

Isomerization of olefins by phosphine-substituted ruthenium complexes and influence of an ‘additional gas’ on the reaction rate

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Abstract

Phosphine-substituted ruthenium carbonyls have often been used as catalytic precursors in reactions such as the hydrogenation or the hydroformylation of olefins. To collect evidence on the coordination of the olefin as a preliminary step of these reactions we have investigated the isomerization of hex-1-ene, in hydrocarbon solvent, in the presence of the phosphine-substituted ruthenium carbonyls $\text{Ru}(\text{CO})_3(\text{PR}_3)_2$, $\text{Ru}_3(\text{CO})_9(\text{PR}_3)_3$ and $\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{PR}_3)_2$ [$\text{R} = \text{Bu}, \text{Ph}$]. When using $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ the rate of the reaction shows a partial first order with respect to the concentration of the catalyst and of the substrate. The activation parameters were also evaluated and the activation entropy is negative. A reaction scheme involving the displacement of a carbonyl ligand with formation of a π -olefin–ruthenium complex is suggested. The rate of the reaction significantly changes if an alcohol is used as solvent. This behaviour is attributed to a modification of the catalytic precursor with formation of a ruthenium hydride. This hypothesis is confirmed by the identification of an alkoxy ruthenium hydride. The isomerization of olefins by phosphine-substituted ruthenium carbonyls is retarded by the presence of an ‘additional gas’ such as dinitrogen. This influence is more evident than the analogous one reported in the hydroformylation reaction: the same pressure of the ‘additional gas’ present in the reaction vessel reduces the rate of the isomerization to a larger extent, i.e. the presence of 1000 bar of nitrogen decreases in otherwise identical experiments the isomerization conversion of hex-1-ene from 95.6% to 25.8%. An analogous effect is also caused by the presence of argon and xenon. Helium, on the other hand, does not display any influence. These data are an indication of an interaction between the ‘additional gas’ and a catalytically active transition metal complex. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemistry of the olefin coordination to transition metal complexes covers a large field of organometallic chemistry and a large part of this subject involves homogeneous catalysis. Some industrial processes that involve interactions between an olefin and a catalyst are: the hydroformylation of olefins [1], the polymerization of ethylene by a one-site organometallic catalyst [2], the stereospecific polymerization of propene [3], metathesis of olefins [4], Wacker–Hoechst oxidation of ethylene [5], and many others (Scheme 1).

The above processes, and other syntheses, involve the

reaction of an olefin with appropriate reagents to produce different chemicals on the basis of the conditions employed. The coordination of the olefin to the catalyst plays an important role in the reaction. If the coordinated olefin isomerizes, different products may be formed [6].

Different mechanisms are reported for the isomerization process connected with the use of different catalytic systems or reaction conditions. The usual hypothesis to explain the migration of a double bond through the alkyl chain of an olefin involves the intervention of a metal (i.e. Rh, Ru, Co) hydride as catalyst. Through several addition–elimination steps a thermodynamically stable mixture of olefins is obtained [7].

A different mechanism may be suggested when the starting catalyst is not a metal hydride or when an hydride cannot be formed in a preliminary step of the

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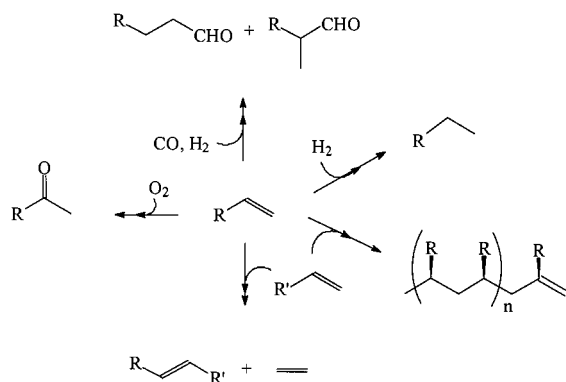
reaction. The formation of a π -olefin metal complex is suggested, followed by the formation of a π -allyl system coordinated to a metal hydride complex. The system evolves and isomeric olefins are obtained [8].

Other different isomerization mechanisms are reported in the literature to explain the results obtained in catalytic reactions such as the hydroformylation of olefins [9–11].

The isomerizing activity of a metal complex may affect the regioselectivity of the reaction (as reported in the hydroformylation of olefins) or may give rise to a less reactive regioisomer.

Other examples are reported where the olefin isomerization plays an important role in synthetic chemistry to afford products from more easily synthesized intermediate as reported for the synthesis of N-protected 1,2,3,4-tetrahydropyridazine [12,13] or the formation of 1,4-dicyanobutane from butadiene and HCN [14].

In this paper we report the results of an investigation on the isomerization of an olefin such as hex-1-ene in the presence of an organometallic ruthenium complex.



Scheme 1. Olefins as raw materials in the synthesis of chemicals.

Table 1
Hex-1-ene isomerization in the presence of ruthenium catalysts: influence of catalyst^a

Catalyst	Code	Conversion (%)		
		353 K	373 K	393 K
$\text{Ru}(\text{CO})_3(\text{P}^n\text{Bu}_3)_2$	1	5.9	34.8	94.9
$\text{Ru}_3(\text{CO})_9(\text{P}^n\text{Bu}_3)_3$	2	19.1	69.4	97.1
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	3	25.1	53.4	91.7
$\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$	4	0.0	97.0	97.6
$\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{P}^n\text{Bu}_3)_2$	5	0.0	0.0	6.5
$\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{PPh}_3)_2$	6	0.0	0.0	0.0

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; $p(\text{He})$: 5 bar at 293 K; reaction time: 3 h.

2. Results and discussion

The catalysts tested were mononuclear or cluster phosphine-substituted Ru(0) carbonyl complexes $\text{Ru}(\text{CO})_3(\text{P}^n\text{Bu}_3)_2$ (**1**), $\text{Ru}_3(\text{CO})_9(\text{P}^n\text{Bu}_3)_3$ (**2**), $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**), $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (**4**) or mononuclear Ru(II) compounds $\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{P}^n\text{Bu}_3)_2$ (**5**) and $\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{PPh}_3)_2$ (**6**). These complexes were chosen in consideration of their activity in hydrogenation processes of C=C and C=O double bonds in which the activation of the double bond is one of the preliminary steps. Their solubility in organic solvents and the presence of the phosphine and carbonyl ligands render these complexes appropriate to investigate the formation of intermediates under reaction conditions through spectroscopic methods. The kinetic and the activation parameters were also evaluated. Complexes with no hydridic hydrogen atoms were chosen because we want only fair catalytic activity in order to be able to evaluate, as a final goal of this investigation, the influence of an 'additional gas' on the rate of the reaction.

