

Hydrogenation and isomerization of 1-hexene with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$

Kai Dallmann*, Regina Buffon

Instituto de Química, Unicamp. P.O. Box 6154, 13083-970 Campinas, SP, Brazil

Received 12 October 2000; received in revised form 9 March 2001; accepted 9 March 2001

Abstract

Both $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ were tested in their ability to hydrogenate and isomerize 1-hexene at 30, 60 and 90°C in the presence and absence of H_2 . The effect of excess PPh_3 was studied and interpreted by the different capacity of the cluster to replace CO by PPh_3 against CO. Some reactions under irradiation with visible light were also performed. The cluster mixtures obtained in hydrogenation reactions were characterized by IR spectroscopy and shown to contain $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1-4$). Main isomerization products were *trans*-2-hexene (up to 61%), *cis*-2-hexene (up to 23%) and *trans*-3-hexene (up to 20%). At H_2 -pressures of 32 and 48 psi, $\text{Ru}_3(\text{CO})_{12}$ was more active in hydrogenation, at 16 psi $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ was the better hydrogenation catalyst. 2-Methyl-1-pentene (up to 4%) and 2-methylpentane (up to 0.55%) were identified as by-products. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Isomerization; $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$

1. Introduction

It is well known that ruthenium cluster compounds, among these such with phosphine ligands, are catalytic active in a wide range of reactions, including hydrogenation and isomerization of olefins, e.g. [1–16]. Surprisingly, $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$, one of the best known substitution products of $\text{Ru}_3(\text{CO})_{12}$, is less investigated, which gives rise to study and compare its activity to that of $\text{Ru}_3(\text{CO})_{12}$. In several works dealing with 1-hexene isomerization and hydrogenation, besides 1-hexene, only *n*-hexane and *cis*- and *trans*-2-hexene are mentioned as reaction products; *trans*-3-hexene, the second stable of the linear hexenes [17,18], and branched isomers are disregarded even

in recent literature (presumably because of separation difficulties due to the use of inadequate gas chromatography columns). Thus, another aim of this work was to get some information about the selectivity of these catalysts. Finally, we added PPh_3 to some of our reaction mixtures to study its effect on catalyst activity and to characterize the resulting cluster mixtures.

2. Experimental

2.1. Materials

The compound $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ was prepared as described in [19], $\text{Ru}_3(\text{CO})_{12}$ (Strem Chemicals) and PPh_3 (Merck) were commercial and used as received.

* Corresponding author. Fax: +55-19-3788-3023.
E-mail address: rbuffon@iqm.unicamp.br (K. Dallmann).

Toluene was dried over sodium before use, 1-hexene (Aldrich, 97%) was stored over 4 Å molecular sieves.

2.2. Catalytic experiments

The catalytic hydrogenation experiments were performed in a 65 ml Fisher–Porter bottle. In a typical hydrogenation reaction 1.35 ml (10.47 mmol) of 1-hexene, 6.0 mg (0.0094 mmol) of $\text{Ru}_3(\text{CO})_{12}$ or 12.6 mg (0.0094 mmol) of $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ were dissolved in 5 ml toluene and the reaction mixture was purged three times with H_2 before starting. Reactions without hydrogen were performed under argon, in glass tubes (2 cm \times 20 cm) containing a rubber septum. In reactions under H_2 , for every reported time a new reaction was performed. If not communicated otherwise, all reactions were carried out under exclusion of light. For experiments under irradiation, light bulbs (visible light) with 7 and 60 W of emission power were employed. Because reproducibility of results strongly depends on the purity of reaction vessels, the glassware was washed with boiling HCl/HNO_3 mixtures before every run. In a blank experiment (90°C, 15 h, 16 psi H_2 , 10.47 mmol 1-hexene, 5 ml toluene), the reaction vessel was 100% inactive either in hydrogenation or in isomerization.

