

Catalysis studies of $\text{Ru}_3(\text{CO})_{12}$ substituted with $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$

Bernardo Fontal*, Ricardo Hernández, Trino Suárez, Marisela Reyes and Fernando Bellandi

Laboratorio Organometálicos, Departamento de Química, Facultad de Ciencias
Universidad de Los Andes, Mérida, Venezuela. Telf: 074- 401380; Fax: 074- 401286
E-mail: fontal@ciens.ula.ve

Abstract

$\text{Ru}_3(\text{CO})_{12}$ substituted with $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppp) isomerizes 1-hexene mainly to the kinetic product cis-2-hexene and smaller amounts of trans-2-hexene, but complete reduction to n-hexane is favored under stronger hydrogenation conditions ($P_{\text{H}_2} > 200$ psi, $T > 85^\circ\text{C}$, catalyst concentration > 100 ppm). Cyclohexene is hydrogenated to cyclohexane and cyclohexanone to cyclohexanol under stronger reaction conditions. These results differ from reactions with unsubstituted $\text{Ru}_3(\text{CO})_{12}$ which favors the trans-2-hexene isomer at lower H_2 pressure and mononuclear Ru dppp complexes which show only the hydrogenation product under similar reaction conditions.

Key words: Ru complexes, homogenous hydrogenation and isomerization catalysis, and bidentate phosphines.

Estudios de catálisis de $\text{Ru}_3(\text{CO})_{12}$ sustituido con $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$

Resumen

$\text{Ru}_3(\text{CO})_{12}$ sustituido con $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppp) isomeriza 1-hexeno principalmente al producto cinético cis-2-hexeno y menores cantidades de trans-2-hexeno, pero reducción completa a n-hexano se favorece bajo condiciones mas fuertes de hidrogenación ($P_{\text{H}_2} > 200$ psi, $T > 85^\circ\text{C}$, concentración de catalizador > 100 ppm). Ciclohexeno se hidrogena a ciclohexano y ciclohexanona a ciclohexanol bajo condiciones mas severas de reacción. Estos resultados difieren de la reacción con $\text{Ru}_3(\text{CO})_{12}$ no sustituido que favorece el isómero trans-2-hexeno a presiones de H_2 más bajas y de complejos de Ru dppp mononucleares que muestran solo el producto de hidrogenación bajo condiciones de reacción similares.

Palabras clave: Complejos de Ru, catálisis de hidrogenación e isomerización homogénea, fosfinas bidentadas.

Introduction

Terminal olefin isomerization to an internal olefins mixture occurs with ruthenium and osmium clusters, $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$), and the clusters substituted with monodentate phosphines have been used previously as catalysts in several reactions [1]. Isomerization of 1-pentene in refluxing hexane to give mainly trans-2-pentene is of particular interest for our work [2].

$\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{L}$ clusters give similar results. [3]. Isomerization rates are solvent dependent, decreasing in the following order: chlorobenzene $>$ benzene $>$ toluene $>$ cyclohexane $>$ mesitylene [4]. The $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ clusters give different isomer ratios under photolytic conditions [5]. The terminal olefin, 1-hexene, produces a 76% trans and 24% cis ratio using $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ as catalyst [6]. Sanchez-Delgado *et al.* have reported 1-hexene hydrogenation

tion to n-hexane with $\text{Ru}_3(\text{CO})_{12}$ [7]. Cyclohexene, a cyclic olefin model in hydrogenation studies, gives cyclohexane using several osmium carbonyl clusters [8]. Cyclohexane is obtained from cyclohexene with the following substituted Ru clusters: $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$, $\text{Ru}_3(\text{CO})_7(\text{PPh}_3)_2(\text{C}_6\text{H}_4)$ [9], $\text{H}_3\text{Ru}_4(\text{CO})_{10}(\text{dppm})_2$ (dppm = $\text{PhPCH}_2\text{PPh}_2$), $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppm})$ [10a], $\text{H}_2\text{Ru}_3(\text{E})(\text{CO})_5(\text{dppm})_2$ (E = O, S) [10b]. Cyclohexanone is hydrogenated to cyclohexanol with $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$ [11] and $\text{Ru}_3(\text{CO})_8(\text{PPh}_2)-[\text{PPh}(\text{C}_5\text{H}_4\text{N})]$ [12]. Both unsaturated groups in cyclohex-1-en-2-one are hydrogenated with $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ and $\text{Ru}_3(\text{CO})_7(\text{PPh}_3)_2(\text{C}_6\text{H}_4)$ [9]. The presence of ligands capable of stabilizing metal clusters during catalytic reactions is considered important [13]. Polydentate phosphine ligands could be useful for cluster stabilization, but little work has been reported on the effect of these ligands on cluster catalysis. In our laboratory we have been studying the catalytic behavior of Ru complexes with polydentate phosphines [14]. In other studies we have reported the catalytic reactions with Ru carbonyl cluster in the presence of one and two dppm ligands and the tripodal $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ ligand [15]. In this paper we report catalytic reactions with $\text{Ru}_3(\text{CO})_{12}$ in the presence of bis-1,3(diphenylphosphino)propane ($\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2 = \text{dppp}$) under hydrogenation conditions.