Particular attention was devoted to evaluating the influence of 'additional gases', such as N_2 , He, Ar or Xe, on the isomerization rate. Our aim was to evaluate if, as reported for the hydroformylation of an olefin in the presence of a cobalt complex [15], the 'additional gas' affects the rate of olefin isomerization in the presence of a ruthenium catalyst.

2.1. Isomerization of an olefin in the presence of ruthenium complexes

The influence of temperature, reaction time, catalyst concentration, and substrate concentration on the catalytic activity of ruthenium complexes was tested in the isomerization of hex-1-ene. These variables were evaluated by changing each one of the parameter at a time while the other conditions were kept constant. In each test, the conversion of the substrate and the composition of the reaction products were determined. No optimization of the reaction was performed at this stage of the investigation.

2.1.1. Influence of the catalytic precursor

The data on the catalytic activity of complexes **1–6** are reported in Table 1. Among the mononuclear Ru(0) complexes, **1** shows a lower catalytic activity than **3**. The catalytic activity of the ruthenium clusters **2** and **4** is very different from that of **3**. The increase of the catalytic activity of **2** as a function of temperature is higher than that of **3**, giving a conversion of 19.1% at 353 K and 97.1% at 393 K.

At 373 K, in the presence of **2**, the amount of hex-2-enes [(Z) + (E)] is largely preponderant with respect to hex-3-enes [(Z) + (E)] with a molar ratio 20:1. This ratio is higher than that (3:1) obtained in the presence of **3**.

Table 2
Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (**3**): influence of temperature^a

T (K)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
333	7.5	92.5	3.3	2.6	0.0	1.6
353	25.1	74.9	10.6	8.4	2.8	3.3
373	53.4	46.6	24.2	17.1	6.0	6.1
393	91.7	8.3	37.7	32.0	10.4	11.6

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; *p*(He): 5 bar at 293 K; reaction time: 3 h.

Table 3
Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (**3**): influence of reaction time^a

Reaction time (h)	T (K)	Conversion (%)	Reaction products composition (%)				
			Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
3	333	7.5	92.5	3.3	2.6	0.0	1.6
14	333	25.8	74.2	10.8	9.5	1.6	3.9
24	333	39.1	60.9	15.8	13.2	4.9	5.2
48	333	52.3	47.7	20.3	17.7	7.4	6.9
1.5	353	25.8	74.2	10.9	8.9	2.2	3.8
3	353	35.6	64.4	14.6	11.3	4.6	5.1
6	353	56.6	43.4	24.2	17.5	7.1	7.8
9	353	70.0	30.0	29.8	22.1	8.5	9.6
18	353	93.9	6.1	36.3	36.9	9.6	11.1
56	353	97.4	2.6	27.1	49.1	5.5	15.7
122	353	97.9	2.1	18.6	55.6	3.8	19.9
146	353	98.1	1.9	18.6	55.9	3.7	19.9

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; *p*(He): 5 bar at 293 K.

Complex **4** is catalytically inactive at 353 K (Table 1), but at 373 K it provides an almost quantitative isomerization of hex-1-ene (97.0%). At this temperature the ratio between hex-2-enes [(Z) + (E)] and hex-3-enes [(Z) + (E)], as reported for **2**, is very high, i.e. 10:1, with (E)-hex-2-ene as the largely predominant stereoisomer (64.0%).

The Ru(II) complex Ru(CO)₂(OAc)₂(PⁿBu₃)₂ (**5**) is a poor catalyst even at 393 K: only 6.5% conversion was obtained (Table 1). Let us recall, however, that, at this temperature, complex **5** is partially transformed into Ru₂(CO)₄(OAc)₂(PⁿBu₃)₂ (**7**), catalytically active in the isomerization of hex-1-ene [16]. As a consequence, the isomerization noticed in the presence of **5** may be attributed to the formation of **7**.

Compound **6** is not catalytically active for the isomerization of hex-1-ene in the range of temperatures tested.

2.1.2. Influence of reaction parameters

The data reported above show that complex **3** is a fairly good catalyst and, therefore, the influence of different reaction parameters in the isomerization of linear hexenes was tested in the presence of **3**.

2.1.2.1. Reaction temperature. The influence of temperature on the catalytic activity of **3** is reported in Table 2. A temperature of 333 K is necessary to obtain a detectable conversion of the substrate. The conversion increases from 7.5% at 333 K up to 91.7% at 393 K. All linear isomers of hex-1-ene were formed and their amount increases almost ten times when the temperature is raised from 333 to 393 K.

2.1.2.2. Reaction time. At 333 K, the conversion increases from 7.5 to 52.3% when the reaction time increases from 3 to 48 h (Table 3). Taking into account a first-order reaction rate, the integrated equation

$$kt = \ln[a_0/a_0(1-x)] \quad (1)$$

can be obtained, where a_0 is the initial concentration of the substrate, t is the reaction time and x is the percentage conversion. Plotting $\ln[100/(100-x)]$ as a function of time, a linear relation was obtained with $k = 4.28 \times 10^{-6} \text{ s}^{-1}$. The linear relation is in agreement with a partial first-order reaction rate with respect to the substrate concentration.

The amount of (Z)-hex-2-ene increases from 3.3% after 3 h to 20.3% after 48 h; similarly, (E)-hex-2-ene

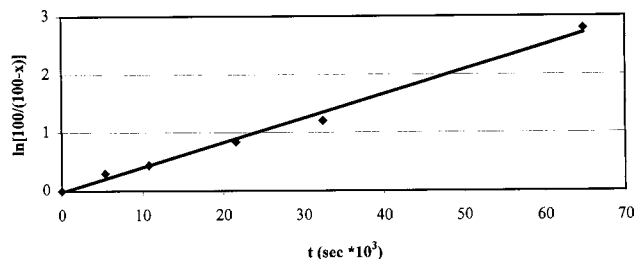


Fig. 1. Hex-1-ene isomerization in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**). Rate constant k_c at 353 K as a function of time (data from Table 3). x : conversion %. For the linear regression $y = ax + b$, $a = 4.22 \times 10^{-5}$, $r^2 = 0.992$. The specific rate is $k_c = 4.22 \times 10^{-5} \text{ s}^{-1}$.

increases from 2.6 to 17.7%, and (*Z*)-hex-3-ene increases from 0.5 to 7.4%, whereas (*E*)-hex-3-ene changes from 1.5 to 6.9%.

Another set of tests was performed at 353 K, and the data are reported in Table 3. Using Eq. (1), a first-order reaction rate has been obtained with a specific rate of $k = 4.22 \times 10^{-5} \text{ s}^{-1}$ (Fig. 1). The specific rate increases ten times as the temperature increases by 20 K. The thermodynamic equilibrium mixture of olefins (Table 3) was obtained after a reaction time of 122 h.

