The reactivity of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_{12})$ and $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{12}H_{19})$

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Abstract

The reactivity of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_{12})$ (**1**) and $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{12}H_{19})$ (2) with hydrogen and carbon monoxide was studied at elevated temperatures. Also the catalytic activity of **1** in homogeneous hydrogenation of 1-hexene was studied. At the lower carbon monoxide pressures compounds **1** and **2** converted to $Ru_3(CO)_{12}$ while at higher pressures they tend to fragmentate to the other ruthenium carbonyl compounds. Under a hydrogen atmosphere **1** and **2** converted to $H_4Ru_4(CO)_{12}$ and at higher pressures tend to fragmentate to insoluble black precipitate. Complex **1** has a moderate activity in homogeneous hydrogenation of 1-hexene. Its activity is dependent on the temperature: activity increases when the temperature goes up. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cluster; Ruthenium; Olefin; Reactivity; Hydrogenation; Homogeneous

1. Introduction

Ruthenium cluster compounds have been used as catalyst precursors in several catalytic reactions for example carbonylation of alcohols [1,2], isomerization and hydrogenation of olefins [3–6], water gas shift reaction [7] and hydroformylation [8], especially in homogeneous catalysis. Reactivity tests under conditions where cluster compounds might be expected to display catalytic activity give useful information of their shape during and after the catalytic reactions. Usually under carbon monoxide the simple metal carbonyl clusters tend to fragmentate to lower nuclearity carbonyl compounds or insoluble metal particles while under hydrogen atmosphere the behaviour is more complicated including both fragmentation reactions and formations of new hydride derivatives of metal carbonyl complexes.

We have now studied reactivity of cyclic olefin derivatives of $Ru_3(CO)_{12}$, $H_2Ru_3(CO)_9$-(C_8H_{12}) (**1**) and $HRu_3(CO)_9(C_{12}H_{19})$ (**2**) [9], under carbon monoxide and hydrogen atmosphere and the catalytic activity of **1** in the hydrogenation of 1-hexene reaction. Earlier we have studied the reactivity of $HRu_3(CO)_{12}$-1,3-dithiacyclohexane [10] towards CO and H_2 and found that it has a moderate activity in the hydrogenation of 1-hexene [5].

One aim of the work was the stabilization of the $Ru_3(CO)_{12}$ cluster with suitable ligand for catalytic reaction conditions. On the other hand

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the substitution of the carbonyl ligands by lightly stabilizing ligands does not necessarily stabilize the cluster framework. The replacement of CO by weakly bound ligands can indeed increase the reactivity of the new cluster complexes. [11]

2. Experimental

2.1. General comments

$Ru_3(CO)_{12}$ [12], $H_2Ru_3(CO)_9C_8H_{12}$ [9] and $HRu_3(CO)_9C_{12}H_{19}$ [9] were prepared with the literature procedures. All manipulations were carried out under nitrogen atmosphere and solvents were deoxygenated with nitrogen gas for fifteen minutes before use. All solvents were p.a. grade and they were stored over molecular sieves. IR-spectra were recorded on a Nicolet 750 FT-IR-spectrometer and ^1H and ^{13}C NMR spectra on a Bruker AMX-400 or a Bruker AM-250 spectrometer in d_6-acetone with TMS as an internal reference.

2.2. Reactions of **1** and **2** with carbon monoxide and hydrogen

The reactions with a H_2 or CO gas were done in a 100 ml round bottom reaction vessel. The examined complex was weighed (~ 20–30 mg) into the reaction vessel and the flask was charged with nitrogen. The solvent was added with a double-ended needle and the reaction vessel was stirred magnetically and warmed with an oil bath to the appropriate temperature. Hydrogen or carbon monoxide was bubbled trough the solution via a thin needle. Temperature was raised with $10°C$ steps for H_2 reactions and $20°C$ steps for CO reactions (reaction conditions of the experiments are introduced in Table 1). Reactions were carried out at each temperature for one hour. After each step the mixture was analyzed with IR.

