

# Catalytic studies with ruthenium clusters substituted with diphosphines

## Part I. Studies with $\text{Ru}_3(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$

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### Abstract

The catalytic precursor  $\text{Ru}_3(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{dppm})$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) isomerizes 1-hexene mainly to the kinetic product *cis*-2-hexene at low  $\text{H}_2$  pressure, and to *n*-hexane at higher hydrogenation conditions. The overall first order rate constant on substrate is  $0.11 \text{ min}^{-1}$ . The compound hydrogenates other unsaturated groups in good yield. Turnover frequency studies indicate cluster catalysis. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Ruthenium cluster; Bidentate phosphines; Hydrogenation and isomerization catalysts

### 1. Introduction

Catalytic studies with metal clusters is an area of recent research [1,2]. Terminal olefin isomerization to a mixture of internal olefins has been done with  $\text{Ru}_3(\text{CO})_{12}$  and the cluster substituted with monodentate phosphines [2]. Isomerization of 1-pentene with  $\text{Ru}_3(\text{CO})_{12}$  in refluxing hexane gave mainly *trans*-2-pentene [3].  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and  $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{L}$  (L = monodentate phosphine) clusters gave similar results [4]. Under photolytic conditions  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  gave different isomer ratios [5]. Sanchez-Delgado et al. have reported 1-hexene hydrogenation to *n*-hexane with  $\text{Ru}_3$

$(\text{CO})_{12}$  [6]. Cyclohexene is hydrogenated to cyclohexane with the following substituted Ru clusters:  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ ,  $\text{Ru}_3(\text{CO})_7(\text{PPh}_3)_2(\text{C}_6\text{H}_4)$  [7],  $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppm})$ , ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ )  $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppm})$  [8],  $\text{H}_2\text{Ru}_3(\text{E})(\text{CO})_5(\text{dppm})_2$  (E = O, S) [9]. The presence of ligands capable of stabilizing the cluster is considered important, especially during catalytic reactions [1]. Polydentate phosphine ligands could be useful for cluster stabilization, but little work has been reported on the effect of these ligands on cluster catalysis. The diphosphine  $\text{dppm}$  has been used in the synthesis of many mononuclear and cluster complexes a few of which has been used in homogenous catalysis [10–14]. In our laboratory we have been studying the catalytic behavior of Ru complexes with polydentate phosphines [15–20]. In other stud-

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ies we reported the catalytic reactions of the Ru carbonyl cluster in the presence of bis-1,3(diphenylphosphino)propane ( $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2 = \text{dppp}$ ) [21]. In this paper we report the reactions of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  under hydrogen pressure.

## 2. Experimental

### 2.1. Synthesis of $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$

Several synthetic methods were tried to compare the percent yield and the ease of preparation. All the gases used are high purity, reagents are analytical grade and all solvents were appropriately dried before use.

(a) Preparation via diphenylketyl radical,  $\text{Ph}_2\text{C}_2\text{O}^-$ . The preparation of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  by this method has been reported by Bruce et al. [22].  $\text{Ru}_3(\text{CO})_{12}$  was prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Strem Chemicals) and CO (Matheson, UAP grade) according to the literature method [23]. Sodium diphenylketyl was prepared prior to use reacting benzophenone (91 mg, 0.5 mmol) in very dry THF (Aldrich, 20 ml) and very finely divided metallic sodium under Ar with stirring for 2 h. The very intense violet solution had a concentration near 0.025 mmol/ml of  $\text{Ph}_2\text{C}_2\text{O}^-$ . In a typical synthesis,  $\text{Ru}_3(\text{CO})_{12}$  (150 mg, 0.234 mmol) and the dppm (Strem Chemicals) ligand (90 mg, 0.234 mmol) are dissolved in dry THF (20 ml) with stirring at 40°C in Schlenk glassware. The diphenylketyl solution is added dropwise with syringe and the reaction followed by the disappearance of  $\text{Ru}_3(\text{CO})_{12}$  metal carbonyl IR bands (P.E. 1725-X FTIR). After solvent evaporation, the residue is separated on silica gel column chromatography, eluted with a 50/50 THF/hexane mixture. The brown–red fraction is recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane to give red–brown crystals of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (214 mg, 94.2% yield). IR:  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2080(m), 2040(sh), 2010(s), 1998(sh), 1958(m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (Varian T-60)  $\delta$  7.1–7.6 (m,  $\text{C}_6\text{H}_5$ ), 4.3 (t,

$\text{CH}_2$ ;  $J_{\text{PH}} = 11$  Hz); Mass Spectra (solid, HP 5988A GC-MS) molecular ion at 969.8 amu, decomposition pattern of consecutive CO loss and ligand fragmentation. The compound decomposes between 174 and 176°C.

