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Catalytic activity of cluster ruthenium complexes: oligomerization of ethylene *

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Abstract

[$Ru_3(CO)_{12}$], one of a series of ruthenium carbonyls tested, shows good catalytic activity in the oligomerization of ethylene in several organic solvents at temperatures above 80°C and olefin pressures exceeding 5 atm. Olefin conversions up to 90% are reached. C_4–C_{12} olefins are the main reaction products, with prevalence of the C_4 species. Branched isomers are prevalent among the higher oligomers. Evidence has been obtained for a key role for ruthenium hydride intermediates in this catalytic cycle.

1. Introduction

Ruthenium carbonyl clusters have been used repeatedly and successfully to activate C=C, C=O, C=N double bonds in organic substrates. Several isomerization [1–6], hydrogenation [7–10], and hydroformylation [11–13] procedures have been developed using such complexes as catalysts.

Evans *et al.* [14] reacted [$Ru_3(CO)_{12}$] with ethylene, at atmospheric pressure and 100°C, and obtained ruthenium cluster complexes containing acetylenic or vinylidenic ligands with 4 or 6 carbon atoms. The formation of these ligands suggests that oligomerization of ethylene takes place in the presence of [$Ru_3(CO)_{12}$].

The following complexes were isolated [14]: [$Ru_3H_2(CO)_9(MeC{\equiv}CMe)$], [$Ru_3H_2(CO)_9(EtC{\equiv}CEt)$], and [$Ru_3H(CO)_9(MeCCHCEt)$].

Jackson *et al.* [15] reacted $Ru_3(CO)_{12}$ with ethylene (30 atm) in n-heptane at 150°C and obtained clusters of a higher complexity, such as [$Ru_4(CO)_{12}(MeC{\equiv}CMe)$] or [$Ru_6C(CO)_{15}(CH_3CH{=}CH{-}CH{=}CHCH_3)$]. In this case, as in the earlier example, dimerization and trimerization of ethylene are involved.

However, the publications cited above do not give any indication of the ability of such systems to activate the catalytic oligomerization of ethylene.

Interest in the oligomerization of lower olefins has increased in recent years [16] and we therefore thought it of interest to investigate this reaction in order to evaluate its possibilities.

The oligomerization of ethylene has been obtained by using transition metal catalysts [17–21] (mainly nickel, *cf.* [17,18,22–26], or by using Ziegler-Natta type catalysts [17,18,21–23,27,28]. In very few cases metal clusters have been used [29–32].

2. Results

Preliminary experiments on the oligomerization of ethylene in n-heptane in the presence of [$Ru_3(CO)_{12}$] were made in conditions similar to those used by Evans *et al.* [14] but at a higher ethylene pressure. The ethylene pressure, 20 atm at room temperature, reached a maximum of 70 atm under reaction conditions and dropped almost to zero after 3 h, when ethylene conversion was nearly complete. The reaction products were mainly C_4 and C_6 olefins. This result shows that [$Ru_3(CO)_{12}$] does act as catalyst in this system.

Experiments using different solvents at different temperatures (Table 1) show that the reaction generally starts at temperatures above 100°C and show an

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* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contribution to organometallic chemistry and its applications in organic synthesis.

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induction period dependent on both the solvent and the temperature. However, in cyclohexane, the oligomerization starts at 80°C, whereas in toluene 150°C is required.

Ethylene conversion is high in all solvents. Both reaction rate and conversion increase with the temperature. Only with very long reaction times does the olefin conversion exceed 90%.

In protic solvents the reaction rate is higher than in hydrocarbons. The addition of even a small amount of an alcohol to a toluene solution of the catalytic system enhances the activity.

Ethane and acetone were detected among the products in experiments using propan-2-ol as solvent. This indicates that the catalytic system may induce hydrogen-transfer during oligomerization.