The reactions with CO or H_2 at higher pressures were carried out in a 100 ml autoclave (Berghof with teflon liner, containing a Berghof Bar 845 temperature control unit). The examined complex was weighed (~ 20–30 mg) and packed into the autoclave and dissolved in toluene (5–14 ml). The autoclave was closed and charged with carbon monoxide or hydrogen gas (50 bar). After the reaction the pressure was released and the autoclave was opened and the reaction mixture was analyzed with IR and NMR-spectrometers.

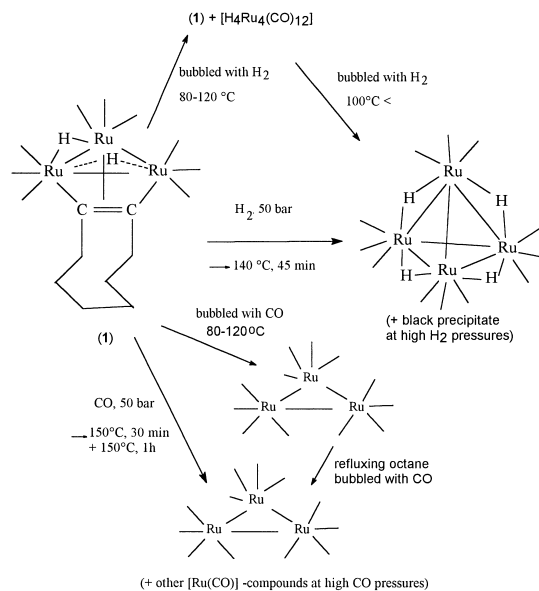### 2.3. Hydrogenation of 1-hexene catalyzed with **1**

$H_2Ru_3(CO)_9C_8H_{12}$ was weighed (8 mg) and packed with toluene as solvent (4 ml) and 1-hexene (10 ml) into an autoclave (Berghof, containing a Berghof Bar 845 temperature control unit) in a N_2-filled glove box. The autoclave was charged with H_2 (50 bar, purity of hydrogen $> 99.99\%$) and heated for one hour (15 min) after the temperature was risen to the set value (72–$170°C$). After the reaction the auto-

Table 1
Reaction conditions

Experiment	Compound	Solvent	Reaction gas	Temperature (°C)	Pressure (atm)
1	**1**	Toluene	H_2	50–110	1
2	**1**	Octane	H_2	110–130	1
3	**1**	Toluene	H_2	117	50
4	**1**	Octane	CO	60–130	1
5	**1**	Toluene	CO	146	50
6	**2**	Toluene	H_2	50–110	1
7	**2**	Octane	H_2	110–120	1
8	**2**	Toluene	H_2	146	50
9	**2**	Octane	CO	60–130	1
10	**2**	Toluene	CO	148	50

clave was cooled down to room temperature with liquid nitrogen, the pressure was released, and the reaction mixture was analyzed.

Analysis was carried out with a gas chromatograph (Hewlett Packard Series II 5890 using Chrompack OV 1-column: 50 m, Ø 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). Separated amounts of *trans*-3-hexene and hexane were obtained with ^{13}C NMR spectroscopy in deuterocloroform as solvent and TMS as reference. The final results were computed using both procedures (NMR and GC).

3. Results and discussion

3.1. The reactions of **1** and **2** with carbon monoxide

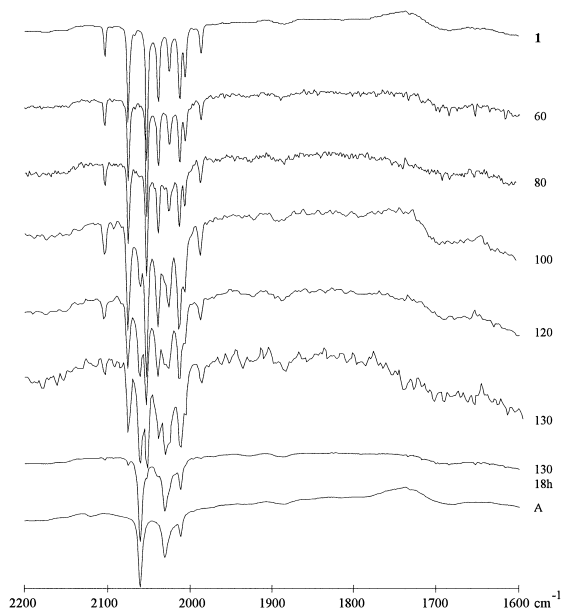Under bubbling of CO compound **1** stayed unchanged up to 80°C according to IR, Fig. 1.

