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Olefin hydrogenation and isomerization catalysed by $Ru_3(CO)_{12}$ and its derivatives. Cluster *vs.* non-cluster catalysis

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Abstract

The systems $Ru_3(CO)_{12} \cdot nL$, ($L = PPh_3$, CH_3CN, $(EtO)_3Si(CH_2)_3NH_2$; $n = 0–3$, 15) have been employed as catalysts and/or catalyst precursors for thermal hydrogenation and isomerization reactions of 1-octene under moderate reaction conditions (1 atm at 70°C or below). In the hydrogenation reaction the system $Ru_3(CO)_{12}/15CH_3CN$ showed the highest activity, with turnover numbers up to 1000. For this system the kinetics indicated that the hydrogenation occurs via a lower nuclearity catalytic species formed by fragmentation of the mother cluster. On the other hand the isomerization reaction occurs, after a 10–20 min induction period, by higher-nuclearity catalytic species. The isomerization gave *trans*-2-octene only, and none of the *cis*-isomer. The effects of other factors on the rates of hydrogenation and isomerization reactions are described.

1. Introduction

The use of metal- and mixed-metal atom clusters as catalysts for thermal and photochemical reactions is attracting increasing interest [1]. Industrially important processes such as hydroformylation [2], hydrogenation [3] and isomerization [4] reactions have been reported to be promoted by clusters as catalysts and/or catalyst precursors.

The complex $Ru_3(CO)_{12}$ (1) and its derivatives have been reported to be catalysts for olefin hydrogenation reactions under relatively high pressures of H_2 (*ca.* 20 atm or higher) [3,5–7]. Spectroscopic analysis of the catalytic solutions after the reactions showed that the cluster remained unchanged. However, these observations cannot be regarded as cluster catalysis since the catalysis may involve lower nuclearity fragments that are present in very low concentrations and may recombine to yield the mother cluster after completion of the reaction.

We report below our studies of the hydrogenation and the isomerization of 1-octene under relatively mild conditions, (70°C, 1.0 atm), conditions chosen to avoid cluster fragmentation as far as possible. Laine's kinetic criterion [8] has been employed to check whether catalysis involves the intact cluster or higher- or lower-nuclearity species.

2. Experimental details

All chemicals and solvents were purchased from Aldrich Chemical Company Ltd. The infrared spectra were recorded on a Pye Unicam SP 2000 spectrophotometer.

Catalytic reactions were carried out in a 50 ml three-necked round-bottomed flask equipped with a suba-seal stopper, a hydrogen bubbler and a magnetic stirrer, and contained in a thermostated bath. A well-cooled condenser was used to prevent evaporation of components of the reaction mixture. Hydrogenation and isomerization reactions were carried out together in the same reactor.

In a typical catalytic experiment the thermostated reactor was charged with the cluster, the added ligand, the solvent (sufficient to make the total volume 10.0 ml) and the internal standard benzene (5.0 ml). Hydrogen gas was slowly but continuously bubbled (flow rate 2.0 ml min^{-1}) through the stirred mixture, with the pressure in the vessel kept at 1.0 atm. The olefin was then syringed in through the suba-seal stopper.

The choice for benzene as a standard reference was not arbitrary. Benzene has a sharp IR band at 1960

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cm^{-1}, which is in the working range of our measurements; since this band is weak, large amounts (5.0 ml) of benzene were used, and this enabled reproducible measurement of the 1960 cm^{-1} band. Despite the precautions taken to prevent evaporation, it is possible that a little benzene is flushed out of the vessel, but the amounts are insignificant relative to the total quantity present.

The progress of each reaction was monitored by withdrawing at intervals small aliquots of the mixture, immediately chilling them in small stoppered tubes, and subjecting them to IR analysis. The rate of the isomerization was determined from the rate of increase in intensity of the IR band at 960 cm^{-1} (for *trans*-2-octene) relative to that from the internal standard at 1960 cm^{-1}. The rate of the hydrogenation was given by the rate of disappearance of 1-octene, as judged from the change in intensity of the band at 1650 cm^{-1} relative to that from the internal standard at 1960 cm^{-1}, and subtracting the rate of appearance of *trans*-2-octene. For all measurements the appropriate calibration curves were determined.