The reaction product is a mixture of oligomers, mainly C_4 and C_6 olefins, with minor amounts of the higher species C_8, C_{10} and C_{12}. C_4 olefins often exceed 50% of the reaction product, and reach 70–80% in propan-2-ol and cyclohexanol. These butenes are linear and their isomeric distribution approaches the equilibrium composition in all cases. C_6 olefins are 20–30% of the reaction product, and they reach 50% in cyclohexane or chlorobenzene at low temperatures. 3-Methylpentenes are the only C_6 branched isomers detected. C_8–C_{14} olefins are minor reaction products, but their yield increases with temperature and reaches 57% at 210°C in chlorobenzene.

In tests performed under constant pressure of ethylene (180 atm), the catalyst activity in both chlorobenzene and toluene is similar. (~ 18 g in 7 min.) A pressure change from 70 to 180 atm in chlorobenzene causes a six-fold increase in activity, the product com-

TABLE 1. Oligomerization of ethylene in various solvents in the presence of $[Ru_3(CO)_{12}]$ (catalyst precursor 0.94 mmol Ru; solvent 25 ml; benzene as internal standard)

C_2H_4 (g)	Solvent	T (°C)	Reaction time (h)	Conversion (%)	Reaction products (weight %)									
					C_4			C_6		C_8		C_{10}	C_{12}	C_{14}
					A	B	C	D	E	F	G			
9.8	Toluene	150	20	86.4	55.8			31.3		10.0		1.9	1.0	–
					7.8	33.9	58.3	30.7	69.3	24.0	76.0			
9.5	Toluene	180	16	82.7	54.7			25.3		9.8		7.6	2.6	–
					11.6	33.4	55.0	57.0	43.0	31.0	69.0			
9.5	Cyclohexane	80	150	88.8	45.4			49.6		2.3		1.9	0.8	–
					11.0	24.4	64.6	14.6	85.4	11.0	89.0			
9.6	Cyclohexane	150	20	92.3	56.9			33.1		3.8		1.7	3.3	1.2
					9.1	32.0	57.0	30.0	70.0	22.3	77.7			
11.0	Cyclohexanol	100	46	94.2	66.5			29.0		3.0		1.5	–	–
					6.4	26.5	67.1	32.3	67.7	25.0	75.0			
10.4	Cyclohexanol	150	20	90.1	80.7			16.5		1.5		1.3	–	–
					9.1	33.3	57.6	65.8	34.2	37.8	62.2			
11.0	Propan-2-ol	100	40	76.0	77.0			9.9		2.9		5.0	5.2	–
					7.6	30.0	62.4	53.3	46.7	19.2	80.8			
12.6	Propan-2-ol	150	20	80.0	71.8			12.2		6.3		5.1	4.6	–
					11.3	30.5	58.2	30.6	69.4	24.6	75.4			
13.2	Chlorobenzene	100	64	96.5	45.2			51.9		2.9		–	–	–
					7.2	31.9	60.9	15.3	84.7	12.4	87.6			
12.3	Chlorobenzene	150	20	97.1	50.7			37.7		6.1		3.7	1.8	–
					8.9	31.9	59.2	28.0	72.0	22.3	77.7			
9.0	Chlorobenzene	210	7	71.1	28.3			14.6		17.1		15.3	16.6	8.1
					19.3	33.9	46.8	85.3	14.7	20.7	79.3			

A, 1-butene; B, *cis*-2-butene; C, *trans*-2-butene; D, linear C_6; E, 3-methylpentenes; F, linear C_8; G, branched C_8.