Fig. 1. IR of **1** at different temperatures (°C) in octane bubbled with CO, A = $Ru_3(CO)_{12}$.

Scheme 1. Reactions of **1** with H_2 and CO in toluene or octane.

At 100°C the carbonyl frequencies of $Ru_3(CO)_{12}$ at 2060.7, 2030.8 and 2011.7 cm^{-1} appeared in IR and the proportion of $Ru_3(CO)_{12}$ increases when the temperature goes up. After refluxing the mixture in octane overnight (130°C) only the CO-bands due to $Ru_3(CO)_{12}$ were observed in IR. At higher CO pressures **1** changes to $Ru_3(CO)_{12}$ and other unidentified Ru(CO)-complexes, Scheme 1. After the reaction IR-spectra from the reaction mixture contains five signals: 2060.7 m, 2039.8 sh, 1990.3 m, 1956.5 vs and 1701.4 m. The plate cromatographic separation of the reaction mixture gave only the yellow band of $Ru_3(CO)_{12}$, the rest was not eluated with common organic solvents.

Under bubbling of CO compound **2** also remained unchanged up to 120°C (Fig. 2). In refluxing octane (130°C) it forms $Ru_3(CO)_{12}$ in an overnight reaction (21 h) like **1**. Unlike for **1** there are no signals of $Ru_3(CO)_{12}$ present in IR after the reaction made at higher temperatures and pressures. Compound **2** obviously decomposes to the mixture of Ru(CO)-complexes, Scheme 2, since after the reaction IR-spectra from the reaction mixture contains six new unidentified metal–carbonyl bands at 2097.4 w,
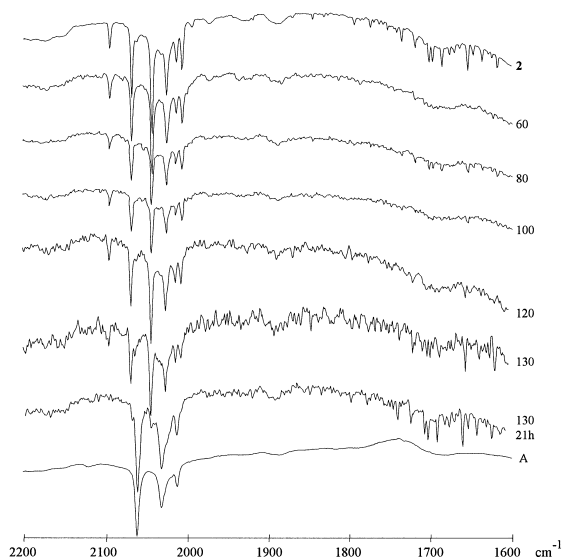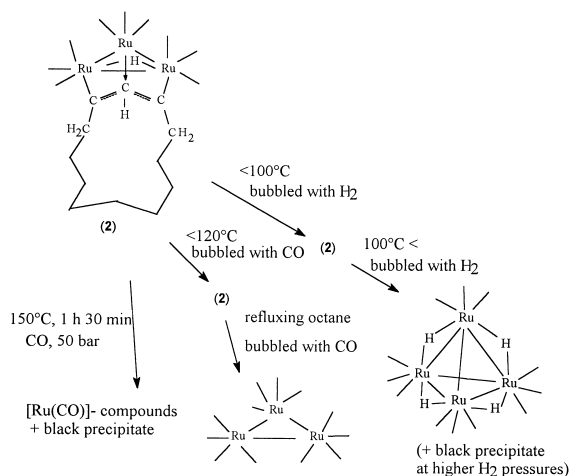
Fig. 2. IR of **2** at different temperatures (°C) in octane bubbled with CO, A = $Ru_3(CO)_{12}$.

