Alkene isomerization by non-hydridic phosphine substituted ruthenium carbonyl carboxylates

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Abstract

The behaviour of phosphine substituted ruthenium carbonyl carboxylates in the presence of hex-1-ene has been followed by IR and NMR spectroscopies. The complex $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ reacts at room temperature with a large excess of hex-1-ene giving the $Ru_2(CO)_4(MeCO_2)_2(PBu_3)$(hex-1-ene) compound. The same complex is formed from $Ru_2(CO)_4$-$(MeCO_2)_2(PBu_3)_2$ and hex-1-ene at 80°C. Mononuclear $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$ is not transformed under the same conditions. Catalytic tests performed at 80°C in the presence of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ or $Ru_2(CO)_4$-$(MeCO_2)_2(PBu_3)_2$ indicate that these complexes display almost the same catalytic activity in hex-1-ene isomerization in agreement with the formation of the same intermediate. Working in the presence of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ at 80°C, an 85% conversion was obtained after 70 h. The isomeric olefins had a *trans/cis* ratio of 4.5. A reaction scheme has been suggested to rationalise the behaviour of these complexes. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition metal complexes are used as catalytic precursor in reactions such as the hydroformylation, hydrogenation, hydrocyanation and polymerisation of olefins [1]. The activation of an alkene by coordination to the metal is the initial step: it may be followed by the isomerization of the starting material.

The driving force for the latter reaction is the higher stability of the internal olefins compared with that of the terminal ones [2]. The isomerization of the olefin may, in many of the reactions above reported, affect both selectivity and reaction rate.

Alkene isomerization catalysed by transition metal complexes has been interpreted in several ways. The most favoured hypothesis involves the reaction of a metal hydride with an olefin to give a π-olefin metal complex which by subsequent addition/elimination steps makes the alkene isomerization possible [3–6]. This mechanism involves the formation and decomposition of an alkyl metal complex.

Other different ways may be operative in specific cases: In the cobalt catalysed hydroformylation of olefins, alkyl metal complex decomposition has been ruled out as a step respon-

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sible of the formation of isomeric products. In this reaction, both hydrogen and unsaturation shift have been attributed to a π-complex between the olefin and the cobalt carbonyl hydride, with no release of free olefin. When the σ-alkylcobalt complex is formed, it reacts with CO and hydrogen giving the corresponding aldehydes [7].

An alternative isomerization process involving a vinyl-metal intermediate has also been proposed to rationalise the results of the hydroformylation of deuterated olefins in the presence of dicobalt octacarbonyl [8].

The formation of a π-allylic metal intermediate has also been suggested in the isomerization of the coordinated olefin from a non hydrido precursor [6,9,10].

Since the isomerization plays an important role in the reactions of alkenes catalysed by transition metal complexes, we have started an investigation on the isomerization of this substrate in the presence of some ruthenium carbonyl carboxylates to evaluate the role played by this reaction in catalytic processes.

2. Results and discussion

Ru(I) and Ru(II) phosphine substituted carbonyl carboxylates, such as $Ru_2(CO)_4(MeCO_2)_2$-$(PBu_3)_2$, $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$, are catalytically active in the hydrogenation and hydroformylation of olefins. They were chosen for the present investigation in consideration of the amount of information already available on their behaviour in the presence of hydrogen and/or carbon monoxide [11–19].

The behaviour of these complexes in the presence of hex-1-ene was followed by IR and NMR techniques. The system was investigated over a fairly wide range of temperatures (20–140°C). Infrared spectra were recorded in situ by using an infrared cell, directly connected with the pressure vessel in which the isomerization process was taking place. Samples were

collected at appropriate time intervals and gas chromatographic (GC) analyses of the solutions were performed. In this way, the concentration of the olefinic component was followed and the results could be correlated with the spectroscopic data. Whenever possible, the behaviour of the same complexes were examined by NMR spectroscopy with the aim to gain more information on the intermediates detected by IR.

2.1. Behaviour of ruthenium carbonyl carboxylates in the presence of an olefin

All tests were carried out in a pressure vessel using a *n*-heptane solution containing both the complex under examination and hex-1-ene. The solution was gradually heated from 20°C to 140°C. The transformations of the metal carbonyls and of the olefin were followed by IR spectroscopy, tracing the evolution of CO, and C=C stretching vibrations in the 2200–1500 cm^{-1} range and the C–H stretching between 3200 and 3000 cm^{-1}.

2.1.1. $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene

2.1.1.1. Spectroscopic IR investigation. The behaviour of a *n*-heptane solution of $Ru_4(CO)_8$-$(MeCO_2)_4(PBu_3)_2$ and hex-1-ene was investigated.