The data reported were also confirmed by using a higher substrate concentration in a series of isochronous experiments carried out at 353 K with a substrate concentration in the range between 0.40 and 1.60 M, while the other reaction conditions remained unchanged. The conversion is a linear function of the initial concentration of the substrate, confirming the first-order reaction rate.

The data collected between 333 and 353 K show that the (*E*)-hex-3-ene/(*Z*)-hex-3-ene ratio increases with temperature, and at higher temperatures the thermodynamic equilibrium is obtained rapidly.

2.1.2.3. Solvent. The following solvents were tested in consideration of their polarity and acidity: acetone,

tetrahydrofuran, 1,4-dioxane, *n*-heptane, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoropropan-2-ol, propan-2-ol, propan-1-ol, ethanol, methanol and butan-1-ol. The results are reported in Table 4.

Complex **3** is only partially soluble in *n*-heptane, methanol and 2,2,2-trifluoroethanol, whereas it is completely soluble in the other solvents employed.

The nature of the solvent greatly affects the isomerization rate of hex-1-ene. A substrate conversion of 9.5% was obtained in a coordinating solvent such as acetone, whereas an 87.7% conversion was obtained in a hydrogen donor solvent such as propan-2-ol. The higher value obtained in propan-2-ol may be tentatively attributed to a transformation of the catalytic precursor in the reaction conditions adopted, and consequently the mechanism changes. In fact a ruthenium hydride complex may be formed in a preliminary step through an oxidative addition of the alcohol to **3**, and this new hydridic complex (Scheme 2) is the catalytically active species having a very high isomerizing activity. IR and NMR spectroscopies, however, do not support the presence of the hypothetical intermediate $[\text{Ru}(\text{H})(\text{CO})_3(\text{PPh}_3)_2][(\text{CH}_3)_2\text{CHO}]$ (**8a**), probably because it is very reactive, or it is formed in a very low concentration (see Section 2.3.1).

The high catalytic activity of hydrido ruthenium complexes [17] supports this hypothesis. A mechanism involving subsequent addition–elimination steps of a C=C double bond on an M–H bond is more efficient than that of one involving the formation of a π -allyl intermediate.

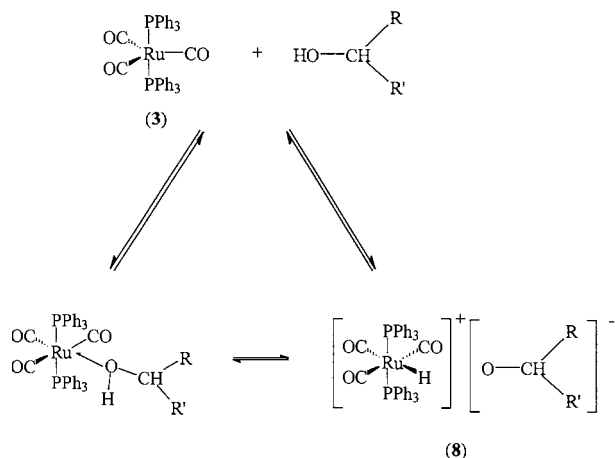
The conversion of the olefin is 46.5% when using ethanol as solvent, a value higher than that obtained using toluene (34.6%). Almost the same value is obtained using propan-1-ol (46.1%) or butan-1-ol (39.3%).

The low conversion (9.5%) obtained in a coordinating solvent such as acetone may be attributed to a competition between the solvent and the substrate for a coordinative place available on the catalyst. By using

Table 4
Hex-1-ene isomerization in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**): influence of solvent^a

Solvent	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(<i>Z</i>)-Hex-2-ene	(<i>E</i>)-Hex-2-ene	(<i>Z</i>)-Hex-3-ene	(<i>E</i>)-Hex-3-ene
(CF_3) ₂ CHOH	8.4	91.6	3.8	4.0	0	0.6
Acetone	9.5	90.5	2.0	5.6	0	1.9
Tetrahydrofuran	11.0	89.0	4.4	3.9	0	2.7
1,4-Dioxane	23.7	76.3	9.1	12.6	0	2.0
Toluene	34.6	65.4	14.7	10.8	4.8	4.3
Butan-1-ol	39.3	60.7	15.0	13.6	5.3	5.4
Propan-1-ol	46.1	53.9	17.2	16.5	6.0	6.4
Ethanol	46.5	53.5	18.6	17.6	4.3	6.0
Propan-2-ol	87.6	12.4	33.2	31.8	10.6	12.0

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; solvent 5.0 ml; $p(\text{He})$: 5 bar at 293 K; reaction time: 3 h.



code	R	R'
a	CH ₃	CH ₃
b	CF ₃	CF ₃
c	H	CF ₃

Scheme 2.

aprotic solvents or solvents having a lower polarity, such as tetrahydrofuran or 1,4-dioxane, respectively, the conversion increases to 11.0 and 23.7%.

2.1.2.4. Substrate. The catalytic activity of **3** in the isomerization of different olefinic substrates has been tested using all linear isomers of hex-1-ene. The isomerization of the linear regioisomers of hex-1-ene after 3 h is undetectable. If the reaction is carried out for a much longer time (122 h), however, a thermodynamic mixture of hexenes may be obtained (Table 3). It is evident that the steric hindrance around the double bond of an internal olefin plays a fundamental role; hex-1-ene in fact may be easily coordinated to the catalyst to form a π -olefin ruthenium complex and isomerized. (*Z*)-Hex-2-ene, the isomer having a lower steric hindrance among the regioisomers tested, is much too crowded and is thus less efficiently coordinated to **3**, thereby giving a π complex in lower concentration.

As a consequence, the formation of (*Z*)- or (*E*)-hex-3-ene from hex-1-ene takes place through several reaction steps that do not involve the displacement of the intermediate hex-2-ene from the catalyst.

2.1.2.5. Catalyst concentration. An increase of the catalyst concentration (Table 5) affects the rate of the reaction: the conversion increases from 25.0 to 70.5%. The kinetic equation for a first-order reaction rate, with respect to catalyst concentration, is $k_t[\text{cat}] = \ln[100/(100 - x)]$ where $[\text{cat}]$ is the molar concentration of **3** and the other variables have the meaning given in Eq. (1). Because a linear relation between $\ln[100/(100 - x)]$ and $[\text{cat}]$ was obtained, a partial first-order of the reaction with respect to the catalyst concentration is obtained with a specific rate of $k_{\text{cat}} = 0.025 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

2.1.2.6. Carbon monoxide. Carbon monoxide (5 bar) suppresses the isomerization of hex-1-ene at 393 K.

2.1.2.7. Free triphenylphosphine. The data for the tests performed at 393 K, using free triphenylphosphine, are reported in Table 6. When the P/Ru molar ratio increases from 0 to 5 the isomerization of hex-1-ene decreases from 66.0% to 26.8% respectively. A further increase of the P/Ru ratio from 5 up to 20 results in the opposite trend in the rate of isomerization; it is now increasing, and the conversion reaches a value of 69.7%.