Reactions were monitored using an HP-5890 II gas chromatograph equipped with a flame ionization detector and an $\text{Al}_2\text{O}_3/\text{KCl}$ on fused silica-capillary column (50 m \times 0.32 mm). Under our experimental conditions (head pressure of carrier gas N_2 : 7 psi; temperature of injector, detector and column: 170°C) typical retention times were 15.0 (2-methylpentane, 2m), 15.7 (*n*-hexane, n), 17.4 (*trans*-3-hexene, t3), 17.8 (*trans*-2-hexene, t2), 19.3 (2-methyl-1-pentene, 2m1), 19.5 (1-hexene, h1) and 20.0 min (*cis*-2-hexene, c2), respectively, so that the linear hexenes were well separated, but 2-methyl-1-pentene and 1-hexene were detected as a merged peak. The compounds were identified by knowledge of the retention times of most hexenes, *n*-hexane and 2-methylpentane. In agreement with the thermodynamic stability of the five linear hexenes (t2 > t3 > c2 > c3 > h1 [17,18]), no *cis*-3-hexene was detected in any reaction mixture.

The IR spectra were recorded on a Bomem FT-IR spectrometer model MB-100 (16 scans) with a resolution of 4.0 cm^{-1} and cyclohexane as the solvent.

3. Results and discussion

Ruthenium clusters react with hydrogen forming hydrido cluster species which are believed to be intermediates in both isomerization and hydrogenation reactions. Isomerization of pentenes with $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ has been reported [1]. On the other hand, in hydrogenation of 1-hexene, usually under high pressure (10–50 bar), isomerization is also observed. However, there are no reports concerning the effects of the presence/absence of hydrogen in isomerization reactions. Therefore, we decided to carry out hydrogenation–isomerization with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ under very mild experimental conditions (16–48 psi H_2 , $[\text{Ru}]/[1\text{-hexene}] = 1:371$, 30–90°C).

Phosphinesubstituted ruthenium clusters are active in hydrogenation–isomerization of 1,4-cyclopentadiene at 0.9–1.0 bar, and an excess of PPh_3 has an inhibiting effect in the activity of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [10]. Thus, our aim was also to study the effect of the phosphine substitution at somewhat higher pressures and to see if there were differences in the inhibiting effect of added PPh_3 in the catalytic activity of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ systems.

3.1. Reactions with H_2 (with and without PPh_3) under exclusion of light

Even under low H_2 -pressure (16–48 psi), at 90°C both $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ isomerize or hydrogenate 1-hexene almost quantitatively (Table 1, Fig. 1(A) and (C)), the amount of the hydrogenation product increasing with time and temperature. In diluted solutions, however, hexane formation decreases, as shown for $\text{Ru}_3(\text{CO})_{12}$ in Table 1. At lower H_2 -pressure (16 psi) isomerization with $\text{Ru}_3(\text{CO})_{12}$ is faster than with $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$, and when increasing H_2 -pressure up to 48 psi, $\text{Ru}_3(\text{CO})_{12}$ also becomes a more efficient hydrogenation catalyst (80.1% of *n*-hexane at 48 psi, 15 h, TON = 297/Ru). At higher H_2 -pressures (with presumably high concentration of Ru hydride species in solution) the kinetics of the reaction may be determined by the accessibility to the reactive sites of the Ru framework, which in the case of $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ is expected to be more difficult owing to the bulky PPh_3 ligands.

In all reactions t2 is the main product. The highest percentages of c2 are reached at the beginning of the