TABLE 2. Oligomerization of ethylene in the presence of $[H_4Ru_4(CO)_{12}]$, influence of the reaction time (catalyst precursor 0.94 mmol Ru; toluene 25 ml; benzene as internal standard)

C_2H_4 (g)	*T* (°C)	Reaction time (h)	Conversion (%)	Reaction products (weight %)									
				C_4			C_6		C_8		C_{10}	C_{12}	C_{14}
				A	B	C	D	E	F	G			
7.2	100	3	3.0	51.0			49.0		–		–	–	–
				27.0	13.8	59.2	22.5	77.5					
11.0	100	16	87.0	43.3			48.7		6.9		1.1	–	–
				9.3	28.2	62.5	20.0	80.0	15.0	85.0			
16.6	100	70	87.7	40.1			49.4		7.4		3.1	–	–
				6.8	30.7	62.5	18.6	81.4	14.0	86.0			
14.8	150	3	71.4	53.5			37.3		5.0		4.2	–	–
				10.0	30.7	59.3	26.2	73.8	20.0	80.0			
9.8	150	13	84.5	57.7			28.0		8.9		5.4	–	–
				13.5	33.5	53.0	40.0	60.0	27.0	73.0			
6.0	150	65	87.3	57.8			19.3		11.2		7.8	3.9	–
				11.3	32.7	56.0	39.0	61.0	28.0	72.0			
12.4	180	3	68.1	64.5			26.2		4.8		4.5	–	–
				13.0	33.0	54.0	41.0	59.0	26.4	73.6			
8.4	180	15	83.6	55.4			21.8		9.7		7.8	5.2	0.1
				12.4	33.6	54.0	58.5	41.5	34.0	66.0			
6.2	180	64	89.3	54.1			22.0		10.0		8.0	5.8	0.1
				11.8	33.6	54.6	58.7	41.3	29.0	71.0			

A, 1-butene; B, *cis*-2-butene; C, *trans*-2-butene; D, linear C_6; E, 3-methylpentenes; F, linear C_8; G, branched C_8.

TABLE 3. Oligomerization of ethylene in the presence of various precursors: influence of the tri-n-butylphosphine ligand (P) (toluene 25 ml; benzene as internal standard)

C_2H_4 (g)	Catalyst precursor (mmol Ru compound)	*T* (°C)	Reaction time (h)	Conversion (%)	Reaction products (weight%)					
					C_4			C_6		C_8–C_{12}
					A	B	C	D	E	
9.8	$[Ru_3(CO)_{12}]$	150	20	86.4	55.8			31.3		12.9
	(0.94)				7.8	33.9	58.3	30.7	69.3	
5.2	$[Ru_3(CO)_9P_3]$	150	22	6.0	95.5			4.5		–
	(0.94)				37.4	22.7	39.9	84.4	15.6	
14.8	$[H_4Ru_4(CO)_{12}]$	150	3	71.4	53.5			37.3		9.2
	(0.94)				10.0	30.7	59.3	26.2	73.8	
5.0	$[H_4Ru_4(CO)_8P_4]$	150	24	36.2	91.8			8.2		–
	(0.29)				17.2	32.3	50.5			
12.4	$[H_4Ru_4(CO)_{12}]$	180	3	68.1	64.5			26.2		9.3
	(0.94)				13.0	33.0	54.0	41.0	59.0	
5.0	$[H_4Ru_4(CO)_8P_4]$	180	24	70.0	84.3			15.7		–
	(0.29)				11.3	34.6	54.1			

A, 1-butene; B, *cis*-2-butene; C, *trans*-2-butene; D, linear C_6; E, 3-methylpentenes.

position being unaltered. The catalyst concentration affects the reaction rate but changes the products only slightly: the formation of higher oligomers increases.

The positive influence of a hydrogen donor on the activity of the catalytic system suggests the involvement of hydridic intermediates in the reaction. $[H_4Ru_4(CO)_{12}]$ was therefore tested as catalyst precursor for this reaction. The results obtained (Table 2) confirm this. In its presence the reaction starts at temperatures as low as 100°C, no induction period is observed, and the reaction rate is higher than when using $[Ru_3(CO)_{12}]$. Conversion approaches 90% with the predominant formation of C_4 and C_6 olefins. Trimers decrease in favour of the higher products as temperature and conversion increase. The higher reaction products are mainly branched internal olefins.

