

Hydrogenation of non-activated alkenes catalysed by water-soluble ruthenium carbonyl clusters using a biphasic protocol

David J. Ellis ^a, Paul J. Dyson ^{a,*}, David G. Parker ^b, Thomas Welton ^{c,1}

^a Department of Chemistry, The University of York, Heslington, York YO10 5DD, UK

^b ICI Technology, Research and Technology Centre, PO Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE, UK

^c Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

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Abstract

The use of the water soluble ruthenium clusters $\text{Ru}_3(\text{CO})_{12-x}(\text{TPPTN})_x$ ($x = 1, 2$ or 3) and $\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{TPPTN})$ **4** (TPPTN = $\text{P}\{m\text{-C}_6\text{H}_4\text{SO}_3\text{Na}\}_3$) as catalyst precursors in the hydrogenation of non-activated alkenes under biphasic conditions is described. Each cluster displays activity under moderate conditions, ca. 60 atm. H_2 at 60°C, with catalytic turnovers up to ca. 500. The trinuclear clusters undergo transformation during reaction but can be reused repeatedly without loss of activity. Other methodologies such as ionic liquid–organic and the use of silica supports have been attempted with these clusters but they are less effective than the aqueous–organic regime. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of transition metal carbonyl clusters and their derivatives in homogeneous catalysis is a mature area of research and a number of prominent review articles describing their scope in this area are available [1–3]. Perhaps the most attractive feature of cluster-catalysed processes is that multicentre bond activation may take place that can give rise to different products unavailable by other homogeneous methods. This is well illustrated with reference to the

acylation of aromatic heterocycles using CO and alkenes, which is catalysed by $\text{Ru}_3(\text{CO})_{12}$ [4–6]. It is proposed that activation of the heteroatom at one metal centre and C–H activation at an adjacent metal centre. However, it has also been found that many clusters fragment into mononuclear species during catalytic cycles. This actually represents an important method for generating highly reactive unsaturated metal species that makes a viable alternative to ligand dissociation.

As with mononuclear homogeneous catalysts, the same problems associated with the separation of the catalyst from the product remain. A number of methods have been developed to help

* Corresponding author. Fax: +44-01904-432516; E-mail: pjd14@york.ac.uk

¹ E-mail: t.welton@ic.ac.uk.

facilitate separation mostly based on heterogenising the cluster by attachment to supports such as silica and alumina surfaces [7], and more recently by intrazeolite anchoring [8]. An alternative and well used approach in organometallic chemistry involves aqueous–organic biphasic catalysis in which the catalyst resides in the aqueous phase and separation of the products is achieved simply by decantation [9,10]. However, most homogeneous catalysts are not suited to an aqueous environment and ligands, which induce hydrophilicity, have been developed to circumvent this problem. In this respect, tris(3-sulfonatophenyl)phosphine trisodium salt (TPPTN), is one of the most widely encountered [11] and transition metal catalysed hydrogenation or reduction reactions in water using this ligand, and others, have been reviewed [12]. A number of clusters have already been rendered water soluble using this ligand [13,14]. In this paper, we report on the use of some ruthenium clusters as catalyst precursors for the hydrogenation of non-activated alkenes under biphasic reaction conditions.

