Journal of Organometallic Chemistry, 187 (1980) 391—403

SELECTIVE, HOMOGENEOUS HYDROGENATION OF CYCLOHEPTATRIENE TO CYCLOHEPTENE CATALYZED BY (η^4-CYCLOOCTA-1,5-DIENE)(η^6-CYCLOHEPTA-1,3,5-TRIENE)-RUTHENIUM(0)

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(Received September 4th, 1979)

Summary

In the presence of small amounts of [Ru(η^4-COD)(η^6-C_8H_{10})] (1), cycloheptatriene is hydrogenated to cycloheptene, under one atmosphere of hydrogen at room temperature in homogeneous phase. The formation of a small amount of cyclooctene and the existence of an induction period, which do not occur when [Ru(η^4-COD)(η^6-C_7H_8)] (2) is used as the catalyst, suggest that 2 is the real catalyst. The selectivity of this hydrogenation is 100% in n-hexane as solvent, 99.5% in THF, and low in ethanol. Conversion is quantitative in THF and ethanol, but not more than 65% in n-hexane. In the presence of 1 or 2, cycloheptene is rapidly hydrogenated to cycloheptane in THF and ethanol, but not in n-hexane. A mechanism for these catalytic hydrogenations is proposed, and discussed on the basis of the dominant role of the solvents. Increase of temperature and/or pressure of hydrogen increases the rate of hydrogenation.

Introduction

Although many papers have been published [1] on syntheses, structural studies, and reactivity of transition metal complexes of cyclic polyolefins, reports on their ability as catalysts or catalyst precursors are sparse [2]. The oligomerizations of acetylenes [3] and dienes and the co-oligomerizations of dienes with olefins [4], catalyzed by [Fe(η^4-COT)(η^6-COT)] (COT = cycloocta-1,3,5,7-tetraene), must be mentioned and the cyclooligomerizations of olefins catalyzed by [Ni(η^6-CDT)] (CDT = cyclododeca-1,5,9-treine) [5,6] are also interesting examples.

Ruthenium(0) complexes of cyclic polyolefins have been known for a long time [7—9], but the synthetic methods available, especially in the case of

complexes not containing carbonyl groups, give only limited amounts of products. This is no longer an inconvenience for $[Ru(\eta^4\text{-COD})(\eta^6\text{-}C_8H_{10})]$ (1) (COD = cycloocta-1,5-diene, C_8H_{10} = cycloocta-1,3,5-triene), which is obtained in fairly good yield (60—65%) by reduction of $RuCl_3 \cdot xH_2O$ with zinc dust in boiling ethanol, in the presence of excess of COD [10]. In ruthenium(0) complexes containing η^6-coordinated polyolefins one double bond can be easily displaced from the metal at room temperature by neutral, two electron, ligands, as shown in the following examples [9,11] (NBD = bicyclo[2.2.1]hepta-2,5-diene=norbornadiene):

$$[Ru(\eta^4\text{-NBD})(\eta^6\text{-COT})] + L \rightarrow [RuL(\eta^4\text{-NBD})(\eta^4\text{-COT})]$$

$L = CO, PPh_3, PPhMe_2, PEt_3, P(OMe)_3$

$$[Ru(\eta^4\text{-COD})(\eta^6\text{-}C_8H_{10})] + CO \rightarrow [RuCO(\eta^4\text{-COD})(\eta^4\text{-}C_8H_{10})]$$

This property may play an important role in the possible catalytic activity of $Ru(\eta^6$-polyolefin) complexes, by making available a vacant site for coordination to the metal. Ruthenium(0) complexes containing η^6-bonded COT, i.e. $[Ru(\eta^4\text{-NBD})(\eta^6\text{-COT})]$ and $[Ru(PPh_3)_2(\eta^6\text{-COT})]$, are reported to be active in the homogeneous hydrogenation of monoenes, in contrast to the related ruthenium(0) complexes containing η^4-bonded COT [9]. Similar activity has been reported for $[M(\eta^4\text{-}C_8H_{10})(\eta^5\text{-}C_8H_{10})]^+$ (M = Rh, Ir) [24].

On the basis of these considerations and of previous observations [12] on the role of molecular hydrogen in the substitution of $\eta^6\text{-}C_8H_{10}$ in 1 by several arenes and cyclic polyolefins, we undertook a study on the activity of 1 as a homogeneous hydrogenation catalyst or catalyst precursor. We describe below the features of the selective hydrogenation of cycloheptatriene (C_7H_8) to cycloheptene (C_7H_{12}).

Experimental

IR spectra were obtained in Nujol mulls between caesium iodide plates or in solution in sodium chloride cells, on a Perkin-Elmer 580 spectrophotometer, and calibrated against polystyrene. ^1H NMR spectra were recorded on a Varian-NV-14 or EM-390 spectrometer. Chemical shifts are relative to TMS as internal standard. Gas-chromatographic analyses were carried out on a Perkin-Elmer Sigma 3 apparatus, using a 2 m column packed with Carbowax 1500 or a 4 m column packed with 20% $AgNO_3$-ethyleneglycol on a Chromosorb P support.

