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Hydrogenation of 1-hexene by a triruthenium cluster stabilized with a face-capping 1,3-dithiacyclohexane ligand

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Abstract

Homogeneous hydrogenation of 1-hexene to hexane was studied using a triruthenium cluster containing a face-capping ligand, $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (**1**), as a catalyst precursor. The catalytic activity of **1** was studied as a function of temperature (98–140°C), H_2 pressure (10–60 bar) and catalyst concentration. The highest hydrogenation rate of 0.085 mol/h was measured at 141°C and 60 bar of H_2 pressure. A linear dependence between the catalytic activity of **1** and the H_2 pressure was observed in the pressure range of 10–50 bar, but equalizing at higher pressures (>50 bar). A rise in the temperature causes an increase in catalytic activity but at the same time enhances the fragmentation of **1** and the formation of a brown precipitate. The fragmentation product was not active in hydrogenation but shows moderate isomerization activity. A possible mechanism for the hydrogenation of 1-hexene by **1** is presented.

Keywords: Face-capping ligand; 1-Hexene; Hydrogenation; Homogeneous; Thioether; Ruthenium; Triruthenium cluster

1. Introduction

The hydrogenation of olefins is one of the most frequently examined catalytic reactions in the area of homogeneous catalysis [1]. One of the major problems in homogeneous catalysis by metal clusters is the fragmentation of catalytic substances into lower nuclearity complexes or into colloidal metal particles in rigorous catalytic conditions [2]. A possible approach toward the solution of this problem is the stabilization of the molecular cluster with a stabilizing ligand. We have previously studied some metal clusters with sulphur ligands [3–7]. We have found that in some clusters, terminal SMe_2 ligands can be replaced with carbonyl, but carbon monoxide does not displace the cyclic thioethers in $HRu_3(CO)_9$(1,3-dithiacyclohexane) (**1**), $Ru_3(CO)_9$(1,3,5-trithiacyclohexane) and $Ru_3(CO)_9$(1,4,7-trithiaheptane). In $HRu_3(CO)_9$(1,3-dithiacyclohexane) (**1**) and $Ru_3(CO)_9$(1,3,5-trithiacyclohexane) the face-capping ligands tend to stabilize the otherwise reactive cluster [7]. In addition, we have found that $HRu_3(CO)_9$(1,3-dithiacyclohexane) (**1**) reacts with H_2 when heated in a hydrocarbon solvent [7]. These observations prompted us to study the activity of **1** as an olefin hydrogenation catalyst.

In this work we report studies on the catalytic hydrogenation of 1-hexene using $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (**1**) (Fig. 1) as a catalyst precursor. During the reaction 1-hexene is isomerized to *trans*-2-hexene, *trans*-3-hexene and *cis*-2-hexene and hydrogenated to hexane by

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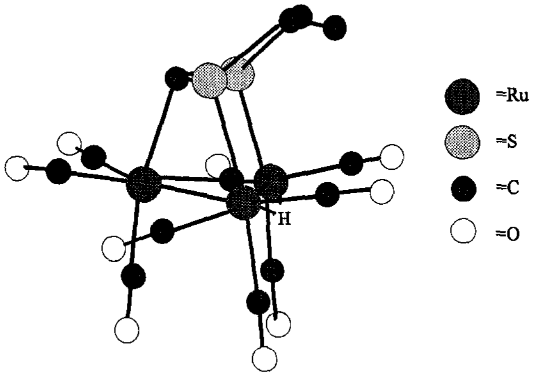


Fig. 1. Structure of $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ [7]. (The hydrogen atoms attached to the carbon atoms of dithiacyclohexane have been omitted for clarity.)

the Ru catalyst. The activity of the catalyst was investigated under different conditions, as a function of temperature, H_2 pressure and concentration of the catalyst.

2. Experimental

Thioether (Aldrich) and the $Ru_3(CO)_{12}$ cluster (Johnson Matthey) were from commercial sources and were used normally without further purification. The catalyst precursor, $HRu_3(CO)_9$–dithiacyclohexane, was prepared according to a published procedure [7]. Solvents: toluene, deuterochloroform and 1-hexene, were commercial reagent grade and p.a. quality.

Before use, toluene and 1-hexene were stored over molecular sieves and nitrogen was bubbled through for 15 minutes to remove oxygen and moisture.