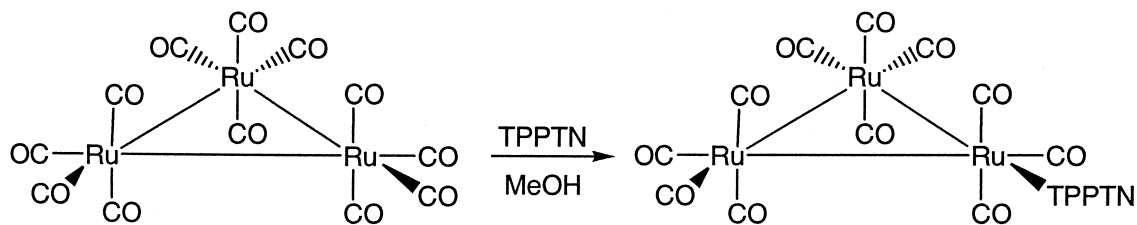
2. Results and discussion

The synthesis and characterisation of a series of water soluble ruthenium clusters, $\text{Ru}_3(\text{CO})_{12-x}(\text{TPPTN})_x$ (where $x = 1$ **1**, 2 **2** or 3 **3**) and $\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{TPPTN})$ **4**, has been reported previously [13,14]. They are prepared in near-quantitative yield from the reaction of $\text{Ru}_3(\text{CO})_{12}$ or $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with the water soluble phosphine $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (TPPTN) in

the appropriate stoichiometry, by heating in methanol under reflux for a few hours (see Scheme 1 as an example).

Related non-aqueous ruthenium clusters have been shown to act as catalyst precursors for the hydrogenation of alkenes [15–19] and therefore we decided to investigate whether clusters **1–4** were suitable catalysts for the hydrogenation of non-activated alkenes under biphasic liquid–liquid conditions. A range of hydrogenations were carried out using clusters **1–4** and they were performed repeatedly to ensure that consistent results were obtained. Catalytic turnovers were assessed using ^1H NMR spectroscopy together with GC analysis, and the turnovers were calculated as the number of moles of substrate converted per mole of catalyst per hour and do not take into account whether fragmentation into mononuclear species takes place. The results for some hydrogenations using clusters **1–4** under aqueous-organic biphasic conditions are listed in Tables 1 and 2. The organic phase consists of the neat substrate and no co-solvents or phase transfer reagents were employed.

Hydrogenation of the alkenes proceeds well at pressures of ca. 60 atmospheres at 60°C . While the turnovers appear low it is worth noting that non-activated alkenes such as these are extremely difficult to hydrogenate using clusters. All four clusters show similar catalytic activity and were inactive in the hydrogenation of aromatic compounds. With the triruthenium clusters, **1–3**, turnovers increased slightly as the number of phosphine ligands increased. Since the nature of the cluster changes during reaction (see below) it is possible that the turnovers



Scheme 1. Synthesis of $\text{Ru}_3(\text{CO})_{11}(\text{TPPTN})$; the other clusters are prepared in a similar fashion.

Table 1
Hydrogenations of alkene substrates using $\text{Ru}_3(\text{CO})_{11}(\text{TPPTN})$ **1**

Substrate	Reaction conditions	Catalyst solution	Moles of substrate/ mole of catalyst	% Conversion of substrate	Catalytic turnover ($\text{mol mol}^{-1} \text{ h}^{-1}$)
Cyclohexene 10 ml	60 atm H_2 60°C 24 h	50 mg in 50 ml H_2O	2330	49% Cyclohexane	48
1-Octene 5 ml	60 atm H_2 60°C 16.5 h	30 mg in 5 ml H_2O	1250	100% Octane	76
1-Decene 5 ml	60 atm H_2 60°C 7 h	30 mg in 30 ml H_2O	1040	21% Decane	32
Styrene 25 ml	60 atm H_2 60°C 17.5 h	30 mg in 10 ml H_2O	8570	100% Ethyl Benzene	490
Benzene 5 ml	90 atm H_2 120°C 24 h	40 mg in 10 ml H_2O	1650	66% Cyclohexane	45

^aComplete decomposition of catalyst to insoluble black material occurred.