(b) Synthesis via thermal reaction. The complex was prepared by a modified version of the reported method [24]. In a typical synthesis,  $\text{Ru}_3(\text{CO})_{12}$  (150 mg, 0.234 mmol), dppm (90 mg, 0.234 mmol) and xylene (Aldrich, 5 ml) in a round bottom flask were heated to 50°C with stirring and then refluxed for 5 h under Ar, giving a red–brown solution. After solvent evaporation, the residue is separated on silica gel column chromatography, eluted with a 3/1  $\text{CH}_2\text{Cl}_2$ /hexane mixture, giving several bands. The larger red–brown band is recrystallized in  $\text{CH}_2\text{Cl}_2$ /hexane to give red–brown  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  crystals (210 mg, 94% yield). Identification similar to (a).

(c) Synthesis via photolysis. In a typical synthesis,  $\text{Ru}_3(\text{CO})_{12}$  (150 mg, 0.234 mmol), dppm (90 mg, 0.234 mmol) in THF (15 ml) are heated to 40°C with stirring for several minutes under Ar. The red orange solution is transferred to a Schlenk tube with a water jacket, covered with Al foil under Ar; a pen Hg UV lamp (Ultra-Violets Products, 114 V, 60 cycle, low intensity) is introduced and photolyzed for about 5 h, the progress of the reaction followed by disappearance of  $\text{Ru}_3(\text{CO})_{12}$  metal carbonyl IR bands. After the reaction is complete, the solvent is reduced under vacuum and silica gel column chromatographed using a 50/50 THF/hexane eluant. The red–brown band is recrystallized in  $\text{CH}_2\text{Cl}_2$ /hexane giving red–brown  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  crystals (216 mg, 95% yield). Identification similar to (a).

(d) Synthesis via  $(\text{CH}_3)_3\text{NO}$  activation. In a typical experiment  $\text{Ru}_3(\text{CO})_{12}$  (150 mg, 0.234 mmol) is dissolved in dry  $\text{CH}_2\text{Cl}_2$  (40 ml) in a Schlenk tube with constant Ar bubbling during the whole reaction. The system is cooled to  $-78^\circ\text{C}$  in a Dewar flask with a  $\text{CO}_2(\text{s})$ /acetone bath. Trimethylamine oxide,  $(\text{CH}_3)_3\text{NO}$  (Aldrich, sublimed three times, 52.6 mg, 0.701

mmol) completely dissolved in  $\text{CH}_2\text{Cl}_2$  (15 ml) was added dropwise via canula to the Ru carbonyl solution at low temperature, the progress of the reaction followed by disappearance of  $\text{Ru}_3(\text{CO})_{12}$  metal carbonyl IR bands. The dppm ligand (90 mg, 0.234 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (15 ml) was added dropwise via canula at low temperature. The Schlenk tube is removed from the cold bath and allowed to warm up slowly to room temperature, heating then to  $40^\circ\text{C}$  during 30 min. After evaporating the solvent, the residue is chromatographed in a silica gel column and the separated fraction recrystallized in a 1/1  $\text{CH}_2\text{Cl}_2$ /hexane mixture, giving red–brown  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  crystals (141 mg, 62% yield). Identification similar to (a). In Table 1, a comparison of the four synthetic methods is presented.

## 2.2. Catalytic trials with $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$

In a typical hydrogenation or isomerization trial,  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg,  $2 \times 10^{-3}$  mmol), 1-hexene (Aldrich, 1 ml, 8 mmol; 4000/1 substrate/catalyst ratio), 5 ml solvent (e.g., ethanol) are mixed in a high pressure stainless steel reactor (10 ml, glass liner, internal magnetic stirrer, 20–2000 psi manometer, Parr Instruments). After purging with  $\text{H}_2$  three times, the

reactor is pressurized to the desired  $\text{H}_2$  pressure, introduced in an oil bath at the desired temperature allowing 5 min for thermal stabilization. At the end of the run the reactor is rapidly cooled and the liquid analyzed by gas chromatography (P.E. AutoSystem 900, PE Nelson software; stainless steel column, 15% tricresyl phosphate on Chromosorb P, 60–80 mesh, 3 m long, 0.6 cm diameter or capillary column Plot fused silica, PoraPlot U, 12.5 m long, 0.53 mm i.d., 0.70 mm o.d.) or GC-MS (HP 5988A GC-MS). Olefin amination was carried out using a 10/1 Ar/ $\text{NH}_3$  mixture. Test reactions with all the other unsaturated substrates were carried out under similar conditions, adjusting the  $\text{H}_2$  pressure, solvent or reaction time as required.