2.1. *General procedure of the hydrogenation*

$HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (**1**) was weighed (0.8–9 mg) and packed with toluene as solvent (4–20 ml) and 1-hexene (20 ml) into an autoclave (Berghof, containing a Berghof Bar 845 temperature-control unit) in a N_2-filled glove-box. Then, the autoclave was charged with hydrogen (10–50 bar, hydrogen purity greater than 99.99%) and heated for one hour (or two hours) after the temperature had risen to the set value (100–140°C) (the temperature rise usually takes about half an hour). After the reaction, the autoclave was cooled with liquid nitrogen, the pressure was released, and the reaction mixture was removed and analyzed.

2.2. *Analysis*

Analysis was carried out with a gas chromatograph (Hewlett Packard Series II 5890 using Chrompack OV 1-column: 50 m, ∅ 0.53 mm, phase thickness 5 μm). Quantitative analysis was carried out with GC by computing the amounts of 1-hexene, *trans*-2-hexene, *cis*-2-hexene and the total amounts of *trans*-3-hexene and hexane (The last two were not separated using GC). Separate amounts of *trans*-3-hexene and hexane were obtained with ^{13}C NMR spectroscopy (Bruker AM-250) in deuterochloroform as solvent. The final results were computed by using both (NMR and GC) procedures. The presence of 1-hexene before and after the hydrogenation was also checked out with IR methods (Galaxy 6020).

3. Results and discussion

3.1. *Effect of H_2 pressure*

If the temperature is high enough (135–140°C), it seems that the higher the H_2 pressure, the greater the activity of the catalyst, until 50 bar (Table 1). When the H_2 pressure was raised to 60 bar, the activity was almost the same as that at 50 bar or even less.

The rise in catalytic activity was almost linear in the range of 10–50 bar, but it seemed to equalize when rising to 60 bar. It seems that the isomerization of 1-hexene is quite easy because it can be accomplished at a rather low (10 bar) pressure. Even at low H_2 pressure, the conversion of 1-hexene was nearly the same as that at a higher pressure. Thus, when the H_2 pressure is raised, the activity of the catalyst increases and the rate of hydrogenation also increases.

3.2. *Effect of temperature*

The temperature effect was studied at a 50 bar H_2 pressure and at a 0.382 mmol/l concentration of the catalyst. The temperature range used was 98–140°C. When the temperature rises, the activity of the catalyst goes up. However, a higher temperature seems to cause fragmentation and precipitation of the catalyst, as we found earlier. Thus, the activity diminishes, because the amount of the active catalyst decreases. Nevertheless, in the temperature range 98–140°C the activity goes up, and it seems to be highest at 140°C, when the reaction time is one hour. Both reactions, isomerization and hydrogenation, need a temperature high enough to proceed, because under 100°C, the total conversion of 1-hexene was rather low.

3.3. *Effect of catalyst concentration*

The effect of the catalyst concentration was studied at 135–140°C and at 50 bar H_2 pressure. Concentration of the catalyst varied in the range of 0.0493–0.683 mmol/l. The rate of the hexane conversion was studied. The growth of the hexane conversion rate is nearly linear until 0.4 mmol/l. At higher concentrations no growth seems apparent. Isomerization takes place nearly quantitatively at low concentration values also, because the total conversion of 1-hexene is 97% even when the concentration is 0.0493 mmol/l.

Table 2
Results of the hydrogenation after one and two hours of reaction

	Time (h)		
	1	2	2[a]
temperature (°C)	140	140	142
total conversion (%)	95.5	98.3	99.5
trans-3-hexene (%)	11.2	13.0	4.2
trans-2-hexene (%)	29.7	33.9	12.3
cis-2-hexene (%)	10.2	11.5	4.1
1-hexene (%)	1.9	1.7	0.5
hexane (%)	47.1	39.9	79.0

[a] Catalyst added after one hour of reaction.

3.4. *Mechanistic aspects of hydrogenation of 1-hexene by* ***1***

High temperature affects the fragmentation and precipitation of the Ru catalyst. The catalytic hydrogenation reaction seems to be homogeneous, since the brown precipitate was not found to be active in catalytic hydrogenation. Its activity was only minimal. The precipitate showed, however, low activity in catalytic isomerization; the total conversion was about 50%. The active catalyst seems to undergo a complete fragmentation during the one-hour reaction, since no increase in the conversion to hexane was observed when the reaction time was two hours. If more catalyst is added to the reaction mixture after one hour, the catalytic hydrogenation continues (Table 2).