At room temperature evidences for the formation of an olefin containing complex Ru_2-$(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ were obtained [absorptions at 2030(vs), 1986(m), 1961(vs) and 1930(vw) cm^{-1}]. It is the main complex in solution after 24 h at 20°C. This complex shows, in the carbonyl stretching region, three bands almost coincident with the first three bands of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ [2030(vs), 1986(m), 1961(vs)] while a fourth absorption is present at 1930(vw) cm^{-1}. This last band has a lower intensity than the fourth band of Ru_4-$(CO)_8(MeCO_2)_4(PBu_3)_2$, at 1919(w) cm^{-1}. In the carboxylates stretching region, an absorp-

tion at 1585(mw) cm^{-1} is present due to $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ having the same intensity as the characteristic absorption of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ [1569(vw) cm^{-1}].

After heating the solution at 80°C (33 h), the equilibrium reported in the following equation shifts to the left as shown by the IR spectrum. In this spectrum, we note two weak absorptions attributable to the presence of $[Ru_2(CO)_4(MeCO_2)_2]_n$ and $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ due to a redistribution of the phosphine on the complexes present in solution. After a long time (57 h) at 80°C hex-1-ene is isomerized.

$$Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2 + olefin$$
$$\rightleftharpoons 2Ru_2(CO)_4(MeCO_2)_2(PBu_3)(olefin)$$
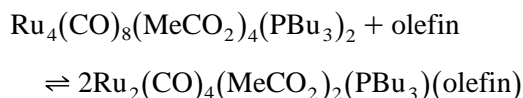
The concentration of the complex $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ was found to decrease when the reaction temperature was increased (100°C for 48 h), but the isomerization activity remained high. No further change was noticed upon heating at 120°C for 15 h.

The GC analyses of the solution at the end of the reaction showed the presence of *cis*-hex-2-ene (20.3%), *trans*-hex-2-ene (51.3%), *trans*-hex-3-ene (17.7%), *cis*-hex-3-ene (4.2%) and hex-1-ene (6.4%).

These results are a clear indication that the reaction between $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene takes place already at room temperature with the formation of the new complex $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ containing coordinated hex-1-ene.

The terminal olefin bound to the ruthenium atom is isomerized at 80°C to an internal olefin. The last one, due to a reduced coordinating ability, is replaced by the terminal olefin. In this way, the isomerization process takes place [20,21]. When the concentration of the starting olefin is low enough then the tetranuclear ruthenium complex $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ is restored.

The complex $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ may be formed by breaking of the oxygen bridges that connect the two $Ru_2(CO)_4$-

$(MeCO_2)_2(PBu_3)$ moieties (Scheme 1). An analogous insertion of a reactant takes place in the reaction of the $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ complex with CO [19] or PBu_3 [12].

The local symmetry of $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ must not be very different from that of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and therefore the IR pattern in the carbonyl stretching region is analogous.

2.1.1.2. Spectroscopic NMR investigation.

The system was investigated by ^{31}P NMR, using a
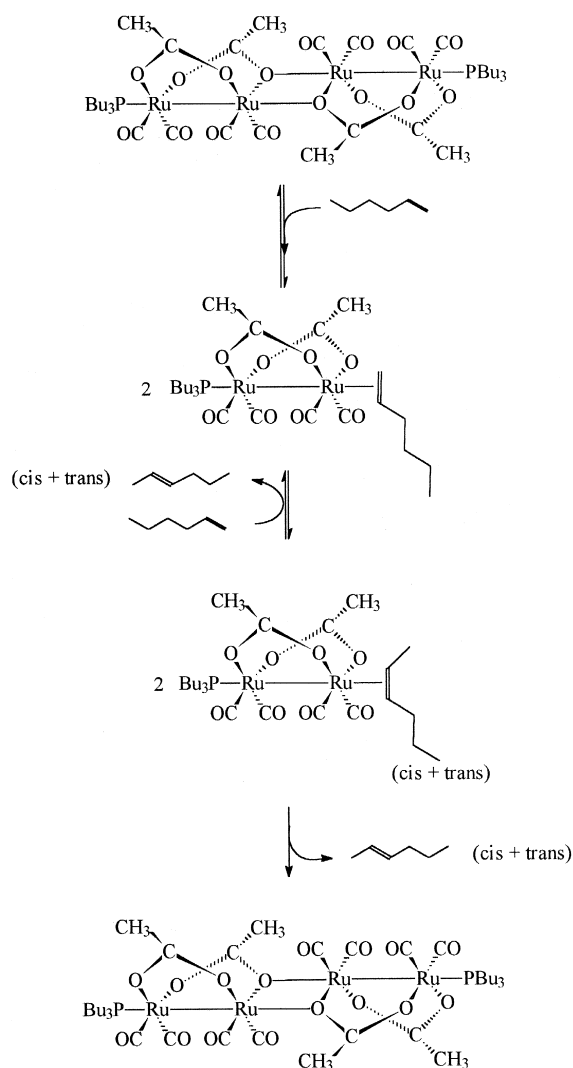
Scheme 1.