The phosphine-substituted derivatives, $[Ru_3(CO)_9(P^nBu_3)_3]$ and $[H_4Ru_4(CO)_8(P^nBu_3)_4]$, have also been tested (Table 3).

In both cases, the presence of the phosphine seems to decrease the activity of the catalyst and to limit the oligomerization to the formation of dimers and trimers with a strong predominance of the former.

A variety of ruthenium carbonyl clusters has also been tested (Table 4). Ruthenium carbide shows little activity, even at high temperatures. Carboxylatoruthenium carbonyl clusters show a very moderate activity, which is diminished by phosphine substitution. With $[Ru_4(CO)_8(CH_3COO)_2(P^nBu_3)_2]$ at 180°C, minor amounts of hexadienes are obtained.

The life of the catalyst has been evaluated by the repeated use of the residues obtained from the crude material after distillation of the reaction products. When the recovery was made with appropriate care (absence of dioxygen, absence of humidity, temperature below 60°C), the catalyst has been reused nine times with only minor losses in activity. In fact, in toluene, the 're-used' catalyst is active at 120°C, compared with 150°C for $[Ru_3(CO)_{12}]$.

3. Discussion

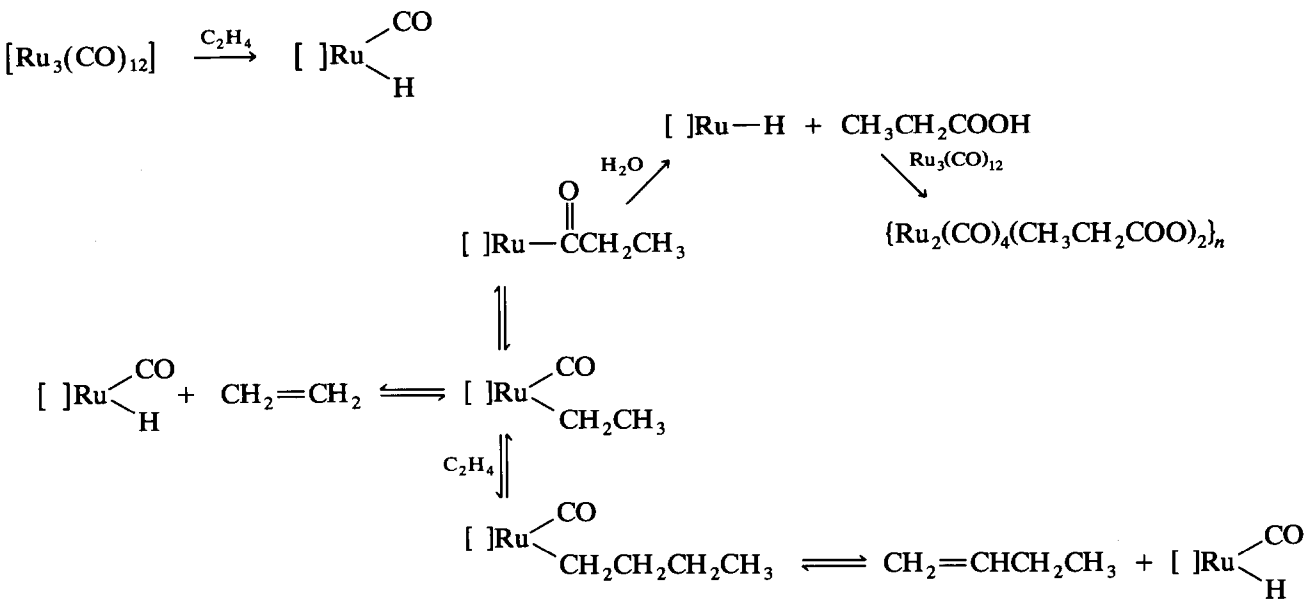
Triruthenium dodecacarbonyl catalyses the oligomerization of ethylene in the liquid phase at temperatures ≥ 100°C. A pressure of at least a few atmospheres is required to provide the olefin concentration