Table 1
Reactions with H₂ under exclusion of light^a

Time (h)	P _{H₂} (psi)	Solvent (ml)	Temperature (°C)	n	h1	t2	t2/t3	t2/c2
Ru ₃ (CO) ₁₂								
0.5	16	5	90	0.6	25.3	46.7	3.7	3.2
1	16	5	90	1.9	5.8	53.5	2.7	3.4
15	16	5	90	7.8	3.6	49.9	2.5	3.4
40	16	5	90	22.6	3.0	41.9	2.5	3.4
15	32	5	90	58.5	1.0	23.3	2.7	3.7
15	48	5	90	80.1	0.6	10.8	2.8	3.8
15	16	10	90	6.7	2.7	51.1	2.6	3.3
15	16	20	90	4.0	5.1	51.6	2.6	3.3
15	16	5	30	0.4	16.9	55.5	4.4	3.8
15	16	5	60	2.6	6.5	53.2	2.7	3.6
Ru ₃ (CO) ₉ (PPh ₃) ₃								
0.5	16	5	90	0.4	78.7	13.2	31.5	1.9
1	16	5	90	0.5	43.6	35.3	16.0	1.9
15	16	5	90	13.4	5.0	47.7	2.8	3.5
40	16	5	90	30.7	2.5	37.5	2.5	3.4
15	32	5	90	29.8	1.6	39.6	2.7	3.5
15	48	5	90	37.8	1.2	35.1	2.7	3.5
15	16	5	30	0.3	69.8	18.5	42.4	1.7
15	16	5	60	1.5	13.5	56.7	10.0	2.5

^a Reaction conditions: solvent, toluene; 10.47 mmol h1; 0.0094 mmol cluster; n, *n*-hexane; h1, 1-hexene; t2, *trans*-2-hexene; t3, *trans*-3-hexene; c2, *cis*-2-hexene.

reaction or at lower temperature (30°C) when the reaction is slower (Table 1 for Ru₃(CO)₉(PPh₃)₃). The same is observed when the reaction is drastically inhibited by addition of high amounts of PPh₃ (vide infra and Table 2). At longer reaction times and 90°C, t2/t3 ratios are between 2.5 and 2.8, t2/c2 ratios are around 3.4, in relatively good agreement

with the results reported by Kallinen et al. [11] for HRu₃(CO)₉(μ₃-η³-1,3-dithiacyclohexane). Formation of t3 strongly depends on temperature. At 30°C the amount of t3 is significantly smaller than at 90°C (Table 1). Small quantities of 2-methyl-1-pentene (around 4%) and of its hydrogenation product, 2-methylpentane (0.1–0.6%), are also formed by skeletal rearrangement.

Table 2
Reactions with H₂ at 90°C under exclusion of light in the presence of PPh₃^a

[PPh ₃]/[cluster]	n	h1	t2	t2/t3	t2/c2
Ru ₃ (CO) ₁₂					
9	1.0	71.1	15.8	50.4	1.4
6	0.8	43.7	32.7	12.8	1.6
1	1.1	5.2	53.0	2.6	3.3
0.33	3.6	3.0	52.5	2.5	3.3
Ru ₃ (CO) ₉ (PPh ₃) ₃					
9	2.1	67.9	16.9	8.6	1.6
6	17.0	6.8	44.9	3.3	3.0
1	19.9	3.6	43.4	2.6	3.2
0.33	21.2	1.9	43.8	2.6	3.4

^a Reaction conditions: solvent, toluene (5 ml); P_{H₂} = 16 psi; reaction time, 15 h; 10.47 mmol h1; 0.0094 mmol cluster.

3.1.1. Effect of excess PPh₃

When adding PPh₃ to the reaction solutions (Table 2, Fig. 1(D)), both hydrogenation and isomerization activity of Ru₃(CO)₁₂ and Ru₃(CO)₉(PPh₃)₃ strongly decrease. This effect can be attributed to the replacement of CO by PPh₃ (IR Fig. 2, below) and is much more drastic for Ru₃(CO)₁₂ than for Ru₃(CO)₉(PPh₃)₃. In Ru-clusters, only one CO is displaced by one PPh₃ on each Ru-atom [20–23]. Thus, in solutions of Ru₃(CO)₁₂ or H₄Ru₄(CO)₁₂ (formed from Ru₃(CO)₁₂ in presence of H₂), three or four CO, respectively, can be set free (one CO for one Ru), whereas in solutions of Ru₃(CO)₉(PPh₃)₃ (which, in presence of H₂, results in mixtures of H₄Ru₄(CO)_{12–n}(PPh₃)_n (*n* = 1–4, preferably *n* =