Solvents were thoroughly degassed, dried over sodio-benzophenone ketyl (benzene, THF, diethyl ether) or sodium/potassium alloy (light petroleum, boiling range 40—60°C, n-hexane), and distilled before use. Cyclic poly- and mono-olefins were distilled under reduced pressure before use. Anhydrous ethanol (Fluka) was used without further treatment. $RuCl_3 \cdot xH_2O$ (39% Ru) was kept under vacuum at room temperature for at least 5 h before use. All apparatus and reagents were carefully degassed by several freeze and thaw cycles. All the syntheses and work-ups of the products were carried out under pure nitrogen unless otherwise specified.

(η^4-cyclooctadiene)(η^6-cyclooctatriene)ruthenium(0) (1)

The preparation of 1 was carried out as follows [10,12]. In a 100 ml flask,

equipped with magnetic bar, condenser, and inlet for nitrogen, $RuCl_3 \cdot xH_2O$ (0.8 g) is dissolved in anhydrous ethanol (10 ml) and COD (8 ml) added. After addition of zinc dust (90% zinc, 2 g) and shaking, the mixture becomes blue-grey and turns red-brown after few minutes. The flask is transferred to an oil bath at 85°C and stirred for 2 h. The mixture is then evaporated to dryness under high vacuum at room temperature, and the residue extracted three times with petroleum (40—60°C boiling range, 8 ml portions). The orange-yellow extract is concentrated to 5 ml and chromatographed on a neutral alumina column (reactivity III) with petroleum. A yellow band is removed and collected while a small red band remains on the top of the column ([Ru-(η^5-C_8H_{11})$_2$] [12]). The yellow solution is concentrated to 5 ml and cooled at —40°C, to give yellow needles which are collected after 24 h and dried. The yellow mother liquor is used as crystallizing solvent for other syntheses. The yield is 60—65%. ^{1}H NMR (in C_6D_6) τ: 4.76 (2 H), 5.28 (2 H), 6.19 (2 H), 7.06 (4 H), 7.78 (8 H), 8.32 (1 H), and 9.18 (1 H). When pure, the compound can be stored indefinitely at —5°C under pure nitrogen.

(η^4-cyclooctadiene)(η^6-cycloheptatriene)ruthenium(0) (2)

Complex 1 (0.15 g) is dissolved in THF (10 ml) and cycloheptatriene (1.5 ml) is added. The mixture is evacuated at —30°C and hydrogen is introduced. After warming to room temperature the mixture is stirred under H_2 atmosphere for 30 min. Evaporation to dryness in high vacuum and at room temperature, and extraction of the residue with petroleum (3 × 3 ml) gives an orange solution and a dark rose residue. The solution is concentrated and chromatographed on an alumina column (reactivity III) with petroleum. After evaporation the orange, oilysh solid is crystallized from petroleum at —30°C, to give pale orange crystals of 2, in 75% yield. ^{1}H NMR (in C_6D_6) τ: 4.50 (2 H), 5.32 (2 H), 6.80 (4 H), 7.25 (2 H), 7.70 (8 H), and 7.55—8.05 (2 H). The dark rose residue (about 15 mg) shows an IR band (nujol mulls) at 1980 cm^{-1}.

Catalytic hydrogenations

a) Cycloheptatriene (C_7H_8) at 1 atm of hydrogen. [Ru(η^4-COD)(η^6-C_8H_{10})] (1) (0.076 g) is placed in a 50 ml flask equipped with a magnetic bar, inlet for gas and a serum cap, and dissolved in 10.5 ml of solvent. The mixture is frozen and 1.1 ml of C_7H_8 are introduced with a microsyringe through the serum cap. The flask is evacuated and transferred to an oil bath equipped with a Beckman thermometer. When the temperature is equilibrated, H_2 is introduced at 1 atmosphere and the mixture stirred. From time to time a sample of the solution is removed with a microsyringe and examined by GLC. For results see below.

b) Cycloheptatriene under pressure. The same procedure as in a) is followed, but using as reactor a 100 ml stainless steel autoclave, equipped with a pressure meter. The autoclave is filled at the desired pressure, then shaken for 5 h and opened, and the mixture analyzed by GLC.

c) Cycloheptene. The procedure described under a) was used.

