

Homo and co-oligomerization of C₂–C₅ olefins in the presence of cluster ruthenium complexes

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Abstract

Propene can be oligomerized using Ru₃(CO)₁₂ as catalytic precursor in solution of a hydrogen donor solvent or in the presence of ethylene. Ethylene–propene mixtures undergo oligomerization in the presence of Ru₃(CO)₁₂ at 120°C with conversions even higher than 80%. Higher olefins do not react in the presence of this catalytic system. Ruthenium hydrides and alkyls are suggested intermediates in this catalytic cycle.

Keywords: Oligomerization; Co-oligomerization; Ruthenium complexes; Catalysis; Olefins

1. Introduction

The oligomerization of propene in the presence of Ziegler–Natta [1–9] or transition metal catalysts [7,10–12], mainly Ni [6,7,13–15] based catalysts, has been reported by different authors. Even higher olefins, from C₄ to C₈, have been subjected to this reaction to give products containing up to 30 carbon atoms [6,7,13,16–22].

The co-oligomerization of the above olefins in the presence of the same catalysts has also been reported [23–25].

Propene and butene oligomerization and co-oligomerization has in fact reached industrial relevance under the name “Dimersol Process” [26,27].

We have previously studied the oligomerization of ethylene and found that Ru₃(CO)₁₂ displays a fair cat-

alytic activity for this reaction [28]. We have now extended our investigation on the catalytic activity of ruthenium clusters to higher olefins, C₃, C₄, C₅, and to their co-oligomerization with ethylene.

2. Results

The oligomerization of propene in the presence of Ru₃(CO)₁₂, tested in different solvents (Table 1), requires a minimum temperature which is higher than the one necessary when using ethylene [28]. The activity of the catalytic system appears to be higher in a hydrogen donor solvent such as propan-2-ol and, surprisingly, also in cyclohexane. Dehydrogenation of a paraffin, *n*-heptane, in the presence of a ruthenium carbonyl carboxylate catalytic system has been observed previously [29]. The reaction rate is approximately the same in both solvents, while the regioselectivity is very different. In cyclohexane 83% of the reaction products consist of branched chain olefins (2-methyl-pentenes).

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Table 1
Oligomerization of propene in various solvents in the presence of $\text{Ru}_3(\text{CO})_{12}$. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; benzene as internal standard

| C_3H_6 (g) | Solvent | T (°C) | Reaction time (h) | Conv. (%) | Reaction products (wt.%) | | | |
|-------------------------------|---------------|-------------|----------------------|--------------|--------------------------|------------------|--------------|-----------------|
| | | | | | C_6 | | C_9 | C_{12} |
| | | | | | linear | 2-methylpentenes | | |
| 20.0 | Toluene | 150 | 20 | 0.1 | 100 | — | — | |
| | | | | | 45.1 | 54.9 | — | |
| 9.0 | Chlorobenzene | 180 | 70 | 42.0 | 55.3 | 31.5 | 13.2 | |
| | | | | | 25.0 | 75.0 | — | |
| 7.0 | Cyclohexane | 180 | 20 | 22.6 | 69.6 | 30.4 | — | |
| | | | | | 17.3 | 82.7 | — | |
| 13.2 | Propan-2-ol | 150 | 22 | 6.1 | 100 | — | — | |
| | | | | | 83.4 | 16.6 | — | |
| 10.4 | Propan-2-ol | 180 | 22 | 19.5 | 100 | — | — | |
| | | | | | 95.2 | 4.8 | — | |

while in propan-2-ol they are mainly linear (95%) (Table 1). Dimers are exclusively formed in this last solvent. Trimers and tetramers are formed in good yield (45%) in chlorobenzene when using prolonged reaction times.

In order to obtain information on the nature of the catalytically active species, we have compared the activity displayed in this reaction alternatively with

$\text{Ru}_3(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and the residue recovered from an oligomerization experiment of ethylene performed in the presence of $\text{Ru}_3(\text{CO})_{12}$ (Table 2). All experiments were carried out in toluene.