The increase of the reaction rate in the presence of a large excess of free phosphine, may be explained by assuming that catalyst **3** is transformed into the more reactive species $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (**9**) [18]. Spectroscopic evidence for the presence of **9** supports this hypothesis. It is not easy to discriminate between $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ($\nu = 1896 \text{ cm}^{-1}$) and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ ($\nu = 1905 \text{ cm}^{-1}$) by IR spectroscopy, because only a strong stretching is present in both cases. The same reaction was therefore carried out in an NMR sample tube (see Section 4.5.4). The ³¹P-NMR spectrum in C₆D₆, after 6 h shows the presence of the starting complex **3** ($\delta = 56.8 \text{ ppm}$), and

Table 5
Hex-1-ene isomerization in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**): influence of catalyst concentration^a

[cat] (mM)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(<i>Z</i>)-Hex-2-ene	(<i>E</i>)-Hex-2-ene	(<i>Z</i>)-Hex-3-ene	(<i>E</i>)-Hex-3-ene
0.1	25.0	75.0	8.1	13.3	1.6	2.0
0.2	33.5	66.5	15.1	12.6	2.9	2.9
0.4	43.8	56.2	20.8	13.2	5.9	3.9
0.8	50.5	49.5	23.3	15.9	6.5	4.8
1.6	60.0	40.0	28.0	17.4	8.7	5.9
3.2	70.5	29.5	34.1	19.8	9.9	6.7

^a Hex-1-ene 490 μl (4.00 mmol); toluene 25.0 ml; substrate/catalyst (molar ratio) = 100; $p(\text{He})$: 5 bar at 293 K; $T = 393 \text{ K}$.

Table 6

Hex-1-ene isomerization in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**): influence of the presence of free phosphine^a

PPh ₃ /Ru molar ratio	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
0.0	60.0	40.0	28.0	17.4	8.7	5.9
0.5	41.4	58.6	22.8	11.1	3.6	3.9
1	42.0	58.0	27.0	12.7	Trace	2.3
2.5	28.4	71.6	17.3	8.1	1.5	1.5
5	26.8	73.2	17.7	8.0	Trace	1.1
7.5	42.0	58.0	27.8	12.9	Trace	1.3
10	46.8	53.2	32.6	12.4	Trace	1.8
20	69.7	30.3	47.4	19.1	1.4	1.8

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 25.0 ml; $p(\text{He})$: 5 bar at 293 K; $T = 393$ K.

free triphenylphosphine ($\delta = -3.99$ ppm) together with a little amount of **9** ($\delta = 50.9$ ppm) (conversion 2.5%). The signals of both free triphenylphosphine and **3** decrease when the reaction time increases, whereas the intensity of the resonance of **9** increases.

Further support to this hypothesis was obtained by carrying out an isomerization experiment in the conditions reported in Table 6 using **9** as catalyst. The conversion of hex-1-ene was 93.6%, whereas in the presence of **3** it was 60.0%.

2.1.2.8. Activation parameter. The data on the influence of temperature (Table 2) were employed to evaluate the activation parameters ΔG^{**} , ΔH^{**} and ΔS^{**} . Plotting the ΔG^{**} values as a function of T (Fig. 2) a straight line was obtained from which the ΔS^{**} ($-167.3 \text{ J mol}^{-1} \text{ K}^{-1} = -39.9 \text{ cal mol}^{-1} \text{ K}^{-1}$) and ΔH^{**} ($58.9 \text{ kJ mol}^{-1} = 14.05 \text{ kcal mol}^{-1}$) values were obtained. These data are related to the *rate-determining step* of the reaction and the negative value of ΔS^{**} is an indication that the transition state involves the formation of a complex having a higher steric hindrance than the starting catalyst. A reaction mechanism is suggested (Scheme 3) to rationalize the data collected and the rate-determining step is assumed to be the coordination of the olefin to the metal forming a π olefin–metal complex. This hypothesis is in agreement with the observed influence of the structure of the substrate on the reaction rate. In fact, whereas hex-1-ene is isomerized, hex-2-enes and hex-3-enes are unchanged in the same conditions, after 3 h.

2.2. Reactivity of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**)

2.2.1. With an alcohol

The reaction of **3** with 1,1,1,3,3,3-hexafluoropropan-2-ol was investigated. The complex **3** is insoluble in this alcohol at room temperature, but it dissolves at 333 K and the new complex **8b**, analogous to **8a**, has been

identified, to which the $[\text{Ru}(\text{H})(\text{CO})_3(\text{PPh}_3)_2][(\text{CF}_3)_2\text{CHO}]$ formulation may be attributed. The IR spectrum shows in fact that **3** is completely transformed into the new compound **8b**, having two absorptions

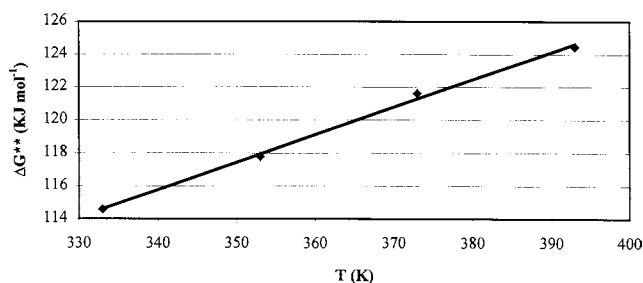
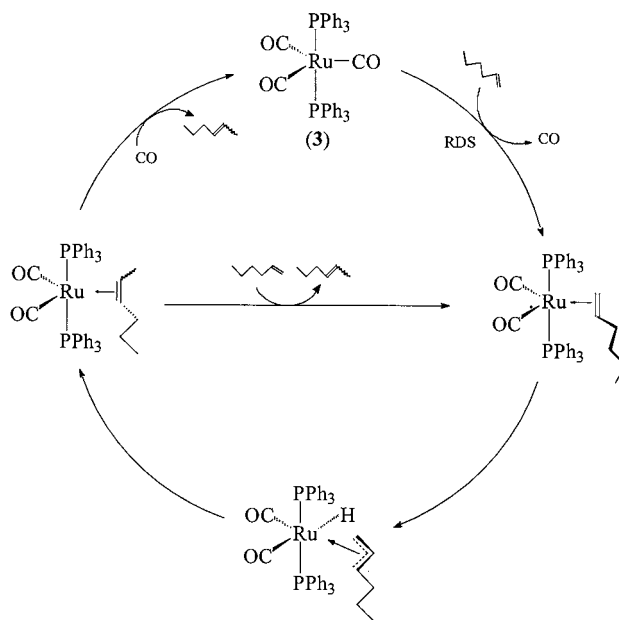


Fig. 2. Hex-1-ene isomerization in the presence of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**3**). Activation parameter (data from Table 2). Linear regression $y = ax + b$, $a = 167.29$, $b = 58\,883.73$, $r^2 = 0.998$. ΔS^{**} : $-167.3 \text{ J mol}^{-1} \text{ K}^{-1}$. ΔH^{**} : 58.9 kJ mol^{-1} .