TABLE 4. Oligomerization of ethylene in the presence of various catalyst precursors (toluene 25 ml; benzene as internal standard)

<table>
<tr><th rowspan="3">C_2H_4(g)</th><th rowspan="3">Catalyst precursor
(mmol Ru compound)</th><th rowspan="3">T(°C)</th><th rowspan="3">Reaction time (h)</th><th rowspan="3">Conversion (%)</th><th colspan="5">Reaction products (weight %)</th></tr>
<tr><th colspan="3">C_4</th><th rowspan="2">C_6</th><th rowspan="2">C_8</th></tr>
<tr><th>A</th><th>B</th><th>C</th></tr>
<tr><td>6.0</td><td>$[Ru_6C(CO)_{17}]$</td><td>150</td><td>70</td><td>7.5</td><td colspan="3">77.3</td><td>22.7</td><td>-</td></tr>
<tr><td></td><td>(1.10)</td><td></td><td></td><td></td><td>10.0</td><td>33.3</td><td>56.7</td><td></td><td></td></tr>
<tr><td>10.0</td><td>$[Ru_6C(CO)_{17}]$</td><td>180</td><td>5</td><td>3.0</td><td colspan="3">82.7</td><td>17.3</td><td>-</td></tr>
<tr><td></td><td>(1.10)</td><td></td><td></td><td></td><td>14.5</td><td>33.2</td><td>52.3</td><td></td><td></td></tr>
<tr><td>8.4</td><td>$\{Ru_2(CO)_4(CH_3COO)_2\}_n$</td><td>150</td><td>5</td><td>18.3</td><td colspan="3">65.8</td><td>33.2</td><td>1.0</td></tr>
<tr><td></td><td>(0.94)</td><td></td><td></td><td></td><td>28.3</td><td>34.2</td><td>37.5</td><td></td><td></td></tr>
<tr><td>6.0</td><td>$[Ru_2(CO)_4(CH_3COO)_2P_2]$ [a]</td><td>100</td><td>18</td><td>0.4</td><td colspan="3">100.0</td><td>-</td><td>-</td></tr>
<tr><td></td><td>(0.24)</td><td></td><td></td><td></td><td>62.0</td><td>6.3</td><td>31.7</td><td></td><td></td></tr>
<tr><td>6.0</td><td>$[Ru_2(CO)_4(CH_3COO)_2P_2]$ [a]</td><td>150</td><td>24</td><td>19.0</td><td colspan="3">90.0</td><td>10.0</td><td>-</td></tr>
<tr><td></td><td>(0.24)</td><td></td><td></td><td></td><td>58.0</td><td>15.0</td><td>27.0</td><td></td><td></td></tr>
<tr><td>6.0</td><td>$[Ru_2(CO)_4(CH_3COO)_2P_2]$ [a]</td><td>180</td><td>72</td><td>60.0</td><td colspan="3">85.1</td><td>10.4</td><td>4.5</td></tr>
<tr><td></td><td>(0.24)</td><td></td><td></td><td></td><td>16.6</td><td>30.0</td><td>53.4</td><td></td><td></td></tr>
<tr><td>7.2</td><td>$[Ru_4(CO)_8(CH_3COO)_4P_2]$ [a]</td><td>100</td><td>23</td><td>2.0</td><td colspan="3">50.0</td><td>50.0</td><td>-</td></tr>
<tr><td></td><td>(0.22)</td><td></td><td></td><td></td><td>46.0</td><td>7.8</td><td>46.2</td><td></td><td></td></tr>
<tr><td>7.2</td><td>$[Ru_4(CO)_8(CH_3COO)_4P_2]$[a]</td><td>150</td><td>15</td><td>28.9</td><td colspan="3">63.2</td><td>36.8 [b]</td><td>-</td></tr>
<tr><td></td><td>(0.22)</td><td></td><td></td><td></td><td>26.6</td><td>20.4</td><td>53.0</td><td></td><td></td></tr>
<tr><td>7.2</td><td>$[Ru_4(CO)_8(CH_3COO)_4P_2]$[a]</td><td>180</td><td>15</td><td>64.2</td><td colspan="3">66.5</td><td>28.1 [c]</td><td>5.4</td></tr>
<tr><td></td><td>(0.22)</td><td></td><td></td><td></td><td>13.0</td><td>27.3</td><td>59.7</td><td></td><td></td></tr>
</table>

A, 1-butene; B, *cis*-2-butene; C, *trans*-2-butene.