With propene, as had been experienced with ethylene [28], hydride species seem to favour, although not to a great extent, the oligomerization reaction. In both cases however the conversion is rather low. The catalyst

Table 2
Oligomerization of propene in the presence of various catalyst precursors. Catalyst precursor 0.94 mmol Ru; toluene 25 ml; T 150°C; benzene as internal standard

| C_3H_6 (g) | Catalyst precursor | Reaction time (h) | Conv. (%) | Reaction products (wt.%) | | |
|-------------------------------|---|----------------------|--------------|--------------------------|------------------|--------------|
| | | | | C_6 | | C_9 |
| | | | | linear | 2-methylpentenes | |
| 20.0 | $\text{Ru}_3(\text{CO})_{12}$ | 17 | 0.1 | 100 | — | — |
| | | | | 45.1 | 54.9 | — |
| 15.0 | $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ | 20 | 2.0 | 100 | — | — |
| | | | | 18.9 | 81.1 | — |
| 16.4 | Preformate ^a | 20 | 29.0 | 96.9 | — | 3.1 |
| | | | | 11.5 | 88.5 | — |
| 14.0 | Preformate ^a | 100 | 33.9 | 94.8 | — | 5.1 |
| | | | | 12.7 | 87.3 | — |

^a The catalyst was recovered in nitrogen atmosphere at 60°C and evaporated under vacuum (from 20 to 0.2 mmHg) from the reaction crude of a previous ethylene oligomerization in the presence of $\text{Ru}_3(\text{CO})_{12}$ in toluene at 150°C.

recovered from a previous oligomerization experiment of ethylene, in contrast, shows a much higher activity, providing 29% conversion to be compared with 2% with $H_4Ru_4(CO)_{12}$ in the same time (around 20h). The reaction however seems not to proceed much further even with this catalytic system since only 34% conversion is achieved in 100h.

Attempts to oligomerize but-1-ene and pent-1-ene in the presence of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ in chlorobenzene and toluene were also made. No oligomers were detected in the reaction medium even after prolonged heating at 180°C. When using as catalyst the residue recovered from a previous oligomerization experiment on ethylene, we could however detect, working in chlorobenzene, the formation of C_8 and C_{12} oligomers from but-1-ene with approximately 9% conversion.

The above results seem to indicate that ethylene helps to transform the ruthenium carbonyl precursor into the catalytically active species for the higher olefins tested also.

We have then investigated the co-oligomerization of ethylene and propene. Both the nature of the products obtained and olefin conversions would in fact provide indications of the role played by ethylene in this reaction.

A first series of co-oligomerization tests on almost equimolecular mixtures of the two olefins was performed at 150°C in various solvents in the presence of $Ru_3(CO)_{12}$ (Table 3). The ratio of C_2/C_3 olefins converted increases from 1.3 to 1.8 and to 2.2 when using cyclohexane, chlorobenzene or toluene respectively as solvents.

Ethylene conversion is at least 90%, while that of propene is generally lower (50%). The reaction products are mixtures of C_4 – C_{10} olefins. They are due to the oligomerization of ethylene (butenes and 3-methylpentenes), of propene (2-methylpentenes) and to the co-oligomerization of the two olefins (C_5 and C_7 olefins). It may be noted that in cyclohexane both ethylene and propylene conversions are high (Table 3).

The composition of the reaction products changes as the olefin conversion proceeds (Table 4). Initially, in fact, C_4 are mainly formed and the C_2/C_3 conversion ratio is rather high. This ratio decreases as the reaction proceeds, and significantly increasing amounts of C_5 and C_7 olefins are formed, indicative of ethylene–propene co-oligomerization.