Kinetic runs: In a 250 ml stainless steel high pressure reactor (Parr Instruments, glass liner, internal stirring, internal thermocouple and sample outlet)  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (20 mg,  $2 \times 10^{-2}$  mmol), 1-hexene (10 ml, 80 mmol; 4000/1 substrate/catalyst ratio), ethanol (solvent, 50 ml), cyclohexane (10 ml, internal standard) were mixed. After purging with  $\text{H}_2$  three times, hydrogen pressure adjusted to 100 psi and 5 min allowed for thermal stabilization ( $90^\circ\text{C}$ ), samples were taken every 5 min during 0.5 h. The samples were immediately quenched and analyzed by gas chromatography.

Table 1  
Synthesis methods for  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$

Synthesis method	Radical	Thermal	Photochemical	Assisted with $(\text{CH}_3)_3\text{NO}$
Yield (%)	94.2	73	95	62
Solvent	THF	Xylene	THF	$\text{CH}_2\text{Cl}_2$
General characteristics	Good yield and selectivity. Less clean reaction. Preparation and handling of radical very air and moisture sensitive.	Acceptable yield. Less selectivity, several products are obtained, that requires separation.	Good yield and selectivity. Very clean reaction. Product separation is simpler.	Acceptable yield and good selectivity. Intermediates are very sensitive. Separation of products more complex.

Table 2  
Hydrogenation and isomerization of 1-hexene

Solvent	Percent <i>n</i> -hexane	Percent 1-hexene	Percent <i>cis</i> -2-hexene	Percent <i>trans</i> -2-hexene
Ethanol	7.1	1.5	72.4	19.1
2-ethoxyethanol	20.9	1.9	59.9	17.3
THF	12.0	34.9	36.5	17.2
Toluene	16.1	58.6	16.5	8.8
Benzene	10.4	66.9	13.7	9.0
Heptane	8.4	66.5	15.5	9.7

Solvent effect. Reaction conditions: solvent (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 2$  h.

A systematic study of several reaction conditions were carried out.

(a) Solvent effect: The following solvents were tried: ethanol, 2-ethoxyethanol, THF, toluene, benzene, heptane. Reaction conditions: solvent (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 2$  h. The results are shown in Table 2. Ethanol was the solvent selected for the other catalytic studies.

(b)  $P_{\text{H}_2}$  effect:  $\text{H}_2$  pressure change results are shown in Fig. 1. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $T = 90^\circ\text{C}$ ,  $t = 2$  h. A 100 psi  $\text{H}_2$  pressure was selected for other catalytic studies.  $\text{H}_2$  pressure effects were also analyzed by the following experiments: (Exp. 1) similar conditions as above, but use pressure changes of Ar (no  $\text{H}_2$  pressure); (Exp. 2) similar conditions as above, but use pressure changes of Ar + 15 psi  $\text{H}_2$ ; (Exp. 3) similar conditions as above, but use pressure changes of Ar/ $\text{H}_2$  (50/50). The results are shown in Table 3.

(c) Temperature effect: Reaction temperature change results are shown in Fig. 2. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $t = 2$  h. A  $90^\circ\text{C}$  temperature was selected for other catalytic studies.

(d) Reaction time effect: Reaction time change results are shown in Fig. 3. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ . A 2 h reaction time was selected for the other catalytic studies.

(e) Amount of catalyst effect: Amount of catalyst change results are shown in Fig. 4. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 2$  h. A catalyst amount of 2 mg (about 4000/1 substrate/catalyst ratio) was selected for other catalytic studies.

(f) Hydrogenation of 2-hexene (11% *cis*/89% *trans* thermodynamic isomer mixture): A trial reaction was run with the isomer mixture. Reaction conditions: Ethanol (5 ml), 2-hexene (1 ml isomer mixture), cyclohexane (1 ml, internal standard),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ . Product distribution: after 6 h: *cis*-2-hexene (15%), *trans*-2-hexene (50%), 1-hexene (35%); after 24 h: *cis*-2-hexene (73%), *trans*-2-hexene (15%), *n*-hexane (12%).

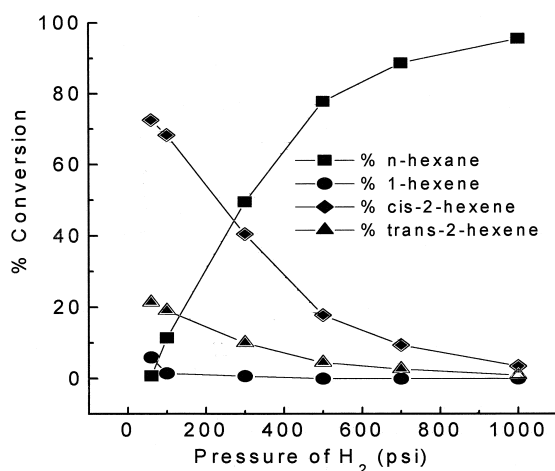


Fig. 1. Hydrogenation and isomerization of 1-hexene.  $\text{H}_2$  pressure effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $T = 90^\circ\text{C}$ ,  $t = 2$  h.

