

Catalytic studies with ruthenium clusters substituted with diphosphines

Part II. Studies with $\text{Ru}_3(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$

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Received 23 November 1998; accepted 17 March 1999

Abstract

The catalytic precursor $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) shows activity with 1-hexene favoring isomerization to *cis*-2-hexene at lower hydrogen pressures and complete hydrogenation at higher temperature and pressure. The reaction is first order on substrate with a $k_{\text{eff}} = 1.59 \times 10^{-3} \text{ min}^{-1}$. Turnover studies indicate cluster catalysis. The catalytic activity has been demonstrated for other unsaturated organic substrates. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium cluster; Bidentate phosphines; Hydrogenation; Isomerization catalysts

1. Introduction

The $\text{Ru}_3(\text{CO})_{12}$ clusters with bis(diphenylphosphino)methane (dppm) has been synthesized with one [1] and two bidentate ligands [2] as well as reports on thermal rearrangement of the coordinated ligands [3–7] and reaction with O_2 [8,9]. The diphosphine dppm has been used in many mononuclear and cluster complexes synthesis, a few of which has been used in homogenous catalysis [10–13]. Catalytic studies

with metal clusters is an area of recent research [14,15]; the presence of ligands capable of cluster stabilization is considered important during catalytic reactions and polydentate phosphines could be used for that task. One example of this is the use of $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppm})$ [6], and $\text{H}_2\text{Ru}_3(\text{E})(\text{CO})_5(\text{dppm})_2$ ($\text{E} = \text{O}, \text{S}$) [16] in olefin activation. In our laboratory we have been studying the catalytic behavior of Ru complexes with polydentate phosphines [17–22], including reactions of Ru carbonyl clusters with bis-1,3(diphenylphosphino)propane ($\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2 = \text{dppp}$) [23]. In Part I of the studies we reported the catalytic reactions with $\text{Ru}_2(\text{CO})_{10}(\text{dppm})$ [24]. In this paper we report the reactions of $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (**1**) under hydrogen pressure.

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2. Experimental

2.1. Synthesis of $Ru_3(CO)_8(dppm)_2$

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.

2.1.1. Preparation via diphenylketyl radical, $Ph_2C_2O^-$

The preparation of $Ru_3(CO)_8(dppm)_2$ by this method has been reported by Bruce et al. [2] $Ru_3(CO)_{12}$ was prepared from $RuCl_3 \cdot 3H_2O$ (Strem Chemicals) and CO (Matheson, UAP grade) according to the literature method [25]. 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 has a concentration near 0.025 mmol/ml of $Ph_2C_2O^-$. In a typical synthesis, $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and the dppm (Strem Chemicals) ligand (60.1 mg, 0.156 mmol) are dissolved in dry THF (15 ml) with stirring at 40°C in Schlenk glassware. The diphenylketyl solution (5 ml) is added dropwise with syringe and the reaction followed by the disappearance of $Ru_3(CO)_{12}$ metal carbonyl IR bands (P.E. 1725-X FTIR). After solvent evaporation, the residue is separated on silica gel flush column chromatography, eluted with a 3/1 hexane/ CH_2Cl_2 volume mixture. The dark brown-red fraction is recrystallized from CH_2Cl_2 /hexane to give red-brown crystals of $Ru_3(CO)_8(dppm)_2$ (66.7% yield). IR: $\nu(CO)$ (THF) 2023 (m), 1979 (vs), 1970 (s), 1946 (m) cm^{-1} , 1H NMR (CD_2Cl_2) (Varian T-60) δ 7.1–7.6 (m, C_6H_5), 4.2–4.3 (t, CH_2 ; $J_{PH} = 11$ Hz). The compound decomposes between 176 and 179°C.

2.1.2. Synthesis via thermal reaction

In a typical synthesis, $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol), dppm (60.1 mg, 0.156 mmol) and

freshly distilled xylene (Aldrich, 15 ml) in a round bottom flask were heated to 65°C with stirring for 4 h under Ar, giving a dark red-brown solution. After solvent evaporation, the residue is separated on silica gel flush column chromatography, eluted with a 3/1 volume hexane/ CH_2Cl_2 mixture. The larger red-brown band is recrystallized in CH_2Cl_2 /hexane to give red-brown $Ru_3(CO)_8(dppm)_2$ crystals (89.7% yield). Identification similar to Section 2.1.1.