Results and discussion

IR analysis of solutions of [Ru(η^4-COD)(η^6-C_8H_{10})] (1) in n-hexane, alcohols or THF after treatment for few minutes with hydrogen, shows the presence of a broad band in the range 1983—1975 cm^{-1}, indicative of Ru—H bond formation. Dark, insoluble material eventually appears if the treatment with hydrogen is prolonged, while in aromatic solvents replacement of η^6-C_8H_{10} by the arene occurs *. If the hydrogenation is carried out in n-hexane, in the presence of cycloheptatriene, [Ru(η^4-COD)(η^6-C_7H_8)] (2) is obtained [12], while gas chromatographic analysis of condensable products as reaction proceeds, gives the results summarized in Table 1. A small amount of cyclooctene (C_8H_{14}) is also produced. Although no hydrogenation of the arenes occurs under these conditions **, the presence of cyclooctene in both cases suggests that the replacement of η^6-C_8H_{10} by arenes and cycloheptatriene in 1, in the presence of hydrogen, follows a similar pathway. In principle, cyclooctene could be formed by hydrogenation of the coordinated cyclooctadiene. However the recovery in high yields of the substitution products [Ru(η^4-COD)(η^6-arene)] and [Ru(η^4-COD)(η^6-C_7H_8)] (2), respectively, and the absence of C_8H_{14} when the hydrogenation is carried out in the presence of catalytic amount of 2 in place of 1, rule out this possibility.

As shown in Table 1, complex 1 is a catalyst or catalyst precursor for the selective hydrogenation of cycloheptatriene to cycloheptene under very mild conditions. The reaction mixture remains homogeneous for about 6 h, slow decomposition occurring after that time with concurrent decrease of the rate of hydrogenation. Conversion is limited to about 65%.

Catalytic hydrogenation of polyenes (mostly dienes) to monoenes is usually a step in the complete hydrogenation to the saturated hydrocarbons [16—19]. The selectivity of the process is determined, in most cases, by thermodynamic parameters related to the better binding ability of dienes compared to monoenes, so that the rate constant of the first hydrogenation step (i.e. the formation of monoene) is consistently higher than the rate constant of the second step (the complete hydrogenation). Examples of selectivity, refering to catalysts which hydrogenate dienes to monoenes but are inactive towards monoenes, have been reported (see, for instance ref. 20). Our experiments in n-hexane and other solvents are better interpreted in terms of the first type of proposals, as shown in the discussion.

In the hope of improving the conversion we examined this catalytic hydrogenation in other solvents. In ethanol the mixture remains homogeneous and a conversion of 100% is reached, with a higher rate of hydrogenation. Selectivity is lost however, since cycloheptane is also produced, the ratio cycloheptane/cycloheptene increasing with time *** (Table 2 and Fig. 1).

These results suggest that in ethanol two catalytic processes are operating,

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* Gas-chromatographic analysis of the condensable products reveals the presence of arene and small amount of cyclooctene.

** Hydrogenation of arenes to cyclic saturated hydrocarbons occurs readily in the presence of other ruthenium complexes, namely [Ru(η^4-C_6Me_6)(η^6-C_6Me_6)] [13], [RuHCl(PPh_3)(η^6-C_6Me_6)] [14], and [Ru(η^6-C_6Me_6)(μ-H)$_2$(μ-Cl)Ru(η^6-C_6Me_6)]Cl [15].

*** Experiments carried out in methanol and isopropanol gave comparable results.

TABLE 1

CATALYTIC HYDROGENATION OF CYCLOHEPTATRIENE IN THE PRESENCE OF 1 [a] IN n-HEXANE

Time (h)	Conversion (%)	C_7H_{14} (%)	C_7H_{12} (%)
6	33.3	0	100
15	51.2	0	100
24	60.2	0	100
28	62.3	0	100
40	65.0	0	100

[a] [1] = 1.01×10^{-2} *M*, C_7H_8/1 molar ratio = 46. Temperature = 20°C.

TABLE 2

CATALYTIC HYDROGENATION OF CYCLOHEPTATRIENE IN THE PRESENCE OF 1 [a] IN ETHANOL

Time (h)	Conversion (%)	C_7H_{14} (%)	C_7H_{12} (%)
2	11.2	40	60
4	35.5	60	40
6	57.2	70	30
8	76.8	80	20
15	100	97	3

[a] [1] = 1.07×10^{-2} *M*, C_7H_8/1 molar ratio = 43. Temperature = 20°C.