increase as all the fragmentation products in $\text{Ru}_3(\text{CO})_9(\text{TPPTN})_3$ remain hydrophilic as each Ru-centre has a water-solubilising phosphine ligand attached. Under more forcing conditions, $\text{Ru}_3(\text{CO})_{11}(\text{TPPTN})$ was found to hydrogenate benzene, but it was subsequently found that colloidal ruthenium was the active catalytic species. Previous studies have shown that oxidation of the phosphine to the oxide may take place and the phosphine oxide stabilises colloidal particles [20]. Cluster **1** was also used to hydrogenate styrene to ethylbenzene and the turnover for this is somewhat higher than that of the other alkenes; this is due to the activating influence of the phenyl ring. The most notable difference between clusters **1–3** and the tetra-ruthenium-hydrido cluster **4** is the increased turnover for the hydrogenation of cyclohexene. In general, all the turnovers were rather disappointing, although similar in magnitude to related single-phase cluster systems. However, there is no loss of catalytic activity with repeated use of catalysts **1–4** and this is illustrated in Fig. 1 for cluster **1**. In addition, there is not loss of ruthenium from the system, which clearly

has potential economic and environmental benefits.

Spectroscopy reveals that **4** remains unchanged after separation from the post reaction mixture, however, fragmentation during reaction cannot be ruled out. $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ was found to be the active species when the trinuclear cluster $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_8\text{H}_{12})$ is used as the catalyst precursor for the hydrogenation of 1-hexene [15]. Attempts to increase catalytic turnovers using co-solvents, that have previously been demonstrated to increase activity in biphasic reactions [21], did not give rise to higher activities. In addition, the presence of phase transfer agents such as large cations merely precipitated the cluster from solution.

Fragmentation of $\text{Ru}_3(\text{CO})_{12-x}(\text{TPPTN})_x$ (where $x = 1$ **1**, 2 **2** or 3 **3**) into catalytically active mononuclear species during reaction takes place. Increasing the concentration of the cluster does not increase the catalytic turnover and this may be ascribed to cluster fragmentation [22]. In addition, clusters **1–3** are red in colour while the compounds extracted after reaction, while remaining water soluble, are brown. The brown

Table 2
Hydrogenations of alkene substrates using clusters **2–4**

Substrate/catalyst	Reaction conditions	Catalyst solution	Moles of substrate/ mole of catalyst	% Conversion of Substrate	Catalytic turnover ($\text{mol mol}^{-1} \text{ h}^{-1}$)
Cyclohexene 10 ml/ 2	60 atm H_2 60°C 24 h	30 mg in 10 ml H_2O	2660	35% Cyclohexane	39
1-Octene 10 ml/ 2	60 atm H_2 60°C 23 h	50 mg in 10 ml H_2O	2190	100% Octane	95
Cyclohexene 5 ml/ 3	60 atm H_2 60°C 17 h	20 mg in 10 ml H_2O	5580	23% Cyclohexane	74
1-Octene 10 ml/ 3	60 atm H_2 60°C 17 h	30 mg in 10 ml H_2O	4800	22% Octane	61
Cyclohexene 10 ml/ 4	60 atm H_2 60°C 4 h	40 mg in 10 ml H_2O	3170	32% Cyclohexane	252
1-Octene 10 ml/ 4	60 atm H_2 60°C 8 h	40 mg in 10 ml H_2O	1980	16% Octane	40

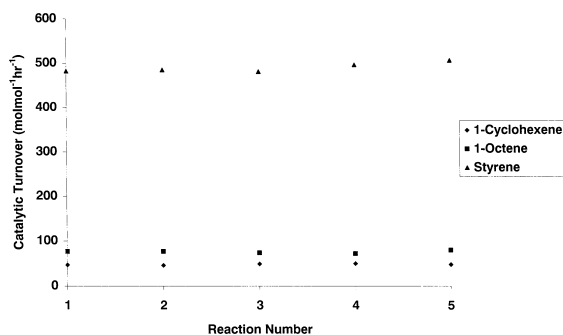


Fig. 1.