2.1.3. Synthesis via photolysis

In a typical synthesis, $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol), dppm (60.1 mg, 0.156 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 48 h, the reactions progress of the reaction followed by disappearance of $Ru_3(CO)_{12}$ metal carbonyl IR bands. After the reaction is complete, the solvent is reduced under vacuum and silica gel flush column chromatographed using a 3/1 volume hexane/ CH_2Cl_2 eluant. The red-brown band is recrystallized in CH_2Cl_2 /hexane giving red-brown $Ru_3(CO)_8(dppm)_2$ crystals (56% yield). Identification similar to Section 2.1.1.

2.1.4. Synthesis via $(CH_3)_3NO$ activation

In a typical experiment $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) is dissolved in dry CH_2Cl_2 (40 ml) in a Schlenk tube with constant Ar bubbling during the whole reaction. The system is cooled to $-78^\circ C$ in a Dewar flask with a $CO_2(s)$ /acetone bath. Trimethylamine oxide, $(CH_3)_3NO$ (Aldrich, sublimed three times, 47 mg, 0.64 mmol) completely dissolved in CH_2Cl_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 $Ru_3(CO)_{12}$ metal carbonyl IR bands. The dppm ligand (120 mg, 0.32 mmol) dissolved in CH_2Cl_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°C during 30 min. After evaporating the solvent, the residue is chromatographed in a silica gel column and the separated fraction recrystallized in a 3/1 hexane/CH₂Cl₂ mixture, giving red-brown Ru₃(CO)₈(dppm)₂ crystals (61% yield). Identification similar to Section 2.1.1. In Table 1, a comparison of the four synthetic methods is presented.

2.2. Catalytic trials with Ru₃(CO)₂(dppm)₂

In a typical hydrogenation or isomerization trial, Ru₃(CO)₈(dppm)₂ (2 mg, 1.54 × 10⁻³ mmol), 1-hexene (Aldrich, 1 ml, 8 mmol; 5000/1 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 H₂ three times, the reactor is pressurized to the desired H₂ 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 (PE 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, BTR-CW (Carbowax BTR), 30 m long, 1 mm internal diameter, or GC-MS (HP 5988A GC-MS). Olefin amination was carried out using a 10/1 Ar/NH₃ mixture. Test reactions with all the other unsaturated sub-

Table 2
Hydrogenation and isomerization of 1-hexene: solvent effect

Solvent	<i>n</i> -Hexane (%)	<i>cis</i> -2-Hexene + <i>trans</i> -2-hexene (%)	Total (%)
Ethanol	46.8	53.0	99.9
Methanol	54.2	21.4	75.6
2-Methoxyethanol	18.4	34.8	53.2
Acetone	20.1	30.5	50.6
THF	25.0	44.7	69.8
Benzene	4.7	15.8	20.5
Toluene	3.4	11.5	14.9

Reaction conditions: solvent (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂ (2 mg), P_{H₂} = 500 psi, T = 90°C, t = 2 h.

strates were carried out under similar conditions, adjusting the H₂ pressure, solvent or reaction time as required.

2.2.1. Kinetic runs

In a 250-ml stainless steel high pressure reactor (Parr Instruments, glass liner, internal stirring, internal thermocouple and sample outlet) Ru₃(CO)₈(dppm)₂ (20 mg, 1.54 × 10⁻² mmol), 1-hexene (10 ml, 80 mmol; 5000/1 substrate/catalyst ratio), ethanol (solvent, 50 ml), cyclohexane (10 ml, internal standard) were mixed. After purging with H₂ three times, hydrogen pressure adjusted to 500 psi and 5 min allowed for thermal stabilization (90°C), samples were taken every 5 min during 45 min. The samples were immediately quenched and analyzed by gas chromatography.

A systematic study of several reaction conditions were carried out.

2.2.1.1. Solvent effect. The following solvents were tried: ethanol, 2-ethoxyethanol, THF, to-

Table 1
Synthesis methods for Ru₃(CO)₈(dppm)₂

Synthesis method	Radical	Thermal	Photochemical	Assisted with (CH ₃) ₃ NO
Yield (%)	66.7	89.7	56	61
Solvent	THF	xylene	THF	CH ₂ Cl ₂
Reaction time	30 min	4 h	48 h	2 h
Stability in solution	good	good	moderate	low
Product separation	simple	simple	more difficult	more difficult
Procedure	elaborate	simple	simple	elaborate