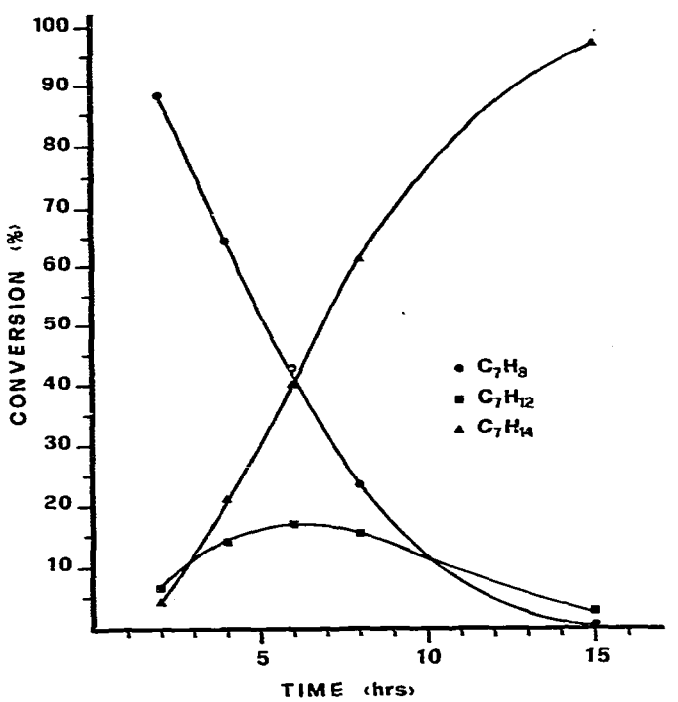


Fig. 1. Catalytic hydrogenation of cycloheptatriene to cycloheptene and cycloheptane, in ethanol, in the presence of 1; [1] = 1.07×10^{-2} *M*, [C_7H_8] = 0.465 *M*, temperature 20°C, p_{H_2} = 1 atm.

possibly involving two active intermediates. Since in the experiments in n-hexane, formation of a dark rose precipitate is associated with the absence of cycloheptane, it is reasonable to assume that the selectivity of the hydrogenation in the latter solvent is due to decomposition of the species possibly active in the hydrogenation of C_7H_{12}.

Experiments carried out in THF confirm the dominant role of the solvents in promoting or quenching complete hydrogenation. As shown in Table 3, the selectivity is maintained at about 99.5%, cycloheptane being formed only when cycloheptatriene is practically absent. Conversion is quantitative.

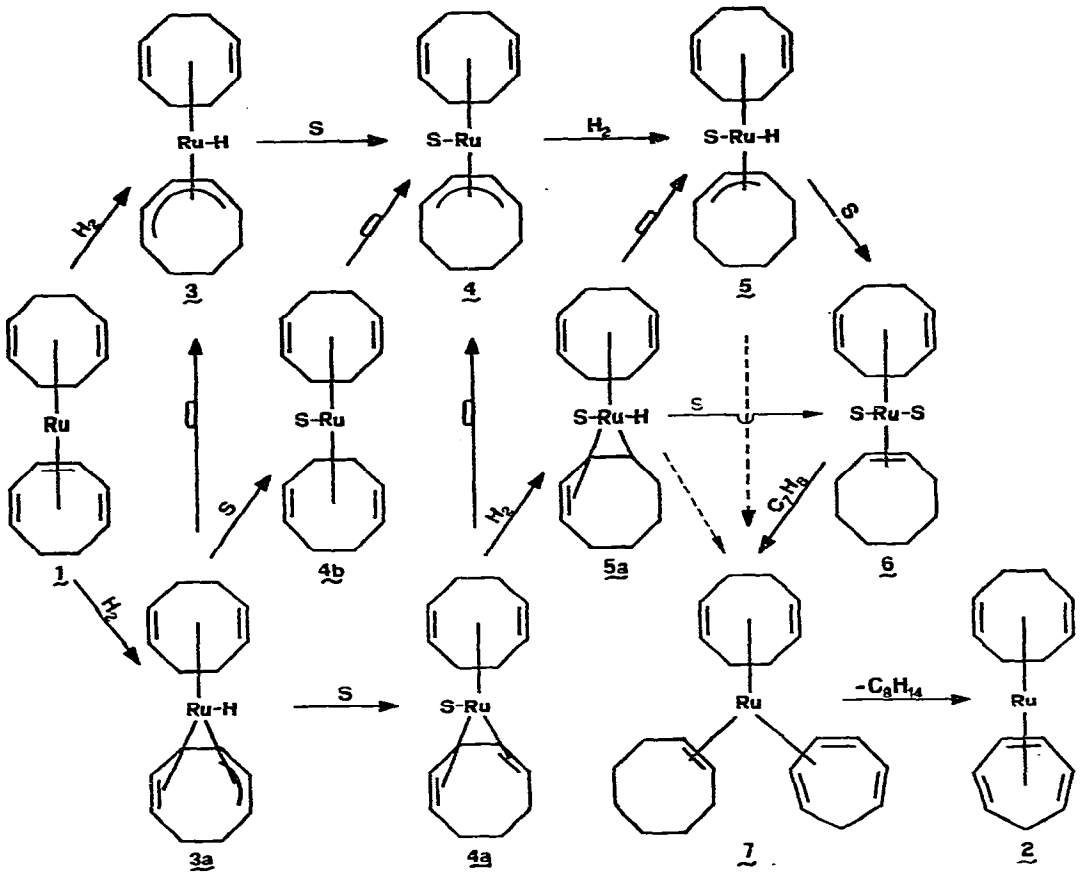
Comparison of the results obtained in the three solvents provides some insight into the mechanism of hydrogenation, although we are not confident that reliable kinetic parameters can be obtained from our data. While the formation of cycloheptane probably follows the same path in each solvent, the selectivity of the process, i.e. the absence of cycloheptane, is solvent dependent. The first step is probably the addition of hydrogen to 1 with formation of a dienyl hydrido ruthenium(II) complex (3) (Scheme 1). A related complex $[RuH(PPh_3)_2(\eta^5\text{-}C_6H_7)]$ (C_6H_7 = cyclohexadienyl) has been recently isolated and characterized by X-ray analysis [21]. Insertion of the coordinated dienyl unit into the Ru—H bond should give the dieneruthenium(0) complex 4, which is coordinatively unsaturated. The vacant site in 4 can, however, be occupied by a molecule of solvent or alternatively by η^2-cycloheptatriene. The latter possibility appears very likely in the case of n-hexane owing to its low coordinating ability. Coordinatively unsaturated complexes of ruthenium(0) are known. An interesting example is $[Ru(PPh_3)_2(\eta^2\text{-}C_8H_7)_2]$ [22] (C_8H_8 = styrene). Coordination around the metal is best described in terms of a highly distorted tetrahedron [23], but molecules of solvent are found between two crystallographic independent molecules of the complex. Therefore considering the larger steric hindrance of the two triphenylphosphines and of the two styrenes compared to the ligands in 4, it is likely that the complex is not coordinatively unsaturated in our case. Further addition of hydrogen to give 5, followed by insertion of the enyl into the Ru—H bond and concomitant coordination of cycloheptatriene in η^4-fashion should give 7. If S in 5 is a molecule of solvent the formation of 7 may occur through 6. Expulsion of cyclooctene produces 2. Although the mechanism of substitution of $\eta^6\text{-}C_8H_{10}$ with $\eta^6\text{-}C_7H_8$ described above appears plausible, other intermediates can give the same final product. For instance the dienyl complex can have the isomeric form 3a. Depending on the position of insertion