The influence of the reaction temperature has also been investigated (Tables 4–6). The reaction starts already at 100°C in cyclohexane, while a temperature of 150°C is necessary in toluene. In aromatic solvents like benzene and toluene the conversion of ethylene reaches 90% and that of propene up to 60%. In cyclohexane, on the contrary, the conversion of propene may also exceed 80% (Table 5). In chlorobenzene higher temperatures

Table 3
Co-oligomerization of ethylene and propene in various solvents in the presence of $Ru_3(CO)_{12}$. Catalyst precursor 0.94mmol Ru; solvent 25 ml; reaction time 20h; T 150°C; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{mol C_2H_4}{mol C_3H_6}$ | Solvent | Conv. (%) | | Reaction products (wt.%) | | | | | | | | | | | | | | | | | | |
|--------------|--------------|---------------------------------|---------------|-------------------------|-------------------------|--------------------------|------|------|------|------|------|------|------|------|------|---|---|-----|-------|-------|----------|-----|-----|--|
| | | | | $\frac{C_2H_4}{C_3H_6}$ | $\frac{C_3H_6}{C_3H_6}$ | C_4 | A | B | C | D | E | F | G | H | I | L | M | N | C_8 | C_9 | C_{10} | | | |
| 8.2 | 11.6 | 1.03 | Cyclohexane | 96.7 | 86.2 | 1.3 | 13.5 | | | | | 36.6 | 36.4 | | | | | 7.3 | | | 3.7 | 2.5 | — | |
| | | | | 8.7 | 32.6 | 58.7 | 38.3 | 61.7 | 16.8 | 67.9 | 15.3 | 17.2 | 82.8 | 11.9 | 88.1 | | | | | | | | | |
| 6.4 | 10.4 | 0.92 | Chlorobenzene | 91.4 | 51.3 | 1.8 | 26.4 | | | | | 40.6 | 20.7 | | | | | 4.3 | | | 3.6 | 3.2 | 1.2 | |
| | | | | 8.8 | 32.7 | 58.7 | 43.8 | 56.2 | 27.3 | 46.5 | 26.2 | 25.1 | 74.9 | 22.5 | 77.5 | | | | | | | | | |
| 5.6 | 6.7 | 1.25 | Toluene | 89.0 | 50.0 | 2.2 | 25.3 | | | | | 38.2 | 18.0 | | | | | 5.6 | | | 6.6 | 3.4 | 1.9 | |
| | | | | 9.4 | 33.0 | 57.6 | 39.4 | 60.6 | 31.7 | 38.7 | 29.6 | 34.0 | 66.0 | | | | | | | | | | | |

A: 1-Butene; B: cis-2-butene; C: trans-2-butene; D: C_5 linear; E: methylbutenes; F: C_6 linear; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched; M: C_8 linear; N: C_8 branched.