Results and discussion

3.1. The hydrogenation reaction

Cluster **1** did not on its own catalyse the 1-octene hydrogenation reaction under the conditions used (Table 1). Addition of PPh_3 to the cluster significantly increased the rate of reaction, as can be seen from Table 1. For various ratios **1**/$nPPh_3$, that with $n = 3$ showed the highest activity, with turnover numbers of up to 450 within 100 min. The formation of the deep red species $Ru_3(CO)_9(PPh_3)_3$ by direct reaction of **1** with $3PPh_3$ has been reported [9]. The ligand $(EtO)_3Si(CH_2)_3NH_2$ was tried owing to its ability to act as a linkage ligand; it did not activate the hydrogenation but did activate the isomerization as shown in Table 1.

Addition of the ligand CH_3CN significantly enhanced the rate of hydrogenation. High turnover numbers (up to 1000 within 50 min) were obtained for the **1**/$15CH_3CN$ system (Table 1). The addition of CH_3CN to the yellow solution of **1** gave a dark-orange colour corresponding to that of $Ru_3(CO)_{11}(NCMe)$ (**2**) [10], but as the reaction proceeded the colour gradually changed to a light yellow, corresponding to that of $Ru_3(CO)_{10}(NCMe)_2$ (**3**) [11]. Use of a 15-fold excess of the ligand CH_3CN is necessary to protect the cluster **3** [10]. Working with catalytic concentrations (about 1.0×10^{-3} M or lower) of **3** it was not easy to see all IR bands characteristic of this cluster. The band at *ca.* 2018 cm^{-1} could be observed, however, since it is known to be a relatively very strong band [10].

Due to its high activity and selectivity towards hydrogenation, the **1**/$15CH_3CN$ catalytic system was employed throughout all of this work unless otherwise stated. Clusters **2** and **3** are known to react with unsaturated hydrocarbons such as phenylacetylene [10–12].

None of the catalytic systems described above showed any activity in the hydrogenation of internal olefins such as *trans*-2-octene.

In hydrogenation of 1-octene the catalytic system **1**/$15CH_3CN$ showed markedly higher activity than other reported systems of similar nature. Other catalysts required higher H_2 pressures. Süss-Fink reported that ethylene and propylene were hydrogenated in the presence of $HRu_3(CO)_{11}^-$ under 20 bar of H_2 with turnover numbers of 350 and 255, respectively, within

TABLE 1. Effect of type of added ligand on the hydrogenation reaction of 1-octene [a]

Entry	L	1/L	Turnover number values with time (min)							
			10	15	20	30	40	50	60	100
1	None	1/0	0	0	0	0	0	0	0	0
2	PPh_3	1/3	36		428					450
3	PPh_3	1/4	0	0	0	0	0	0	54	
4	PPh_3	1/5	0	0	0	0	0	0	0	0
5	PPh_3	1/9	0	0	0	0	0	0	0	0
6	RNH_2 [b]	1/1	0	0	0	0	0	0	0	0
7	RNH_2	1/0.5	0	0	0	0	0	0	0	0
8	RNH_2	1/2	0	0	0	0	0	0	0	0
9	CH_3CN	1/1		435			447			
10	CH_3CN	1/3			99					237
11	CH_3CN	1/15	352		703	857	978			
12	CH_3CN	1/20			205				415	

[a] Reaction conditions: dioxane (2.65 ml)/benzene (5.0 ml), H_2 (1.0 atm), 1-octene (2.35 ml, 1.5 M), at 70°C, using **1** (0.01 g, 1.56×10^{-3} M).
[b] $R = (EtO)_3Si(CH_2)_3$–.