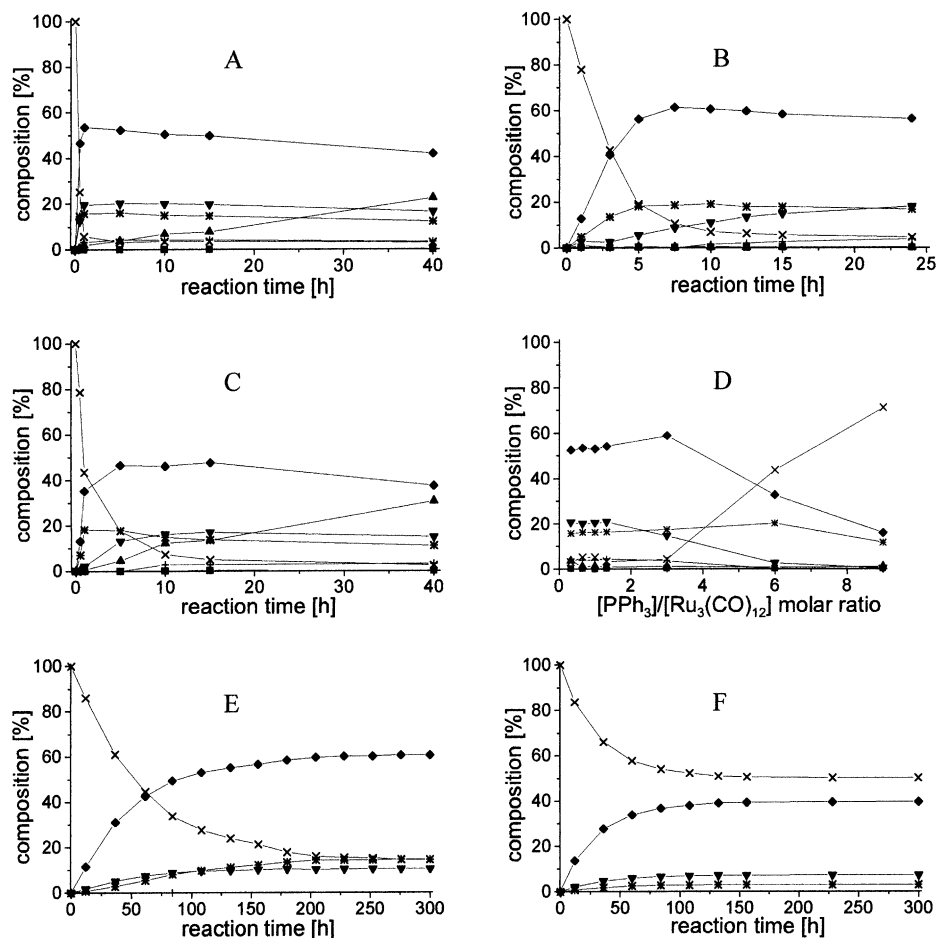


Fig. 1. Isomerization/hydrogenation of 1-hexene under different conditions. (A): Ru₃(CO)₁₂, P_{H₂} = 16 psi, 90°C, without light; (B): Ru₃(CO)₁₂, without H₂, 90°C, without light; (C): Ru₃(CO)₉(PPh₃)₃, P_{H₂} = 16 psi, 90°C, without light; (D): Ru₃(CO)₁₂, P_{H₂} = 16 psi, 90°C, influence of PPh₃; (E): Ru₃(CO)₁₂, without H₂, 7 W lamp, 30°C; (F): Ru₃(CO)₁₂, without H₂, 60 W lamp, 30°C; (-■-) 2-methylpentane; (-+-) 2-methyl-1-pentene; (-*-) *cis*-2-hexene; (-×-) 1-hexene; (-▲-) *n*-hexane; (-◆-) *trans*-2-hexene; (-▼-) *trans*-3-hexene.

