# (η$^6$-Naphthalene)(η$^4$-cycloocta-1,5-diene)ruthenium(0) as efficient catalytic precursor for the isomerization of methyl linoleate under mild conditions

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## Abstract

The Ru(η$^6$-naphthalene)(η$^4$-cycloocta-1,5-diene) complex, **1**, in the presence of acetonitrile, is able to promote the isomerization of methyl linoleate under mild conditions (60°C) with high yields. Using aprotic solvents (hexane) the reaction is very selective, by-products like methyl oleates and polymers are formed in negligible amounts. A remarkable long-lived catalytic activity has been observed. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Linoleic acid is one of the most common fatty unsaturated acid present in vegetable oils [1]. It contains two, not conjugated double bonds, both of ($Z$) stereochemistry, in the $C_9$ and $C_{12}$ positions (Chart 1).
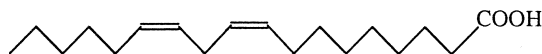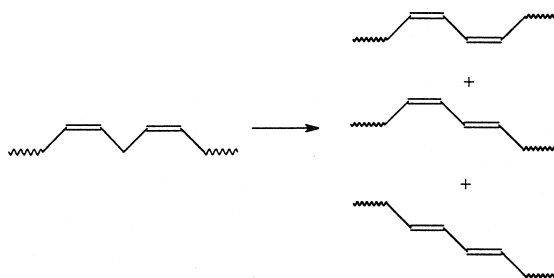


(Z,Z)-9,12-Octadecadienoic acid (Linoleic acid)

Chart 1.

The isomerization reaction of the double bonds to yield conjugated dienes (Scheme 1) is of industrial relevance. In the manufacturing of edible hydrogenated fats it has been observed that the conjugation

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Scheme 1.

under hydrogenation conditions represents a necessary step prior the reduction of a double bond [2–12]. In addition, the oils containing conjugated double bonds are important constituents of paints and varnishes giving to these materials improved drying properties and high alkali and water resistance [1,13,14].

For all these reasons, the catalytic isomerization of its derivative methyl linoleate, ML, has been the subject of longstanding investigations and a variety of transition metal-based systems of chromium [12,15], iron [16], ruthenium [13,14,17–19], rhodium [17–22], palladium [21], platinum [21], operating as heterogeneous or homogeneous catalysts, have been employed. In this frame it has been found that the isomerization is complicated by side reactions that can give monoenes and polymeric materials in large amounts.

Additional studies have pointed out the high catalytic activity of ruthenium-based homogeneous catalysts in this reaction. Carbonyl clusters, $Ru_3(CO)_{12}$ and $Ru_4H_4(CO)_{12}$, furnish at 80°C in propan-2-ol high conversions of ML to conjugated dienes and monoenes, the last deriving from a competitive hydrogen transfer reaction between the solvent and ML [23,24]. Using octane as solvent the selectivity in conjugated dienes is increased while the ML conversion is reduced [23]. Ruthenium alkoxides, obtained in situ by reaction of $RuCl_3$ hydrated and alcohols, are also catalytically active [25]. However, the high temperatures (155°C–185°C) necessary to get good conversions are responsible of the formation of polymeric materials and monoenes in large amounts.

We recently reported that the ruthenium(0) complex $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$, **1** ($C_{10}H_8 =$ naphthalene; $C_8H_{12} = 1,5$-cyclooctadiene) in the presence of acetonitrile is an useful catalytic precursor for the isomerization of double bonds under mild conditions [26,27]. Complex **1** is characterized for the lability of the $\eta^6$-naphthalene–ruthenium bond and, in acetonitrile, the arene is easily displaced from ruthenium leaving coordination sites on the metal more accessible for the incoming reagent [26–29]. It appears then as a promising catalytic precursor for the easy isomerization of ML and we report here the results obtained in such a reaction.

## 2. Experimental

Hexane was dried by refluxing over Na/K alloy under argon before distillation. Anhydrous methanol was obtained by drying with $CaH_2$ and distillation. Acetonitrile was purified by distillation from $CaH_2$ and $P_4O_{10}$. The complex $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$, **1**, was prepared as already reported [28]. The complexes $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ (arene=benzene and *p*.cymene) were made by reacting

the corresponding $[RuCl_2(\eta^6\text{-arene})]_2$ compounds with $C_8H_{12}$ and $Na_2CO_3$ in propan-2-ol [30] and identified by comparison their ^{1}H-NMR spectra with authentic materials [31]. Methyl linoleate (Fluka product) was pure at 99%; it was degassed and stored under argon before use.