TABLE 2. Effect of type of solvent on olefin hydrogenation reaction using **1**/CH_3CN (1/15) catalytic system [a]

Entry	Solvent	Turnover number values with time (min)			
		10	20	30	40
1	dioxane/benzene	352	703	857	978
2	THF/benzene	128			230
3	heptane/benzene		64	64	
4	DMSO/benzene	0	0	0	0
5	CCl_4/benzene	0	0	0	0

[a] Reaction conditions: 1-octene (2.35 ml, 1.5 M), H_2 (1.0 atm), benzene (5.0 ml), solvent (2.65 ml), **1** (0.01 g, 1.546×10^{-3} M) and CH_3CN (23.46×10^{-3} M) at 70°C.

15 h, [7]. In our work, complex **2** showed turnover numbers of up to 1000 within only 50 min. It should be noted, however, that in our work the 1-octene hydrogenation was accompanied by isomerization to yield *trans*-2-octene (*vide infra*). Despite this complication, the high activity makes the catalyst potentially valuable for industrial purposes.

The hydrogenation was carried out in various solvents (Table 2). The rate of the reaction fell in the order: dioxane > THF > heptane ≫ DMSO, CCl_4. The trend does not show any significant effect of the polarity of the solvent, probably because of the dominance of benzene (5.0 ml) in the solvent mixture.

The effect of change in temperature on the rate of the hydrogenation was studied in the range 55–70°C. Below 50°C, no hydrogenation reaction was detected. From plots of ln (initial rates) against 1/*T* (K) the activation energy was calculated and found to be 69.2 kJ/mol.

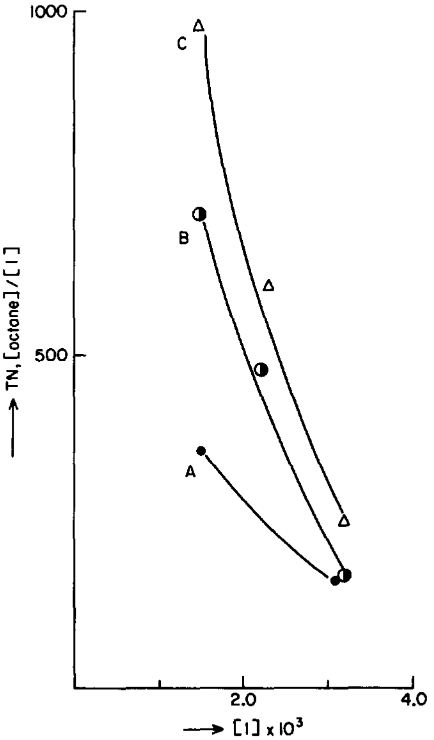

Fig. 1. Plots of TN values *vs.* [**1**] for the hydrogenation reaction of olefin at 70°C in dioxane (2.65 ml)/benzene (5.0 ml) using H_2 (1.0 atm) and 1-octene (2.35 ml). (a) After 10.0 min; (b) after 20.0 min; (c) after 40.0 min. 1/15CH_3CN systems were used.

To see if the hydrogenation reaction involved intact cluster or fragment catalytic species, Laine's kinetic criteria [8] were used. Plots of turnover number (TN) values *vs.* cluster concentration at various reaction times were constructed, and are shown in Fig. 1. Curves a–c show that as the cluster concentration is increased, there is a steep decrease in the TN value. Even though the reactions were conducted under relatively mild conditions (70°C, 1.0 atm), the plots clearly indicate

TABLE 3. Effect of type of added ligand on the olefin isomerization reaction [a]