Scheme 3.

at 2078(s) and 2056(s) cm^{-1} attributable to $\nu(\text{C}=\text{O})$ and another band at 1485 cm^{-1} attributed to $\nu(\text{C}-\text{H})$ of a ruthenium alkoxide. The formation of **8b** (Scheme 2) is confirmed by $^1\text{H-NMR}$: a triplet at $\delta = -6.1$ ppm may be unequivocally attributed to a hydridic proton coupled with two equivalent phosphine ligands with a $^2J_{\text{P-H}} = 15.1$ Hz. The spin system (AX_2) and the coupling constant are in agreement with a hydride in a cis position with respect to the phosphorus atoms. Only one singlet, at $\delta = 36.7$ ppm, is present in the $^{31}\text{P-NMR}$, confirming that the two phosphinic ligands are equivalent. The $^{13}\text{C-NMR}$ spectrum shows a triplet at $\delta = 191.9$ ppm ($^2J_{\text{C-P}} = 13$ Hz) in agreement with two equivalent carbonyl groups coupled with two cis phosphinic ligands. Another resonance attributable to a carbonyl group is present at $\delta = 189.8$ ppm. The resonances of the alkoxy group are not detected because the complex is formed in a solution of 1,1,1,3,3,3-hexafluoropropan-2-ol.

A 1 mM solution of **8b** shows the same conductivity as an equimolar solution of sodium acetate. The mass spectrum of the complex shows a cluster of peaks attributed to $[\text{RuH}(\text{CO})_3(\text{PPh}_3)_2]^+$ (m/z 711).

The reaction between **3** and 1,1,1,3,3,3-hexafluoropropan-2-ol is reversible: when the solvent is removed the starting complex **3** is completely restored.

The higher stability of compound **8b**, compared with that of **8a**, is in agreement with its lower catalytic activity in the isomerization of hex-1-ene: using **3** as catalytic precursor and 1,1,1,3,3,3-hexafluoropropan-2-ol as solvent the olefin conversion is only 6.5%. It is known that perfluoroalkoxy complexes are more stable than the corresponding non-fluorinated compounds [19]. For instance $\text{Rh}(\text{H})(\text{PPh}_3)_4$ reacts with 1,1,1,3,3,3-hexafluoropropan-2-ol to give the corresponding rhodium alkoxide [19] and $\text{Ru}(\text{H}_2)(\text{PPh}_3)_4$ reacts with 2,2,2-trifluoroacetophenone to form the stable $\text{Ru}(\text{H})[\text{OCH}(\text{CF}_3)\text{Ph}](\text{PPh}_3)_4$ complex [19].

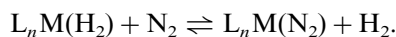
The behaviour of **3** in 2,2,2-trifluoroethanol is analogous to that shown in 1,1,1,3,3,3-hexafluoropropan-2-ol. The complex **3** dissolved is completely transformed into the new complex $[\text{Ru}(\text{H})(\text{CO})_3(\text{PPh}_3)_2][\text{CF}_3\text{CH}_2\text{O}]$ (**8c**), as shown by the IR spectrum of the solution: only two absorptions are present, in the $\nu(\text{CO})$ region, at 2066 and 2010 cm^{-1} . Owing to the stability of **8c**, and to the low solubility of **3** in this solvent, the isomerization of hex-1-ene is 8.4%.

2.2.2. With PPh_3

Using $^{31}\text{P-NMR}$ spectroscopy, the conversion of **3** into **9** was tested on a solution of **3**, hex-1-ene and PPh_3 . After 6 h the amount of **9** is 2.5%, and its conversion increases to 13.3% after 24 h, 21.1% after 89 h and 30.3% after 144 h.

2.3. Influence of an 'additional gas' on the hydroformylation of olefins

An additional gas, that is not involved in the catalytic cycle of the reaction but which may obstruct it, has recently been used to single out the elementary steps of a catalytic reaction. An appropriate amount of an 'additional gas' such as N_2 , Ar or Xe, has been shown to reduce considerably the rate of hydroformylation of olefins in the presence of dicobalt octacarbonyl [15]. The influence of such 'additional gas' has been explained on a molecular basis [15]: the 'additional gas' may compete with a reactant for a coordinatively unsaturated position on the catalyst to form a complex that is kinetically inactive. The amount of catalyst available for the catalytic reaction is therefore reduced and, as a consequence, the reaction rate is decreased. This role may be easily explained when the 'additional gas' is nitrogen if, for instance, we consider the equilibrium:



It is completely shifted to the right in the presence of a high concentration of nitrogen, as reported by Sacco and Rossi [20]. When the reaction is carried out in the presence of Ar or Xe an effect analogous to that reported for nitrogen has been noticed: the rate of the reaction is considerably reduced [15]. These results may be attributed to an interaction between Ar or Xe with the catalytically active cobalt species in agreement with the explanation reported for the influence of nitrogen. Ar- or Xe-containing transition metal complexes have been identified, usually by spectroscopic methods, in a solid matrix at low temperature [21], in a solution of liquefied noble gas [21b,22] or in the gaseous state [21b].

We have now tested the eventual influence of an 'additional gas' on the isomerization rate of hex-1-ene in the presence of **3** as catalyst.

2.3.1. Nitrogen

The influence of nitrogen (pressures between 0 and 1000 bar) on the rate of hex-1-ene isomerization was tested in isochronous experiments performed at 373 K, in the presence of **3**. The results are reported in Table 7. A 55.9% conversion was obtained in a reference test; the conversion is reduced to 44.1% when adding nitrogen at a pressure of 244 bar and it decreases progressively to 9.4% when the nitrogen pressure is increased to 1032 bar.