2038.9 vs, 1997.8 m, 1960.2 s, 1937.8 sh and 1708 m. With both compounds there was also some insoluble black precipitate formed in reaction vessel indicating the decomposition of the cluster frameworks.

Thus, both compounds, **1** and **2**, are stable at elevated temperatures, **1** up to 80°C and **2** up to 120°C, under CO atmosphere. At higher temperatures CO can replace the olefin ligand, thus forming the parent cluster $Ru_3(CO)_{12}$. These

results are similar to that found for $H_2Ru_3(CO)_9(NPh)$, which under CO atmosphere (10 bar, 30°C, 2 h) converts to $Ru_3(CO)_{12}$ [13]. At higher CO pressures both compounds, **1** and **2**, start to decompose to other ruthenium carbonyl compounds.

3.2. The reactions of **1** and **2** with hydrogen

In the reaction of **1** with H_2 the IR-spectra in the carbonyl stretching region stayed unchanged up to 70°C. At 80°C a new band appeared at 2098 cm^{-1}. Its intensity increased when the temperature of the reaction was increased to 90°C. At 110°C this new unidentified signal at 2098 cm^{-1} was clearly visible, Fig. 3, also the signals of $H_4Ru_4(CO)_{12}$ (2081, 2052 and 2031 cm^{-1}) started to appear. At 120°C the signal at 2098 cm^{-1} disappeared and at 130°C only the signals of $H_4Ru_4(CO)_{12}$ were observed in IR. Thus under hydrogen atmosphere compound **1** forms first a mixture of the starting cluster, some unidentified compound and $H_4Ru_4(CO)_{12}$ and then at the higher temperatures converts to $H_4Ru_4(CO)_{12}$, Fig. 3 and Scheme 1. Moreover, in the reactions above 90°C some insoluble
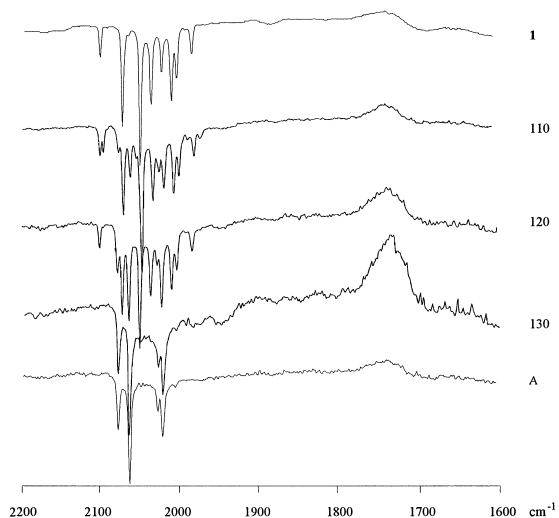

Scheme 2. Reactions of **2** with H_2 and CO in toluene and octane.

Fig. 3. IR of **1** at different temperatures (°C) in toluene or octane bubbled with H_2, A = $H_4Ru_4(CO)_{12}$.

black precipitate appeared indicating the decomposition of the cluster complexes. Under 50 bar pressure of H_2 the reaction of **1** with H_2 produces $H_4Ru_4(CO)_{12}$ and some insoluble black precipitate.

For complex **2** under H_2 atmosphere the IR-spectra stayed unchanged up to 70°C. At 80°C the signals of $H_4Ru_4(CO)_{12}$ appeared in IR. Above this temperature a mixture of **2** and $H_4Ru_4(CO)_{12}$ is present up to 100°C. At 110°C only $H_4Ru_4(CO)_{12}$ is left in solution according to the IR, Fig. 4 and Scheme 2. During the reaction of **2** with H_2 there also appeared some unidentified insoluble black precipitate.