TABLE 3

CATALYTIC HYDROGENATION OF CYCLOHEPTATRIENE IN THE PRESENCE OF 1 [a], IN THF

Time (h)	Conversion (%)	C_7H_{14} (%)	C_7H_{12} (%)
5	28.3	0	100
8	69.1	0.1	99.9
10	83.2	0.1	99.9
20	100	0.5	99.5
35	100	60	40

[a] [1] = 1.09×10^{-2} *M*, C_7H_8/1 molar ratio = 44. Temperature = 20° C.

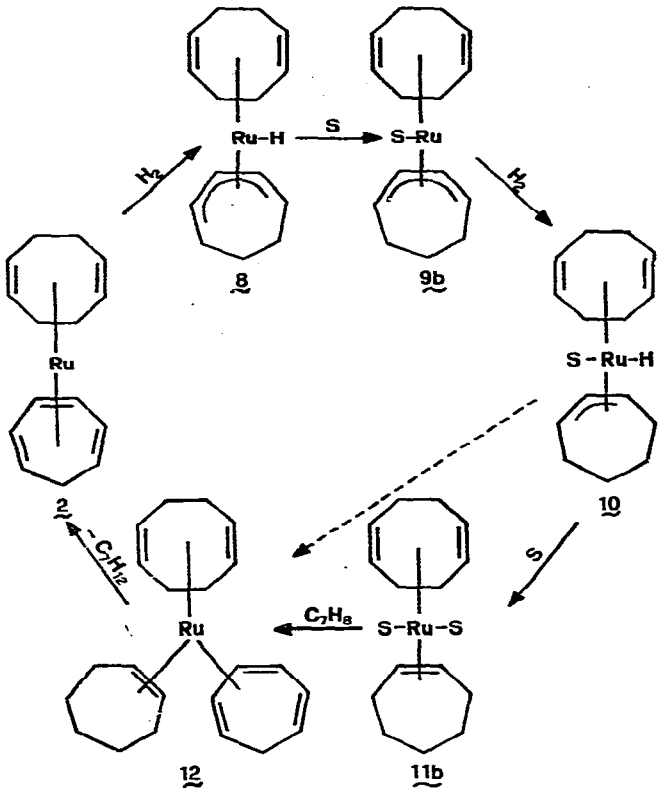


SCHEME 1. Proposed mechanism of formation of 2 from 1. If S in 4 and 5 is η^2-cycloheptatriene, intermediate 6 can be omitted (see discussion).

of the allyl unit into the Ru—H bond of 3a, either 4a or 4b is then formed. While further addition of hydrogen can be accomplished with 4a to give 5a, which eventually isomerizes to 5, isomerization of 4b to 4 must occur before hydrogenation. The yield of 2 from 1 is, indeed, high enough to exclude hydrogenation of coordinated 1,5-COD. In the presence of $[PdCl(PPh_3)_2(\eta^3\text{-allyl})]_2$ 1,5-COD is isomerized to 1,3-COD, before being hydrogenated, selectively, to cyclooctene [20].

Although we have no experimental data (attempts to isolate possible intermediates during the various hydrogenations were unsuccessful) to enable a choice to be made between 3 and 3a, and between 4, 4a, and 4b, we prefer the first mechanism discussed. In any case the formation of 2, the real catalytic species in the selective hydrogenation of cycloheptatriene, initiates the catalytic cycle described in Scheme 2 *. That 2 is the real catalyst is demonstrated by the absence of the short induction period in the hydrogenation experiments (see Figs. 2 and 3) when 2 is used directly as catalyst in place of 1. The rates of hydrogenation in the two cases are comparable.