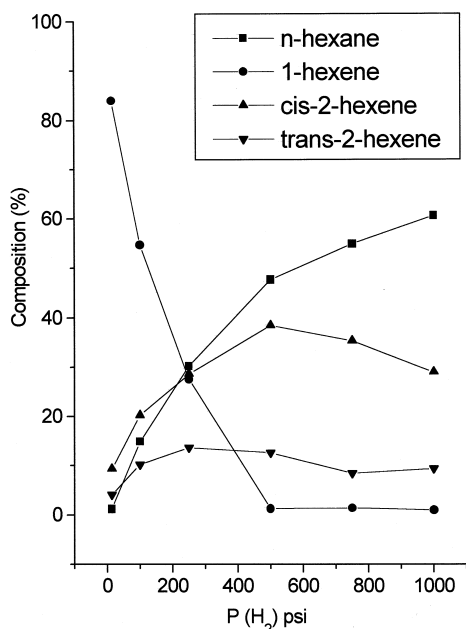


Fig. 1. Hydrogenation and isomerization of 1-hexene: H₂ pressure effect. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂ (2 mg), T = 90°C, t = 2 h.

luene, benzene. Reaction conditions: solvent (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂

Table 3

Hydrogenation and isomerization of 1-hexene: (Ar + H₂) pressure effect

	n-Hexane (%)	1-Hexene (%)	cis-2-Hexene (%)	trans-2-Hexene (%)
<i>Experiment 1 H₂ = 1 atm (time, h)</i>				
2	1.2	85.4	9.3	4.1
6	4.6	61.9	22.8	10.7
13	4.7	31.8	45.4	18.1
24	4.9	9.4	67.2	18.5
48	5.2	5.8	68.9	20.1
<i>Experiment 2 500 psi (Ar / H₂ relation)</i>				
1:1	15.4	57.3	20.2	7.1
2:1	22.3	40.5	24.7	12.5
3:1	30.1	27.3	27.4	15.2
4:1	33.6	21.5	30.6	14.3
<i>Experiment 3 (Ar / H₂, psi)</i>				
250/250	13.8	60.7	19.3	6.2
500/500	29.1	32.2	26.6	12.1
750/750	42.3	9.1	35.2	13.4
1000/1000	48.4	1.9	36.9	12.8

Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂ (2 mg), T = 90°C, t = 2 h (experiments 1 and 3), P_{H₂} = 1 atm (experiment 1) and P_{total} = 500 psi (experiment 2).

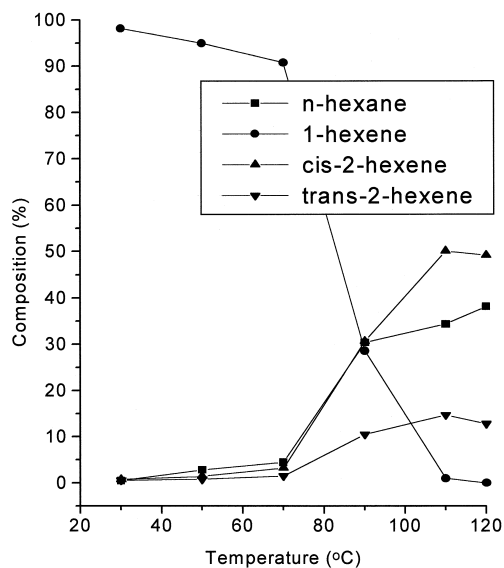


Fig. 2. Hydrogenation and isomerization of 1-hexene: temperature effect. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂ (2 mg), P_{H₂} = 250 psi, t = 2 h.

(2 mg), P_{H₂} = 500 psi, T = 90°C, t = 2 h. The results are shown in Table 2. Ethanol was the solvent selected for the other catalytic studies.

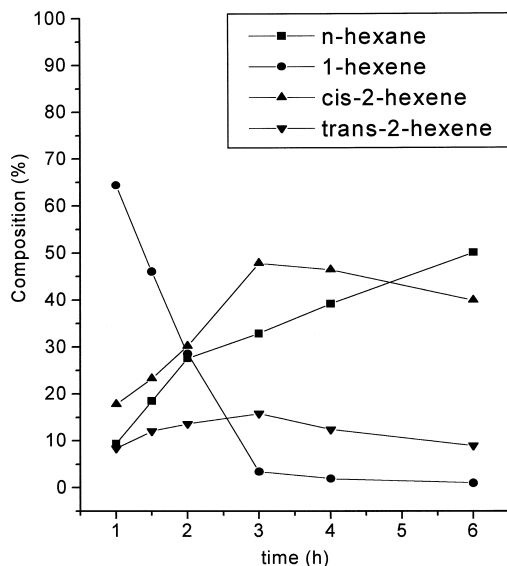


Fig. 3. Hydrogenation and isomerization of 1-hexene: reaction time effect. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), Ru₃(CO)₈(dppm)₂ (2 mg), P_{H₂} = 250 psi, T = 90°C.