n-heptane solution of $Ru_4(CO)_8(MeCO_2)_4$-$(PBu_3)_2$ and hex-1-ene (molar ratio $Ru_4(CO)_8$-$(MeCO_2)_4(PBu_3)_2$/hex-1-ene = 1:500) in a nitrogen atmosphere. The spectra were recorded using a NMR sample tube containing a coaxial insert stem filled with C_6D_6 for the internal lock of the FT-NMR instrument.

The initial complex (singlet at 3.8 ppm) disappeared completely after 15 min at room temperature and two new resonances were present: a very broad singlet at 8.7 and a narrow singlet at 7.2 ppm. The last resonance was initially of moderate intensity then gradually increased with respect to that one at 8.7 in the course of the reaction.

The IR spectrum, recorded on a sample of this solution, confirmed the presence of Ru_2-$(CO)_4(MeCO_2)_2(olefin)(PBu_3)$. The GC analysis of the solution, after a reaction time of 21 h at room temperature, does not indicate the presence of isomerized hexenes.

These data seem to indicate that the complex containing the olefin is easily formed at room temperature, but that isomerized olefins are not released at this temperature even if formed.

After heating the solution at 80°C for 7 h, the singlet at 7.2 ppm in the ^{31}P NMR spectrum increases if compared with that at 8.7 ppm.

The GC analyses of the samples collected after heating the solution at 80°C for 7, 14, 24, 32 and 70 h (Table 1) indicate that the amount of internal hexenes increases with the reaction time.

The broad singlet at 8.7 ppm in the ^{31}P NMR is not easily assigned. In our opinion, this resonance may be attributed to $Ru_2(CO)_4(MeCO_2)_2$-$(olefin)(PBu_3)$ solvated by the large amount of free olefin present in solution. This interpretation is in agreement with the observation that the intensity of this singlet decreases when the concentration of hex-1-ene is reduced due to its isomerization at 80°C.

In order to have more information on Ru_2-$(CO)_4(MeCO_2)_2(olefin)(PBu_3)$, an experiment was carried out with $Ru_4(CO)_8(MeCO_2)_4$-$(PBu_3)_2$ and a stoichiometric amount of hex-1-ene in C_6D_{12}. The solution was monitored by ^{31}P NMR. The amount of olefin in solution was then gradually increased up to a molar ratio olefin/ruthenium complex = 500:1. Using a 1:1 substrate/catalyst ratio a low transformation of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ into $Ru_2(CO)_4$-$(MeCO_2)_2(olefin)(PBu_3)$ (singlet at 7.2 ppm) was noticed (2.3%). The molar olefin/catalyst ratio was then increased up to 50 and the system heated to 40°C. The relative concentration of $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ slowly increased as reported in Table 2.

On increasing the molar olefin/catalyst ratio up to 200, the signal at 8.7 ppm and the singlets at 4.3 (now enlarged due a solvation effect of the excess of olefin present in solution) and 7.2 ppm appeared in the ^{31}P NMR spectrum. By increasing further the molar olefin/catalyst ratio up to 250, the singlet at 4.3 ppm decreased if compared with that at 8.7 ppm and a complete conversion of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ is obtained when the olefin/catalyst molar ratio reaches 500.

In the ^{13}C NMR spectrum of this last solution, there are resonances at 206.5, 205.0 and 186.6 ppm attributable to carbonyl and carboxylato ligands present in the new ruthenium complex.

The low stability of $Ru_2(CO)_4(MeCO_2)_2$ $(olefin)(PBu_3)$, however, does not allow its recovery from the solution and due to the high concentration of free olefin in solution, the other resonances of this complex cannot be detected by ^1H and ^{13}C NMR.

Table 1
Isomerization of hex-1-ene in the presence of $Ru_4(CO)_8$-$(MeCO_2)_4(PBu_3)_2$. Reaction product composition
Hex-1-ene: 12.0 mmol, catalyst: 23.6 μmol, *n*-heptane: 3 ml, *T*: 80°C.
Test carried out in an NMR sample tube.

Time (h)	Conversion (%)	Internal hexenes *trans / cis* ratio
7	12.2	4.08
14	21.3	3.44
24	32.2	3.24
32	43.9	3.30
70	85.0	4.45

Table 2
Behaviour of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ in the presence of hex-1-ene. Ruthenium complex composition percentage at various olefin concentrations
$Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$: 12 μmol, C_6D_{12}: 3 ml.
Test carried out in an NMR sample tube.

$Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$/olefin molar ration	T (°C)	Time (h)	Composition (%)	
			$Ru_2(CO)_4(MeCO_2)_2(PBu_3)(olefin)$	$Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$
1:1	20	0.25	2.3	97.7
1:2	20	0.25	2.7	97.3
1:6	20	0.25	3.5	96.5
1:6	40	5.00	3.7	96.3
1:30	40	2.00	4.7	95.3
1:50	40	4.00	8.6	91.4

The GC analyses of the solution at the end of this experiment showed the absence of isomeric hexenes in agreement with the previous test performed at low temperature.

2.1.2. $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ and hex-1-ene

No change in the system was detected up to 80°C. At this temperature, while a solution of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ alone is thermally stable [18], in the presence of hex-1-ene a new ruthenium derivative showing IR absorptions at 2030(w) and 1961(w) cm^{-1} was formed after 24 h. The complex is the same formed from $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene as reported in paragraph 1.1. Its formation is now apparently more difficult. Hex-1-ene must in fact substitute a phosphine ligand in the coordination sphere of the ruthenium complex. In the course of the reaction the intensity of the absorptions due to hex-1-ene decreased and, at the same time, a new absorption at 3020(s) cm^{-1} appeared, which may be ascribed to the isomerized hexenes.

Increasing the reaction temperature (100°C for 24 h) resulted in enhanced isomerization of hex-1-ene as indicated by the higher intensity of the band at 3020 cm^{-1}. Furthermore, an increase of the absorptions due to the new complex was noticed when compared with those of the starting $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$.

At a higher temperature (120°C for 24 h), the system exhibited further evolution and after 53 h, an absorption compatible with the presence of cis-hex-2-ene was present [1655(sh) cm^{-1}]. No other changes were detected upon heating the solution at 140°C for 24 h. After cooling at room temperature, the solution showed IR absorptions due to $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$, $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and to the new complex $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$ in small concentration.

GC analysis of the solution recovered at the end of the test showed the presence of trans-hex-3-ene (16.1%), cis-hex-3-ene (6.5%), cis-hex-2-ene (20.5%) and trans-hex-2-ene (47.9%) together with hex-1-ene (9.0%).

These results are in keeping with the formation of the ruthenium complex $Ru_2(CO)_4$-$(MeCO_2)_2(olefin)(PBu_3)$ at 80°C by replacement of a phosphine ligand by the olefin. The olefin bound to the ruthenium complex isomerizes from terminal to internal one due to the relative stability of these isomers. A complex bearing the internal olefin may be more sterically crowded than the one bearing the terminal olefin. The internal olefin may thus be displaced by the terminal one present in solution, thus completing the isomerization cycle [20,21].

These intermediates however are present in small concentration due to the low coordinating ability of the olefin with respect to the phos-

Scheme 2.
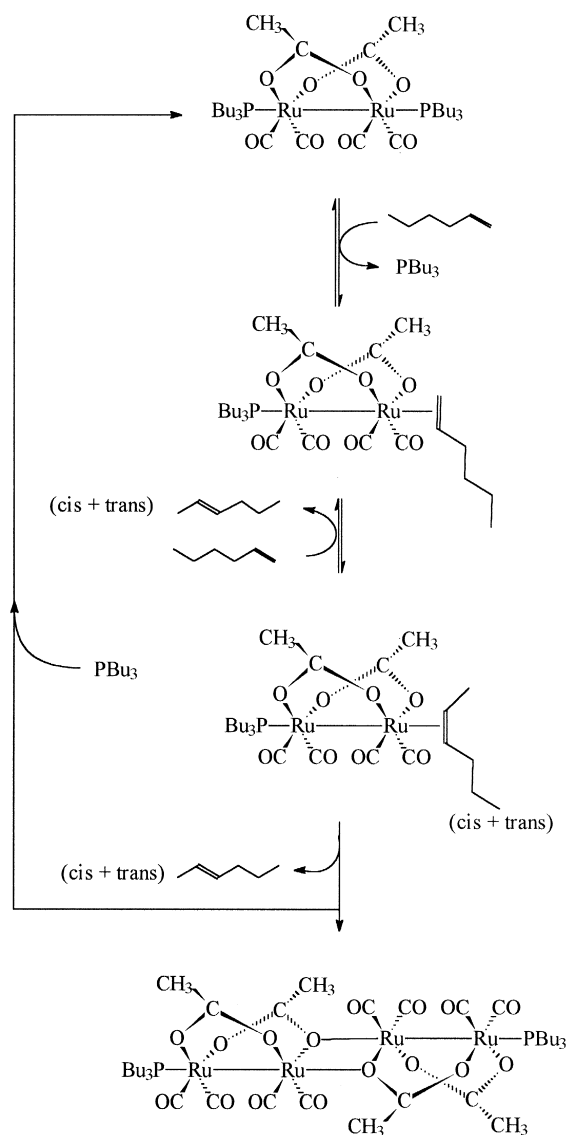
phine ligand and therefore are detected with difficulty.