### 3. Results and discussion

#### 3.1. Synthesis of $Ru_3(CO)_{10}(dppm)$

The several synthetic methods tried for the synthesis of  $Ru_3(CO)_{10}(dppm)$  and shown in Table 1, indicate that the complex can be obtained in good yield using the diphenylketyl radical and photochemical activation. Lesser yields are observed with the thermal reaction, since this method is less selective and various products are obtained, and with  $(CH_3)_3NO$  there is good selectivity, but decomposition of the trimethylamine Ru carbonyl intermediate lowers the overall yield. The first two methods are thus recommended.

#### 3.2. Catalytic results

(a) Solvent effect: As shown in Table 2, under the reaction conditions used, more polar and better coordinating solvents like ethanol, THF and 2-ethoxyethanol give better overall yields, favoring the isomerization reaction with *cis*-2-hexene in greater percentage. Less polar solvents with lesser coordinating ability like toluene, benzene and heptane, give less overall yields and less marked product selectivity. This solvent behavior indicates a possible stabiliza-

tion of polar and/or coordinatively unsaturated intermediates in the catalytic cycle. The tendency to favor the *cis*-2-isomer clearly indicates an important steric requirement during the catalytic cycle.

(b)  $P_{H_2}$  effect: The isomerization reaction is greatly favored at low  $H_2$  pressure, giving predominantly the *cis*-2-hexene isomer (Fig. 1). At 100 psi  $H_2$  pressure, all the 1-hexene substrate has been consumed, mainly to give the internal isomers, and some hydrogenation product, *n*-hexane, its concentration increasing as  $H_2$  pressure increase; the concentration of isomers decreases rapidly and at 1000 psi  $H_2$  pressure, the main product is the saturated alkane. To test further the  $H_2$  pressure behavior, especially the low pressure region, several reactions in the presence of Ar were carried out (Table 3). In the absence of  $H_2$ , only the isomerization reaction favoring the *cis*-2-hexene isomer is observed in low yield; this process does not consume hydrogen and increases slightly with increasing Ar pressure to a maximum overall yield of about 30% when the total pressure reaches 1000 psi. When a 15 psi partial  $H_2$  pressure is included, the overall yield improves and increases slightly with increasing total pressure (Ar + 15 psi  $H_2$ ), still favoring isomerization of 1-hexene mainly to the *cis*-2-hexene

Table 3  
Hydrogenation and isomerization of 1-hexene

Ar pressure (psi)	Percent <i>n</i> -hexane	Percent 1-hexene	Percent <i>cis</i> -2-hexene	Percent <i>trans</i> -2-hexene
0	0.3	99.8	0	0
15	0.3	90.4	6.5	2.8
100	0.3	81.8	12.3	5.6
500	0.3	76.6	17.0	6.0
1000	0.4	71.0	20.8	7.9
Ar + 15 psi $H_2$				
100	2.4	13.5	58.2	25.9
500	2.5	11.0	65.2	22.4
1000	2.5	5.5	70.3	21.7
Ar + $H_2$ (50/50)				
15	4.6	6.8	61.7	19.1
100	35.6	2.6	43.4	16.3
500	47.7	1.8	42.1	8.4
1000	48.9	0.7	41.8	8.6

(Ar +  $H_2$ ) pressure effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $Ru_3(CO)_{10}(dppm)$  (2 mg),  $T = 90^\circ C$ ,  $t = 2$  h.

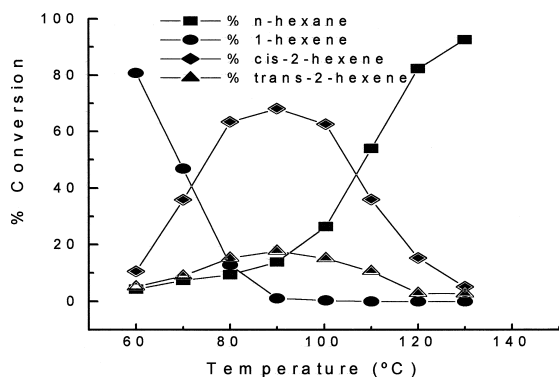


Fig. 2. Hydrogenation and isomerization of 1-hexene. Temperature effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $t = 2$  h.

isomer, and very little hydrogenation product. When a 50/50 Ar/ $\text{H}_2$  mixture is used, the product distribution is the expected isomerization favoring *cis*-2-hexene at lower partial hydrogen pressure and increases in the hydrogenation product, *n*-hexane, as the hydrogen partial pressure increases. There is a greater proportion of isomers at the higher  $\text{H}_2$  pressures when using an Ar/ $\text{H}_2$  mixture than when an equivalent pure hydrogen pressure is used. It becomes apparent that the isomerization route in the catalytic cycle can be activated in the absence of hydrogen pressure, probably via hydrogen abstraction from the  $\pi$ -bonded olefin to form a  $\pi$ -allyl intermediate; this route gets enhanced