Experimental

Synthesis

Preparation of $\text{Ru}_3(\text{CO})_{12}/\text{dppp}$: $\text{Ru}_3(\text{CO})_{12}$ (0.156 mmol, 100 mg, Strem Chem.) was refluxed in petroleum ether (59-60, 200 ml, Aldrich) under N_2 with dppp (0.313 mmol, 128.9 mg, Strem Chem) for several hours; $\text{Ru}_3(\text{CO})_{12}$ consumption was followed by carbonyl bands disappearance using FTIR. (PE 1725-X). An orange yellow solution formed that gave three main bands (yellow (corresponding to compound **1**), light violet (compound **2**), and orange (compound **3**)) in thin layer chromatography (3:1 hexane/ CH_2Cl_2 as eluant). A variation of the synthetic method, utilizes the above mixture with slow addition of $(\text{CH}_3)_3\text{NO}$ (11.7 mg, in $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (3:1, 200 ml) to give a wine red solution. Compounds **1**, **2** and **3** are obtained by preparative

thin layer chromatography. A red orange compound (**2**) crystallizes in CH_2Cl_2 and corresponds to the compound used in the catalytic studies. This compound shows IR bands characteristic of the dppp ligand and ν_{CO} bands at: 2100 (sm), 2070 (m, sharp), 2010 cm^{-1} (m, sharp); 1940 (st, broad). The spectrum is similar to cluster compounds with one bidentate ligand bridging two Ru atoms [15]. The compound does not crystallize well enough for x-ray diffraction.

Hydrogenation reactions

In a typical reaction, $\text{Ru}_3(\text{CO})_{12}/\text{dppp}$ (comp. **2**) (1 mg), the substrate (1 ml) and the appropriate solvent (7 ml) (catalyst concentration 1mg/8 ml, ca. 140 ppm) were placed in the glass container of a high pressure reactor (12 ml, stainless steel, Parr Inst. Co.). The reactor was previously purged three times with H_2 , and filled to the desired H_2 initial pressure (estimated at the working temperature) heated in a silicon oil bath to the desired working temperature and stirred with a magnetic stirrer. After the required reaction time, the reactor is introduced in an ice-water mixture; the reaction solution (clear yellow, no turbidity) is passed through a small silica gel column (60-80 mesh, 5 cm, 1/4" o.d.) to separate the metal catalyst. The solution is separated and the different products identified by gas chromatography (P.E. Autosystem, thermal conductivity and FID detector). For 1-hexene, cis-2-hexene, trans-2-hexene and cyclohexene substrates, the reaction products were separated using a stainless steel column (trimesyl phosphate 15% on Chromosorb P, 80-100 mesh, 3m long, 1/8" d); for the cyclohexanone substrate, the reaction products were separated using a stainless steel column (Carbowax 1540 10% on Chromosorb WHP, 3m long, 1/8" o.d.).

A systematic study using different reaction conditions was carried out.

a) Solvent effect: The following solvents were tried: benzene, acetone, THF, ethanol, dioxane. The reaction conditions are given in Table 1. The results are shown in Table 2. THF was the solvent selected for the other catalytic studies.

b) P_{H_2} effect: The results due to H_2 pressure changes are shown in Figure 1. Reaction conditions are given in Table 1. A 500 psi H_2 pres-

Table 1
Reaction conditions for the catalytic reactions.