[a] P = tri-n-butylphosphine. [b] Mono-olefins (35.2%), hexadienes (1.6%). [c] Mono-olefins (26.1%), hexadienes (2.0%).



Scheme 1.

in solution necessary for a satisfactory reaction rate. In fact in the experiments performed at atmospheric pressure, no catalytic reaction was observed. At 180–200 atm, the catalyst activity (moles of ethylene converted per mole of Ru per hour) is higher than 100.

The product composition (olefin distribution) is affected mainly by reaction temperature and olefin concentration. The reaction product consists mainly of C_4–C_{12} olefins, the C_4/C_6 ratio at moderate conversions increasing with temperature. At high conversions, the participation of the products initially formed in a subsequent reaction becomes evident, affecting the product composition. The fraction of higher olefins increases at the expense of the C_6 olefins. However, when the ethylene conversion is almost complete, further heating of the system does not cause any alteration in the product composition.

$[H_4Ru_4(CO)_{12}]$ is more active catalytically than

TABLE 5. Oligomerization of ethylene in the presence of different catalyst precursors (catalyst precursor 0.94 mmol Ru; solvent 25 ml; $T = 150°C$; benzene as internal standard)

C_2H_4 (g)	Catalyst precursor	Solvent	Reaction time (h)	Conversion (%)	Reaction products (weight %)							
					C_4			C_6	C_8	C_{10}	C_{12}	C_{14}
					A	B	C					
7.8	$\{Ru(CO)_4\}_n$	Cyclohexane	20	83.2	46.7			24.0	9.9	7.8	6.5	5.1
					18.4	26.3	55.3					
7.8	$\{Ru(CO)_4\}_n$	Chlorobenzene	20	77.3	32.3			25.0	15.1	10.6	8.6	8.4
					18.4	26.3	55.3					
8.8	$[\{Ru(CO)_3Cl_2\}_2]$	Toluene	72	53.4	70.2			9.4	8.7	6.6	5.1	–
					23.9	26.3	49.8					
10.4	$[\{Ru(CO)_3Cl_2\}_2]$	Chlorobenzene	72	53.6	76.7			9.0	5.4	4.8	4.1	–
					10.7	32.9	56.4					
11.4	$\{Ru_2(CO)_4(CH_3CH_2COO)_2\}_n$	Toluene	5	58.5	61.5			36.0	2.5	–	–	–
					21.4	23.1	55.5					
10.0	$\{Ru_2(CO)_4(CH_3CH_2COO)_2\}_n$	Chlorobenzene	5	46.0	55.6			42.4	2.0	–	–	–
					26.5	24.5	49.0					

A, 1-butene; B, *cis*-2-butene; C, *trans*-2-butene.

$[Ru_3(CO)_{12}]$. This suggests that hydride species are involved in the catalytic cycle. The induction period encountered when using $[Ru_3(CO)_{12}]$ may be rationalized by the requirement for the formation of the hydride species by hydrogen abstraction from the substrate. Support for this hypothesis is provided by the facility of the reaction with hydride and the detection of acetone when the reaction is carried out in propan-2-ol.

The isolation of $[Ru_3H_2(CO)_9(CH{\equiv}CH)]$ by Evans *et al.* [14] from the crude product of the reaction between $[Ru_3(CO)_{12}]$ and ethylene at atmospheric pressure in refluxing ^{n}heptane further supports this hypothesis. However, the mixture of complexes in the crude product of an oligomerization reaction carried out at 150°C in toluene in the presence of $[Ru_3(CO)_{12}]$ is different from that obtained when working in Evans' conditions judging from the IR spectra.