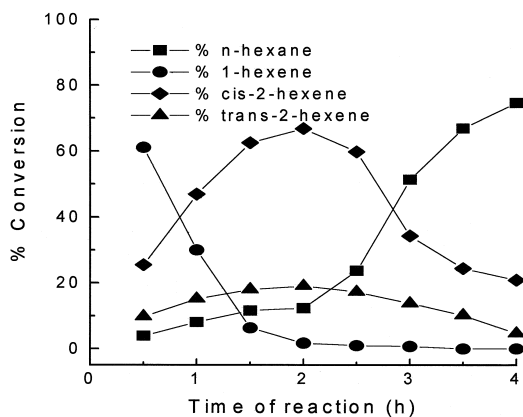


Fig. 3. Hydrogenation and isomerization of 1-hexene. Reaction time effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ .

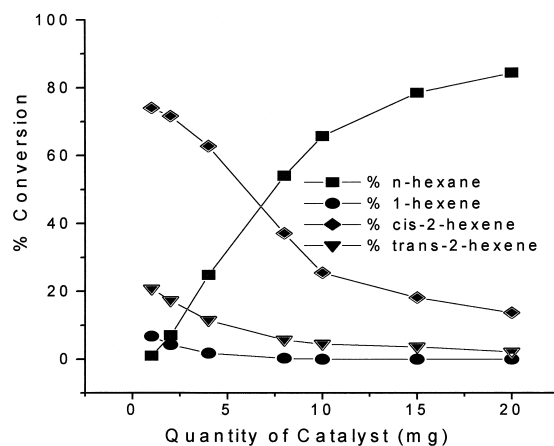


Fig. 4. Hydrogenation and isomerization of 1-hexene. Amount of catalyst effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $P_{\text{H}_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 2$  h.

under low hydrogen pressure, or a different mechanism, sharing a common  $\sigma$ -alkyl intermediate with the hydrogenation path could start dominating the reaction.

(c) Temperature effect: The overall yield is low at  $60^\circ\text{C}$  and increases rapidly with increasing temperature (Fig. 2). The isomerization reaction increases more rapidly, greatly favoring the *cis*-2-hexene isomer and reaching a maximum percent conversion at about  $90^\circ\text{C}$ . At this temperature all the substrate has been transformed to products. This is indicative that some minimum activation energy is required for the isomerization reaction to proceed, probably associated to ligand loss, like a CO group or phosphorus dissociation, to produce the coordinatively unsaturated species required for substrate substitution in the catalytic cycle. The hydrogenation reaction increases slowly with the temperature rise, and more rapidly after  $90^\circ\text{C}$  with a concomitant decrease in isomerization products, *n*-hexane being the dominant product at  $130^\circ\text{C}$ , the highest temperature tried. The higher temperature required for the hydrogenation reaction to proceed indicates a higher activation energy for this reaction path, most likely associated with ligand dissociation and  $\text{H}_2$  activation necessary for  $\text{H}_2$  oxidative addition in the catalytic cycle.

(d) Reaction time effect: The reaction progress with time is shown in Fig. 3. After 30 min, the percent overall conversion is already near 40%, with greater proportion of isomerization and favoring the *cis*-2-hexene internal isomer. After 2 h the reaction is practically complete, with the maximum production of *cis*-2-hexene. After this time complete hydrogenation to *n*-hexane increases rapidly, the internal isomers likewise being hydrogenated as the reaction proceeds. These results indicate that the isomerization reaction is faster than hydrogenation, the initial alkane being produced by hydrogenation of the terminal 1-hexene olefin and when this is consumed, the internal olefins that are more difficult to hydrogenate get reduced to alkane.

(e) Amount of catalyst effect: A reaction using 1 mg of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  as catalyst precursor, under the reaction conditions used, produces more than 90% conversion, predominating the *cis*-2-hexene isomerization product (Fig. 4). As the amount of Ru complex is increased, more hydrogenation product is observed, being the predominant product when 20 mg of compound are used. As the substrate/catalyst ratio decreases, more active sites are introduced, increasing the probability for complete olefins hydrogenation, including the internal olefins produced more rapidly during the isomerization process.