The isomerization reaction is faster than the hydrogenation to hexane, because after one hour

Table 1
Catalytic activity of the Ru catalyst in different conditions

P (bar)	Turnover[a] (h^{-1})	*T* (°C)	Turnover[a] (h^{-1})	*C* (mmol/l)	Rate[b] (mmol/h)
10	2080	98	1530	0.0493	18.4
20	3390	113	2370	0.0846	23.6
30	4440	121	5990	0.234	32.2
40	6000	128	6030	0.315	48.1
50	7210	129	5910	0.382	70.9
60	6790	131	4710	0.683	75.3
		136	6160		
		140	6910		

[a] Turnover = mmol hexane formed (mmol of added catalyst)$^{-1}$ h^{-1}.
[b] Rate = rate of hexane formation in mmol h^{-1}.

the isomerization reaction is nearly quantitative, but only about 50% hexane has been formed. Due to the fragmentation of the catalyst, the hydrogenation to hexane is not complete in a one-hour reaction.

The proposed mechanism for the catalytic hydrogenation is shown in Scheme 1. The catalytic hydrogenation starts when alkene migrates near the metal atom of the cluster. One CO group dissociates and H_2 binds in the free coordination site with an oxidative addition (1. in Scheme 1). Then, the catalytic cycle continues with an oxidative addition of alkene and at the same time one more CO group dissociates (2.). A migratory insertion of hydride to alkene takes place (3.). After reductive elimination of the alkane, the unstable cluster either fragments or returns to the catalytic cycle with an addition of two CO groups (4.). The isomerization of 1-hexene results from the migratory insertion of a double bond, which can occur at the metal center, probably with the hydride mechanism [8].

The hydrogenation mechanism is supported by observing the reaction of **1** with H_2 in $CHCl_3$ [7]. When **1** is exposed to H_2 in chloroform at 60°C, $(\mu_2\text{-H})_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3[S_2CH(CH_2)_3]$ (**2**) (Fig. 2) is formed. In the presence of H_2, compound **1** presumably forms an unstable hydride, which in the presence of $CHCl_3$ acts as a hydrogen atom donor to give the corresponding metal chloride **2** and CH_2Cl_2 [7]. Shapley et al. have also presented a similar catalytic cycle with the $H_2Os_3(CO)_{10}$ cluster, which catalyses the hydrogenation of alkene reaction [9].

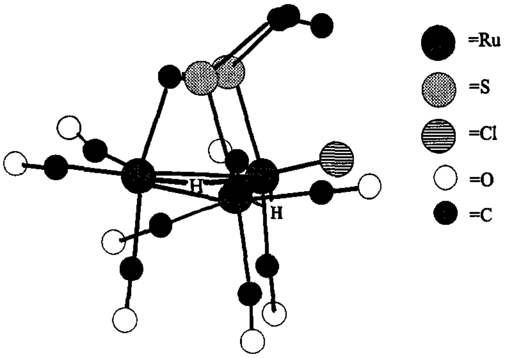
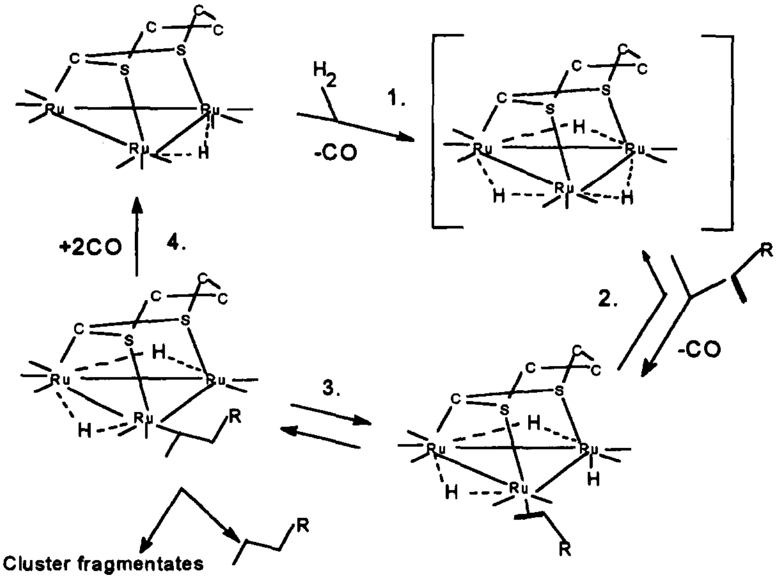


Fig. 2. Structure of $(\mu_2\text{-H})_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ [7]. (The hydrogen atoms attached to the carbon atoms of dithiacyclohexane have been omitted for clarity.)

In conclusion, $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ is a moderately active catalyst in the hydrogenation of 1-hexene. Our observations show that up to 100°C, the face-capping ligand, 1,3-dithiacyclohexane, stabilizes the triruthenium cluster framework. We are now searching for other ligands that could stabilize the triruthenium cluster from fragmentation even at higher temperatures.



Scheme 1. Mechanism of the hydrogenation of 1-hexene by the Ru catalyst.

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