Entry	L	1/L	Turnover number values with time (min)							
			10	15	20	30	40	50	60	100
1	None	1/0	51		307	530				
2	PPh_3	1/3	600		1100					
3	PPh_3	1/4	0	412	677	970			1132	
4	PPh_3	1/5	0	0	0	0			0	
5	PPh_3	1/9	0	0	0	0	0	0	0	
6	RNH_2 [b]	1/1	0	0	77	330		700		
7	RNH_2	1/0.5	205	364						
8	RNH_2	1/2	0	0	0			531		772
9	CH_3CN	1/1	0				805		1070	
10	CH_3CN	1/3	0	0	19	307	384			818
11	CH_3CN	1/15	0	116	160	160	160		160	
12	CH_3CN	1/20	0	0	434				780	

[a] Reaction of conditions: same as those in Table 1. [b] R = $(EtO)_3Si(CH_2)_3$–.

that catalysis occurred by lower nuclearity fragment species, not by an intact cluster.

These results are in accordance with earlier reports. It was observed [16] that **1** fragments into mono- and di-nuclear derivatives when exposed to unsaturated hydrocarbons at 80°C or above. However, at temperatures below this **1** is not affected by olefins. In our work the susceptibility of **2** towards olefins at temperatures below 80°C is presumably due to the effect of CH_3CN; as stated earlier, this ligand activates **1** towards reactions with olefins [13,17].

Fully detailed kinetic and other mechanistic studies have yet to be carried out. However, use of the method of initial rates gave a reaction order of -2.0 with respect to 1-octene (for 1-octene concentrations of < 2.0 M and $\mathbf{1}/15CH_3CN$ concentration of 1.546×10^{-3} M, in dioxane/benzene at 70°C, at H_2 1.0 atm).

3.2. *The isomerization reaction*

In the absence of H_2 and other added ligands, **1** showed no significant catalytic activity for the 1-octene isomerization. Under 1 atm H_2, the isomerization occured without any hydrogenation in the absence of ligands (Table 3). Turnover numbers of up to 530 within 30 min were obtained. These results suggest that H_2 activates **1** as a catalyst in the isomerization reactions, in accordance with other reports [3,5,10,13–15]. Complex **1** by itself is known not to activate olefins under the conditions we used. When certain other additives are present, such as Et_3SiH, Ph_2PH, PPh_3 and CH_3CN, **1** does catalyse the isomerization. In our work, the sole product of the isomerization was *trans*-2-octene.

Table 3 shows the range of ligands tested. For the $\mathbf{1}/n PPh_3$ system, the rate of isomerization reaction varied in the order $1/n = 1/4 > 1/3 \gg 1/5, 1/9$. The ligand $(EtO)_3Si(CH_2)_3NH_2$ also enhanced the rate of isomerization when used in a 1/1 ratio. This could be potentially useful for studies of the catalytic behaviours of **1** supported on solid surfaces. Work is now in progress here to study the effect of poly(siloxane)-supported **1** in olefin isomerizations and hydrogenations with this ligand providing the linkage to the surface.

The activating effect of CH_3CN on **1** for the isomerization reaction is less than that of PPh_3. In fact, CH_3CN activated the hydrogenation more than the isomerization reactions. It is noteworthy that the ligands PPh_3 and $(EtO)_3Si(CH_2)_3NH_2$ selectively activate in the isomerization reactions, whereas CH_3CN selectively activates the hydrogenation. Therefore, by appropriate choice of ligand it may become possible to control the direction taken by the reaction.

The isomerization reaction was studied concurrently with the hydrogenation reaction. Since the catalyst $\mathbf{1}/15CH_3CN$ showed highest activity in hydrogenation, it was also used for the isomerization unless otherwise stated.

TABLE 4. Effect of solvent on olefin isomerization using $\mathbf{1}/CH_3CN$ (1/15) [a]

Entry	Solvent	Turnover number values with time (min)							
		10	15	20	30	40	50	60	100
1	dioxane/benzene	0	0	116	160	160	160		
2	THF/benzene	0		217		600			
3	heptane/benzene	0	339	614	1151				
4	DMSO/benzene	0	0	0	0	0	0		
5	CCl_4/benzene	0	0	0	0	0	0		

[a] Reaction conditions: same as those in Table 2.