When the terminal olefin was almost completely converted, a low amount of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ was formed, probably due to the coupling of two $Ru_2(CO)_4(MeCO_2)_2(PBu_3)$ moieties formed by the loss of the internal olefin from the complex. A thermal transformation of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ into $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ may be excluded because it takes place at a higher temperature (140°C) [18]. The following reaction scheme may be suggested (Scheme 2).

2.1.3. $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$ and hex-1-ene

No changes were observed up to 80°C. At 100°C, the formation of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ in low concentration was noticed in agreement with the thermal behaviour of mononuclear ruthenium carbonyl carboxylates when heated in hydrocarbon solution [17]. Such a behaviour was unaffected by the presence of a free olefin in solution. No further changes were observed upon heating the solution up to 120°C.

The GC analyses of a sample collected after heating at 100°C confirmed that the starting olefin was unchanged. In a sample collected after heating at 120°C, we could detect a moderate isomerization of the starting olefin (21.0%) with formation of cis- and trans-hex-2-ene (12.7% and 8.3%, respectively). Such an isomerization may be associated with the formation of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ in low con-

Table 3

Isomerization of hex-1-ene in the presence of $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$. Product composition after various reaction times
Hex-1-ene: 23.76 mmol, catalyst: 47.27 μmol, $p(N_2)$: 5 atm, n-heptane: 30 ml, T: 80°C.
Test carried out in a pressure vessel.

Time (h)	Hex-1-ene (%)	trans-hex-2-ene (%)	cis-hex-2-ene (%)	trans-hex-3-ene (%)	cis-hex-3-ene (%)
6	96.1	2.5	0.7	–	0.7
24	78.7	13.3	6.9	0.6	0.5
48	72.2	18.2	8.1	1.0	0.5
72	58.3	24.9	14.9	1.5	0.4

Table 4
Isomerization of hex-1-ene in the presence of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$. Products composition after various reaction times
Hex-1-ene: 23.76 mmol, catalyst: 93.96 μmol, $p(N_2)$: 5 atm, n-heptane: 30 ml, T: 80°C.
Test carried out in a pressure vessel.

Time (h)	Hex-1-ene (%)	trans-hex-2-ene (%)	cis-hex-2-ene (%)	trans-hex-3-ene (%)	cis-hex-3-ene (%)
6	97.2	1.7	0.5	–	0.6
24	85.6	8.8	4.7	0.4	0.5
48	70.9	18.6	9.0	0.9	0.6
72	57.8	28.1	11.8	1.7	0.6

centration which, as above reported (paragraph 1.2), isomerizes olefins.

2.2. Catalytic activity of ruthenium carbonyl carboxylates in the isomerization of hex-1-ene

The isomerization of hex-1-ene in the presence of $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$, $Ru_2(CO)_4$-$(MeCO_2)_2(PBu_3)_2$ and $Ru_4(CO)_8(MeCO_2)_4$-$(PBu_3)_2$ has been investigated to relate the behaviour evidenced by spectroscopic results with the catalytic activity of these complexes.

The experiments were carried out in a pressure vessel at 80°C. Samples of the solution were collected at various time intervals and analysed by GC. All isomeric linear hexenes were separated and quantitatively determined.

The results obtained when using Ru_4-$(CO)_8(MeCO_2)_4(PBu_3)_2$ as catalytic precursor are reported in Table 3. After 72 h at 80°C trans-hex-2-ene (24.9%), cis-hex-2-ene (14.9%), trans-hex-3-ene (1.5%) and cis-hex-3-ene (0.4%) were formed. It must be pointed out that cis-hex-3-ene even if present after 6 h, never exceeds 1%. This behaviour must be ascribed to the kinetic and thermodynamic control of this reaction. The cis-isomer initially formed by elimination from the ruthenium complex is subsequently isomerized to the thermodynamically more stable trans-isomer.

An analogous behaviour was noticed when using the binuclear complex $Ru_2(CO)_4$-$(MeCO_2)_2(PBu_3)_2$ (Table 4) in agreement with the hypothesis that the same catalytic intermediate is formed starting from both the binuclear or the tetranuclear precursor.

The small differences in the conversion of isomeric olefins may be easily ascribed to different ways of formation of the catalytically active intermediate.