The reduction of the isomerization rate of hex-1-ene may be attributed to the formation of a ruthenium complex containing nitrogen (Scheme 4) that, in the reaction conditions tested, is unable to coordinate the olefin. As a consequence, the amount of catalytically active ruthenium complex is reduced. Using an increas-

Table 7

Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (3): influence of nitrogen as additional gas^a

Nitrogen (bar)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
0	55.9	44.1	24.4	19.2	4.8	7.5
244	44.1	55.9	19.8	14.6	4.7	5.0
504	29.6	70.4	13.4	9.0	4.3	2.9
740	17.7	82.3	8.8	6.5	Trace	2.4
1032	9.4	90.6	4.3	3.4	Trace	1.7

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; *T* = 373 K; reaction time: 3 h.

ing pressure of nitrogen, the amount of the nitrogen-containing ruthenium complex increases and this reduces the concentration of the ruthenium complex catalytically active in the hex-1-ene isomerization. An analogous behaviour was reported by Pennella and Banks [23] in the isomerization of pent-1-ene catalysed by [Ru(H₄)(PPh₃)₃] or [Ru(H₂)(N₂)(PPh₃)₃] complex. The presence of nitrogen does not affect the isomeric distribution of the olefins formed, i.e. the (*Z*)/(*E*) ratio remains constant (Table 7). The hex-3-enes obtained from hex-1-ene must be formed directly from the starting olefin coordinated to the ruthenium complex and, therefore, this process is not influenced by the presence of nitrogen. These data support the hypothesis that the catalyst active for olefin isomerization is not modified by the presence of nitrogen, but that there is only a competition between nitrogen and the olefin to a coordinatively unsaturated position of the catalyst.

2.3.2. Argon

The results for the influence of argon are reported in Table 8. The conversion of the olefinic substrate is reduced to 48.8% in the presence of argon at a pressure of 240 bar, and to 8.6% with a pressure of 910 bar. This behaviour of argon is analogous to that reported for nitrogen, and is in agreement with the almost identical ionization potentials of these two gases, even if, at the same partial pressure, argon shows a higher solubility in toluene [24]. As a consequence, a simple correlation between the data obtained with these two gases is not possible due to their different solubility and compressibility factors [24].

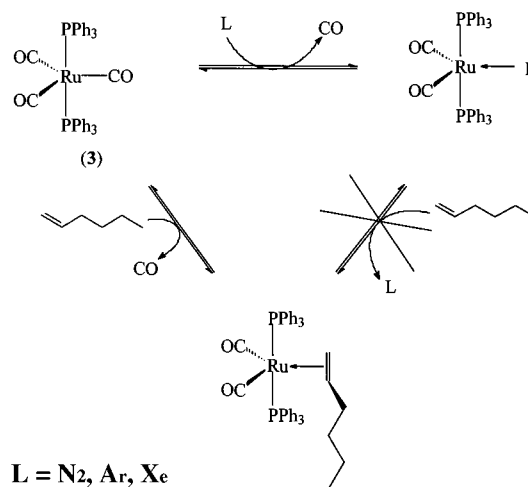
2.3.3. Helium

The results for the influence of helium as ‘additional gas’ are reported in Table 9. Almost no influence was observed up to a pressure of 669 bar of He as additional gas. By increasing the pressure of helium to 835 bar, however, the conversion increases (83.9%), and a further increase is obtained at 976 bar (89.5%). The data obtained between 835 and 976 bar of helium are not easily rationalized. In the mechanism reported in

Scheme 3 the transition state may be approached with a molar volume lower than the sum of the volumes of the starting complex and the olefin, and, as a consequence, it is facilitated by increasing the total pressure. However, this is only a suggestion, and further data would be necessary to confirm this hypothesis.

2.3.4. Xenon

The influence of xenon as ‘additional gas’ has been evaluated using different experimental conditions with respect to those adopted with the other additional gases previously reported due to the different critical temperature of this gas. The results are reported in Table 10. The behaviour of xenon is in line with that reported for nitrogen and argon, even if the total pressure of this experiment is very low. The amount of xenon in solution affects the conversion of the olefinic substrate that is reduced from 47.0% in the absence of xenon to 41.7% when 2.2 g of xenon is added and to 32.8% when the amount of xenon is 9.4 g.



Scheme 4.

Table 8
Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (**3**): influence of argon as additional gas^a

Argon (bar)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
0	55.9	44.1	24.4	19.2	4.8	7.5
240	48.8	51.2	22.8	14.4	6.4	5.2
487	32.2	67.8	14.1	10.8	3.2	4.1
766	15.2	84.8	6.9	5.3	~0	3.0
910	8.6	91.4	3.7	3.1	~0	1.8

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; T = 373 K; reaction time: 3 h.

Table 9
Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (**3**): influence of helium as additional gas^a

Helium (bar)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
5	55.9	44.1	24.4	19.2	4.8	7.5
257	61.0	39.0	26.2	20.2	7.6	7.0
509	61.1	38.9	27.8	20.0	6.6	6.7
669	62.6	37.4	26.7	20.9	7.6	7.4
835	83.0	17.0	35.9	27.3	9.9	9.9
976	89.5	10.5	37.1	30.8	10.0	11.6

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; T = 373 K; reaction time: 3 h.

Table 10
Hex-1-ene isomerization in the presence of Ru(CO)₃(PPh₃)₂ (**3**): influence of xenon as additional gas^a

Xenon (g)	Conversion (%)	Reaction products composition (%)				
		Hex-1-ene	(Z)-Hex-2-ene	(E)-Hex-2-ene	(Z)-Hex-3-ene	(E)-Hex-3-ene
0	47.0	53	21.9	14.6	6.0	4.5
2.2	41.7	58.3	19.3	12.4	5.5	4.5
3.5	38.8	61.2	19.3	11.0	3.9	4.6
4.5	38.1	61.9	18.5	10.9	5.0	3.7
5.9	37.9	62.1	19.2	11.1	3.2	4.4
9.4	32.8	67.2	16.8	9.4	3.0	3.6

^a Catalyst: 28.4 mg (0.040 mmol); hex-1-ene 490 μl (4.00 mmol); substrate/catalyst (molar ratio) = 100; toluene 5.0 ml; T = 353 K; reaction time: 3 h.

3. Conclusions

The Ru(0) complexes Ru(CO)₃(PⁿBu₃)₂ (**1**), Ru₃(CO)₉(PⁿBu₃)₃ (**2**), Ru(CO)₃(PPh₃)₂ (**3**), Ru₃(CO)₉(PPh₃)₃ (**4**) are catalytically active in the isomerization of hex-1-ene to hex-2-enes and hex-3-enes, whereas the Ru(II) complexes Ru(CO)₂(OAc)₂(PⁿBu₃)₂ (**5**) and Ru(CO)₂(OAc)₂(PPh₃)₂ (**6**) show a low or negligible isomerization activity. The reaction shows a low regioselectivity: all possible linear isomers are formed.

The higher activity of **3** with respect to **1** may be explained taking into account that:

1. the steric hindrance of the PBu₃ ligands in **1** is higher than the PPh₃ phosphine in **3** and, as a consequence, the coordination of the olefin is more difficult;
2. the higher basicity of tri-*n*-butylphosphine, if compared with triphenylphosphine, increases the stability of complex **1** with respect to **3** and, as a consequence, **1** is less prone to release a carbonyl ligand to start a catalytic cycle.