* Formation of isomeric hydrido- and olefin-ruthenium complexes as is shown in Scheme 1 is also possible in Scheme 2.



SCHEME 2. Proposed catalytic cycle in the selective hydrogenation of C_7H_8 to C_7H_{12}, in the presence of 2. If S in 9b and 10 is η^2-cycloheptatriene, intermediate 11b can be omitted (see Discussion).

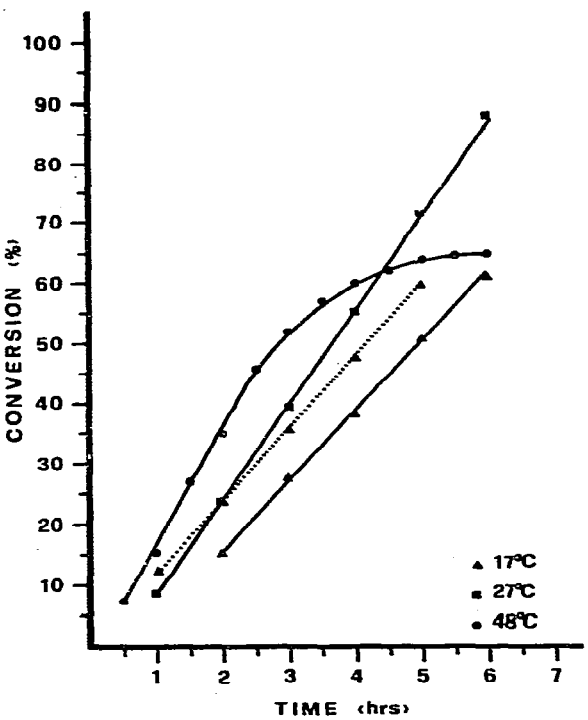


Fig. 2. Catalytic hydrogenation of cycloheptatriene to cycloheptene, in THF, (full lines, in the presence of 1, dotted line, in the presence of 2) [1] or [2] = 2.08×10^{-2} M, $[C_7H_8] = 0.915$ M, $p_{H_2} = 1$ atm (Conversion % against time).

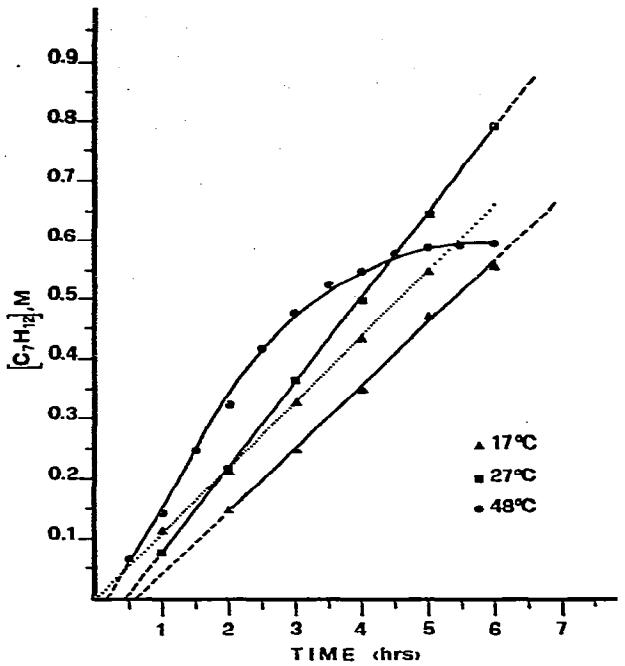
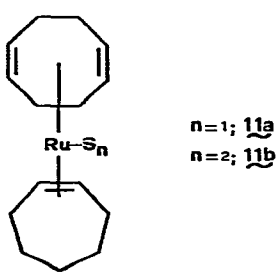


Fig. 3. Catalytic hydrogenation of cycloheptatriene to cycloheptene, in THF, (full lines, in the presence of 1, dotted line, in the presence of 2) [1] or [2] = 2.09×10^{-2} *M*, $[C_7H_8] = 0.915$ *M*, $p_{H_2} = 1$ atm. (Moles of C_7H_{12} against time).

If in the intermediate 9b (Scheme 2) we assume that a molecule of solvent is coordinated, the second uptake of hydrogen followed by insertion of the enyl unit into the Ru—H bond should give a solvato, sixteen electron intermediate (11a) or, more likely, a disolvato intermediate 11b. Whichever is the