The data obtained confirm that the mononuclear complex $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$ does not isomerize olefins even after a long reaction time (144 h) at 80°C. Its behaviour was not investigated at higher temperatures because this complex is then transformed into the binuclear $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ [14], which is active in this reaction.

3. Conclusions

The activity of ruthenium carbonyl carboxylates in the catalytic isomerization of hex-1-ene provides an indication of the coordinating ability of these complexes towards linear olefins.

When using a terminal olefin a π-olefin metal complex may be thought as the first reaction step. It is followed by the activation of a hydrogen atom on the carbon atom in α-position with respect to the double bond leading to the formation of a π-allylic system, in keeping with the mechanism reported for a non hydridic catalyst (Scheme 3) [6,9,10]. Addition of the M−H bond to one of the carbon atoms of the allylic system gives rise either to the initial π metal complex or to another π metal complex containing the isomerized olefin. The internal olefin thus formed is then replaced in the complex by the terminal one to minimise the steric hindrance,

Scheme 3.
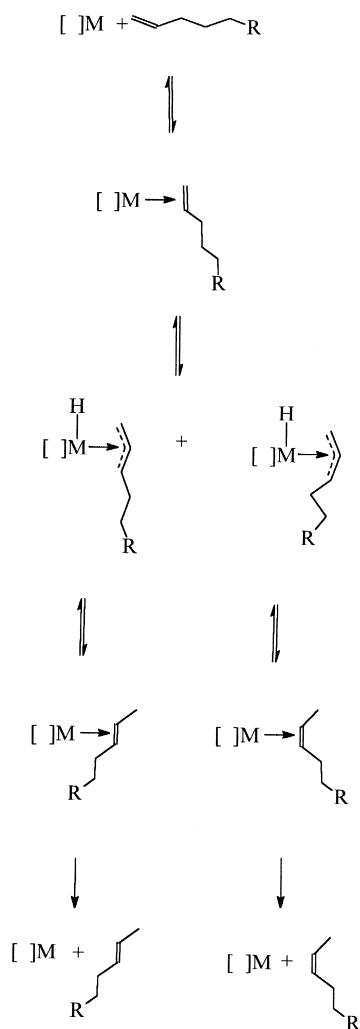
thus, producing a complex presumably more stable [2,20,21].

Among Ru(I) complexes considered, the tetranuclear one is able to activate the olefin by opening the oxygen bridge that keeps together the two $Ru_2(CO)_4(MeCO_2)_2(PBu_3)$ moieties. A similar behaviour has been found in the reaction of this complex with CO [19] or a phosphine [12]. This catalyst however becomes active in the olefin isomerization only at 80°C.

The binuclear complex gives rise to the formation of the same intermediate by displacement of a phosphine but this process requires more energy and a higher temperature (80°C).

The mononuclear Ru(II) specie, due to its higher stability, does not show any tendency to coordinate the olefin and therefore has no catalytic activity in the isomerization of hex-1-ene.

4. Experimental

Quantitative analyses of the reaction products were performed by GC using a Perkin-Elmer Model 1022 autosystem gas-chromatograph, equipped with a PPG column (Ucon oil LB 550X on Chromosorb W 15%, i.d. 1/8 in, length 2 m) and with a Perkin-Elmer Model 8320 capillary gas-chromatograph, equipped with an Al_2O_3 PLOT column (Al_2O_3 deactivated with KCl, i.d. 0.32 mm, length 50 m). 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 having a GC14A capillary column chromatograph and a QP2000 mass detector. The chromatograph was equipped with a CP-Sil8 50 m capillary column.

IR spectra were recorded with a Perkin-Elmer Model 580B IR spectrometer connected with a Perkin-Elmer 3600 Data system.

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

Hex-1-ene was purified by elution through a neutral Al_2O_3 (70–230 mesh) chromatographic column, then distilled under nitrogen had b.p. 62°C.

Tri-*n*-butylphosphine (Aldrich) was purified by distillation prior to use. Had b.p. 159°C/60 mm Hg.

Solvents: benzene and *n*-heptane were dried according to Vogel [22].

Other reagents and solvents were commercial products used without further purification.

The following catalysts were prepared according to the literature, their spectroscopic characteristics were in agreement with the data reported: $Ru(CO)_2(CH_3COO)_2(PBu_3)_2$ [13], $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ [23], $Ru_4(CO)_8$-$(CH_3COO)_4(PBu_3)_2$ [12].

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

4.1. Behaviour of ruthenium complexes

4.1.1. By IR spectroscopy

The investigation of the behaviour of ruthenium complex was carried out using a stainless steel pressure reactor (125 ml) with a pressure gauge and two stopcocks. The air was evacuated from the vessel, then a *n*-heptane solution of the complex under examination, and hex-1-ene, was introduced and finally nitrogen (5 atm) was added from a high-pressure cylinder.