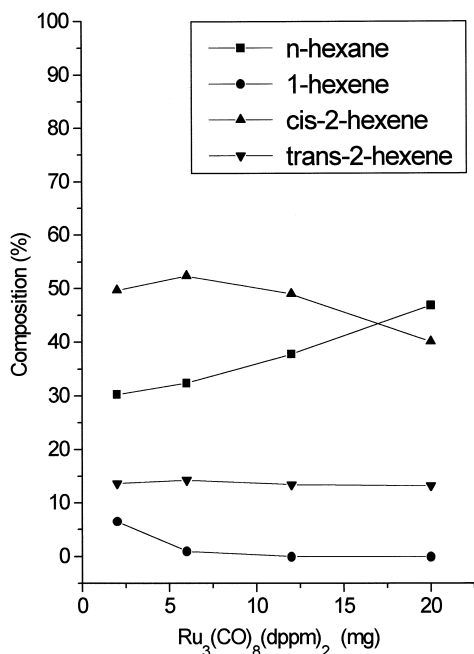


Fig. 4. Hydrogenation and isomerization of 1-hexene: amount of catalyst effect. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $P_{H_2} = 250$ psi, $T = 90^\circ\text{C}$, $t = 3$ h.

2.2.1.2. P_{H_2} effect. H_2 pressure change results are shown in Fig. 1. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $Ru_3(CO)_8(dppm)_2$ (2 mg), $T = 90^\circ\text{C}$, $t = 2$ h. A 250-psi

H_2 pressure was selected for other catalytic studies. H_2 pressure effects were also analyzed by the following experiments. Experiment 1: similar conditions as above, but used 1 atm H_2 pressure and 48 h total time. Experiment 2: similar conditions as above, but used 500 psi total pressure of ($Ar + H_2$) with different Ar/H_2 relations. Experiment 3: similar conditions as above, but used pressure changes of Ar/H_2 (1/1). The results are shown in Table 3.

2.2.1.3. Temperature effect. Reaction temperature change results are shown in Fig. 2. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $Ru_3(CO)_8(dppm)_2$ (2 mg), $P_{H_2} = 250$ psi, $t = 2$ h. A 90°C temperature was selected for other catalytic studies.

2.2.1.4. Reaction time effect. Reaction time change results are shown in Fig. 3. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $Ru_3(CO)_8(dppm)_2$ (2 mg), $P_{H_2} = 250$ psi, $T = 90^\circ\text{C}$. A 2- or 3-h reaction time was selected for the other catalytic studies.

2.2.1.5. Amount of catalyst effect. Amount of catalyst change results are shown in Fig. 4.

Table 4

Catalysis study of 1-hexene with $Ru_3(CO)_{12}/H_2$ pressure effect: in situ production of complexes

	<i>n</i> -Hexane (%)	1-Hexene (%)	<i>cis</i> -2-Hexene (%)	<i>trans</i> -2-Hexene (%)
(a) $Ru_3(CO)_{12}/H_2$ pressure (psi)				
15	2.6	93	3.2	1.2
100	15.6	32.1	42.0	10.3
200	26.6	10	45.1	18.3
300	55.1	1	35.6	8.3
500	66.4	0	27.7	5.9
(b)				
$Ru_3(CO)_{12}/dppm$ (1:2 mole ratio)/100 psi	6.4	1.4	73.2	19.0
$Ru_3(CO)_{10}(dppm)^a/100$ psi	7.1	1.4	72.4	19.1
$Ru_3(CO)_{12}/dppm$ (1:4 mole ratio)/100 psi	17.6	49.8	19.2	13.4
$Ru_3(CO)_{12}/dppm$ (1:4 mole ratio)/250 psi	35.2	20.6	31.9	12.3
$Ru_3(CO)_8(dppm)_2/100$ psi	14.9	54.7	20.2	10.2
$Ru_3(CO)_8(dppm)_2/250$ psi	30.2	27.6	28.6	13.6

^aRef. [24].

Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $Ru_3(CO)_{12}$ or $Ru_3(CO)_{12}/dppm$ (2 mg), $T = 90^\circ\text{C}$, $t = 2$ h, $P_{H_2} = 100$ or 250 psi (reaction b).

Table 5
Catalyst stability studies

	<i>n</i> -Hexane (%)	1-Hexene (%)	<i>cis</i> -2-Hexene (%)	<i>trans</i> -2-Hexene (%)
(a) Reaction in presence of Hg				
Catalyst/500 psi	47.7	1.3	38.4	12.6
Catalyst + Hg/500 psi	43.5	10.6	35.7	10.2
Catalyst/1000 psi	60.6	2.0	29.0	8.4
Catalyst + Hg/1000 psi	55.4	4.3	27.8	12.5
(b) Catalyst reuse				
Number of reuses: 1	49.5	0.2	39.6	10.7
Number of reuses: 2	48.2	0	40.2	11.6
Number of reuses: 3	46.3	6.7	37.0	10.0

Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (2 mg), 1 drop Hg (reaction a); $T = 90^\circ\text{C}$, $t = 2$ h, $P_{\text{H}_2} = 500$ psi (reactions a and b) or 1000 psi (reaction a).

Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $P_{\text{H}_2} = 250$ psi, $T = 90^\circ\text{C}$, $t = 3$ h. A catalyst amount of 2 mg (about 5000/1 substrate/catalyst ratio) was selected for other catalytic studies.

2.2.1.6. 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), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (2 mg), $P_{\text{H}_2} = 250$ psi, $T = 90^\circ\text{C}$. Product distribution: after 36 h: *cis*-2-hexene (68%), *trans*-2-hexene (23%), 1-hexene (5%); *n*-hexane (4%).

2.2.1.7. In situ production of $\text{Ru}_2(\text{CO})_8(\text{dppm})_2$. In order to test the possible formation of (1) in situ, several reactions were carried out with $\text{Ru}_3(\text{CO})_{12}$ and different proportions of dppm ligand. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $\text{Ru}_3(\text{CO})_{12}/\text{dppm}$ (2 mg, different molar relations), $P_{\text{H}_2} = 100$ psi, $T = 90^\circ\text{C}$, $t = 2$ h. The results are shown in Table 4.

2.2.1.8. Stability studies of $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$. In order to test the stability of the cluster complex studied, reactions were carried out in the presence of small amounts of metallic mercury [26,27]. Reactions conditions: ethanol (5 ml),

1-hexene (1 ml, 0.67 g), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (2 mg), $P_{\text{H}_2} = 500$ and 1000 psi, 1 drop liquid Hg, $T = 90^\circ\text{C}$, $t = 2$ h). The results are shown in Table 5a. In order to test the degree of catalyst decomposition, several reactions were carried

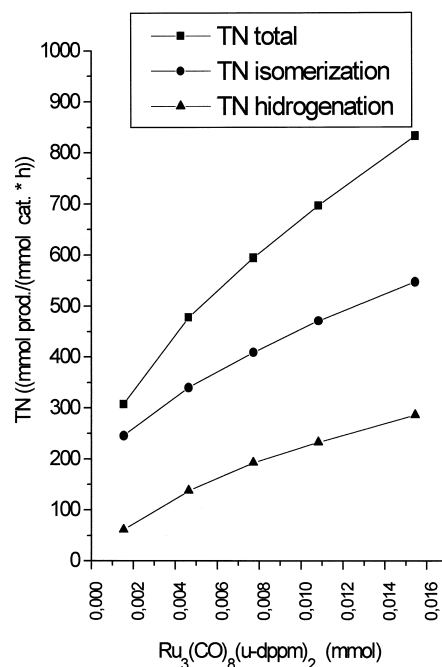


Fig. 5. Hydrogenation and isomerization of 1-hexene: turnover frequency (millimoles product/(millimoles catalyst)(minutes)) vs. amount of catalyst (millimoles). Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), cyclohexane (1 ml, internal standard) $P_{\text{H}_2} = 500$ psi, $T = 90^\circ\text{C}$, $t = 0.5$ h.

out reusing the separated catalyst for three consecutive times. After the reaction, the solution was evaporated to dryness, the residue washed several times with pentane and vacuum dried before reuse. Reaction conditions: ethanol (5 ml), 1-hexene (1 ml, 0.67 g), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (initial 2 mg, then re-covered), $P_{\text{H}_2} = 500$ psi, $T = 90^\circ\text{C}$, $t = 2$ h). The results are presented in Table 5b. Several reactions were carried out increasing the number of millimoles of $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ 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), $P_{\text{H}_2} = 500$ 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 is presented in Fig. 5.

3. Results and discussion

3.1. Synthesis of $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$

The several synthetic methods tried for the synthesis of $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ and shown in Table 1 indicate that the complex can be obtained in good yield using the diphenylketyl radical and thermal reaction. Lesser yields are observed with photochemical activation and with $(\text{CH}_3)_3\text{NO}$ 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

3.2.1. Solvent effect

As shown in Table 2, under the reaction conditions used, more polar and better coordinating solvents like ethanol, methanol, THF and 2-ethoxyethanol give better overall yields, while less polar solvents with lesser coordinating ability like toluene, benzene and acetone, give less overall yields. All the better solvents favor the isomerization products, except methanol that

shows a greater amount of hydrogenation product. This solvent behavior indicates a possible stabilization of polar and/or coordinatively unsaturated intermediate in the catalytic cycle.