Reaction	Reaction Conditions
a) Solvent Effect	7 ml solvent, 1 ml (0.67 g) 1-hexene, 1 mg catalyst, P _{H2} = 500 psi (34.5 atm), T= 95°C, time = 60 min.
b) H ₂ Pressure Effect Experiment 1)	1 ml 1-hexene, 7 ml THF, 1 mg catalyst; T= 95°C, time = 60 min. Previous treatment: 7 ml THF, 1 mg of catalyst, 100 psi H ₂ , T= 95°C, time = 60 min. Afterwards: add 1 ml 1-hexene, P _{H2} = 100 psi, T= 95°C, time = 60 min.
Experiment 2)	Previous treatment as Exp. 1). Afterwards: add 1 ml 1-hexene, P _{N2} = 100 psi, T= 95°C, time = 60 min.
Experiment 3)	No previous H ₂ treatment. 7 ml THF, 1 mg catalyst. Add 1 ml 1-hexene, P _{N2} = 100 psi, T= 95°C, time = 60 min.
c) Temperature effect	1 ml 1-hexene, 7 ml THF, 1 mg catalyst, P _{H2} = 500 psi, time = 60 min.
d) Reaction time effect	1 ml 1-hexene, 7 ml THF, 1 mg catalyst, P _{H2} = 500 psi, T= 95°C.
e) Amount of catalyst effect	1 ml 1-hexene, 7 ml THF, P _{H2} = 500 psi, T= 95°C, time = 60 min.
f) Hydrogenation of 2- hexenes	1 ml cis/ trans 2-hexene mixture, 7 ml THF, 1 mg catalyst, P _{H2} = 500 psi, T= 95°C, time = 60 min.
g) Hydrogenation of cyclohexene	1 ml cyclohexene, 7 ml THF, P _{H2} = 500 psi, T= 95°C, time= 60 min.
h) Hydrogenation of cyclohexanone	1 ml cyclohexanone, 7 ml THF, 1 mg catalyst, T= 95°C, time = 60 min.

sure was selected for other catalytic studies. Isomerization/ hydrogenation ratio changes with H₂ pressure are shown in Figure 1a. H₂ pressure effects were also analyzed by running three experiments: Exp. 1, Exp. 2 and Exp. 3 and the reaction conditions are shown in Table 1. The results for these three experiments are shown in Figure 2.

c) Temperature effect: The results for changes in the reaction temperature are shown in Figure 3. Reaction conditions are given in Table 1. A 95°C temperature was selected for other catalytic studies.

d) Reaction time effect: The results for changes in reaction time are shown in Figure 4. Reaction conditions are given in Table 1. A 60 minutes reaction time was selected for the other catalytic studies.

e) Amount of catalyst effect: The results for changes in the amount of catalyst are shown in Figure 5. Reaction conditions are given in Table 1. A catalyst concentration of ca. 140 ppm (1 mg/7 ml) was selected for other catalytic studies.

f) Hydrogenation of 2 hexenes (11% cis/89% trans isomer mixture): A trial reaction was run with the isomer mixture. Reaction conditions are given in Table 1. Product distribution after 1 hour: trans-2-hexene (48%), cis-2-hexene (42%), n-hexane (10%). The results as a function of reaction time are shown in Figure 6

g) Hydrogenation of cyclohexene: Reaction conditions are given in Table 1. Product distribution after 1 hour: cyclohexene: 73.5%; cyclohexane: 26.5%.

h) Hydrogenation of cyclohexanone: The hydrogenation results as a function of P_{H2} are shown in Figure 7. Reaction conditions are given in Table 1.

Results and Discussion

Hydrogenation results

a) Solvent effect: The percent conversion (Table 2) follows the coordinating capacity of the solvents (THF > 1,4 Dioxane > ethanol > acetone > benzene), thus showing that nonpolar and poorly

coordinating solvents such as benzene give low percent conversion; more polar and coordinating solvents like THF, dioxane and ethanol give a greater conversion, favoring complete hydrogenation to n-hexane with increasing solvent polarity and favoring isomerization to cis-2-hexene over trans-2-hexene. Reaction in acetone gives intermediate conversion. The isomerization percentage reaches a maximum with the more polar ethanol (Table 2), favoring the trans-2-hexene isomer and is lowest with THF. The effect of polar coordinating solvents could indicate solvent stabilization of coordinatively unsaturated intermediates in the catalytic cycle.

b) P_{H_2} effect: At low hydrogen pressure (at 100 psi, Figure 1), total conversion is intermediate (49%); the isomerization compounds are the main products, with cis-2-hexene (16%) pre-

dominating, a smaller quantity of trans-2-hexene (10%) and low (22%) complete hydrogenation to n-hexane. As the P_{H_2} increases from 100 to 700 psi, there is a gradual increase in complete hydrogenation coming mainly from 1-hexene and after 400 psi the isomerization products get hydrogenated but at a slower rate. Above 400 psi, the conversion is complete and the hydrogenation to n-hexane levels off, being still incomplete (85% n-hexane) at the highest pressure tried (700 psi). The isomerization/hydrogenation (isom/hydr.) relation decreases as the P_{H_2} increases (Figure 1a). Reactions carried out below 50 psi show the following results:

- P_{H_2} = 20 psi, time = 6 hr, gives 30% conversion, isom./hydr. ratio = 2.08 (Other conditions: 1 ml 1-hexene, 7 ml THF, 1 mg catalyst, $T = 95^\circ\text{C}$).