2–3) [20]) the amounts of free CO should be minimal, becoming quite clear that the concentration of free CO in a Ru₃(CO)₁₂/PPh₃ solution must be much more higher than in a solution of Ru₃(CO)₉(PPh₃)₃/PPh₃. In contrast to PPh₃, the very nucleophilic CO is small enough to compete for active sites of the Ru framework. The catalyst poisoning effect of even small concentrations of CO has been shown in the isomerization of pentenes with H₄Ru₄(CO)₁₂ [1,3]; the same effect for an excess of PPh₃ has been shown in hydrogenation–isomerization experiments of pentadienes with Ru₃(CO)₁₀(PPh₃)₂ [10]. Thus, the presence

of PPh₃ decreases the activity of the cluster, especially when [cluster]/[PPh₃] = 1:9, in which case the preference for t2 and t3 is less pronounced (Table 2).

3.1.2. Spectroscopic characterization of formed cluster mixtures

Comparison of the IR spectra (Fig. 2(a) and (b)) of cluster mixtures obtained after the catalytic experiments suggests that Ru₃(CO)₁₂ in the presence of H₂ (and h1) gives mixtures of Ru₃(CO)₁₂ and H₄Ru₄(CO)₁₂. At longer reaction times, more H₄Ru₄(CO)₁₂ is formed. In the same reaction conditions,

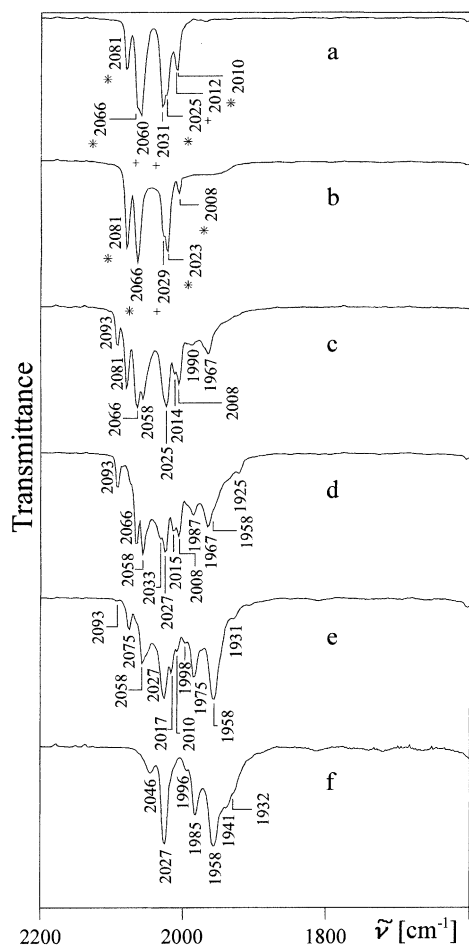


Fig. 2. FT-IR spectra of reaction solutions: (a) $\text{Ru}_3(\text{CO})_{12}$, 0.5 h, 16 psi H_2 ; (b) $\text{Ru}_3(\text{CO})_{12}$, 40 h, 16 psi H_2 ; (c) $[\text{Ru}_3(\text{CO})_{12}]/[\text{PPh}_3] = 1:0.33$; (d) $[\text{Ru}_3(\text{CO})_{12}]/[\text{PPh}_3] = 1:1$; (e) $[\text{Ru}_3(\text{CO})_{12}]/[\text{PPh}_3] = 1:3$; (f) $[\text{Ru}_3(\text{CO})_{12}]/[\text{PPh}_3] = 1:9$. Other conditions as stated in Tables 1 and 2. (+) Absorption of $\text{Ru}_3(\text{CO})_{12}$; (*) absorption of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$.