The GLC analyses were performed on a Perkin Elmer Sigma 3 B gas chromatograph, equipped with a flame ionization detector, using a neopentylglicolsuccinate column (3 m × 2.5 mm, $T = 190°C$) on Chromosorb W AW-DMCS, 80/100 mesh. Nitrogen was employed as carrier gas (Flowrate = 30 ml/min). Methyl palmitate was used as internal standard to evaluate the polymer content.

^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer at 200 MHz. Chloroform-*d* was used as solvent and chemical shifts were determined relative to internal $Si(CH_3)_4$ ($\delta = 0$ ppm). The ^{1}H-NMR experiment was performed on a solution of **1** (0.015 g, 0.045 mmol) in tetrahydrofuran-$d_8$ (99.5 at.% D; 0.6 ml) in a 5 mm o.d. NMR tube to which methyl linoleate (0.015 ml, 0.045 mmol) and acetonitrile-$d_3$ (99.95 at.% D; 0.047 ml, 0.9 mmol) were added. The growth in the signals of the products was monitored on a Varian Gemini 200 spectrometer at various probe temperature in the range 25°C to 45°C.

## 2.1. Isomerization reactions

The isomerization experiments were carried out under argon in a two-necked round-bottomed flask fitted with a reflux condenser and equipped with a magnetic bar and a serum cap. The solution was heated in a constant temperature bath ($\pm 0.2°C$). In a typical experiment, **1** (0.02 g, 0.06 mmol) was placed in the reaction vessel and dissolved in hexane (10 ml). Acetonitrile (0.063 ml, 1.2 mmol) was added and the solution was stirred for some minutes at room temperature. Methyl linoleate (2 ml, 6 mmol) and methyl palmitate (0.1 ml) were introduced and the solution was heated at 60°C. The progress of the reaction was checked by removing liquid samples through the serum cap with a syringe and analyzing them by GLC and by ^{1}H NMR, recording the spectrum of the residue obtained after the removal of the solvent by vacuum evaporation. The composition of the reaction mixtures, calculated by these techniques, resulted very similar ($\pm 3\%$). The data reported in Table 1 refer to the GLC analyses.

Table 1
Isomerization of methyl linoleate with $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ complexes **1–3**[a]

| Run | Catalyst | Solvent | Conversion (%) | Reaction products[b] | | Turn over frequencies[c] |
|-----|----------|---------|----------------|----------------------|---|--------------------------|
| | | | | Conjugated dienes | Monoenes | |
| 1 | **1** | hexane | 100 | 95 | 3 | 3.9 |
| 2[d] | Reaction mixture of run **1** | hexane | 100 | 92 | 5 | 3.8 |
| 3[e] | **1** | hexane | 5 | 5 | – | 0.2 |
| 4[f] | **1** | hexane | 10 | 10 | – | 0.4 |
| 5[g] | **1** | methanol | 100 | 45 | 50 | 2.2 |
| 6 | **2** | hexane | 5 | 5 | – | 0.2 |
| 7 | **3** | hexane | 5 | 5 | – | 0.2 |

[a]Reaction conditions: $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$, 0.06 mmol; methyl linoleate, 2 ml (6 mmol); $CH_3CN$, 0.063 ml (1.2 mmol); solvent (20 ml); time, 24 h; temperature, 60°C.
[b]The other products are polymeric materials.
[c]Moles of conjugated dienes/moles of $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})\times h$.
[d]Fresh methyl linoleate (2 ml) has been added.
[e]Carried out at room temperature.
[f]Carried out without acetonitrile.
[g]Reaction time, 20 h.