A satisfactory picture of the intermediates formed under our conditions cannot yet be given because of the difficulties encountered in their separation and recovery. We have, however, been able to isolate the carboxylato-complex $\{Ru_2(CO)_4(CH_3CH_2COO)_2\}_n$.

The formation of this complex in the catalytic cycle requires an intermediate Ru–H bond which, by addition of ethylene, gives the ethyl derivative (Scheme 1). This may be transformed into the corresponding propionyl compound by addition of carbon monoxide or give but-1-ene by ethylene insertion and subsequent β-hydrogen elimination. Mechanisms of this type have already been suggested for olefin oligomerization catalysed by nickel or other metals [17,18,22,33–36].

The propionyl derivative reacts with water to give propionic acid which, with $[Ru_3(CO)_{12}]$, may form the propanoato derivative [37] that we isolated. However, this compound shows (Table 5) a lower catalytic activity than $[Ru_3(CO)_{12}]$ in the oligomerization of ethylene. It may be one of the catalytically active species, although not an important one.

Chlorinated ruthenium derivatives have not been detected in the crude products from experiments carried out in chlorobenzene. Although their formation cannot be excluded, they probably are not relevant to the reaction course: $[\{Ru(CO)_3Cl_2\}_2]$ shows a very poor catalytic activity and different selectivity compared with $[Ru_3(CO)_{12}]$.

After heating $[Ru_3(CO)_{12}]$ in chlorobenzene at 160°C for several hours, the only ruthenium derivative recovered was its decomposition product $[Ru_6C(CO)_{17}]$ [15,38,39]. $[Ru_6C(CO)_{17}]$ has never been detected in the oligomerization crude products in chlorobenzene, and has itself shown negligible catalytic activity (Table 4). $\{Ru(CO)_4\}_n$, the insoluble form of $[Ru_3(CO)_{12}]$, reacts with ethylene under pressure to give similar results to $[Ru_3(CO)_{12}]$ (Table 5), in keeping with the behaviour shown with carbon monoxide or tri-*n*-butylphosphine or hydrogen [40]. The catalyst precursor $[Ru_3(CO)_{12}]$ may be recovered as such from the reaction residue after treating it with carbon monoxide (80 atm) and hydrogen (50 atm) at 150°C in methanol solution.

The predominant formation of internal olefins in our experiments confirms the high isomerization activity of ruthenium catalysts, also considered responsible for the absence of linear higher olefins from the reaction products.

The phosphine derivatives of $[Ru_3(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$ have a lower activity than the parent compounds and a different selectivity. The reaction products are almost exclusively C_4 olefins, predominantly internal isomers, indicating the retention of considerable isomerizing activity in these catalysts.

4. Experimental details

GLC analyses were performed on a Perkin-Elmer 8320 instrument; GLC-mass spectra were recorded with an HP 5970A spectrometer.

4.1. Materials

Ethylene and all reference compounds were commercial products. All solvents were purified in the usual manner [41].

4.2. Catalyst precursors

$[Ru_3(CO)_{12}]$ [42], $[H_4Ru_4(CO)_{12}]$ [43], $[Ru_3(CO)_9(P^nBu_3)_3]$ [44], $[H_4Ru_4(CO)_8(P^nBu_3)_4]$ [43], $[Ru_6C(CO)_{17}]$ [38], $[\{RuCl_2(CO)_3\}_2]$ [45], $\{Ru(CO)_4\}_n$ [40], $\{Ru_2(CO)_4(CH_3COO)_2\}_n$ [37], $\{Ru_2(CO)_4(CH_3CH_2COO)_2\}_n$ [37], $[Ru_2(CO)_4(CH_3COO)_2(P^nBu_3)_2]$ [37] and $[Ru_4(CO)_8(CH_3COO)_2(P^nBu_3)_2]$ [46] were prepared as described in the literature.