The reaction vessel was connected through a stainless steel capillary coil (total volume 2 ml) to an IR cell capable to withstand high pressure and temperature, equipped with NaCl windows. The whole system (reaction vessel, coil, IR cell) was kept at the same temperature. All spectra were recorded, at chosen time intervals, after abundant flushing of both coil and IR cell with the solution from the vessel. The solvent absorption bands were compensated using a variable thickness IR cell.

At the end of the experiment, the GC analyses of the solution were performed using the Al_2O_3 PLOT column kept at 140°C for 1 min, then heated up to 160°C at a rate of 1°C/min and kept at this temperature for 1 min.

4.2. $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene

4.2.1. By IR spectroscopy

A *n*-heptane solution (60 ml) of $Ru_4(CO)_8$-$(MeCO_2)_4(PBu_3)_2$ (120 mg, 0.094 mmol) and

hex-1-ene (6 ml, 0.048 mol) was introduced in the autoclave, then N_2 up to 5 atm at 20°C.

After 24 h at room temperature, the starting complex was almost completely transformed into $Ru_2(CO)_4(MeCO_2)_2(olefin)(PBu_3)$: The IR spectrum shows bands, in the 2200–1500 cm^{-1} region, at 2030(vs), 1986(m), 1961(vs), 1930(vw) and 1585(mw) cm^{-1}.

After heating at 80°C for 33 h, there was a low increase in the concentration of $Ru_2(CO)_4$-$(MeCO_2)_2(olefin)(PBu_3)$ with respect to Ru_4-$(CO)_8(MeCO_2)_4(PBu_3)_2$ and the formation of trace amounts of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ and $[Ru_2(CO)_4(MeCOO)_2]_n$. Further heating at the same temperature (24 h), then at 100°C (48 h) caused an increase of the concentration of $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ and the presence of the absorptions due to isomerized olefins. Further heating at 120°C for 15 h did not show any change.

As previously described, the GC analyses of the solution at the end of the experiment, showed the presence in solution of hex-1-ene (6.4%), *cis*-hex-3-ene (4.2%), *trans*-hex-3-ene (17.7%), *cis*-hex-2-ene (20.3%) and *trans*-hex-2-ene (51.3%).

4.2.2. By NMR spectroscopy

The reactivity tests analysed by NMR spectroscopy were carried out in a screw cap NMR sample tube (10 mm). The air was evacuated from the tube and substituted with nitrogen. The catalyst, the solvent (*n*-heptane or C_6D_{12}) and the olefin were introduced then the PTFE/rubber septum cap was tightened. The reaction was monitored by ^{31}P NMR spectroscopy at various time intervals and after heating up to the desired temperature.

4.2.2.1. $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene in a n-heptane solution. In the screw cap NMR sample tube, a *n*-heptane solution (3 ml) containing $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ (30 mg, 0.024 mmol) and hex-1-ene (1.5 ml, 0.012 mol) was introduced. After 15 min at room tem-

perature, the complex $Ru_2(CO)_4(MeCO_2)_2$-(olefin)(PBu_3) was formed.

The ^{31}P NMR spectrum recorded on this solution, after the introduction of a capillary tube containing C_6D_6, display a singlet at 7.2 ppm attributable to the complex $Ru_2(CO)_4$-$(MeCO_2)_2$(olefin)(PBu_3) and another singlet at 8.7 ppm, attributable to a solvation of this complex. This last singlet is the prevailing signal of the spectrum.

The IR spectrum (*n*-heptane) of a sample of the solution shows bands at 2030(vs), 1986(m), 1961(vs), 1930(vw) and 1585(mw) cm^{-1} due to $Ru_2(CO)_4(MeCO_2)_2$(olefin)(PBu_3).

After heating at 80°C *cis*-hex-2-ene and *trans*-hex-2-ene are present in the solution. In the ^{31}P NMR spectrum, the intensity of the singlet at 7.2 ppm is increased if compared with that of the singlet at 8.7 ppm. The results of the GC analyses of the solution at various time intervals, carried out as previously described, are reported in Table 1.

4.2.2.2. $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ and hex-1-ene in a C_6D_{12} solution.

In the screw cap NMR sample tube, a C_6D_{12} solution (3 ml) containing $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$ (15 mg, 0.012 mmol) was introduced, then a stoichiometric amount of hex-1-ene was added recording the ^{31}P NMR spectrum at room temperature.

The starting complex reacts with hex-1-ene (molar ratio Ru/olefin = 1) giving a low amount of the complex containing the olefin as shown by the singlet at 7.2 ppm in the ^{31}P NMR. The intensity of this resonance is almost unchanged even after 10 days. By increasing the amount of hex-1-ene, the singlet at 7.2 ppm increases. The relative amounts of the products evaluated by the relative intensities of the resonances in the ^{31}P NMR spectra are reported in Table 2.