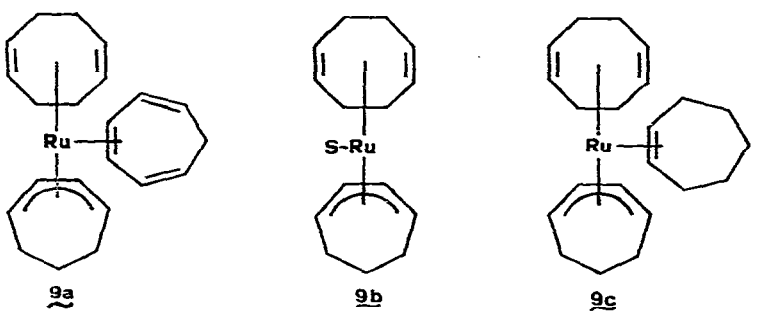


n=1; 11a
n=2; 11b

case, cycloheptatriene, a better bidentate coordinating ligand, can replace the molecules of solvents to give 12, from which cycloheptene should be easily displaced to reform 2. However, when THF is the solvent, after the complete conversion of C_7H_8 to C_7H_{12}, further hydrogenation occurs and cycloheptane is rapidly formed. Addition of cycloheptatriene just before the conversion $C_7H_8 \rightarrow C_7H_{12}$ is complete, inhibits formation of C_7H_{14} and the added cycloheptatriene is again converted into cycloheptene. Under similar experimental conditions, cycloheptene is indeed rapidly hydrogenated in THF to cycloheptane in the presence of catalytic amount of 1. The results obtained in THF thus

parallel in terms of mechanism, the formation of both C_7H_{12} and C_7H_{14} in ethanol. The inhibition to the hydrogenation to cycloheptane in THF, caused by the presence of cycloheptatriene (Table 3), is evidently not observed in ethanol (Table 2). In n-hexane the decomposition of the intermediate which catalyzes the production of cycloheptane allows a selectivity of 100% (Table 1) but a conversion limited to 65%. The most rational explanation of this observation is the preferential coordination of cycloheptene when present in excess with respect to cycloheptatriene, and subsequent decomposition of the species initially formed. An alternative explanation, that the n-hexane disolvato complex **11b** decomposes when the C_7H_8/C_7H_{12} ratio is less than one, is less attractive because of very low coordinating ability of n-hexane. Accordingly no hydrogenation of cycloheptene is obtained after 12 h in n-hexane, in the presence of **1**. Moreover, removal of condensable products from the reaction residue resulting from the synthesis of **2** in THF and subsequent extraction with n-hexane, gives a rose-brown, insoluble material [ν(Ru—H) at 1980 cm^{-1}] in small amount. Attempts to promote hydrogenations of unsaturated cyclic C_7 hydrocarbons in THF in the presence of this hydride * were unsuccessful, in keeping with the other results of the catalytic hydrogenations in n-hexane.

Competition among solvent, cycloheptatriene, and cycloheptene for coordination to the metal must be invoked during the various steps of the catalytic cycles. Of interest is to decide at what stage of the cycle of Scheme 2 the catalytic process which gives cycloheptane starts. It is reasonable to assume that this must be after the addition of the second molecule of hydrogen. In fact whatever is the form of the intermediate **9**, i.e.:

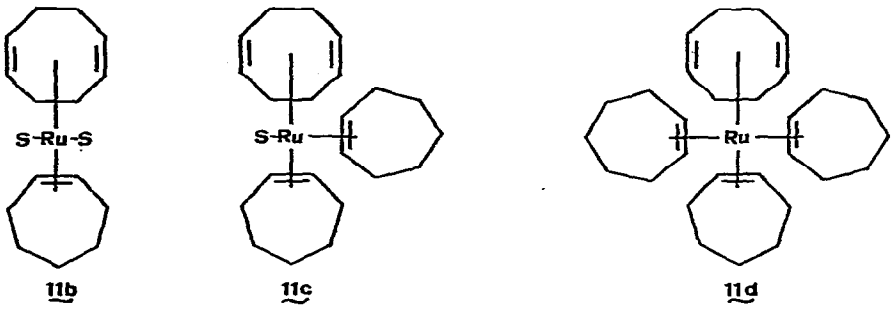


9a **9b** **9c**

further steps must be addition of hydrogen and insertion of the enyl moiety into the Ru—H bond, as suggested previously, to give **11**. Excluding intermediate **9a**, which clearly points to the catalytic cycle of Scheme 2, the possible combinations arising from **9b** and **9c** by addition of solvent or cycloheptene are shown as **11b**, **11c** and **11d**.

We must assume that THF is preferentially coordinated compared with cycloheptene, so that it can be easily displaced from **11b** only by the better coordinating η^4-cycloheptatriene to give **12**. When cycloheptatriene is pratically absent, further addition of hydrogen can occur and production of cycloheptane begins through the cycle **11b** $\rightleftharpoons$ **13a** (Scheme 3). With ethanol as solvent, there is evidently no discrimination between cycloheptene, cycloheptatriene and