compounds are air stable and show similar catalytic activity as the precursors even after repeated use. It has not been possible to fully characterise the brown compounds. The IR spectra (ν_{CO}) for these compounds are similar regardless of the substrate employed in the hydrogenation; the carbonyl stretching frequencies merely move to slightly lower wavenumbers. This could be due to any of several phenomena including the formation of substitution products, reduction to anions or degradation into lower nuclearity species. NMR spectroscopy and electrospray mass spectrometry were used to try and delineate which of these transformations had occurred. The ^1H NMR spectra of the samples showed a very similar range of peaks due to the phenyl rings of the ligand in the range of 7.3–8.5 ppm and no evidence of coordinated alkenes, alkyls or hydride ligands was found. ^{31}P NMR spectroscopy also showed that changes had taken place but it was not possible to make any assignments. The ESMS of clusters **1–3** have been reported previously [14]. Anions corresponding to the intact parent ion in which one sodium cation has been lost are readily identified where low cone voltages are applied. No fragmentation is observed unless the cone voltage is increased and, as such, the technique is very sensitive to identifying impurities. The post-reaction samples of **1** to **3** only showed ligand based peaks. Cleavage of the P–C bond with the formation of P–O bonds has been noted before and similar behaviour cannot be ruled out here [23].

Ionic liquids represent an alternative series of catalyst support solvents to water, which are immiscible with a wide range of organic solvents [24]. A variety of air and moisture stable systems have been developed that are liquid at ambient temperatures and this has led to their deployment in a number of processes [25]. We found that transition metal–carbonyl complexes and clusters react in chloroaluminate(III) ionic liquids and the products obtained have yet to be fully characterised. As we have recently obtained some interesting results concerning the hydrogenation of arenes with a cationic ruthenium cluster catalyst in the air stable ionic liquid $[\text{bmim}][\text{BF}_4]$ {where $[\text{bmim}]^+$ = the 1-butyl-3-methylimidazolium cation} [26] we attempted to investigate the reactivity of clusters **1–4** in this solvent. Unfortunately, the clusters were only sparingly soluble and catalytic activity was extremely low. In addition, we have anchored cluster **1** to silica but this was found to be a less effective catalyst than when used under aqueous–organic conditions.

3. Experimental

The clusters $\text{Ru}_3(\text{CO})_{12-x}(\text{TPPTN})_x$ (where $x = 1$ **1**, 2 **2** or 3 **3**) and $\text{Ru}_4(\text{CO})_{11}(\text{TPPTN})$ **4** were prepared according to the literature methods [14]. Infrared spectra were recorded using a Mattson Research Series 1 FTIR instrument. NMR spectra were recorded on a JEOL JNM-EX270 FT-NMR instrument. ES-MS were recorded using a VG Platform II mass spectrometer using water as the mobile phase at a flow rate of 0.1 ml min^{-1} . Nitrogen was used as the nebulising and drying gas. Samples were introduced as aqueous solutions, and spectra were recorded with skimmer cone voltages between 10 and 50 V. GC were obtained on a Perkin-Elmer Autosystem instrument using a Perkin-Elmer stainless steel column (2 m) packed with 5% Carbowax 20M on Chromasorb WHP AW (DCMS treated) using *n*-decane as an internal standard.

Hydrogenations were carried out in a Parr stainless steel autoclave (300 ml) fitted with either a glass or PTFE liner. The water soluble catalyst in use was added directly to the autoclave followed by addition of the required amount of degassed water. The autoclave was then sealed, purged with nitrogen and then the substrate was added through the liquid inlet port via a syringe. The autoclave was then purged thoroughly with hydrogen gas (99.9995% purity) and the appropriate reaction pressure was then set at room temperature. The autoclave was then heated to the required reaction temperature and stirring was commenced for the period required. After reaction, the autoclave was allowed to cool and the pressure released. The contents were then separated into organic and aqueous phases for analysis. ^1H NMR and GC were used to assess catalytic turnovers. Where required, mercury (ca. 1 ml) was also added to act as a selective poison to colloids that might be produced in situ during the course of the reaction.

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