4.3. Oligomerization experiments

The ethylene oligomerization tests were carried out in a 150 ml stainless steel rocking autoclave heated in a thermostatic oil bath where the temperature could be kept at the chosen value ±1°C.

The catalyst precursor, the solvent and benzene (internal standard) were initially placed in the reaction vessel under dinitrogen, and finally the required amount of ethylene was added. The autoclave was then heated.

The reaction was stopped when required by rapidly cooling the autoclave to room temperature. The residual ethylene and the more volatile products were collected in a gasometer, and the liquid reaction crude product in a cooled Erlenmeyer flask (−50 to −80°C).

When a constant olefin concentration was required in solution, throughout the test ethylene was continuously supplied to the reactor from a high-pressure container.

4.4. *Reaction of ethylene with $[Ru_3(CO)_{12}]$ at atmospheric pressure*

Ethylene was bubbled at atmospheric pressure through a solution of $[Ru_3(CO)_{12}]$ (500 mg) in ^{n}heptane (100 ml) in a glass flask heated at reflux temperature. The effluent gases were condensed in liquid air. After 22 h, the solution was deep red.

Only ethylene and the solvent were present in both effluent and the reaction solution. After elimination of the solvent under reduced pressure from the reaction crude product, a solid was collected which was separated by TLC.

The IR spectra of the products obtained corresponded to those of the complexes reported by Evans *et al.* [14], *i.e.* $[Ru_3H_2(CO)_9(MeC{\equiv}CMe)]$, $[Ru_3H_2(CO)_9(EtC{\equiv}CEt)]$, and $[Ru_3H(CO)_9(MeCCHCEt)]$.

4.5. *Re-use of the catalytic system*

$[Ru_3(CO)_{12}]$, the solvent, and ethylene were placed in the usual manner in the autoclave which was then heated to 150°C. When the pressure had dropped to 5 atm, the autoclave was rapidly cooled to −20°C, the residual ethylene was collected in a gasometer and the liquid reaction crude product recovered and kept under dinitrogen. The liquid components in the crude product were distilled gradually, lowering the pressure from 20 to 0.2 mmHg, so that the temperature should not exceed 60°C. The solid residue was recovered by addition of 25 ml of solvent and transferred to the autoclave as catalyst for a subsequent oligomerization test. The oligomerization was repeated several times following the same procedure.

After heating at 150°C under 80 atm CO and 50 atm H_2, the residue was completely transformed into $[Ru_3(CO)_{12}]$.

4.6. *Analytical procedures and identification of the reaction products*

The conversion of ethylene was determined through GLC analyses of both the residual gases and the liquid crude product, both before and after hydrogenation. The analysis of the gases was performed using a 25 m capillary dimethyl silicone fluid (DSF) column kept at 20°C. The composition of the liquid recovered was determined using the same column, kept at 20°C for 10 min, then heated to 200°C at a rate of 5°C/min. The amounts of the components were calculated using calibration curves obtained by mixing the C_4, C_6, C_8, C_{10}, C_{12} and C_{14} olefins, one by one, with a known amount of benzene as internal standard.

The crude product was hydrogenated by simply heating it at 150°C under 150 atm of dihydrogen. The product was then analysed in the same way as the initial crude product.

When necessary olefins were identified through their GLC-mass spectra [47]. The isomeric composition of C_4 olefins was determined by GLC using a 50 m "Al_2O_3 Plot" capillary column at 120°C. The ratio of linear to branched-chain olefins in the C_6 and C_8 clusters was determined from the hydrogenated crude product. All C_6 and C_8 saturated hydrocarbons were identified by their GLC-mass spectra [47]. Some C_6 and C_8 dienes were detected by GLC and GLC-mass spectra in the liquid reaction crude product recovered from the oligomerization of ethylene at constant pressure.

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