Table 4
Co-oligomerization of ethylene and propene in the presence of $Ru_3(CO)_2$ in toluene. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{mol C_2H_4}{mol C_3H_6}$ | Conv. (%) | | T (°C) | Reaction time (h) | Reaction products (wt.%) | | | | | | | | | | | |
|-----------------|-----------------|---------------------------------|-----------|----------|-------------|----------------------|--------------------------|------|------|------|------|------|------|------|------|------|------|--|
| | | | C_2H_4 | C_3H_6 | | | A | B | C | D | E | F | G | H | I | L | | |
| 11.4 | 16.6 | 1.02 | 0.61 | 0.14 | 4.5 | 150 | 0.0083 | 54.2 | 30.9 | | | 14.9 | | | — | | | |
| | | | | | | | | 11.3 | 32.5 | 56.2 | 39.8 | 60.2 | 75.1 | 2.0 | 22.9 | | | |
| 6.6 | 6.4 | 1.45 | 25.4 | 10.3 | 3.8 | 150 | 4 | 37.1 | 30.8 | | | 14.4 | | | 2.9 | | | |
| | | | | | | | | 12.4 | 32.1 | 55.5 | 36.0 | 64.0 | 27.3 | 46.5 | 26.2 | 25.1 | 74.9 | |
| 5.6 | 6.7 | 1.25 | 89.0 | 50.0 | 2.2 | 150 | 20 | 25.3 | 38.2 | | | 18.0 | | | 6.6 | | | |
| | | | | | | | | 9.4 | 33.0 | 57.6 | 39.4 | 60.6 | 31.7 | 38.7 | 29.6 | 34.0 | 66.0 | |
| 5.4 | 6.2 | 0.87 | 90.0 | 47.0 | 1.7 | 150 | 70 | 26.0 | 34.6 | | | 16.8 | | | 7.6 | | | |
| | | | | | | | | 10.2 | 34.0 | 55.8 | 42.2 | 57.8 | 32.2 | 42.2 | 25.6 | 18.1 | 81.9 | |
| 7.4 | 6.3 | 1.76 | 80.2 | 51.0 | 2.8 | 150 | 70 | 27.0 | 35.0 | | | 21.0 | | | 5.6 | | | |
| | | | | | | | | 10.0 | 31.8 | 58.2 | 41.0 | 59.0 | 25.0 | 40.5 | 34.5 | 22.4 | 77.6 | |
| 6.8 | 7.0 | 1.45 | 70.0 | 41.1 | 2.5 | 180 | 15 | 34.0 | 28.5 | | | 15.1 | | | 4.4 | | | |
| | | | | | | | | 10.1 | 35.2 | 54.7 | 50.1 | 49.9 | 35.2 | 38.3 | 26.5 | 16.8 | 83.2 | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C_5 linear; E: methylbenzenes; F: C_6 linear; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched.

Table 5
 Co-oligomerization of ethylene and propene in the presence of $\text{Ru}_3(\text{CO})_{12}$ in cyclohexane. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{\text{mol C}_2\text{H}_4}{\text{mol C}_3\text{H}_6}$ | Conv. (%) | | T (°C) | Reaction time (h) | Reaction products (wt. %) | | | | | | | | | | | | | |
|-------------------------------|-------------------------------|---|------------------------|------------------------|-------------|----------------------|---------------------------|------|------|------|------|------|------|------|------|------|------|---|------|--|
| | | | C_2H_4 | C_3H_6 | | | A | B | C | D | E | F | G | H | I | L | M | N | | |
| 5.2 | 7.6 | 1.06 | 94.0 | 75.0 | 100 | 64 | 13.0 | | 49.0 | 28.4 | | 7.5 | | | 2.1 | | | | | |
| 13.0 | 11.1 | 1.76 | 98.3 | 80.8 | 120 | 20 | 7.1 | 29.1 | 63.8 | 35.0 | 65.0 | 13.6 | 50.0 | 36.4 | 13.8 | 86.2 | 10.7 | | 89.3 | |
| 8.2 | 11.6 | 1.03 | 96.7 | 86.2 | 150 | 20 | 16.3 | | 42.3 | 30.0 | | 7.1 | | | 3.0 | | | | 1.3 | |
| | | | | | | | 7.2 | 30.8 | 62.0 | 37.3 | 62.7 | 14.9 | 55.3 | 29.8 | 15.4 | 84.6 | 13.4 | | 86.6 | |
| | | | | | | | 13.5 | | 36.6 | 36.4 | | 7.3 | | | 3.7 | | | | 2.5 | |
| | | | | | | | 8.7 | 32.6 | 58.7 | 38.3 | 61.7 | 16.8 | 67.9 | 15.3 | 17.7 | 82.8 | 11.9 | | 88.1 | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C_5 linear; E: methylbutenes; F: 3-methylpentenes; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched; M: C_8 linear; N: C_8 branched.

