The Ru(η^6 -naphthalene)(η^4 -1,5-cyclooctadiene)/ acetonitrile system as a homogeneous catalytic precursor for the fast isomerization of 1,5-cyclooctadiene and 1-hexene *

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Abstract

1,5-Cyclooctadiene and 1-hexene undergo isomerization to 1,3-cyclooctadiene and (E)-/(Z)-2-hexene, respectively, with high turnover number in the presence of the complex Ru(η^6 -naphthalene)(η^4 -1,5-cyclooctadiene) and acetonitrile. This high catalytic activity is observed only using acetonitrile as co-catalyst. A possible reaction mechanism, based on results from an ^{1}H and ^{2}H NMR study of the isomerization, is presented.

Introduction

In recent years various arene-transition metal compounds in which a mononuclear or polynuclear aromatic molecule is η^6 -bonded to the metal have been prepared [1]. Polynuclear arenes are generally less firmly bonded to the metal than mononuclear arenes [2]; they are easily displaced from the metal by other ligands and their complexes often show catalytic activity under less vigorous conditions than those required for complexes of the corresponding mononuclear aromatic compounds.

Recently [3] convenient syntheses of the complex Ru(η^6 -C $_{10}$ H $_8$)(η^4 -1,5-COD), **1**, (C $_{10}$ H $_8$ = naphthalene; COD = cyclooctadiene) were reported, and it was shown that, in the presence of acetonitrile, naphthalene is readily displaced by mononuclear aromatic compounds.

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* Dedicated to Professor Peter Pauson on the occasion of his retirement.

The lability of η^6-naphthalene is an important factor in the effectiveness of its complexes in homogeneous catalysis, and we have begun a comparison of the catalytic properties of 1 with those of related mononuclear aromatic derivatives. Here we report a study of the catalytic isomerization of 1,5-cyclooctadiene and 1-hexene in the presence of 1 or one of the analogous complexes Ru(η^6-arene)(η^4-1,5-COD), (arene = benzene, 2, and *p*-cymene, 3).

Experimental

The catalytic precursors 1–3 were prepared as previously reported [3,4]. Tetrahydrofuran was dried by refluxing over sodium and LiAlH$_4$ under argon before distillation. (*Care!* *) 1,5-COD and 1-hexene were distilled prior to use and stored under argon. Acetonitrile was purified by distillation from CaH$_2$ and P$_4$O$_{10}$ under argon.

The isomerization experiments were carried out under argon in a two-necked round-bottomed flask equipped with a magnetic bar and a serum cap. In a typical experiment 1 (47.2×10^{-3} g, 0.14 mmol) was placed in the reaction vessel and dissolved in THF (20 ml). Acetonitrile (0.145 ml, 2.8 mmol) was introduced, the solution was stirred for a few minutes at room temperature, and 1,5-COD (1.2 ml, 1×10^{-2} mol) was added. Liquid samples were removed through the serum cap with a syringe and analyzed by GLC on a Dani 6800 chromatograph equipped with 2 m × 0.4 cm columns of 10% SE30 or 10% TCEP or 5% CW 20 M on 60/80 mesh Chromosorb WAW DCMS and a flame-ionization detector; nitrogen was used as carrier gas. Analysis of the products of the 1-hexene isomerization was also carried out by use of a Perkin–Elmer 8500 gas chromatograph equipped with a 12 m × 0.22 mm BP1 capillary column, using helium as carrier gas. The runs at 60°C were carried out in a constant temperature bath (± 0.2°C), the flask being fitted with a reflux condenser.

^{1}H NMR studies were carried out on solutions of 1 in THF-d_8 in a 5 mm o.d. NMR tube to which were added CD$_3$CN and 1,5-COD. The growth in the signals of the products was monitored on a Varian VXR-300 NMR spectrometer at various probe temperatures in the range -20°C to 30°C. The ^{2}H NMR spectra were recorded at 46 MHz on a Varian VXR-300 spectrometer.

Results and discussion

The results obtained in the isomerization of 1,5-COD to 1,3-COD at 20°C and 60°C catalyzed by complexes 1–3 are shown in Table 1. Complex 1 is very active in the presence of acetonitrile. At 20°C isomerization to 1,3-COD is complete after 240 min, with a turnover number of 0.3 min^{-1} (run 1). The catalytic activity increases as the molar ratio CH$_3$CN/1 is increased (runs 2–4) and reaches a maximum at $n = 20$ (run 4, turnover number = 0.48 min^{-1}). The presence of acetonitrile is essential for high catalytic activity; isomerization is very slow in its absence. Thus at 20°C only 4% of 1,3-COD is formed in 24 hours, and at 60°C only 18% of 1,3-COD in 3 hours (runs 5 and 6). At the end of the reaction the

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* A referee has pointed out that refluxing of solutions of LiAlH$_4$ in THF can be very hazardous, and should be avoided.