3.2.2. P_{H_2} effect

As shown in Fig. 1, at low H_2 pressure the main products are the isomerization compounds, favoring the *cis*-2-hexene isomer, that remains an important product up to 500 psi H_2 pressure. As the H_2 pressure increases the overall yield increases and the hydrogenation product is favored, the internal isomers being hydrogenated after the 1-hexene substrate is consumed. Allowing a longer reaction time using 1 atm of H_2 pressure, produces almost exclusive the isomerization reaction, with a 69% *cis*/20% *trans* ratio after 48 h (Table 3, experiment 1). Diluting the hydrogen with an inert gas (Ar) has a yield lowering effect compared with the reactions with pure H_2 , but product relations remain similar, that is, *cis*-2-hexene being favored at lower partial pressures and increasing *n*-hexane yield as H_2 pressure increases and the *cis* isomer always favored over the *trans* (Table 3, experiments 2 and 3). It becomes apparent that the isomerization route in the catalytic cycle gets activated at a lower hydrogen pressure, and the selectivity toward the kinetic product, *cis*-2-hexene, indicates an important steric requirement during isomer formation. The results confirm that internal olefins are more difficult to hydrogenate than terminal ones.

3.2.3. Temperature effect

The reaction only proceeds at a reasonable rate after 70°C , and increases rapidly favoring the *cis* isomer, obtaining complete reaction at 110°C , with almost 50% yield of *cis*-2-hexene (Fig. 2). Both the hydrogenation and isomerization reaction paths require heating to overcome activation barriers, most likely the activation of the cluster compound by CO loss, corroborated by the complete reaction inhibition in the presence of 1 atm of carbon monoxide gas. The similar activation behavior could indicate the

presence of a common reaction intermediate in the catalytic cycle.

3.2.4. Reaction time effect

The reaction progress with time is shown in Fig. 3. The internal *cis* isomer appears first in the reaction and becomes the main product, accounting for almost half of the reaction products after 3 h, when the terminal olefin is completely consumed. After this time, the olefin reduction product, *n*-hexane, keeps increasing as the *cis*-2-hexene and *trans*-2-hexene get hydrogenated. The product distribution with time indicates that the isomerization rate is faster than the hydrogenation at 250 psi H₂ pressure and 90°C.

3.2.5. Amount of catalyst effect

With 2 mg of Ru₃(CO)₈(dppm)₂ as catalyst precursor, under the reaction conditions used, more than 90% conversion is obtained, with 50% of the *cis*-2-hexene isomerization product (Fig. 4). As the amount of (**1**) is increased, more hydrogenation product is observed, being the predominant product when 20 mg of compound are used. As the amount of catalyst is increased, more active sites are introduced, increasing the probability for complete olefins hydrogenation, including the internal olefins produced more rapidly during the isomerization process.

3.2.6. Hydrogenation of 2-hexenes

The test reaction with the thermodynamic 2-hexene mixture (11% *cis*/89% *trans*) show that after 36 h the isomer composition is reversed (68% *cis*/23% *trans*), indicating that the internal olefins can enter the catalytic cycle and be equilibrated with the other products in reversible reactions. The reverse reaction is slower indicating that the internal olefins coordinate with more difficulty due to steric reasons.

3.2.7. In situ production of Ru₃(CO)₈(dppm)₂

The results of the test reactions using Ru₃(CO)₁₂ and variable amounts of dppm ligand are shown in Table 4. The reaction of 1-hexene with Ru₃(CO)₁₂ and variable H₂ pres-

sure shows and initial increase in isomerization product, favoring *cis*-2-hexene, but after 200 psi the hydrogenation product predominates (Table 4a). After 300 psi, the Ru carbonyl cluster decomposes under the reaction conditions used. A 1/2 Ru₃(CO)₁₂/dppm molar ratio gives predominantly the *cis*-2-hexene isomerization product and no complex decomposition is observed (Table 4b). The dppm substituted cluster does not show decomposition signs up to 1000 psi H₂ pressure, indicating that the bidentate ligand stabilizes the trinuclear cluster. This behavior is analogous to the reaction products obtained with Ru₃(CO)₁₀(dppm) under similar reaction conditions [24]; this suggests that the compound produced in situ is similar to that diphosphine substituted Ru cluster. Increasing the molar ratio to 1:4 gives a different product distribution, with less total percent yield and more similar hydrogenation/isomerization ratios. The similarity of these results and those obtained with the catalytic precursor Ru₃(CO)₈(dppm)₂, including the changes observed when the H₂ pressure changes from 100 to 250 psi, could indicate that a similar compound is produced in situ when the molar relation is 1:4.