Under H_2 atmosphere both Ru_3-olefin clusters, **1** and **2**, change to $H_4Ru_4(CO)_{12}$. These results are similar to those found for HRu_3-$(CO)_9(C_{12}H_{15})$, which under H_2 atmosphere (100°C/100 atm/24 h) forms $H_4Ru_4(CO)_{12}$ and cyclododecane [14]. Also under H_2 atmosphere complexes $Ru_4(CO)_{12}C_8H_{10}$, $Ru_4(CO)_{11}C_8H_{10}$ and $Ru_4(CO)_{12}C_8H_{12}$ were converted to H_4Ru_4-$(CO)_{12}$ in toluene or cyclohexane at 80–90°C. In addition in the reaction of $Ru_4(CO)_{11}C_8H_{10}$ and $Ru_4(CO)_{12}C_8H_{12}$ compound **1** was formed. [15] A temperature high enough is needed for the reorganization of compounds **1** and **2** to take place (>70°C). The reaction presumably includes dissociation of the olefin ligand and the

fragmentation of the cluster core before the reorganization, which includes the addition of hydride ligands and building up the H_4Ru_4-$(CO)_{12}$ cluster. The dissociation of the olefin ligands rather than carbonyl groups at elevated temperatures was due to the weaker bond between Ru–C(olefin) than Ru–C(car-bonyl).

The transformation of both starting clusters **1** and **2** under CO atmosphere at elevated temperatures under rigorous reaction conditions to $Ru_3(CO)_{12}$ and other Ru(CO)-compounds was expected. These results show that $H_2Ru_3(CO)_9$-C_8H_{12} and $HRu_3(CO)_9C_{12}H_{19}$ clusters are not very highly stabilized with olefin ligands under hydrogen or carbon monoxide atmosphere. They seem to be converted under H_2 and CO atmospheres at elevated temperatures quite easily to $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively. Steric effects of the olefin ligand influence the stability of the $Ru_3(CO)_{12}$ olefin clusters. Compound **2** seemed to be more stable under CO atmosphere than compound **1**. This is obviously due to the different bonding mode: the bonding via μ_3-η^3-CCHC-linkage in **2** stabilizes better the cluster framework than the μ_3-η^2-bonding mode in **1** under CO atmosphere. Under H_2 atmosphere both compounds begin to convert to $H_4Ru_4(CO)_{12}$ at the same temperature.

3.3. Hydrogenation of 1-hexene catalyzed with 1

The catalytic activity of $H_2Ru_3(CO)_9C_8H_{12}$ in the hydrogenation of 1-hexene was studied in the temperature range of 72–170°C. Under 100°C the conversion of 1-hexene to hexane was low and the isomerization of 1-hexene to *trans*-2-hexene, *cis*-2-hexene and *trans*-3-hexene was the principal reaction, Table 2 and Fig. 5. The total conversion including the isomerization and hydrogenation increased when the temperature went up. The total conversion was 99.9% at 110°C. Above 100°C the catalytic activity of **1** in hydrogenation of 1-hexene increased sharply, Fig. 6, being 2600 mol(mol Ru
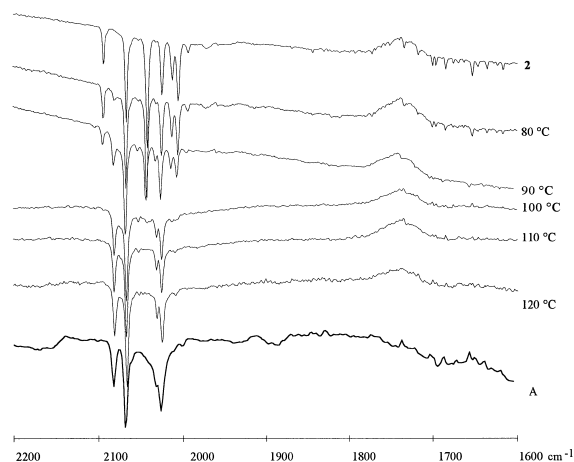

Fig. 4. IR of **2** at different temperatures (°C) in toluene or octane bubbled with H_2, A = $H_4Ru_4(CO)_{12}$.