Table 2
Solvent effect. Product distribution (%)^a

Solvent	1-hexene	cis-2-hexene	trans-2-hexene	n-hexane	%isom/%hydrog
THF	0	17	3	80	20 / 80
1,4 Dioxane	1	24	7	68	31.3 / 68.7
Ethanol	3	25	29	43	55.7 / 44.3
Acetone	32	16	9	43	36.8 / 63.2
Benzene	65	7	3	25	28.6 / 71.4

a) 7 ml solvent, 1ml (0.67 g) 1-hexene, 1 mg catalyst, $P_{H_2} = 500$ psi (34.5 atm), $T = 95^\circ\text{C}$, $t = 60$ min.

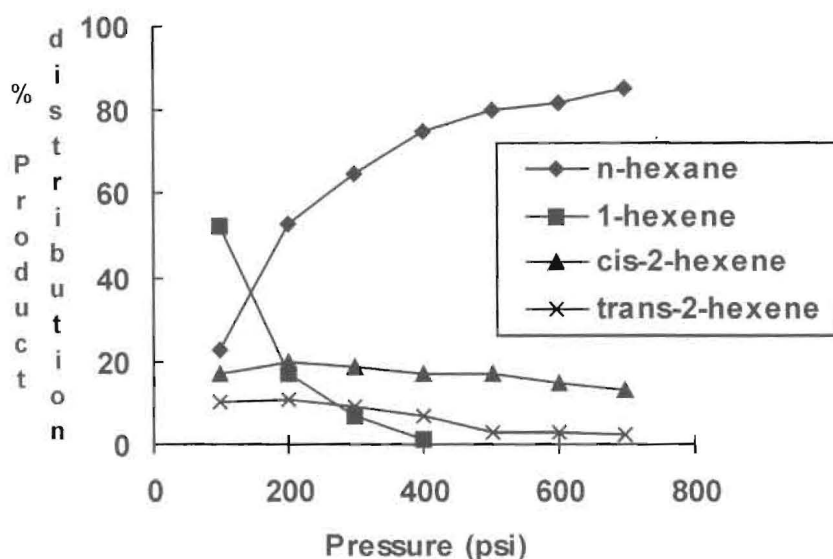


Figure 1. Hydrogenation of 1-hexene. H_2 pressure effect (psi) (1 mg catalyst, 1 ml 1-hexene, 7 ml THF, $T = 95^\circ\text{C}$, time = 60 min).

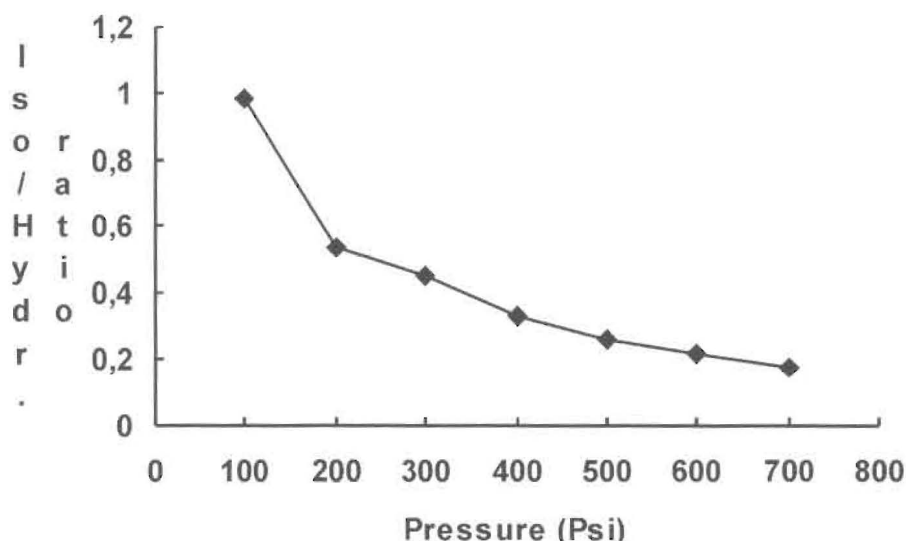


Figure 1a. Hydrogenation of 1-hexene. H_2 pressure effect. Isomerization/Hydrogenation ratio (1 mg catalyst, 1 ml 1-hexene, 7 ml THF, $T = 95^\circ\text{C}$, time = 60 min).

- $P_{\text{H}_2} = 20$ psi, time = 24 hr, gives 60% conversion and isom./hydr. ratio = 2.77.
- $P_{\text{H}_2} = 5$ psi, time = 24 hr, gives 20% conversion and isom./hydr. ratio = 3.41.

These results indicate that the isomerization products are favored at lower pressures, always giving a greater proportion of the cis-2-hexene isomer.