3.2.8. Stability studies of Ru₃(CO)₈(dppm)₂

In homogenous catalysis studies there is always the possibility that the reaction is carried out by another species derived from cluster fragmentation or metallic particles from complex decomposition rather than the original cluster complex. This is verified by observing the final solution under the microscope and by running a test reaction in the presence of metallic mercury with similar reaction conditions (Table 5a). When Hg is used the change in percent yield for the different products is less than 5% at the two H₂ pressures tried, discarding metallic Ru as the active catalyst. Another test that is useful to determine the degree of catalyst decomposition is to separate the complex after the catalytic reaction and reuse it under similar reaction conditions. The results shown in Table

5b indicate that after three catalyst reuses, the activity has decreased only slightly.

The plot of turnover frequency vs. millimoles of catalyst presented in Fig. 5 for isomerization and hydrogenation results show an increase in turnover frequency as the amount of Ru complex increases, but the slopes are different. The increasing tendency is interpreted as indicative of cluster catalysis rather than produced by active fragments of lower nuclearity [25]. This supports the idea that the catalysis is being carried out by the cluster complex. The $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ complex loses CO and benzene groups on thermolysis reactions in refluxing aromatic solvents giving $\text{Ru}_3(\mu\text{-H})(\mu\text{-P}(\text{C}_6\text{H}_5)\text{CHP}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))(\text{CO})_7(\text{dppm})$ and $\text{Ru}_3(\mu_3\text{-P}(\text{C}_6\text{H}_5))(\text{CHP}(\text{C}_6\text{H}_5)_2)(\text{CO})_7(\text{dppm})$ [6,7]. Our reaction conditions does not favor the thermolysis reaction, but these rearranged thermolysis products cannot be excluded as possible intermediates. These complexes are presently being tested using our reactions conditions to investigate their catalytic behavior.

3.2.9. Kinetic results

The first order plot for the kinetic studies in the isomerization and hydrogenation of 1-hexene, following the disappearance of the substrate 1-hexene is shown in Fig. 6. The results indicate first order on substrate with an apparent rate constant value of $1.59 \times 10^{-3} \text{ min}^{-1}$ for the total reaction. This results is about 100 times slower than the value obtained for the $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ complex [24], perhaps indicative of a greater steric crowding presented by the complex $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ to 1-hexene π bonding.

3.3. Catalysis with other substrates

The $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ complex was explored in its catalytic activity with other organic substrates and the results are summarized in Table 6. Terminal olefins like 1-hexene are hydrogenated more rapidly than internal olefins or cyclic olefins like cyclohexene. Alkynes require stronger conditions for the first hydro-

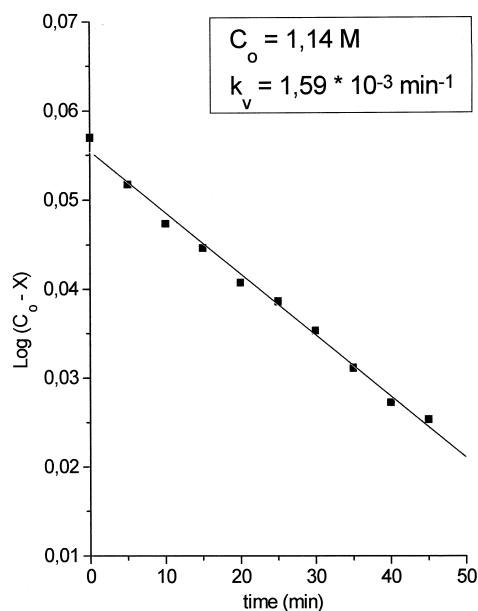


Fig. 6. Hydrogenation and isomerization of 1-hexene: kinetic results. Reaction conditions: ethanol (50 ml), 1-hexene (10 ml, 6.7 g), cyclohexane (10 ml, internal standard), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (20 mg), $P_{\text{H}_2} = 500 \text{ psi}$, $T = 90^\circ\text{C}$.

genation to the alkenes. 1-Hexyne hydrogenates to 1-hexene and some *n*-hexane and little isomerization, but 2-hexyne produces mainly the *trans*-2-hexene, some *n*-hexane and little *cis*-2-hexene; this result indicates some special steric conditions, that are presently being studied. Aromatic compounds like benzene or carbonyl groups as in acetone or cyclohexanone require higher hydrogen pressures for hydrogenation to occur with moderate reaction yield. With allylic alcohol, double bond migration to form the carbonyl group occurs in good proportion, but the competing complete reduction reaction also occur in good proportion. For α,β 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. The results indicate that the Ru complex studied does not show strong regioselectivity in its hydrogenating activity. A test reaction under hydroformylation conditions with 1-hexene, favors the linear aldehyde with intermediate overall percent yield. Hydrogenation of nitriles, such as