## 3. Results and discussion

The results obtained in the isomerization of methyl linoleate (ML) with $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$, **1**, and other $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ complexes (arene=benzene, **2**, and *p*-cymene, **3**) are reported in Table 1. Using complex **1** as catalytic precursor, in the presence of acetonitrile (molar ratios ML/**1** = 100 and $CH_3CN/\mathbf{1}$ = 20) in hexane as solvent, the conversion was complete after 24 h at 60°C giving the conjugated products in high selectivity (95%, run 1). Methyl oleate [23] is also formed in small amount (3%) and the polymeric materials are obtained only in traces. At the end of the reaction the red brown mixture is clear and it does not contain solids in suspension. The catalyst remains active and, if fresh methyl linoleate is added, it is isomerized at the same rate (run 2). The reaction also proceeds at room temperature but it is remarkably slower than at 60°C (conv. 5% after 24 h, run 3). The presence of acetonitrile is an essential requisite to achieve high catalytic activity. In fact, without acetonitrile, only a conversion of 10% was obtained (run 4). The isomerization of methyl linoleate with **1** in the presence of acetonitrile at 60°C has been also performed in methanol (run 5), since alcohols are generally used as solvents in this reaction with other ruthenium catalysts [23,25]. After 20 h methyl linoleate is completely converted to a mixture of conjugated dienes (45%) and methyl oleate (50%).

The change in composition with time observed in the runs 1 and 5 is reported in the Fig. 1a and b, respectively. It can be observed that the isomerization of ML is faster in methanol than in hexane (conv. 40% against 27% after 2 h). In hexane (Fig. 1a) conjugated dienes are selectively obtained and methyl oleate is formed in very small amount only after long time (12 h). In methanol (Fig. 1b), after 4 h, the formation of monoenes becomes the main reaction and the amount of conjugated dienes in solution decreases.

These results clearly indicate that the chemical properties of the solvent have a considerable importance in determining the composition of the reaction mixture. According to the literature report [17–19,23,25], the monoenes, formed in large amount with methanol, derive from the hydrogenation of the dienes by hydrogen transfer from the alcohol (Eq. (1)).



$$\text{(1)}$$
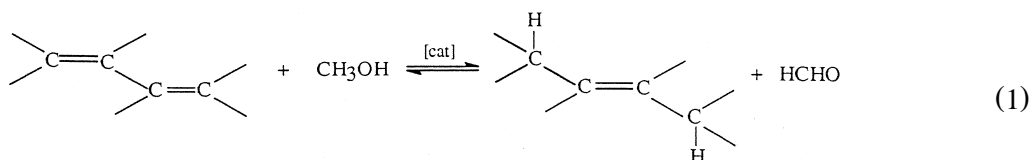
In this frame it is important to note that arene ruthenium complexes are efficient catalysts in this reaction [24,32]. The small amount of monoenes obtained working in hexane probably arises from the disproportionation of the diene with formation of trienes which were detected by GLC. Similar results have been obtained in the isomerization of ML with metal carbonyls of chromium [15,16] and of ruthenium [23].

In order to gain information on the course of the isomerization, the reaction between **1** and methyl linoleate (molar ratio = 1) has been studied by ^{1}H NMR at different temperature both without and with acetonitrile. In the first experiments we examined the reaction in cyclohexane-$d_{12}$, chemically similar to hexane, but solubility problems and limited miscibility with acetonitrile, already observed in the arene-exchange reaction between **1** and aromatic hydrocarbons [28], made this solvent not suitable for the study. The reaction has been examined in THF-$d_8$, a solvent successfully employed in similar experiments [26,27].
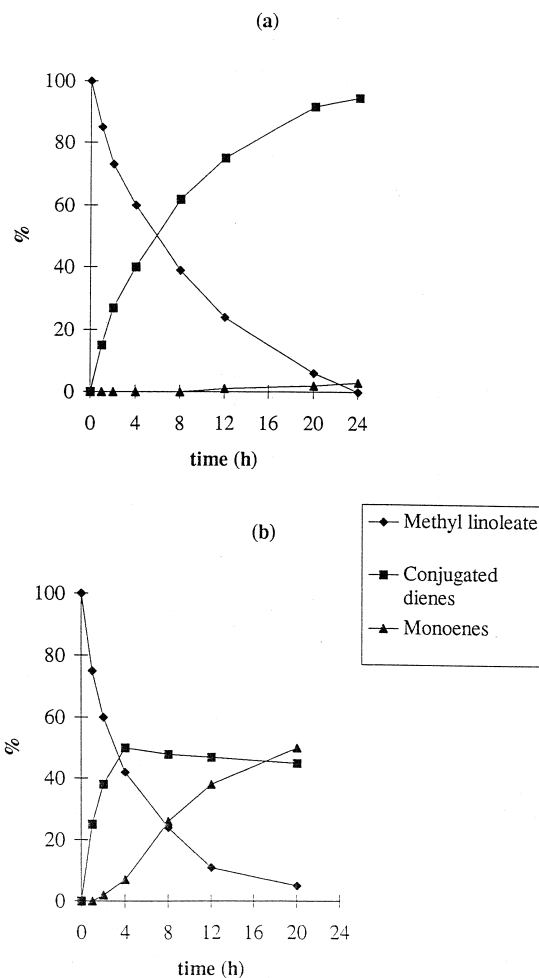
(a)