The results shown in Figure 2, indicate that a hydrogen pressure is required for the isomerization reaction to take place, since very little or no reaction is observed in the presence of a N_2 pressure, probably indicative of a Ru hydride intermediate. The small % conversion observed with a previous H_2 pressure treatment (Exp. 2) could indicate that the hydride intermediate could be formed in situ, but is unstable without H_2 pressure during reaction.

c) Temperature effect: At temperatures below 65°C there is a very small conversion (Figure 3). The isomerization and hydrogenation products increase gradually up to 95°C ; here total conversion is already close to 100%, hydrogenation to n-hexane is near 80% and a smaller quantity of isomerization products (cis-2-hexene (18%) and trans-2-hexene (2%)). At temperatures above 95°C , the hydrogenation reaction dominates at the expense of the isomerization products, being close to 89% at 105°C , the highest temperature studied.

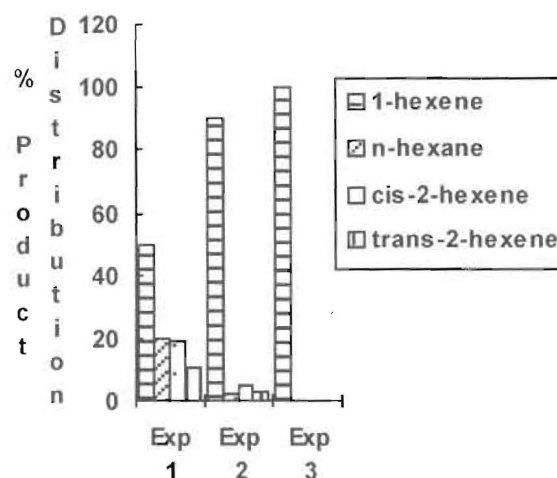


Figure 2. Hydrogenation of 1-hexene. H_2 pressure effect (1 mg catalyst, 1 ml 1-hexene, 7 ml THF, $T = 95^\circ\text{C}$). Exp. 1 and 2, previous treatment $P_{\text{H}_2} = 100$ psi, time = 60 min.

Exp. 1: $P_{\text{H}_2} = 100$ psi, time = 60 min;
 Exp. 2: $P_{\text{N}_2} = 100$ psi, time = 60 min.;
 Exp. 3: No previous treatment,
 $P_{\text{N}_2} = 100$ psi, time = 60 min.

d) Reaction time effect: 1-hexene is consumed rapidly producing mainly the hydrogenation product and smaller amounts of isomerization products (Figure 4). After 15 minutes the product distribution is approximately the same percentage for the three products, then n-hexane increases up to 75% after 1 hour. The cis-2-hexene isomer reaches a maximum (20%) after

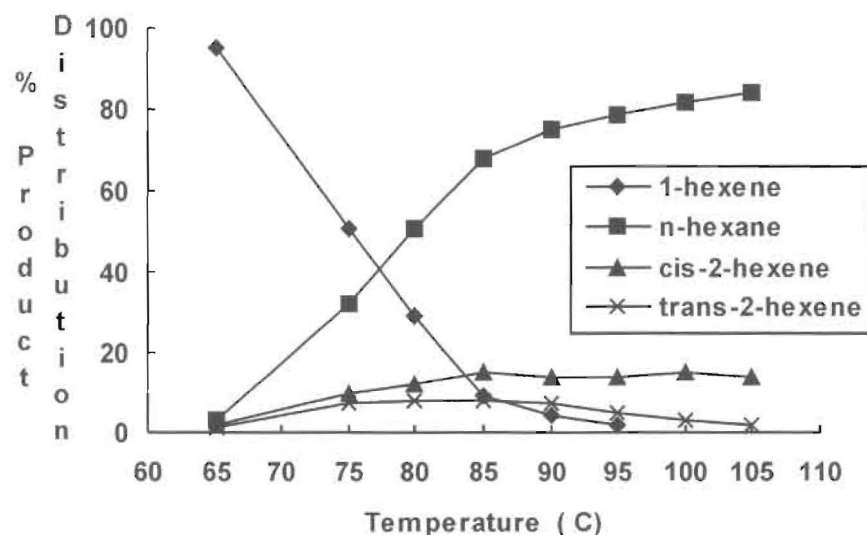


Figure 3. Hydrogenation of 1-hexene. Temperature effect (1 mg catalyst, 1 ml 1-hexene, 7 ml THF, P_{H_2} = 500 psi, time = 60 min).