In the presence of **3** a pseudo-first-order reaction rate is obtained with respect to the substrate and catalyst concentrations. The large influence of carbon monoxide on the reaction rate suggests that the activation of the

olefin may involve the displacement of a carbon monoxide molecule present in **3** with formation of a π -olefin–ruthenium complex. This compound may evolve towards the formation of a π -allyl hydride ruthenium complex, in agreement with the suggestion reported by Valle et al. [25], from which it is possible to restore the starting π -olefin–ruthenium complex or an analogous complex containing the isomerized olefin. Owing to its higher steric hindrance the internal olefin is displaced by the terminal one, and the complex formed starts another catalytic cycle.

An alcohol used as solvent affects the catalytic activity of complex **3** because it causes the formation of a hydridic ruthenium complex that changes the catalytic cycle. In fact, a ruthenium hydride is formed in the reaction between 1,1,1,3,3,3-hexafluoropropan-2-ol and **3**.

In consideration of the fact that hex-2-ene and hex-3-ene are not isomerized after a reaction time of 3 h in the presence of **3**, the (*E*)- and (*Z*)-hex-3-enes formed in the isomerization of hex-1-ene are not obtained through several addition–elimination steps. These olefins must be formed through a multistep isomerization process that does not involve the displacement of the intermediate isomerized olefin bound to the catalytic intermediate. To isomerize internal olefins a very long reaction time is necessary.

An additional gas, such as nitrogen, present in appropriate concentration in the reaction medium reduces the rate of the reaction. In consideration of the mechanism suggested, the role played by an ‘additional gas’ is an interaction with the ruthenium complex forming an intermediate that, in the condition tested, is unable to activate an olefin. Whereas helium has no influence on the reaction, at least up to 650 bar, the presence of argon causes an effect analogous to that reported for nitrogen. The different behaviour observed in the presence of helium and argon rules out the hypothesis that the different reaction rate is attributable to the high pressure employed. Furthermore, the influence of xenon, having an effect analogous to that of nitrogen or argon, but at a low pressure, confirms that a high pressure of the ‘additional gas’ is only necessary to obtain the appropriate concentration of the gas in solution.

The reduction of the reaction rate cannot be attributed to an increase of the volume of the solution due to the ‘additional gas’ dissolved in the solvent. The amount of nitrogen dissolved in toluene, when 1000 bar of nitrogen is employed, increases the volume of the solution of 20% and this dilution of the solution does not explain the data obtained.

The reduction of the reaction rate in the presence of an ‘additional gas’ may be ascribed to an interaction between the ‘additional gas’ and the catalytic specie in agreement with the hypothesis formulated to explain an

analogous effect in the hydroformylation of olefin catalysed by $\text{Co}_2(\text{CO})_8$ [15].

The following considerations may be formulated:

- an interaction between a ruthenium carbonyl complex and an ‘additional gas’ is possible, in agreement with the hypothesis reported for the hydroformylation of cyclohexene in the presence of a cobalt complex, even if different reaction conditions are employed;
- competition between an ‘additional gas’ and an olefin is possible in addition to those between the ‘additional gas’ and hydrogen or carbon monoxide [15] previously reported;
- the methodology to carry out experiments in the presence of an ‘additional gas’ is very useful for showing, in a catalytic cycle, weak interactions between the substrate and the transition metal complex.

4. Experimental

A Shimadzu GC14 chromatograph equipped with a PPG column (Ucon oil LB 550X on Chromosorb W 15%, i.d. 1/8", length 4 m) and with a Perkin–Elmer Model 8320 capillary gas-chromatograph, equipped with a Chrompack Al_2O_3 PLOT column (Al_2O_3 deactivated with KCl, i.d. 0.32 mm, length 50 m) were used for quantitative analyses of the reaction product. The instruments had FID detectors. In consideration of the analogy of the products examined, no correction factors were introduced. The identity of the products was confirmed by GC–MS using a Shimadzu apparatus with a GC14A capillary column chromatograph and a QP2000 mass detector. The chromatograph was equipped with a CP-Sil8 50 m capillary column.

The conductivity determination was carried out using an Analytical Instrument 111 conductivity meter with Orion 99.01.01 cell having a cell constant 1.00 cm^{-1} .

Electrospray mass was carried out using a Perkin–Elmer Sciex Api 365 system.

IR spectra were recorded with a Perkin–Elmer mod. 1760 FTIR spectrometer.

^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^1H -NMR, at 75.429 MHz for ^{13}C -NMR and at 121.421 MHz for ^{31}P -NMR, using solutions in appropriate solvents. SiMe_4 was used as external standard for ^1H - and ^{13}C -NMR, H_3PO_4 (85%) for ^{31}P -NMR (signals reported as positive downfield to the standard). ^{13}C - and ^{31}P -NMR spectra were acquired using a broad band decoupler.

Hex-1-ene was purified by elution through a neutral Al_2O_3 (70–230 mesh) chromatographic column, then distilled under nitrogen, and had a b.p. of 335 K.

(*Z*)-Hex-2-ene, (*E*)-hex-2-ene, (*Z*)-hex-3-ene and (*E*)-hex-3-ene were purified as reported for hex-1-ene.

Tri-*n*-butylphosphine (Aldrich) was distilled prior to use; b.p. 431–433 K/60 mmHg

Solvents: toluene, methanol, ethanol, propan-2-ol, butan-1-ol, and *n*-heptane were dried according to Vogel [26]. 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-hexafluoro-propan-2-ol were dried on molecular sieves and distilled prior to use.

Other reagents and solvents were commercial products and used without further purification. The following gases were used: nitrogen, Sol Centro product with a purity of 99.996%; argon, Sol Centro product with a purity of 99.998%; xenon, Rivoira product with a purity of 99.997%; helium, Sol Centro product with a purity of 99.998%.

All experiments, unless otherwise specified, were carried out under a nitrogen atmosphere using the Schlenk technique.

The following catalysts were prepared according to the literature; their spectroscopic characteristics were in agreement with the data reported: Ru(CO)₃(P^{*n*}Bu₃)₂ (**1**) [27], Ru₃(CO)₉(P^{*n*}Bu₃)₃ (**2**) [28], Ru(CO)₃(PPh₃)₂ (**3**) [29], Ru₃(CO)₉(PPh₃)₃ (**4**) [30], Ru(CO)₂(OAc)₂(P^{*n*}Bu₃)₂ (**5**) [31,32], and Ru(CO)₂(OAc)₂(PPh₃)₂ (**6**) [33].