$\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ gives an IR similar to that reported for a mixture of $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{H}_4\text{Ru}_4(\text{CO})_9(\text{PPh}_3)_3$ [20]. Fig. 2(c)–(f) show the IR spectra of cluster mixtures obtained in hydrogenation of h1 with $\text{Ru}_3(\text{CO})_{12}$ at different $[\text{cluster}]/[\text{PPh}_3]$ ratios. In this case the addition of PPh_3 also leads to mixtures which contain several clusters $\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1-4$). The change of intensity in absorption bands from Fig. 2(c)–(f) is due to a higher exchange rate of CO against PPh_3 . IR spectra of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n =$

1–4) are in good agreement with those reported in the literature [20,22]. The IR spectra for cluster mixtures obtained in the hydrogenation with $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ in the presence of PPh_3 were similar. Thus, in reactions under H_2 a Ru_4 cluster framework is built, with H_2 preventing the scission of the Ru_3 unit into mononuclear complexes. But it should be noted that the catalytically active species may be different from those isolated afterwards.

3.2. Reactions at 90°C without H_2 under exclusion of light

3.2.1. $\text{Ru}_3(\text{CO})_{12}$

The $\text{Ru}_3(\text{CO})_{12}$ isomerizes h1 at 90°C within 15 h almost quantitatively (Table 3, Fig. 1(B)) and the proportions of isomeric hexenes are similar to those observed in reactions with H_2 . The c2 reaches again its highest percentage at short reaction times and lower temperatures (30 and 60°C). The drastically decreased formation of t3 at 30 and 60°C in comparison to 90°C shows that its formation is thermally induced. In the 90°C reaction both t2 and c2 reach a maximum concentration (7.5 h, 61.4% and 10 h, 19.2%, Table 3, Fig. 2(b)) and then are converted into t3. Also small quantities of 2-methyl-1-pentene are observed (4.3% after 500 h, 90°C). After 15 h, 90°C, the solution is still orange-yellow (but becomes colorless at longer reaction times), showing in the IR spectrum mainly the typical pattern of $\text{Ru}_3(\text{CO})_{12}$ and just a few peaks of degradation products.

Since isomerization is always faster when the reaction is performed under H_2 , it is clear that it takes place via H-transfer from a hydrido cluster to the coordinated olefin.

Table 3
Reactions of $\text{Ru}_3(\text{CO})_{12}$ without H_2 and under exclusion of light^a

Time (h)	Temperature (°C)	h1	t2	t2/t3	t2/c2
1	90	77.9	12.9	4.4	2.7
3	90	42.8	40.6	16.0	3.0
15	90	5.7	58.4	3.9	3.3
100	90	3.9	56.1	3.0	3.3
500	90	3.5	54.7	2.7	3.2
15	30	97.9	1.6		3.3
325	30	27.7	55.4	105.0	3.4
15	60	36.8	47.5	90.1	3.1

^a Reaction conditions: solvent, toluene (5 ml); 10.47 mmol h1; 0.0094 mmol cluster.

3.2.2. $Ru_3(CO)_9(PPh_3)_3$

The behavior of $Ru_3(CO)_9(PPh_3)_3$ is quite different without H_2 , the cluster being nearly inactive at 30, 60 and 90°C (maximal 8.8% consumption of h1 after 15 h at 90°C). At 90°C the red–violet $Ru_3(CO)_9(PPh_3)_3$ is no longer present in solution (almost nothing at 60°C, nearly completely present at 30°C), being replaced by yellow products and consumption of h1 stops in the first hour. According to Keeton et al [24], mononuclear complexes are formed when heating $Ru_3(CO)_9(PPh_3)_3$ in hydrocarbons.

The lack of reactivity when the Ru_3 unit is decomposed shows that an intact cluster framework is essential for catalytic isomerization. Moreover, when remaining intact at 30°C, isomerization with $Ru_3(CO)_9(PPh_3)_3$ is faster in the presence of H_2 and the so formed hydrido cluster compounds. Without H_2 isomerization of h1 is slower with $Ru_3(CO)_9(PPh_3)_3$ than with $Ru_3(CO)_{12}$. Since in the absence of H_2 isomerization only can occur by the formation of a π -allyl intermediate [25], it seems that the presence of PPh_3 in $Ru_3(CO)_9(PPh_3)_3$ inhibits its formation.