(b)



Fig. 1. Isomerization of methyl linoleate catalyzed by Ru($\eta^6$-naphthalene)($\eta^4$-cycloocta-1,5-diene)/acetonitrile at 60°C. (♦) Methyl linoleate; (■) conjugated dienes; (▲) monoenes. (a) In hexane (run 1, Table 1). (b) In methanol (run 5, Table 1).

*Without acetonitrile*. In the Fig. 2a and b the ^{1}H-NMR spectra of complex **1** in THF-$d_8$ at room temperature and of the mixture obtained adding ML to this solution are shown, respectively. The solution was slowly heated to 45°C and no changing in the spectrum was observed after 1 h indicating that the reaction between **1** and ML does not occur in these conditions.

*With acetonitrile*. On addition of acetonitrile-$d_3$ (twenty equivalents) to this solution at room temperature, new signals appeared at 7.45 ppm and 7.85 ppm, due to free naphthalene, while the intensity of the resonances of **1** decreases (Fig. 2c). A slow isomerization of ML to conjugated dienes was successively observed as indicated by the appearance of the signals between 4.7 ppm and 6.4 ppm of the olefinic protons of the conjugated dienes (Fig. 2d). Raising the temperature to 45°C the isomerization was complete after 3 h, as shown by the disappearance of the resonances at 2.78 ppm and 5.33 ppm due, respectively, to the methylenic protons, =CH–C$H_2$–CH=, and the olefinic protons of ML (Fig. 2e). In addition, the spectrum shows that: (i) the resonances of free naphthalene had increased, indicating that the arene has been displaced from ruthenium during the isomerization and (ii) the resonances of $\eta^4$-C$_8$H$_{12}$ at 2.05 ppm and 3.38 ppm are still present, pointing out that this ligand had remained bonded to the metal during and at the end of the reaction contributing to the
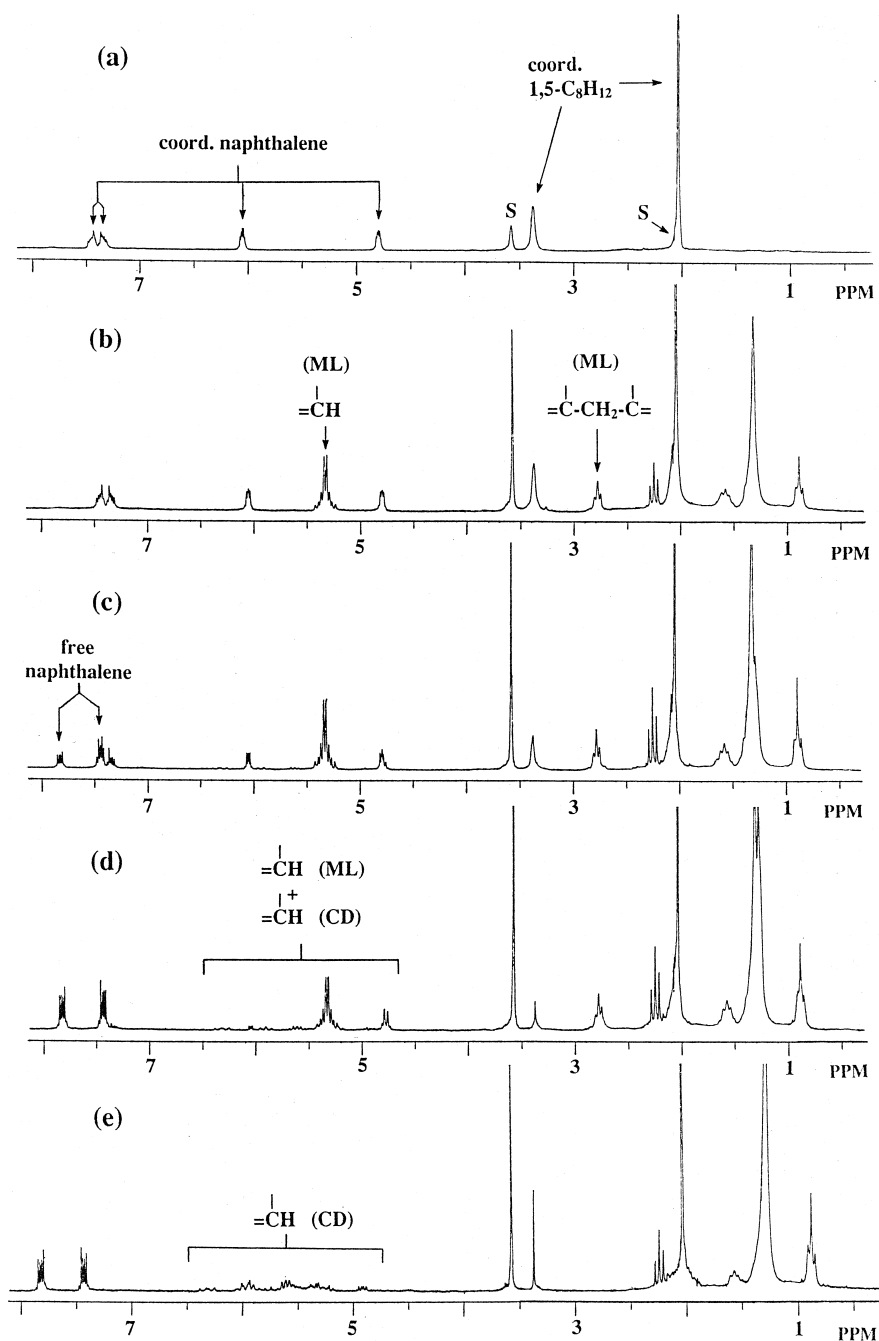
Fig. 2. $^1$H-NMR spectra (THF-$d_8$, 25°C) relative to the isomerization of methyl linoleate, ML, to conjugated dienes (CD): (a) Ru($\eta^6$-naphthalene)($\eta^4$-cycloocta-1,5-diene), **1**; (b) complex **1** + ML; (c) complex **1** + ML + acetonitrile-$d_3$, initial step; (d) reaction mixture after one hour; (e) end of the isomerization ($T = 45$°C). S = solvent.