Ru(CO)₂(PPh₃)₃ (**9**) was synthesized according to the following procedure: the acetato (**6**) was converted in the dihydride complex H₂Ru(CO)₂(PPh₃)₂ (**10**) as reported by Frediani et al. [34]. On adding pentane a white cream solid was obtained and the solution was separated by filtration. A solution of complex **10** (0.263 mmol) and PPh₃ (1.841 mmol) in methanol (7 ml) was refluxed for 2 h. The yellow solid was filtered, washed with anhydrous ethanol and anhydrous *n*-hexane and dried under vacuum. The IR, ¹H- and ³¹P-NMR spectra of **9** are in agreement with the data reported in the literature [35,36].

4.1. Catalytic isomerization

The tests were carried out in a 50 ml glass vial placed in a stainless steel rocking autoclave having a capacity of 150 ml. Air was evacuated and a solution containing the catalyst and the olefin was introduced in the glass vial under a nitrogen atmosphere. The autoclave was sealed and helium was then added up to 5 bar. The autoclave was heated in an thermostatic oil bath at the prefixed temperature and rocked for the established time. After a rapid cooling to room temperature, the gases were vented and the solution collected and analysed by GC as indicated above. The results of the catalytic experiments are reported in Tables 1–5.

4.2. Catalytic isomerization in the presence of free triphenylphosphine

The experiments were carried out in a Parr autoclave

having a capacity of 125 ml. A toluene solution (25 ml) containing **3** (0.040 mmol), hex-1-ene (4.0 mmol) and triphenylphosphine was introduced by suction in the vessel, then helium was added up to 5 bar. The autoclave was heated at the prefixed temperature and the solution stirred. After a rapid cooling to room temperature, helium was vented and the solution collected and analysed by GC as indicated above. The data obtained are reported in Table 6.

4.3. Catalytic isomerization in the presence of CO

The experiment was carried out in a Parr autoclave having a capacity of 125 ml. A toluene solution (25 ml) containing **3** (0.040 mmol), hex-1-ene (4.0 mmol) was introduced by suction into the vessel, then CO was added up to 5 bar. The autoclave was heated and rocked at 393 K. After a rapid cooling to room temperature, CO was vented and the solution collected and analysed by GC as indicated above; only hex-1-ene was present.

4.4. Catalytic isomerization in the presence of an additional gas

The tests were carried out in a stainless steel rocking autoclave having a capacity of 27.5 ml. Air was evacuated and, in a nitrogen atmosphere, a toluene solution containing the catalyst and the olefin was introduced. The autoclave was sealed and the ‘additional gas’ was introduced, up to the pressure required. The autoclave was electrically heated at the prefixed temperature and rocked for the established time. After a rapid cooling to room temperature, the ‘additional gas’ was vented and the solution collected and analysed by GC as indicated above. The results are reported in Tables 7–10.

4.5. Reactivity of ruthenium complexes

4.5.1. Ru(CO)₃(PPh₃)₂ and hex-1-ene

A solution of Ru(CO)₃(PPh₃)₂ (**3**) (0.042 mmol) in C₆D₆ (0.6 ml) was introduced in an NMR sample tube and the ³¹P-NMR spectrum was collected. Hex-1-ene (1.43 mmol) was added and the sample tube heated at 333 K for 14 h. ³¹P- and ¹H-NMR spectra were recorded at hourly intervals. The ³¹P-NMR spectra showed the presence of only one signal at 56.3 ppm, in keeping with the presence of only **3**. The ¹H-NMR spectra collected at various time intervals showed the presence of an increasing amount of isomeric olefins.

4.5.2. Ru(CO)₃(PPh₃)₂ and (CF₃)₂CHOH

A suspension of Ru(CO)₃(PPh₃)₂ (**3**) (35.1 μmol) in (CF₃)₂CHOH (1 ml) was introduced in an NMR sample tube in which a capillary tube containing C₆D₆ was present for lock purposes. The sample tube was heated at 333 K for 8 h. The ³¹P-, ¹H-NMR, and IR spectra

were recorded every 30 min. A new product **8b** was obtained, after 30 min, having the following characteristic data: ^{31}P -NMR $\delta = 36.7$ ppm; ^1H -NMR $\delta = -6.1$ (t, 1H, $^2J_{\text{P-H}} = 15.1$ Hz) ppm; ^{13}C -NMR $\delta = 191.9$ (t, CO, $^2J_{\text{C-P}} = 13$ Hz), 189.8 (s, CO) ppm. No further changes were shown. The IR spectrum [(CF₃)₂CHOH as solvent] in the 2200–1400 cm⁻¹ region displays absorptions at 2078(s), 2056(s), 1485(s) cm⁻¹. An electro-spray mass spectrum of the complex shows cluster of peaks centred at *m/z* (intensity% in parentheses): 711 (20) [RuH(CO)₃(PPh₃)₂]⁺, 654 (50) [Ru(CO)(PPh₃)₂]⁺, 626 (100) [Ru(PPh₃)₃]⁺, and 363 (16) [Ru(PPh₃)₂]⁺.

A 1 mM solution of this complex shows the same conductivity ($0.58 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 289 K) as an equimolar solution of sodium acetate.

The solvent was distilled at reduced pressure and the residue dissolved at room temperature in C₆D₆. The ^{31}P -, ^1H -, ^{13}C -NMR and IR spectra confirm the presence of Ru(CO)₃(PPh₃)₂ as the only complex in solution.

4.5.3. Ru(CO)₃(PPh₃)₂ and CF₃CH₂OH

A suspension of Ru(CO)₃(PPh₃)₂ (**3**) (35.1 μmol) in CF₃CH₂OH (1 ml) was introduced in a vial under nitrogen. The IR spectrum (CF₃CH₂OH as solvent) in the 2200–1800 cm⁻¹ region displays absorptions at 2066(s), 2010(s) cm⁻¹. The solvent was distilled at reduced pressure and the residue dissolved at room temperature in C₆D₆. The ^{31}P -, ^1H -NMR, and IR spectra confirm the presence of Ru(CO)₃(PPh₃)₂ as the only complex in solution.

4.5.4. Ru(CO)₃(PPh₃)₂ and PPh₃

A solution of Ru(CO)₃(PPh₃)₂ (**3**) (7.2 μmol), hex-1-ene (0.72 mmol), and PPh₃ (0.072 mmol) in C₆D₆ (1 ml) was introduced in an NMR sample tube and analysed by ^{31}P -NMR. The spectrum in C₆D₆, after 6 h at 373 K, showed the presence of the starting complex **3** ($\delta = 56.8$ ppm), and free triphenylphosphine ($\delta = -3.99$ ppm) together with 2.5% of **9** ($\delta = 50.9$ ppm). The signals of free triphenylphosphine and **3** decrease in the course of the reaction, while the signal due to **9** increases. The following conversions were obtained: 13.3% after 24 h, 21.1% after 89 h and 30.3% after 144 h.

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