 Table 6
 Co-oligomerization of ethylene and propene in the presence of $\text{Ru}_3(\text{CO})_{12}$ in chlorobenzene. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{\text{mol C}_2\text{H}_4}{\text{mol C}_3\text{H}_6}$ | Conv. (%) | | T (°C) | Reaction time (h) | Reaction products (wt. %) | | | | | | | | | | | | | |
|-------------------------------|-------------------------------|---|------------------------|------------------------|-------------|----------------------|---------------------------|------|------|------|------|------|------|------|------|------|------|---|------|--|
| | | | C_2H_4 | C_3H_6 | | | A | B | C | D | E | F | G | H | I | L | M | N | | |
| 14.4 | 14.2 | 1.50 | 72.4 | 45.4 | 120 | 9 | 24.0 | | 46.7 | 23.1 | | 4.7 | | | 0.7 | | | | 0.8 | |
| | | | | | | | 8.3 | 28.9 | 62.8 | 39.3 | 60.7 | 19.3 | 24.9 | 55.8 | 39.0 | 61.0 | 65.5 | | 34.5 | |
| 11.8 | 15.0 | 1.18 | 84.3 | 60.4 | 120 | 20 | 16.9 | | 45.7 | 28.3 | | 4.6 | | | 1.8 | | | | 1.7 | |
| | | | | | | | 10.6 | 32.3 | 57.1 | 44.8 | 55.2 | 17.1 | 48.8 | 34.1 | 15.8 | 84.2 | 48.2 | | 51.4 | |
| 10.2 | 13.8 | 1.10 | 30.9 | 4.6 | 150 | 0.1 | 67.6 | | 23.2 | 7.6 | | 1.6 | | | — | | | | — | |
| | | | | | | | 22.9 | 24.8 | 52.3 | 86.2 | 13.8 | 43.8 | 16.4 | 39.8 | 22.1 | 77.9 | | | | |
| 9.8 | 12.8 | 1.15 | 52.9 | 24.1 | 150 | 3 | 28.7 | | 44.1 | 18.4 | | 4.7 | | | 1.1 | | | | 1.8 | |
| | | | | | | | 12.6 | 36.7 | 50.7 | 41.5 | 58.5 | 28.3 | 25.6 | 46.1 | 19.9 | 80.1 | 63.3 | | 36.7 | |
| 9.8 | 15.3 | 1.04 | 92.3 | 60.3 | 150 | 70 | 15.7 | | 43.8 | 25.6 | | 7.8 | | | 4.1 | | | | 2.2 | |
| | | | | | | | 10.9 | 35.7 | 53.4 | 47.3 | 52.7 | 29.7 | 26.5 | 43.8 | 29.4 | 70.6 | 50.3 | | 49.7 | |
| 13.4 | 17.0 | 1.18 | 58.8 | 22.1 | 180 | 3 | 26.6 | | 32.8 | 21.7 | | 7.2 | | | 4.0 | | | | 3.6 | |
| | | | | | | | 11.6 | 32.1 | 56.3 | 56.3 | 43.7 | 42.0 | 12.4 | 45.6 | 28.0 | 72.0 | 59.2 | | 40.8 | |
| 5.0 | 6.8 | 1.10 | 78.4 | 46.9 | 180 | 20 | 25.8 | | 34.3 | 19.1 | | 9.2 | | | 4.3 | | | | 4.9 | |
| | | | | | | | 12.0 | 33.2 | 54.8 | 55.2 | 44.8 | 40.0 | 38.1 | 21.9 | 28.2 | 71.8 | 43.4 | | 56.6 | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C_5 linear; E: methylbutenes; F: 3-methylpentenes; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched; M: C_8 linear; N: C_8 branched.