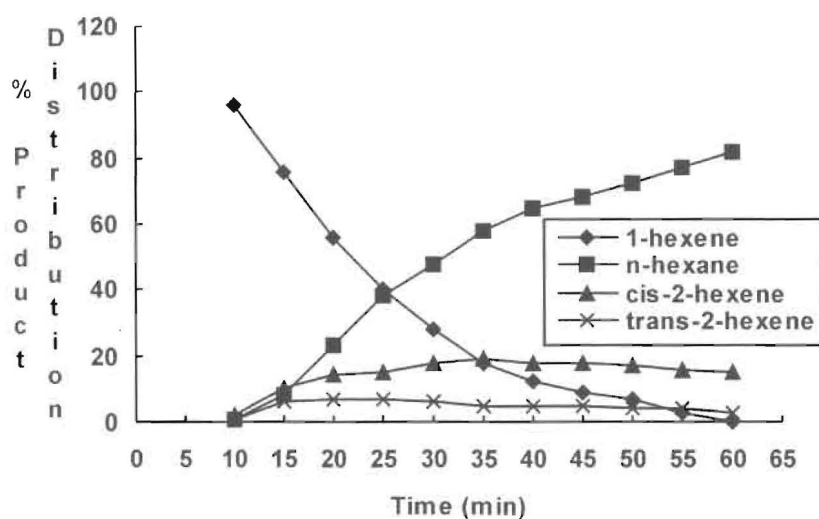


Figure 4. Hydrogenation of 1-hexene. Reaction time effect (1 mg catalyst, 1 ml 1-hexene, 7 ml THF, P_{H_2} = 500 psi, T = 95°C).

35 minutes, and then decreases. In the linear portion of the decreasing curve (consumption) for 1-hexene (between 10 and 25 min) there is a consumption of 0.292 moles of 1-hexene for mg of catalyst per minute. A catalytic frequency of 321 min^{-1} is calculated (assuming a molecular weight of 1010 g/mol for compound **2**, possibly $\text{Ru}_3(\text{CO})_{10}(\text{dppp})$). For the hydrogenation curve, in the linear range (15- 35 min), 0.180 mmoles of n-hexane are produced per mg of catalyst per minute, giving an approximate catalytic frequency of 200 min^{-1} .

e) Amount of catalyst effect: The percent conversion is low (only 10%, mainly hydrogenation product) for concentrations below 25 ppm (Figure 5); there is an increase in total reaction rate as the catalyst concentration increases, giving mainly hydrogenation product, with a large increase after 100 ppm and leveling off after 150 ppm. The isomerization products increase more slowly, favoring cis-2-hexene. At the highest concentration tried (200 ppm), an apparent equilibrium mixture (85% n-hexane, 13% cis-2-hexene and 2% trans-2-hexene) is observed. This behav-

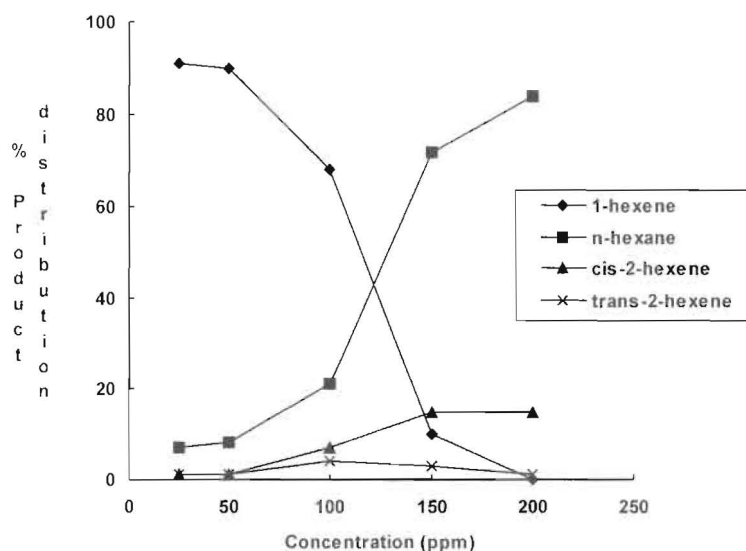


Figure 5. Hydrogenation of 1-hexene. Amount of catalyst effect (1 ml 1-hexene, 7 ml THF, $P_{\text{H}_2} = 500$ psi, $T = 95^\circ\text{C}$, time = 60 min).