3.3. Reactions at 30°C under irradiation and without H_2

For irradiation experiments we chose visible light because the electronic spectrum of $Ru_3(CO)_{12}$ is dominated by an intense absorption band centered at 392 nm ($\epsilon \approx 7.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and $Ru_3(CO)_9(PPh_3)_3$ exhibits an intense visible absorption maximum at 506 nm ($\epsilon \approx 14 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [26,4]. It appeared that under irradiation conversion of h1 to the linear isomers also depends on the lifetime of the Ru_3 unit. The more intense the light power the faster solutions of $Ru_3(CO)_{12}$ become colorless (formation of $Ru(CO)_5$, [27]) and isomerization stops (Table 4, Fig. 1(E) and (F)). Thus, isomerization is more efficient and also faster with a 7 W than with a 60 W daylight bulb (85.5 and 49.8% conversion of h1 after 300 h). Both t2/t3 and t2/c2 ratios differ significantly from those obtained at 90°C. More t2 is formed and concentration of t2 increases with the power of emission light. The t3 concentrations lower than in reactions at 90°C show again the temperature dependence of t3 formation. In contrast, $Ru_3(CO)_9(PPh_3)_3$ is nearly inactive (4% of h1 conversion with 7 W, 5.2%

Table 4
Reactions with $Ru_3(CO)_{12}$ under irradiation at 30°C without H_2 ^a

Time (h)	h1	t2	t2/t3	t2/c2
7 W lamp				
12	85.1	11.5	6.9	14.2
36	61.1	31.0	6.1	11.1
84	33.8	49.4	5.6	6.1
156	21.3	56.6	5.6	4.7
300	14.5	60.6	5.8	4.2
60 W lamp				
12	83.6	13.7	6.6	19.6
36	66.0	27.7	6.0	16.0
84	54.0	36.7	5.6	13.6
156	50.6	39.3	5.5	13.1

^a Reaction conditions: solvent, toluene (5 ml); 10.47 mmol h1; 0.0094 mmol cluster.

with 60 W, each after 300 h) due to rapid formation of yellow products (cleavage of the Ru_3 unit [7]).

4. Conclusions

Isomerization of 1-hexene with $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(PPh_3)_3$ takes place only when the cluster framework remains intact. When the Ru–Ru bonds of the cluster are disrupted, as in reactions of both clusters under irradiation or when $Ru_3(CO)_9(PPh_3)_3$ is used in the absence of H_2 , mononuclear compounds are formed and isomerization stops. The presence of H_2 has two effects in isomerization reactions: firstly, in the presence of H_2 stable active ruthenium hydrido clusters are formed; secondly, these hydrido clusters also show a higher rate in 1-hexene isomerization than the nonhydrido compounds, indicating that isomerization by the hydrido cluster compounds proceeds by H-transfer to the coordinated olefin. The catalytic activity of both $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(PPh_3)_3$ in hydrogenation and isomerization is hindered by an excess of PPh_3 . $Ru_3(CO)_9(PPh_3)_3$ is more tolerant against the addition of PPh_3 than $Ru_3(CO)_{12}$, since no CO is replaced by PPh_3 and so no free CO comes in solution to block active coordination sites. In the hydrogenation–isomerization reaction, first t2 and c2 are formed, and the concentration of the second reaches its highest concentrations at the beginning of the reaction. The t3 isomer, often not mentioned, is formed almost at higher temperature from c2 and t2

and reaches up to 20% of the product mixture after long reaction times.

Acknowledgements

Financial support from FAPESP, as well as a fellowship to K. Dallmann, is gratefully acknowledged.