Table 7

Co-oligomerization of ethylene and propene in the presence of $\text{Ru}_3(\text{CO})_{12}$ in chlorobenzene at different ethylene/propene molar ratios. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; 7 150 °C; reaction time 20 h; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{\text{mol C}_2\text{H}_4}{\text{mol C}_3\text{H}_6}$ | Conv. (%) | Reaction products (wt.%) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|-------------------------------|-------------------------------|---|-----------|---|--------------|------|---|--------------|---|---|--------------|---|---|--------------|---|--|--------------|------|------|--------------|--|--|-----------------|--|--|-----------------|--|--|-----------------|--|------|------|------|--|--|--|--|--|--|--|--|--|--|-----|------|------|--|--|--|--|--|--|--|--|--|--|-----|------|--|--|--|--|--|--|--|--|--|--|--|--|
| | | | | $\frac{\text{mol C}_2\text{H}_4 \text{ conv.}}{\text{mol C}_3\text{H}_6 \text{ conv.}}$ | C_4 | | | C_5 | | | C_6 | | | C_7 | | | C_8 | | | C_9 | | | C_{10} | | | C_{11} | | | C_{12} | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | A | B | C | D | E | F | G | H | I | L | M | N | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.8 | 15.0 | 0.08 | 25.0 | 1.8 | 1.1 | 48.2 | | | | | | | | | | | | 2.2 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 10.1 | 35.5 | 54.4 | 48.1 | | | | | | | | | | | | 51.9 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.4 | 13.6 | 0.26 | 49.1 | 9.3 | 1.4 | 45.2 | | | | | | | | | | | | 14.8 | 3.2 | | | | | | | | | | | | 1.1 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 9.7 | 36.3 | 54.0 | 46.3 | | | | | | | | | | | | 53.7 | 33.8 | | | | | | | | | | | | 50.1 | 16.1 | 27.7 | | | | | | | | | | | | 72.3 | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.0 | 7.0 | 0.64 | 69.1 | 27.7 | 1.6 | 42.4 | | | | | | | | | | | | 17.0 | 4.3 | | | | | | | | | | | | 4.0 | 1.8 | | | | | | | | | | | | 1.5 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 10.4 | 37.4 | 52.2 | 47.4 | | | | | | | | | | | | 52.6 | 32.7 | | | | | | | | | | | | 54.3 | 13.0 | 23.2 | | | | | | | | | | | | 76.8 | 20.6 | | | | | | | | | | | | 79.4 | | | | | | | | | | | | |
| 6.4 | 10.4 | 0.92 | 91.4 | 51.3 | 1.8 | 40.6 | | | | | | | | | | | | 20.7 | 4.3 | | | | | | | | | | | | 3.6 | 3.2 | | | | | | | | | | | | 1.2 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 8.8 | 32.7 | 58.5 | 43.8 | | | | | | | | | | | | 56.2 | 27.3 | | | | | | | | | | | | 46.5 | 26.2 | 25.1 | | | | | | | | | | | | 74.9 | 22.5 | | | | | | | | | | | | 77.5 | | | | | | | | | | | | |
| 8.2 | 6.6 | 1.86 | 92.3 | 75.6 | 2.3 | 32.6 | | | | | | | | | | | | 20.3 | 6.9 | | | | | | | | | | | | 4.1 | 3.2 | | | | | | | | | | | | 1.9 | 1.8 | | | | | | | | | | | | 1.1 | | | | | | | | | | | | | |
| | | | 9.6 | 36.4 | 54.0 | 44.8 | | | | | | | | | | | | 55.2 | 40.3 | | | | | | | | | | | | 35.3 | 24.4 | 28.3 | | | | | | | | | | | | 71.7 | 24.1 | | | | | | | | | | | | 75.9 | | | | | | | | | | | | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C_5 linear; E: methylbutenes; F: C_6 linear; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched; M: C_8 linear; N: C_8 branched.