Table 4 shows the effect of solvent on the isomerization reaction. Dioxane, which was good as a solvent for the hydrogenation reaction, was not good for isomerization. On the other hand, heptane was not good for the hydrogenation but was good for the isomerization. Thus the direction of the reaction may also be controlled by choice of solvent.

Table 5 shows that the isomerization was faster at higher temperatures. At temperatures below 50°C, no isomerization was detected.

Plots of turnover numbers *vs.* cluster concentration were constructed. Figure 2 shows that the TN value (after 20 min) increases with increasing cluster concentration. This means, in accord with Laine's criteria [2,8], that the isomerization reaction involves higher nuclearity cluster catalytic species.

The formation of higher nuclearity clusters is presumably due to combination of lower nuclearity species with remaining mother cluster species. This would account for the fact that, unlike hydrogenation, the isomerization reaction involved relatively prolonged induction times (10–20 min), during which the higher nuclearity cluster species are being formed. Higher nuclearity cluster species such as $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ have been reported to be effective cata-

TABLE 5. Effect of temperature on olefin isomerization reaction [a]

Entry	*T* (°C)	Turnover number values with time (min)							
		10	15	20	30	40	50	60	100
1	70	0	0	116	160	160	160		
2	65	0	0	0		90		185	
3	60	0	0	0	0				430
4	50	0	0	0	0				0
5	40	0	0	0	0				0

[a] Reaction conditions: same as those in Table 4.

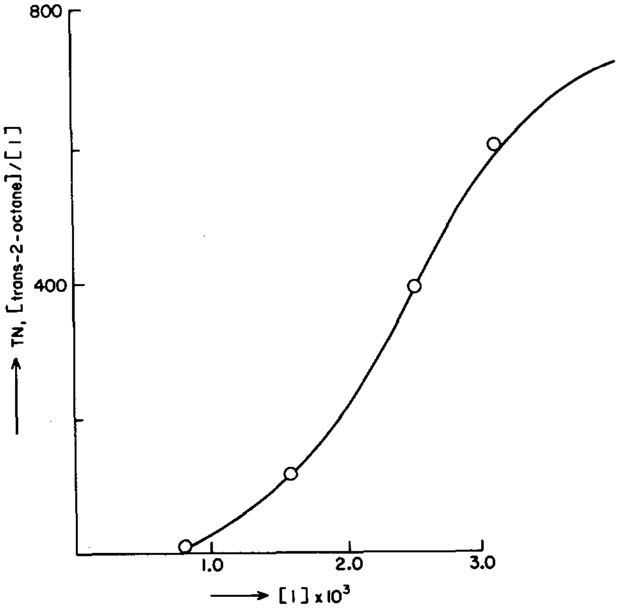

Fig. 2. A plot of TN values *vs.* [**1**] for the isomerization reaction of 1-octene (2.35 ml, 1.5 M) at 70°C in dioxane (2.65 ml)/benzene (5.0 ml) using H_2 (1.0 atm) after 20.0 min. **1**/15CH_3CN systems were used.

lysts for isomerization of terminal olefins [18]. Furthermore, formation of higher nuclearity cluster species, such as $Ru_6(CO)_{17}C$ and $Ru_6(CO)_{14}C$, from **1** when heated in aromatic hydrocarbons has been reported [19–21].

The IR and the visible spectra of the catalytic mixture showed no detectable change during the course of the reaction. This indicates that only a small fraction of the cluster molecules dissociate to give species that catalyse the hydrogenation. Consequently, the higher nuclearity species, which presumably catalyse the isomerization reaction, must be present in even lower concentrations.

Mechanistic studies of cluster catalysis of isomerization of terminal olefins have been reported [22] but are beyond the scope of the present communication. Studies of mechanistic aspects of **1**/ligand systems as homogeneous and as supported catalysts are in progress.

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