Table 2
The contents (mol%) of the liquid products and 1-hexene after the hydrogenation reaction of 1-hexene at different temperatures[a]

T (°C)	1-hexene	t-2-hexene	t-3-hexene	c-2-hexene	Hexane	Conversion	Hydrogenation activity[b]
72	91.3	3.81	0.73	1.99	2.17	8.69	48.0
79	87.4	5.96	0.31	3.34	3.00	12.6	67.0
88	79.5	10.7	0.68	6.06	3.05	20.5	68.0
101	24.8	43.4	1.10	22.5	8.18	75.2	139
107	2.74	42.3	16.2	13.3	25.4	97.8	564
117	1.76	33.7	13.2	10.5	40.9	98.2	907
128	1.99	36.3	13.5	12.2	35.9	98.0	1590
138	1.96	31.4	11.8	10.5	44.5	98.0	1970 *
167	1.16	20.2	13.2	7.36	58.1	98.8	2580 *
170	2.39	30.3	10.8	10.8	45.8	97.6	3870[c]

[a]Reaction conditions: $P(H_2) = 50$ bar, solvent = toluene (4 ml), 1-hexene 10 ml (∗20 ml), catalysts (**1**) 8 mg (0.012 mmol), reaction time $t = 1$ h.
[b]Mol hexane$((mol\ Ru)^{-1}\ h^{-1})$.
[c]$t = 0.25$ h.

$h)^{-1}$ at 167°C. The reaction at 170°C with a reaction time of 15 min leads to a even higher activity of 3900 mol(mol Ru h)$^{-1}$.

The rate of the hydrogenation increases at the same time when the starting compound begins to transform to $H_4Ru_4(CO)_{12}$ and at the same temperature in which there is only $H_4Ru_4(CO)_{12}$ left in solution the hydrogenation rate increases sharply. At the lower temperatures the isomerization and the hydrogenation are slow, since the decomposition and the reorganization of the catalyst have not started at these temperatures. The increasing temperature affects the reorganization of the catalyst precursor to active intermediate, but the structure of the real active form is not known. The activity tested for $H_4Ru_4(CO)_{12}$ in the hydrogenation of 1-hexene at 124°C was 593 mol(mol Ru h)$^{-1}$. At the same temperature the activity of **1** was twice as high, namely 1370 mol(mol Ru h)$^{-1}$.
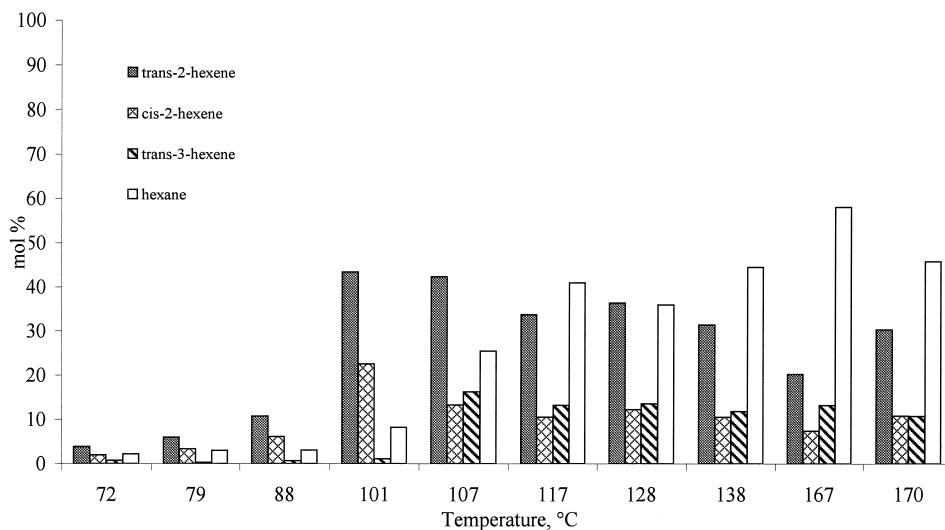