Table 8

Co-oligomerization of ethylene and propene in the presence of $\text{H}_2\text{Ru}_2(\text{CO})_{11}$ at different temperatures in toluene. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; reaction time 20 h; benzene as internal standard

| C_2H_4 (g) | C_3H_6 (g) | $\frac{\text{mol C}_2\text{H}_4}{\text{mol C}_3\text{H}_6}$ | Conv. (%) | $\frac{\text{mol C}_2\text{H}_4 \text{ conv.}}{\text{mol C}_3\text{H}_6 \text{ conv.}}$ | | T (°C) | Reaction products (wt.%) | | | | | | | | | | | | | | | | | | |
|-------------------------------|-------------------------------|---|-----------|---|------------------------|-------------|--------------------------|------|------|--------------|------|------|--------------|------|-----|--------------|------|------|--------------|--|--|--------------|--|--|-----------------|
| | | | | C_2H_4 | C_3H_6 | | C_4 | | | C_5 | | | C_6 | | | C_7 | | | C_8 | | | C_9 | | | C_{10} |
| | | | | A | B | C | D | E | F | G | H | I | L | | | | | | | | | | | | |
| 6.2 | 6.2 | 1.50 | 88.2 | 50.2 | 2.6 | 100 | 22.4 | 46.0 | | | 2.0 | 47.7 | | | 2.0 | 1.0 | | | | | | | | | |
| | | | 9.3 | 28.2 | 62.5 | 28.0 | | | 72.0 | 14.4 | | | 30.3 | 55.3 | | | 4.8 | 95.2 | | | | | | | |
| 6.2 | 7.6 | 1.22 | 87.0 | 44.4 | 2.4 | 150 | 28.9 | 38.7 | | | 16.3 | 8.0 | | | 2.5 | | | 2.0 | | | | | | | |
| | | | 10.0 | 33.1 | 57.9 | 40.3 | | | 59.7 | 28.6 | | | 38.0 | 33.4 | | | 5.0 | 95.0 | | | | | | | |
| 5.8 | 6.4 | 1.36 | 65.6 | 34.2 | 2.6 | 180 | 33.1 | 25.8 | | | 12.3 | 9.8 | | | 5.3 | | | | | | | | | | |
| | | | 12.0 | 32.1 | 55.9 | 52.0 | | | 48.0 | 65.3 | | | 15.0 | 19.7 | | | 15.2 | 84.8 | | | | | | | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C_5 linear; E: methylbutenes; F: C_6 linear; G: 2-methylpentenes; H: 3-methylpentenes; I: C_7 linear; L: C_7 branched.

Table 9
Co-oligomerization of ethylene and 1-pentene in the presence of $\text{Ru}_3(\text{CO})_{12}$ in chlorobenzene. Catalyst precursor 0.94 mmol Ru; solvent 25 ml; T 150°C; benzene as internal standard

| C_2H_4 (g) | C_5H_{10} (g) | mol | | C ₂ H ₄ conv. (%) | mol C ₂ H ₄ conv. | mol C ₅ H ₁₀ conv. | Reaction time (h) | Reaction products (wt.%) | | | | | | | | | |
|-------------------------------|----------------------------------|------------------------|---------------------------|--|--|---|----------------------|--------------------------|------|------|------|------|------|------|------|------|--|
| | | C_2H_4 | C_5H_{10} | | | | | A | B | C | D | E | F | G | H | I | |
| 3.0 | 20.0 | 0.37 | 3.8 | 50.0 | 4.9 | 4.9 | 20 | 31.2 | 29.3 | 56.0 | 17.1 | 24.8 | 24.8 | 5.1 | 5.4 | 12.4 | |
| 1.4 | 7.6 | 0.46 | 6.4 | 62.5 | 4.6 | 4.6 | 72 | 14.7 | 29.3 | 56.0 | 75.9 | 43.7 | 56.3 | 40.0 | 12.0 | 7.7 | |
| | | | | | | | | 29.6 | | | 14.8 | 30.3 | | 5.6 | | | |
| | | | | | | | | 10.9 | 31.7 | 57.4 | 89.5 | 47.6 | 52.4 | 25.8 | 74.2 | | |

A: 1-Butene; B: *cis*-2-butene; C: *trans*-2-butene; D: C₆ linear; E: 3-methylpentenes; F: C₇ linear; G: C₇ branched; H: C₈ linear; I: C₈ branched.

increase the formation of higher molecular weight products (Table 6).