When the molar ratio Ru/olefin is 1:200, the resonance at 7.2 ppm, in the ^{31}P NMR, is the main signal of the spectrum while two broad singlets at 4.3 and 8.7 ppm are present.

Further addition of olefin up to a molar ratio Ru/olefin = 1:250 causes a further increase in the intensity of the singlet at 7.2 ppm. The IR spectrum (C_6D_{12}) recorded on the latter solution shows the bands due to $Ru_2(CO)_4$-$(MeCO_2)_2$(olefin)(PBu_3) as the main signals, while low-intensity bands are attributed to $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$.

When the molar ratio Ru/olefin is 1:500, the singlet at 4.3 ppm disappeared in the ^{31}P NMR spectrum. Due to the large amount of olefin present, the ^1H NMR spectrum does not give any information while the ^{13}C NMR spectrum shows resonances of weak intensity at 186.6 $(MeCO_2)$, 205.0 (Ru–CO) and 206.5 (Ru–CO) ppm that may be attributed to $Ru_2(CO)_4$-$(MeCO_2)_2$(olefin)(PBu_3).

4.2.3. $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$ and hex-1-ene

A *n*-heptane solution (60 ml) of $Ru_2(CO)_4$-$(MeCO_2)_2(PBu_3)_2$ (120 mg, 0.143 mmol) and hex-1-ene (6 ml, 0.048 mol) was introduced in the autoclave and then N_2 up to 5 atm at 20°C.

After heating at 80°C for 24 h, the formation of $Ru_2(CO)_4(MeCO_2)_2$(olefin)(PBu_3) takes place while the concentration of hex-1-ene decreases (absorptions at 1825 and 1645 cm^{-1}) and olefin isomers are formed.

Further transformation of the system is observed when the reaction temperature is raised up to 140°C with an increased concentration of the complex containing the olefin and of the olefin isomers.

When the conversion of hex-1-ene reached 91.0% the vessel was cooled. The following complexes were identified in the solution by IR spectroscopy: $Ru_2(CO)_4(MeCO_2)_2(PBu_3)_2$, $Ru_2(CO)_4(MeCO_2)_2$(olefin)(PBu_3) and $Ru_4(CO)_8(MeCO_2)_4(PBu_3)_2$.

The following compounds were identified by GC analyses: hex-1-ene (9.0%), *cis*-hex-3-ene (6.5%), *trans*-hex-3-ene (16.1%), *cis*-hex-2-ene (20.5%) and *trans*-hex-2-ene (47.9%).

The IR spectrum of $Ru_2(CO)_4(MeCO_2)_2$-(olefin)(PBu_3) (*n*-heptane as solvent) shows absorptions at 2030(vs), 1986(m), 1961(vs), 1930(vw) and 1585(mw) cm^{-1}.

4.2.4. *Ru(CO)$_2$(MeCO$_2$)$_2$(PBu$_3$)$_2$ and hex-1-ene*

A *n*-heptane solution (60 ml) of Ru(CO)$_2$-(MeCO$_2$)$_2$(PBu$_3$)$_2$ (190 mg, 0.280 mmol) and hex-1-ene (6 ml, 0.048 mol) was introduced in the autoclave, then N$_2$ up to 5 atm at 20°C.

The vessel was heated up to 80°C but no change was observed in the IR spectrum. After heating at 100°C, small amounts of Ru$_2$-(CO)$_4$(MeCO$_2$)$_2$(PBu$_3$)$_2$ were formed and the system remains almost unchanged after heating up to 120°C.

The GC analyses, performed as described above on samples collected after heating at temperatures lower than 120°C does not display the presence of isomerized olefins. In the sample collected after heating at 120°C moderate amount of *cis*-hex-2-ene (12.7%) and *trans*-hex-2-ene (8.3%) were present.

4.2.5. *Catalytic isomerization*

The tests were carried out in a stainless steel rocking autoclave having the capacity of 150 ml. The air was evacuated prior to the introduction of the solution containing solvent, catalyst and olefin. Nitrogen was then added up to 5 atm. The autoclave was heated in an oil bath thermostated at the prefixed temperature and rocked for the established time. After a rapid cooling at room temperature, the nitrogen was vented and the solution collected and analysed by GC as above reported. Hex-1-ene, *cis*-hex-2-ene, *trans*-hex-2-ene, *cis*-hex-3-ene and *trans*-hex-3-ene were identified and quantified.

The results of the catalytic experiments are reported in Tables 3 and 4.

Acknowledgements

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