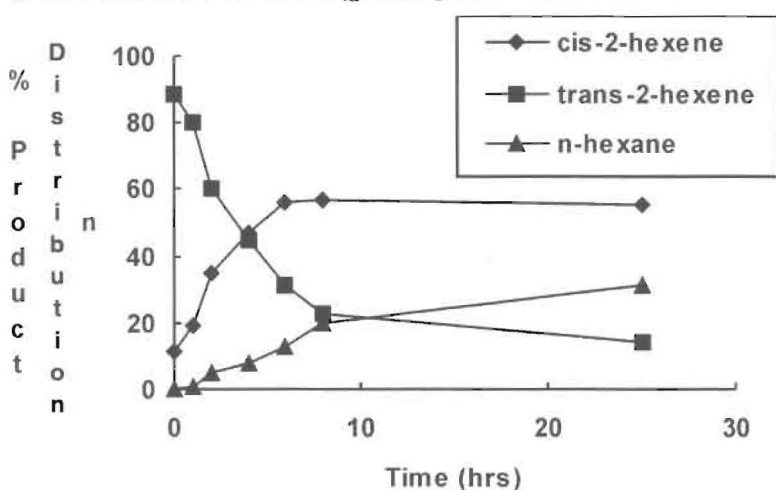


Figure 6. Hydrogenation of 2-hexene (cis/trans mixture). Reaction time effect (1 mg catalyst, 1 ml 2-hexene, 7 ml THF, $P_{\text{H}_2} = 100$ psi, $T = 95^\circ\text{C}$).

ior with change in concentration might evidence cluster catalysis [16].

f) Hydrogenation of the 2-hexene isomer mixture (11% cis/ 89% trans) clearly shows (Figure 6) a tendency favoring the trans to cis isomer conversion and a much slower hydrogenation of these two internal olefins, compared with the terminal 1-hexene. The trans to cis isomerization occurs more rapidly, leveling off after 5 hours, and complete hydrogenation increases slowly. The two isomers appear to decrease at about the same rate, indicating that the hydrogenation rate for both isomers is nearly similar. After 25 hours

at $P_{\text{H}_2} = 100$ psi, the reaction mixture is mainly cis-2 hexene (55%), less trans-2-hexene (15%) and some hydrogenation product, n-hexane (30%).

The results observed with the 2-hexene mixture, clearly indicate that the trans 2-hexene isomer gets equilibrated to a new isomer mixture in which cis-2 hexene predominates. This suggests that the internal olefins enter the catalytic cycle and isomerizes through reversible elementary steps until it reaches an equilibrium mixture characteristic of the cluster catalyst and the reaction conditions used.

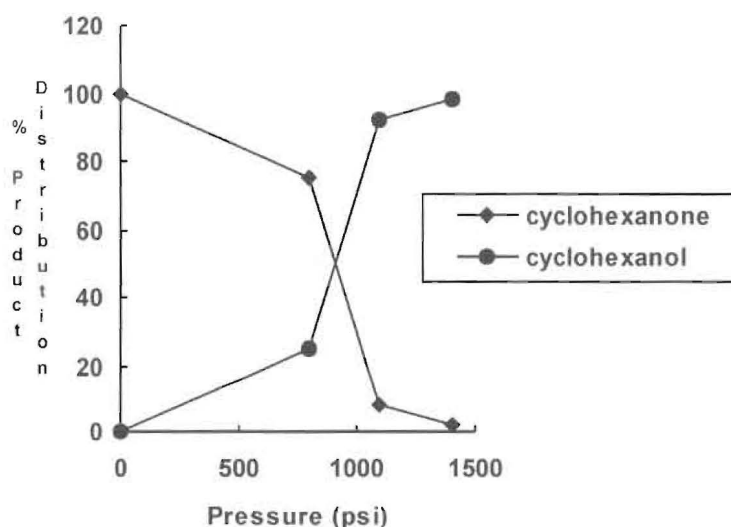


Figure 7. Hydrogenation of cyclohexanone. H_2 pressure effect (1 mg catalyst, 1 ml cyclohexanone, 7 ml THF, $T = 95^\circ C$, time = 60 min).

g) Hydrogenation of cyclohexene is slow, since only 26.5% cyclohexane is observed after 1 hour at $P_{H_2} = 500$ psi and $T = 95^\circ C$, compared with 80% n-hexane from 1-hexene under the same hydrogenation conditions. Cyclic olefins usually hydrogenate more slowly than terminal olefins.

h) The trial reaction with cyclohexanone, shows that compound (**2**) is capable of hydrogenating the carbonyl group to the alcohol, but requires much higher P_{H_2} for complete reduction (e.g. 1400 psi, after 1 hour at $95^\circ C$, see Figure 7). Compound (**2**) shows a higher activity than the analogous compound $(\mu-H)_2Ru_3(CO)_6$ $(\mu-PPh_2CH_2PPh_2)_2$ under similar reaction conditions [17]