The influence of the C₂/C₃ olefin ratio on the reaction course has also been tested by changing this parameter (Table 7). Ethylene being much more reactive than propene, it is possible to convert equimolecular amounts of the two olefins only by using a very low C₂/C₃ ratio. The obvious consequence is also a very low olefin conversion. When the C₂/C₃ olefin ratio increases, the conversion of both olefins increases also.

In fact, a reasonably higher C₂/C₃ ratio causes an increase in the formation of the heavier products which are almost absent when the above ratio is very low.

In the presence of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (Table 8) the C₂-C₃ oligomerization takes place already at 100°C even if toluene is used as solvent. This catalytic precursor provides approximately the same results as $\text{Ru}_3(\text{CO})_{12}$. The catalytic system formed by these two precursors is therefore most probably the same.

The co-oligomerization of C₂/C₅ olefins in the presence of $\text{Ru}_3(\text{CO})_{12}$ may be promoted in chlorobenzene (Table 9).

When the C₂/C₅ ratio is not too high we may notice the formation of C₇, C₉ and C₁₀ olefins.

3. Discussion

Triruthenium dodecacarbonyl does not promote the oligomerization of C₃, C₄ and C₅ olefins under the conditions used for ethylene.

The oligomerization of propene may be promoted using $\text{Ru}_3(\text{CO})_{12}$ as catalytic precursor, working in the presence of hydrogen donors; that of but-1-ene takes place only in the presence of a catalytic system recovered from a previous oligomerization of ethylene.

In propan-2-ol or cyclohexane solution or in the presence of ethylene, propene may be oligomerized or co-oligomerized using $\text{Ru}_3(\text{CO})_{12}$. An appropriate, continuous source of hydrogen must be provided to this system, such as the presence of ethylene, in reagent concentration, to achieve reasonable conversions. Dienes, C₆ and C₈, have in fact been detected when reacting ethylene in the presence of $\text{Ru}_3(\text{CO})_{12}$ [28].

In the case of propene too, as already suggested for ethylene [28], the intermediates involved in this reaction are very likely hydride and alkyl ruthenium carbonyls.

4. Experimental details

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

4.1. Materials

Ethylene, propene, but-1-ene, pent-1-ene and all reference compounds were commercial products. All solvents were purified in the usual manner [30].

4.2. Catalyst precursor

$\text{Ru}_3(\text{CO})_{12}$ [31] and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ [32] were prepared as described in the literature.

4.3. Oligomerization experiments

Propene and but-1-ene oligomerization tests were performed as described for ethylene in a previous paper [28]. In the case of pent-1-ene oligomerization, the olefin was added together with the solvent.

The ethylene/propylene co-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 $\pm 1^\circ\text{C}$.

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

The reaction was stopped when required by rapidly cooling the autoclave. The residual olefins 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).

Working conditions are reported in the tables.

Analytical procedures adopted are reported below.

4.4. Re-use of the catalytic system

$\text{Ru}_3(\text{CO})_{12}$, the solvent and ethylene were placed in the usual manner [28] in the autoclave which was then heated to 150°C for 2 h. Then the autoclave was rapidly cooled to room temperature and the liquid reaction crude recovered under dinitrogen. The liquid components 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 solvent and transferred to the autoclave as catalyst for subsequent oligomerization or co-oligomerization tests.

4.5. Analytical procedure

The conversion of the olefins and the composition of the liquid recovered were determined as described in a previous paper [28]. The amounts of the components were calculated using calibration curves obtained by

mixing the C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , C_{11} and C_{12} . When necessary olefins were identified through their GC mass spectra [33]. The ratio of linear to branched-chain olefins in the C_5 , C_6 , C_7 and C_8 clusters was determined on the hydrogenated crude. All C_5 , C_6 , C_7 and C_8 saturated hydrocarbons were identified by their GC mass spectra [33].

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