text{CO})_{12}]$ and other uncharacterised carbonyl species.

In order to study the roles of $[\text{Ru}_3(\text{CO})_{10-X}(\text{NPh})_{X+1}]$ ($X = 0, 1$) species in the catalytic cycles, it was necessary to find alternative synthetic routes for these complexes so that the above mentioned poor yield reactions could be avoided. Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with nitrosobenzene, a possible intermediate in PhNO_2 reduction reactions, gives much better yields of the above mentioned complexes. While other nitrobenzene derivatives such as *p*-nitroanisole or *p*-dinitrobenzene also react with $[\text{Ru}_3(\text{CO})_{12}]$ to give $[\text{Ru}_3(\text{CO})_{10}(\text{NC}_6\text{H}_4\text{X})]$ ($X = \text{NO}_2, \text{OMe}$) complexes, reaction with 2,4-dinitrotoluene fails to give any isolable carbonyl complexes.

Hydrogenation of $[\text{Ru}_3(\text{CO})_{10}(\text{NPh})]$ (60 °C, 60psi) leads to the formation of $[\text{H}_2\text{Ru}_3(\text{CO})_9(\text{NPh})_2]$ cannot be hydrogenated under these conditions. However, with CO and H_2 (1 : 1) under more drastic conditions (100 °C, 200psi), $[\text{Ru}_3(\text{CO})_9(\text{NPh})_2]$ is converted into a species formulated as $[\text{Ru}_3(\text{CO})_{11}(\text{PhNH}_2)]$ on the basis of analytical, mass spectroscopic and nmr data. Furthermore, reactions of $[\text{Ru}_3(\text{CO})_{10-X}(\text{NPh})_{X+1}]$ ($X = 0, 1$) with CO (100 °C, 600psi) give $[\text{Ru}_3(\text{CO})_{12}]$ quantitatively. The reactions when monitored by g.c.-m.s. (gas chromatography with mass spectrometry) show the formation of PhNCO in both the cases. Similarly, $[\text{Ru}_3(\text{CO})_{12}]$ can be quantitatively generated back by reacting $[\text{H}_2\text{Ru}_3(\text{CO})_9(\text{NPh})]$ or $[\text{Ru}_3(\text{CO})_{11}(\text{PhNH}_2)]$ with CO (60 °C, 400psi). In both the cases elimination of PhNH_2 has been confirmed. Based on the above mentioned stoichiometric reactions a catalytic cycle as shown in Fig. 1 may be proposed for the conversion of nitrobenzene to phenyl isocyanate and aniline.

The isolation of nitrogen capped cluster complexes and the stoichiometric reactions of these derivatives are certainly indicative of participation of cluster

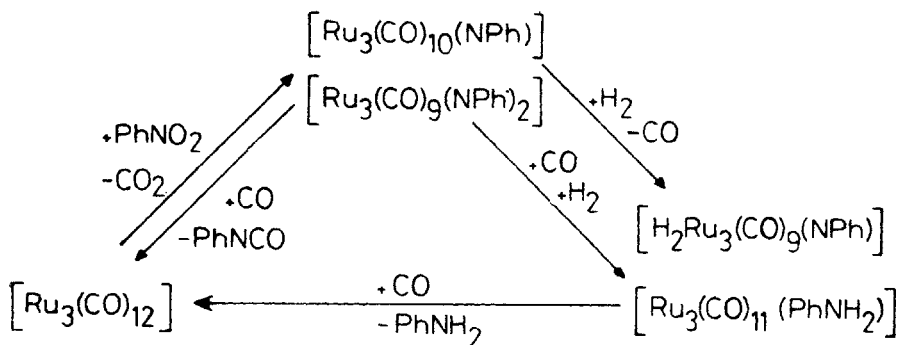


FIG 1

complexes in the catalytic cycle. A catalytic system has recently been reported for the conversion of PhNO_2 to PhNH_2 with CO and H_2O , using a combination of $[\text{Ru}_3(\text{CO})_{12}]$ and bipyridine and orthophenanthroline as the precatalyst.¹² Kinetic studies in this system definitely indicate formation of ruthenium carbonyls of lower nuclearities. In our reaction system where no water is involved, we find addition of 1, 10 phenanthroline does not have noticeable effect on the product yields. This is contrast to what is observed in the system reported by Alessio *et al.*,¹² where without addition of phenanthroline i.e. without the formation of species of lower nuclearity, very little conversion is achieved.

CONCLUSIONS

In the hydrogenation reactions with $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ as the precatalyst a number of ruthenium clusters have been isolated. So far as i.r. characteristics of the reaction systems before and after the reactions are concerned $[\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)]$, an active catalyst, has been found to remain intact.

In the transfer hydrogenation reactions with $[\text{Ru}_3(\text{CO})_{12}]$ as the catalyst precursor, a number of cluster carbonyls have been isolated but there is no definite evidence for their involvement in the catalytic cycles. The transfer hydrogenation system with base however, appear to involve $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ as the active catalyst which again on the basis of i.r. spectroscopic studies remain intact during the course of the reaction.

Although *in situ* i.r. spectroscopic studies has not been done, $[\text{Ru}_3(\text{CO})_{12}]$ used as an active catalyst for PhNO_2 carbonylation can be quantitatively recovered at the end of the reaction, thereby indicating retention of the cluster framework during the reaction. Isolation of cluster intermediates $[\text{Ru}_3(\text{CO})_{10-X}(\text{NPh})_{X+1}]$ ($X = 0, 1$), $[\text{H}_2\text{Ru}_3(\text{CO})_9(\text{NPh})]$ and their stoichiometric reactions with CO and H_2 further supports this conclusion.

EXPERIMENTAL

The catalytic experiments that require higher than atmospheric pressures were carried out in a small Parr pressure reactor. Gas-liquid chromatographic analyses was performed with a Pye-Unicam 204 instrument. G.C.-M.S. experiments were

performed with a HP 5992 unit. I.R. and nmr spectra were recorded on a Perkin Elmer 377 grating spectrophotometer and Bruker 80 MHz C.W. instrument. $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ were prepared according to literature reported procedures.^{13,6} The X-ray structures of various isolated complexes have been reported elsewhere.¹¹ Reported procedures were adopted to show that decomposition to metal particles did not take place under the reaction conditions adopted for any particular catalytic run.¹⁴

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