References

- [1] M. Valle, D. Osella, G.A. Vaglio, *Inorg. Chim. Acta* 20 (1976) 213.
- [2] K.G. Caulton, M.G. Thomas, B.A. Sosinsky, E.L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.* (1976) 4274.
- [3] G.A. Vaglio, M. Valle, *Inorg. Chim. Acta* 30 (1978) 161.
- [4] J.L. Graff, R.D. Sanner, M.S. Wrighton, *J. Am. Chem. Soc.* 101 (1979) 273.
- [5] R.A. Sanchez-Delgado, I. Duran, J. Monfort, E. Rodriguez, *J. Mol. Catal.* 11 (1981) 193.
- [6] G. Süss-Fink, J. Reiner, *J. Mol. Catal.* 16 (1982) 231.
- [7] J.L. Graff, R.D. Sanner, M.S. Wrighton, *Organometallics* 1 (1982) 837.
- [8] P.M. Lausarot, G.A. Vaglio, M. Valle, *J. Organomet. Chem.* 275 (1984) 233.
- [9] A. Basu, S. Bhaduri, H. Khwaja, P.G. Jones, T. Schroeder, G.M. Sheldrick, *J. Organomet. Chem.* 290 (1985) C19.
- [10] M. Castiglioni, R. Giordano, E. Sappa, *J. Organomet. Chem.* 342 (1988) 111.
- [11] K.O. Kallinen, T.T. Pakkanen, T.A. Pakkanen, *J. Mol. Catal. A: Chem.* 99 (1995) 29.
- [12] M. Castiglioni, R. Giordano, E. Sappa, *J. Organomet. Chem.* 491 (1995) 111.
- [13] K.O. Kallinen, T.T. Pakkanen, T.A. Pakkanen, *J. Mol. Catal. A: Chem.* 135 (1998) 233.
- [14] M. Castiglioni, S. Deabate, R. Giordano, P.J. King, S.A.R. Knox, E. Sappa, *J. Organomet. Chem.* 571 (1998) 251.
- [15] G. Gervasio, R. Giordano, D. Marabello, E. Sappa, *J. Organomet. Chem.* 588 (1999) 83.
- [16] B. Fontal, M. Reyes, T. Suárez, F. Bellandi, N. Ruiz, *J. Mol. Catal. A: Chem.* 149 (1999) 87.
- [17] K.B. Wiberg, D.J. Wasserman, *J. Am. Chem. Soc.* 103 (1981) 6563.
- [18] D.W. Rogers, E. Crooks, K. Dejrroongruang, *J. Chem. Thermodyn.* 19 (1987) 1209.
- [19] J.P. Candlin, K.K. Joshi, D.T. Thompson, *Chem. Ind.* 19 (1966) 1960.
- [20] F. Piacenti, M. Bianchi, P. Frediani, E. Benedetti, *Inorg. Chem.* 10 (1971) 2759.
- [21] M.I. Bruce, J.G. Matison, B.K. Nicholson, *J. Organomet. Chem.* 247 (1983) 321.
- [22] S. Aime, M. Botta, R. Gobetto, L. Milone, D. Osella, R. Gellert, E. Rosenberg, *Organometallics* 14 (1995) 3693.
- [23] P. Frediani, C. Faggi, S. Papaleo, A. Salvini, M. Bianchi, F. Piacenti, S. Ianelli, M. Nardelli, *J. Organomet. Chem.* 536/537 (1997) 123.
- [24] D.P. Keeton, S.K. Malik, A. Poë, *J. Chem. Soc., Dalton Trans.* (1977) 233.
- [25] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis*, 2nd Edition, Wiley, New York, 1992.
- [26] M.F. Desrosiers, D.A. Wink, R. Trautman, A.E. Friedman, P.C. Ford, *J. Am. Chem. Soc.* 108 (1986) 1917.
- [27] B.F.G. Johnson, J. Lewis, M.V. Twigg, *J. Chem. Soc., Dalton Trans.* (1975) 1876.