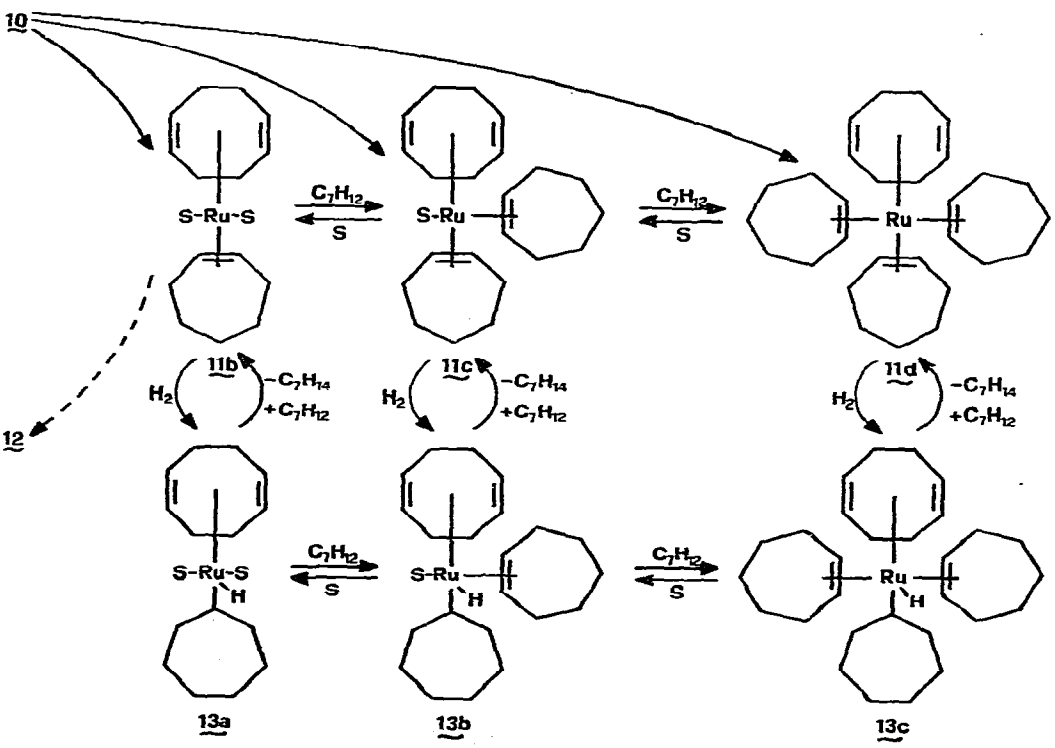
* Note added in proof; this compound is a ruthenium cluster with hydrido bridges.



the solvent. The formation of cycloheptane, in this case, can also occur through 11c or 11d.

A ruthenium(0) complex containing three coordinated molecules of cyclohexene, namely $[Ru(PPh_3)_2(C_6H_{10})_3]$, has been proposed as intermediate in the catalytic disproportion of cyclohexene to benzene and cyclohexane (1 to 2 ratio) [21].

Once we established that THF as solvent gives the best combination of selectivity and conversion, we studied the influence of other factors on the catalytic hydrogenation of cycloheptatriene. In Figs. 2 and 3 are shown the effects of change of temperature. In each case, except when 2 is the catalyst, a small induction period (Fig. 3) is found, which is consistent with the time for



SCHEME 3. Intermediates in the catalytic hydrogenation of C_7H_{12} to C_7H_{14}. The cycle 11b ⇌ 13a is likely with S = THF, the others (11c ⇌ 13b, 11d ⇌ 13c) with S = ethanol.

TABLE 4

EFFECT OF PRESSURE ON THE CATALYTIC HYDROGENATION OF CYCLOHEPTATRIENE IN THE PRESENCE OF 1 [a] IN THF

p_{H_2} (atm)	Conversion (%)	C_7H_{14} (%)	C_7H_{12} (%)
1.0	28.3	0	100
2.7	43.6	0.3	99.7
4.0	51.5	1.1	98.9

[a] Reaction conditions: [1] = 1.09×10^{-2} *M*, C_7H_8/1 molar ratio = 44. Temperature = 20°C. Products analyzed after 5 h.

the production of 2 (Scheme 1). The drastic decrease in the hydrogenation rate after three hours at +48°C is due to decomposition of the catalyst. The turnover number, i.e. the number of moles of substrate hydrogenated per mol of catalyst, calculated from Fig. 3, is 0.082, 0.108, and 0.162 mol/min at 17°C, 27°C, and 48°C, respectively. The value found when 2 is used as catalyst is practically the same (0.086 mol/min at 17°C).

Increase in the pressure of hydrogen also has a positive effect on the conversion (Table 4). Although the limited number of experiments allows only qualitative conclusions, the increase in hydrogen pressure seems to decrease the selectivity of the process slightly.

Finally we observed that dilution substantially decreases the rate of hydrogenation (compare data in Table 3 and Fig. 2), while minor changes are found on varying the concentration of the substrate.

At present we are investigating the catalytic hydrogenations of other substrates (1,5,9-CDT, linear conjugated and unconjugated dienes, 1,3-COD and 1,5-COD) in the presence of 1 to see if the selectivity can be extended to linear polyolefins and to establish the role of conjugated double bonds in these processes.

Acknowledgements

We thank C.N.R. and the Ministero della Pubblica Istruzione for financial support.

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