The results obtained with the hydrogenation reactions studied indicate that compound (**2**), probably $Ru_3(CO)_{10}(dppp)$, used as a catalyst precursor favors the isomerization of 1-hexene at lower H_2 pressures preferentially to the cis-2-hexene isomer, and hydrogenation to n-hexane comes mainly from H_2 addition to 1-hexene and less from hydrogenation of the isomerization products. Hydrogenation activity requires a minimum H_2 pressure; this hydrogenation reaction increases with more polar coordinating solvents, with higher hydrogen pressures, with higher temperatures, with longer reaction times and with greater amounts of catalyst precursor. Under the reaction conditions tried, there is always a proportion of isomerization products pres-

ent, indicative of a lesser tendency for the internal isomers to hydrogenate. The results obtained, especially the higher proportion of cis-2-hexene derived from the isomerization reaction, clearly indicate some selectivity for this isomer, indicative that the catalyst used is sterically directing the reaction. The trans-2-hexene isomer is thermodynamically more stable, and the expected equilibrium must be close to: 75% trans-20% cis-3% 1-ene (similar to that for 1-pentene at $70^\circ C$) [15]. The $Ru_3(CO)_{12}$ cluster isomerizes 1-pentene to an isomer mixture close to the equilibrium values (74% trans-2-pentene, 23% cis-2-pentene and 3% 1-pentene)[2]. The substrate acts as a ligand, giving olefin carbonyl complexes that isomerize 1-pentene, usually at a slower rate. Under hydrogenation conditions, the $Ru_3(CO)_{12}$ cluster hydrogenates 1-hexene clearly to n-hexane [7]. It is known that the Ru cluster changes to $H_4Ru_4(CO)_{12}$ under an H_2 atmosphere [18], it would be interesting to compare the catalytic activity of this hydride cluster. Isomerization of 1-pentene with $H_4Ru_4(CO)_{12}$ is more rapid than with $Ru_3(CO)_{12}$ and favors the trans-2-pentene isomer, the isomerization rate being slower for the cis-2 and trans-2 isomers [3]. The rate decreases in the presence of CO, H_2 pressure, weak acids and polar solvents, but the hydrogenation rate is slower than the isomerization rate. The $H_4Ru_4(CO)_{12}$ cluster in the presence of phosphines produces several substitution products, being the monosubstituted ones ($H_4Ru_4(CO)_{11}L$)

more active in the isomerization of 1-pentene than the parent compound, and favoring the trans-2-pentene isomer (except for $L = \text{P}(\text{OPh})_3$). The order for L was $\text{P}(\text{OEt})_3 > \text{P}(\text{OPh})_3 > \text{PPh}_3$. [19] The complexes with higher ligand substitution ($L = 2, 4$) show a decreased activity. The $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ cluster hydrogenates 2-pentyne at 1 atm. of H_2 , initially to the 1-pentene and cis-2-pentene isomers, but longer reaction times favors the trans-2-pentene isomer. [20] $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{P}(\text{OEt})_3$ and $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{P}(\text{OEt})_3]_3$ hydrogenate 1-pentyne to 1-pentene and smaller quantities of the 2-ene isomers [21]. The reactions with the Ru clusters mentioned above, seem to indicate that in most cases the trans-2 isomer is favored, in contrast with the complex under study that clearly favors the cis-2 isomer.

It is interesting to compare the catalytic behavior of the $\text{Ru}_3(\text{CO})_{12}/\text{dppp}$ complex with the mononuclear compound $\text{RuCl}_2(\text{dppp})_2$ under similar hydrogenation conditions [14e]. 1-hexene is hydrogenated to n-hexane with no isomerization products observed (reaction conditions: solvent THF, $T = 95^\circ\text{C}$, $P(\text{H}_2) = 17 \text{ atm.}$, g substrate/ g catalyst = 3.3/ 0.05, $\text{NH}_4\text{PF}_6 = 0.01 \text{ g}$, reaction time 30 min, % conversion = 40%). Complete conversion to n-hexane is observed at $P_{\text{H}_2} = 350 \text{ psi}$ in ethanol, $T = 95^\circ\text{C}$, time = 30 min. Under comparable conditions, the $\text{Ru}_3(\text{CO})_{12}/\text{dppp}$ system shows 25% of isomer products and 70% hydrogenation products.

Comparisons with the Ru clusters containing the bidentate ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) ($\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ and $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$) [15] shows an analogous behavior such as a marked selectivity toward the cis-2-hexene isomer at lower hydrogen pressure and important hydrogenation activity under stronger reaction conditions.

Conclusions

This observation permits the conclusion that the isomerization reaction catalyzed by compound (2) occurs through a hydride intermediate and the steric requirements imposed by the presence of the bidentate phosphine ligand directs the isomerization reaction to the cis 2-hexene isomer. The trans to cis isomer transformation to a new isomer ratio, favoring the cis isomer, allows

the conclusion that the internal olefin can be equilibrated by incorporation in the catalytic cycle and through a series of reversible elementary steps. The hydrogenation catalytic cycle probably shares a common intermediate with the isomerization cycle, and a higher hydrogen pressure and higher reaction temperature probably favor the reductive elimination of the reduced olefin.

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