Table 6
Catalytic reactions of unsaturated organic substrates with $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$

Substrate	Product (%)	Conditions	Time (h)
<i>(a) Hydrogenation of unsaturated organic substrates</i>			
1-Hexene	<i>n</i> -hexane (60.6) <i>cis</i> -2-hexene (29.0) <i>trans</i> -2-hexene (9.4)	ethanol, 90°C, 1000 psi H ₂	2
1-Hexene	<i>n</i> -hexane (34.3) <i>cis</i> -2-hexene (50.0) <i>trans</i> -2-hexene (14.7)	ethanol, 110°C, 250 psi H ₂	2
1-Hexyne	<i>n</i> -hexane (25.1) 1-hexene (50.7) <i>cis</i> -2-hexene (2.2) <i>trans</i> -2-hexene (2.5)	ethanol, 90°C, 1500 psi H ₂	12
1-Hexyne	<i>n</i> -hexane (11.2) 1-hexene (15.2) <i>cis</i> -2-hexene (2.7) <i>trans</i> -2-hexene (2.3)	ethanol, 90°C, 500 psi H ₂	6
2-Hexyne	<i>n</i> -hexane (24.9) <i>cis</i> -2-hexene (7.7) <i>trans</i> -2-hexene (23.0)	THF, 90°C, 1500 psi H ₂	12
2-Hexyne	<i>n</i> -hexane (19.6) <i>cis</i> -2-hexene (3.0) <i>trans</i> -2-hexene (17.6)	ethanol, 90°C, 500 psi H ₂	6
Cyclohexene	cyclohexane (50.7)	ethanol, 90°C, 1500 psi H ₂	12
Benzene	cyclohexadiene (4.7) cyclohexene (11.2) cyclohexene (25.7)	ethanol, 90°C, 1500 psi H ₂	12
Acetone	isopropanol (26.7)	THF, 90°C, 1500 psi H ₂	12
Cyclohexanone	cyclohexanol (25.9)	THF, 90°C, 1500 psi H ₂	12
Allylic alcohol	propanaldehyde (35.6) propanol (23.2)	THF, 90°C, 500 psi H ₂	12
<i>(b) Hydrogenation of α-β unsaturated aldehydes</i>			
Crotonaldehyde	butyraldehyde (29.2) butanol (21.3) 2-butenol (22.8)	THF, 90°C, 1500 psi H ₂	12
Cinnamaldehyde	3-phenylpropanal (15.6) 3-phenylpropanol (22.5) 3-phenyl-2-propenol (32.3)	THF, 90°C, 1500 psi H ₂	12
<i>(c) Hydroformylation of 1-hexene</i>			
1-Hexene	heptanaldehyde (47.9)	THF, 120°C, 1500 psi H ₂ /CO (1/1)	12
<i>(d) Amine synthesis</i>			
Hydrogenation of nitrile			
Acetonitrile	diethylamine (13.5) triethylamine (21.2)	ethanol, 90°C, 1500 psi H ₂	24
Benzonitrile	benzylamine (42.4)	ethanol, 90°C, 1500 psi H ₂	24
<i>Condensation of NH₃ with alcohol</i>			
CH ₃ OH/NH ₃	dimethylamine (9.4) trimethylamine (12.6)	methanol, 90°C, 1000 psi Ar/NH ₃ (9/1)	48
CH ₃ CH ₂ OH/NH ₃	triethylamine (23.5)	ethanol, 90°C, 1000 psi Ar/NH ₃ (9/1)	48

Reaction conditions: solvent (5 ml), substrate (1 ml), $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ (2 mg/15 mg in alcohol/NH₃ reactions).

acetonitrile and benzonitrile to give the expected amines requires higher H₂ pressure and longer reaction times. With acetonitrile, the scrambling reaction allows production of trimethylamine in moderate yield. The condensation reaction between NH₃ and small alcohols such as methanol and ethanol provides reasonable amine yields under the reaction conditions tried. The Ru₃(CO)₈(dppm)₂ 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. In general, the reactivity of (1) is less than that shown by the complex with only one dppm bidentate ligand, Ru₃(CO)₁₀(dppm) [24], indicative of an important steric condition 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.

Acknowledgements

The present work was financed by Bid-Conicit (Proy. QF-04) Also Conicit (Proy. F-124 for FTIR and Proy. S1 2338 for GC).

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