(f) Hydrogenation of 2-hexenes: The results obtained when the thermodynamic isomer mixture of *trans*-2-hexene and *cis*-2-hexene is placed under the reaction conditions for isomerization of 1-hexene, demonstrates that after sufficient time the kinetic mixture is equilibrated. The results after 6 h, indicate that isomerization

to the terminal olefin is faster than *trans*-*cis* isomerization; after 24 h, the *cis*-2-hexene isomer predominates, and some hydrogenation products have already appeared. This result indicates that the internal olefins can enter the catalytic cycle and be equilibrated with the other products in reversible reactions. The fact that the times required for reaction are longer than when the initial substrate is 1-hexene indicate that the internal olefins are more difficult to coordinate due to steric reasons and that the reverse reaction to  $\pi$ -olefin dissociation in the catalytic cycle is slower.

(g) Stability studies of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ : In homogenous catalysis it is important to verify that the reaction is carried out by the cluster complex rather than by another species derived from cluster fragmentation or metallic particles from complex decomposition.  $\text{Ru}_3(\text{CO})_{12}$  was used in a test reaction under similar reaction conditions. The results are shown in Table 4. The  $\text{Ru}_3(\text{CO})_{12}$  cluster gives a similar catalytic behavior but is less active than  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ , and readily decomposes to metallic particles above 300 psi  $\text{H}_2$  pressure. A test reaction carried out under similar reaction conditions, 100 psi  $\text{H}_2$  but containing  $\text{Ru}_3(\text{CO})_{12}$  (2 mg) and dppm ligand (1.20 mg) gives a higher percent total yield, with the following product distribution: 68.4% *cis*-2-hexene, 16.9% *trans*-2-hexene and 5.9% *n*-hexane; this indicates that a dppm substituted Ru cluster is formed in situ, providing greater thermal stability to the ruthenium carbonyl cluster. The dppm substituted cluster does not show decomposition signs up to 1000 psi  $\text{H}_2$  pressure, indicating that the bidentate ligand stabilizes the trinuclear cluster. This is verified by observing the final reaction solu-

Table 4  
Catalysis study of 1-hexene with  $\text{Ru}_3(\text{CO})_{12}$

$\text{H}_2$ pressure (psi)	Percent <i>n</i> -hexane	Percent 1-hexene	Percent <i>cis</i> -2-hexene	Percent <i>trans</i> -2-hexene
100	12.6	27.0	42.0	18.3
300	55.1	1.0	35.4	8.3
500	66.4	0.0	27.7	5.9

$\text{H}_2$  pressure effect. Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{12}$  (2 mg),  $T = 90^\circ\text{C}$ ,  $t = 2$  h.

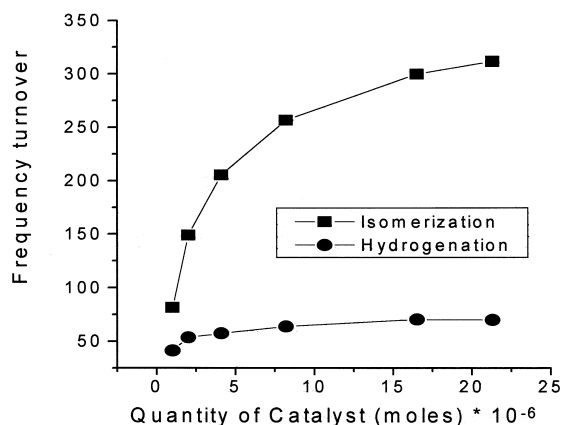


Fig. 5. Hydrogenation and isomerization of 1-hexene. Turnover frequency (millimoles product/(millimoles catalyst)(minutes)) vs. Amount of catalyst (millimoles). Reaction conditions: Ethanol (5 ml), 1-hexene (1 ml, 0.67 g), cyclohexane (1 ml, internal standard)  $P_{H_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 0.5$  h.

tion under the microscope and by running a test reaction in the presence of metallic mercury with similar conditions (ethanol (5 ml), 1-hexene (1 ml, 0.67 g),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (2 mg),  $P_{H_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 2$  h) [25,26]. When Hg is used the change in percent yield for the different products is less than 5%, discarding metallic Ru as the active catalyst.

Several reactions were carried out increasing the number of millimoles of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  and the products analyzed before reaching 40% total conversion (reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), cyclohexane (1 ml, internal standard),  $P_{H_2} = 100$  psi,  $T = 90^\circ\text{C}$ ,  $t = 0.5$  h). A plot of turnover frequency (millimoles of product/(millimoles catalyst) (minutes)) vs. millimoles of catalyst gives an indication of cluster catalysis, possible fragmentation or catalysis by higher nuclearity species [27]. The plot is shown in Fig. 5 for isomerization and hydrogenation results. Both reactions show an increase in turnover frequency as the amount of Ru complex increases, but the slopes are rather different. The increasing tendency is interpreted as indicative of cluster catalysis rather than produced by active fragments of lower nuclearity [27]. The  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  complex can be thermally induced to lose CO

and benzene with reflux at high temperatures in noncoordinating solvents to give species as  $\text{Ru}_3(\mu_3\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))(\text{CO})_8$  [28–30]. Our reaction conditions do not favor cluster decomposition and the solution color remains after reaction, but the presence of species as the thermolysis product above cannot be discarded as possible intermediates. This species is presently being investigated under our reaction conditions to compare its possible catalytic behavior.