formation of a particularly stable catalytic species (see the result of run 2, Table 1). The $^1$H-NMR experiment indicates that, as previously found in the isomerization of olefins [26] and allylic compounds [27], the key step in the isomerization catalyzed by **1** is the replacement of bonded naphthalene by acetonitrile, probably via $\eta^4$- and $\eta^2$-naphthalene–ruthenium intermediates [33], in

this way the substrate can easily reach the metallic center promoting the isomerization reaction. Since the catalytic reaction occurs in a solvent such as hexane which has very low tendency to donate hydrogen atoms, the isomerization probably proceeds stepwise via $\eta^3$-enyl-ruthenium hydride intermediates [34].

It is interesting to note that under the same reaction conditions the complexes Ru($\eta^6$-benzene)($\eta^4$-$C_8H_{12}$), **2**, and Ru($\eta^6$-*p*-cymene)($\eta^4$-$C_8H_{12}$), **3**, containing a mononuclear arene bonded to the metal, are very little effective catalytic precursors (runs 6 and 7, Table 1) pointing out the peculiarity of naphthalene in allowing ligand displacement reactions under mild conditions [33].

When compared to the previously reported ruthenium catalysts [23,25], the Ru($\eta^6$-naphthalene)($\eta^4$-cycloocta-1,5-diene)/acetonitrile system appears as one of the most convenient and long-lived catalyst for the isomerization of methyl linoleate. The selectivity in dienes with conjugated double bonds is very high ($\geq 95\%$) even at complete conversion and additional amounts of fresh methyl linoleate are easily isomerized as in the starting reaction mixture.

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