Fig. 5. The composition of the reaction mixture (mol%) at different temperatures in the hydrogenation of 1-hexene catalyzed by **1** (at 170°C reaction time 15 min, otherwise 1 h).
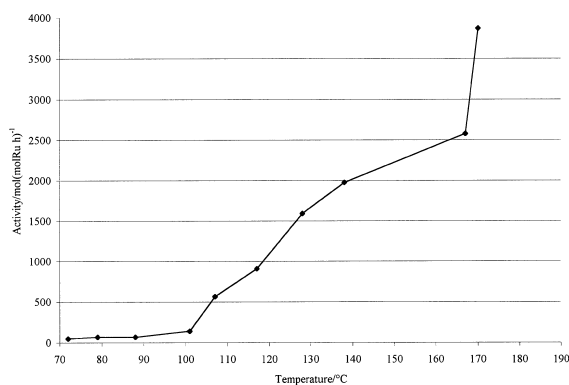
Fig. 6. The hydrogenation activity of $(mol/mol\ Ru\ h^{-1})$ of **1** at different temperatures in the hydrogenation of 1-hexene.

Compound **1** shows a moderate activity in the hydrogenation and isomerization of 1-hexene. It has been known for long time that $H_4Ru_4(CO)_{12}$ and its derivatives are active in isomerization reactions of pentenes, cyclohexene and other unsaturated compounds [3,4,16]. The catalytic isomerization reactions with transition metal complexes are usually considered to proceed by a hydrogen addition–elimination involving σ-alkyl intermediates or by a hydrogen abstraction–addition mechanism involving π-allylic species [3] and with the migratory insertion of a double bond, which can occur at the metal center [4].

4. Conclusions

Cyclic olefin derivatives of $Ru_3(CO)_{12}$, **1** and **2**, are stable up to 70°C under hydrogen and up to 80°C (**1**) and 120°C (**2**) under carbon monoxide atmosphere. The CO or H_2 atmosphere at the elevated temperature leads to the replacement of the olefin ligand and formation of the ruthenium clusters, $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, respectively. The even higher pressures and temperatures cause the formation of the other Ru(CO)-complexes and insoluble precipitates. Compound **1** has a moderate activity in the hydrogenation of 1-hexene. The highest activity was achieved at 170°C being 3900 mol hexane formed$(mol\ Ru)^{-1}\ h^{-1}$.

References

[1] S.J. Choi, J.S. Lee, Y.G. Kim, J. Mol. Catal. 85 (1993) L109.
[2] G. Jenner, G. Bitsi, J. Mol. Catal. 45 (1988) 235.
[3] M. Valle, D. Osella, G.A. Vaglio, Inorg. Chim. Acta 20 (1976) 213.
[4] G.A. Vaglio, M. Valle, Inorg. Chim. Acta 30 (1978) 161.
[5] K.O. Kallinen, T.T. Pakkanen, T.A. Pakkanen, J. Mol. Catal. 99 (1995) 29.
[6] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, p. 329.
[7] A.D. King Jr., R.B. King, D.B. Yang, J. Am. Chem. Soc. 102 (1980) 1028.
[8] J.R. Fox, W.L. Gladfelter, G.L. Geoffroy, Inorg. Chem. 19 (1980) 2574.
[9] K.O. Kallinen, M. Ahlgrén, T.T. Pakkanen, T.A. Pakkanen, J. Organomet. Chem. 510 (1996) 37.
[10] S. Rossi, K. Kallinen, J. Pursiainen, T.T. Pakkanen, T.A. Pakkanen, J. Organomet. Chem. 440 (1992) 367.
[11] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, p. 212.
[12] M.R. Churchill, F.J. Hollander, J.P. Hutckinson, Inorg. Chem. 16 (1977) 2655.
[13] S. Bhaduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick, D. Stalke, J. Chem. Soc. Dalton Trans., 1984, p. 1765.
[14] M.I. Bruce, M.A. Cairns, M. Green, J. Chem. Soc. Dalton Trans., 1972, p. 1293.
[15] A.J. Canty, A.J.P. Domingos, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans., 1973, p. 2056.
[16] G.A. Vaglio, D. Osella, M. Valle, Transition Met. Chem. 2 (1977) 94.