(h) Kinetic results: The first order plot for the kinetic studies in the isomerization and hydrogenation of 1-hexene, following the disappearance of substrate is shown in Fig. 6. The results indicate first order on substrate with an apparent rate constant value of  $0.11 \text{ min}^{-1}$  for the total reaction.

### 3.3. Catalysis with other substrates

The  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  complex was tried with other organic substrates to explore the extent of its catalytic activity. The results are summarized in Table 5. Terminal olefins like 1-hexene and styrene get hydrogenated almost completely at 1000 psi  $\text{H}_2$  pressure and 90 min

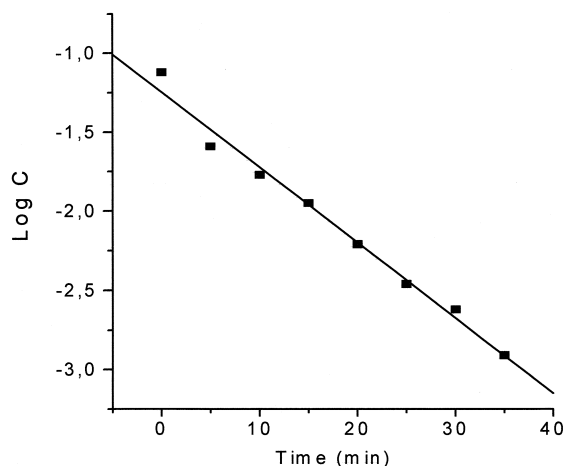


Fig. 6. Hydrogenation and isomerization of 1-hexene. Kinetic results. Reaction conditions: Ethanol (50 ml), 1-hexene (10 ml, 6.7 g), cyclohexane (10 ml, internal standard),  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  (20 mg),  $P_{H_2} = 100$  psi,  $T = 90^\circ\text{C}$ .



Table 5  
Catalytic reactions of unsaturated organic substrates with Ru<sub>3</sub>(CO)<sub>10</sub>(dppm)

Substrate	Product (%)	Conditions	Time (h)
<i>(a) Hydrogenation of unsaturated organic substrates</i>			
1-hexene	<i>n</i> -hexane (91.9), <i>cis</i> -2-hexene (6.5), <i>trans</i> -2-hexene (1.6)	ethanol, 90°C, 1000 psi H <sub>2</sub>	1.5
styrene	ethylbenzene (96.3)	ethanol, 90°C, 1000 psi H <sub>2</sub>	1.5
1-hexyne	<i>n</i> -hexane (52.4), 1-hexene (33.4), <i>trans</i> -2-hexene (5.9), <i>cis</i> -2-hexene (6.3)	ethanol, 90°C, 1500 psi H <sub>2</sub>	5
cyclohexene	cyclohexane (96.2)	ethanol, 90°C, 1000 psi H <sub>2</sub>	2
benzene	cyclohexadiene (1.3), cyclohexene (5.2), cyclohexane (7.8)	ethanol, 90°C, 1500 psi H <sub>2</sub>	24
acetone	isopropanol (32.1)	THF, 90°C, 1600 psi H <sub>2</sub>	18
cyclohexanone	cyclohexanol (37.9)	THF, 90°C, 1600 psi H <sub>2</sub>	18
<i>(b) Hydrogenation of α - β unsaturated aldehydes</i>			
acrolein	propanaldehyde (52.9), propanol (27.3), 2-propenol (4.9)	THF, 90°C, 1600 psi H <sub>2</sub>	8
crotonaldehyde	butyraldehyde (36.3), butanol (22.1), 2-butenol (21.4)	THF, 90°C, 1600 psi H <sub>2</sub>	8
cinnamaldehyde	3-phenylpropanal (12.2), 3-phenylpropanol (17.6), 3-phenyl-2-propenol (46.3)	THF, 90°C, 1600 psi H <sub>2</sub>	8
<i>(c) Isomerization of unsaturated organic substrates</i>			
1-hexene	<i>n</i> -hexane (7.1), <i>cis</i> -2-hexene (72.4), <i>trans</i> -2-hexene (19.1)	ethanol, 90°C, 100 psi H <sub>2</sub>	2
1-hexyne	<i>n</i> -hexane (52.4), 1-hexene (33.4), <i>trans</i> -2-hexene (5.9), <i>cis</i> -2-hexene (6.3)	ethanol, 90°C, 1500 psi H <sub>2</sub>	5
1-methylcyclohexene	methylcyclohexene (15.6), 2-methylcyclohexene (5.4), 3-methylcyclohexene (2.3)	THF, 90°C, 500 psi H <sub>2</sub>	4
allylic alcohol	propanal (33.3), propanol (26.0)	THF, 90°C, 200 psi H <sub>2</sub>	2
<i>(d) Hydroformylation of 1-hexene</i>			
1-hexene	2-methylhexanal (8.4), heptanaldehyde (34.7)	THF, 130°C, 1000 psi H <sub>2</sub> /CO (1/1)	6
<i>(e) Amine synthesis. Hydrogenation</i>			
acetonitrile	ethylamine, diethylamine, triethylamine (20 total)	ethanol, 90°C, 1600 psi H <sub>2</sub>	24
benzonitrile	benzylamine (66.6)	ethanol, 90°C, 1600 psi H <sub>2</sub>	24
nitrobenzene	aniline (42.1)	ethanol, 90°C, 1600 psi H <sub>2</sub>	24
<i>Condensation of NH<sub>3</sub> with alcohol and olefins</i>			
CH <sub>3</sub> OH/NH <sub>3</sub>	CH <sub>3</sub> NH <sub>2</sub> (15)	methanol, 90°C, 1000 psi NH <sub>3</sub> /Ar (10/1)	24
CH <sub>3</sub> CH <sub>2</sub> OH/NH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> (23)	ethanol, 90°C, 1000 psi NH <sub>3</sub> /Ar (10/1)	24
Propylene/NH <sub>3</sub>	propylamine (13.3), isopropylamine (5.8)	THF, 125°C, 30 mg cat, 1000 psi propylene/NH <sub>3</sub> /Ar, 5/10/150	16
1-hexene/NH <sub>3</sub>	hexylamine (16.4), 2-hexylamine (7.2)	THF, 125°C, 30 mg cat, 1-hexene, 1000 psi Ar/NH <sub>3</sub> 15/1	16

Reaction conditions: Solvent (5 ml), substrate (1 ml), Ru<sub>3</sub>(CO)<sub>10</sub>(dppm) (2 mg).

reaction; cyclic olefins like cyclohexene are harder to hydrogenate and take longer to get high percent conversions. Alkynes as 1-hexyne require stronger hydrogenation conditions and more reaction time to attain complete reduction, important yield of the intermediate 1-hexene is observed and small amounts of isomerization products. Aromatic substrates like benzene and ketones as acetone and cyclohexanone are more difficult to hydrogenate, requiring stronger reaction conditions and longer reaction time to get partial reduction. For substrate with two functional groups susceptible of reduction as in  $\alpha,\beta$  unsaturated aldehydes, the hydrogenation results indicate that both the carbon–carbon double bond and the carbonyl group can be hydrogenated, under stronger reaction conditions and longer times. Complete reduction is observed in important yield for acrolein and crotonaldehyde, but for cinnamaldehyde, carbonyl reduction predominates. This results indicate that the Ru complex studied does not show strong regioselectivity in its hydrogenating activity. The isomerization reaction observed with 1-hexene, which favors the *cis*-2-hexene isomer, was extended to other substrates. With 1-hexyne, the stronger reduction conditions required for the first hydrogenation, only allows accumulation of a small percentage of the expected isomers derived from 1-hexene before complete hydrogenation occurs. With 1-methylcyclohexene, only small amounts of isomerization to the 2 and 3 positions are observed. With allylic alcohol, double bond migration to form the carbonyl group occurs in good proportion, but the competing complete reduction reaction is also very prevalent. A test reaction under hydroformylation conditions with 1-hexene, favors the linear aldehyde, with some branched aldehyde produced, but with intermediate overall percent yield. Our research group is interested in the catalytic activity of ruthenium complexes for synthesis of amines. Hydrogenation of nitriles, such as acetonitrile and benzonitrile and nitro groups as in nitrobenzene, to give the expected amines requires higher  $H_2$  pressure and longer

reaction times. With acetonitrile, the scrambling reaction is apparent, and this reaction is being further pursued in our laboratory. The condensation reaction between  $NH_3$  and small alcohols such a methanol and ethanol provides reasonable amine yields under the reaction conditions tried. The reactions between  $NH_3$  and olefins such as propylene and 1-hexene under the reaction conditions tried, give the N–H addition products, with a slight preference for the terminal amine.

The  $Ru_3(CO)_{10}(dppm)$  complex has shown good hydrogenation activity for several unsaturated organic groups, and a strong isomerization tendency for 1-hexene at low hydrogen pressures, favoring the *cis*-2-hexene isomer, indicative of an important steric requirement that could have eventual application in regioselective or stereoselective hydrogenation reactions. The complex also shows an interesting N–H activation capacity that is being explored for specific amine synthesis.

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