Table 1

Isomerization of 1,5-cyclooctadiene with Ru(η^6-arene)(η^4-1,5-COD) complexes, 1-3 [a]

Run	Catalyst	CH$_3$CN (mmol)	$\dfrac{\text{CH}_3\text{CN}}{\text{Catalyst}}$ (mol/mol)	Temperature (°C)	Time (min)	1,3-COD (%)	Number of cycles $\left(\dfrac{\text{mol substrate}}{\text{mol catalyst min}}\right)$
1	1	0.42	3	20	240	100	0.3
2	1	1.4	10	20	180	100	0.4
3	1	2.1	15	20	155	100	0.46
4	1	2.8	20	20	150	100	0.48
5	1	–	–	20	1440	4	0.002
6	1	–	–	60	180	18	0.07
7 [b]	Reaction mix. of run 4		(20)	20	155	100	0.46
8 [c]	1	2.8	20	20	150	76	0.36
9	2	2.8	20	20	1440	–	–
10	2	–	–	20	1440	–	–
11	3	2.8	20	20	1440	–	–
12	3	–	–	20	1440	–	–
13	2	2.8	20	60	180	9	0.036
14	2	–	–	60	180	9	0.036
15	3	2.8	20	60	180	10	0.04
16	3	–	–	60	180	10	0.04

[a] Reaction conditions: Ru(η^6-arene) (η^4-1,5-COD), 0.14 mmol; 1,5-COD, 1.2 ml (10^{-2} mol); THF, 20 ml. [b] Fresh 1,5-COD (1.2 ml) has been added. [c] Carried out in pentane (20 ml).

red-brown solutions are clear, and do not contain suspended solids. This solution maintains its activity unchanged. Additional 1,5-COD is isomerized at the same rate as that observed during the first reaction (run 7).

In contrast to the behaviour of 1, complexes 2 and 3 do not catalyze the isomerization in 24 hours at 20°C (runs 8–11), and at 60°C only 10% of 1,3-COD is obtained in 3 hours (runs 12–15). Moreover, in these conditions acetonitrile has no effect on the rate of isomerization (compare runs 9 and 10, 11 and 12, 13 and 14, 15 and 16). These results indicate that 1 is catalytically more active than 2 or 3, even in the absence of acetonitrile.

Figure 1 shows the change in composition with time for the isomerization of 1,5-COD catalyzed by 1 in the presence of acetonitrile (molar ratio CH$_3$CN/1 = 20). It is noteworthy that 1,4-COD, which is usually observed as an intermediate in this reaction [5], was not detected in this case. The reaction profile is consistent with a first-order process with a rate constant of 2.66×10^{-2} min^{-1}.

Similar results were obtained in the isomerization of 1-hexene (Table 2). In the presence of acetonitrile at 20°C 1-hexene is isomerized by 1 to a 75/25 mixture of (E)-/(Z)-2-hexenes in 120 min, with a turnover number of 0.6 min^{-1} (run 17). No further isomerization of this mixture to (E)- and (Z)-3-hexenes is observed. In absence of acetonitrile the isomerization is very slow (run 18). Complexes 2 and 3, in the presence or absence of acetonitrile, do not catalyze the isomerization of 1-hexene at 20°C (runs 19–22).

Some information on the course of the isomerization of 1,5-COD has been obtained by observing the changes in the ^{1}H NMR resonances of the products and the catalytic precursors at various times in the temperature range −20°C to 30°C.
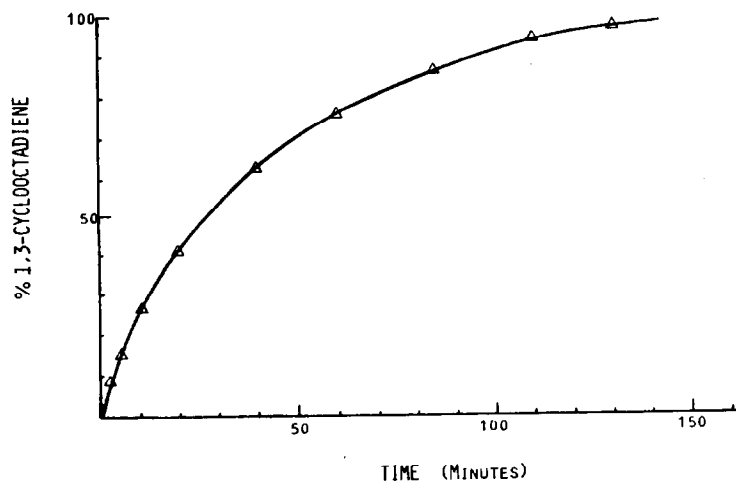
% 1,3-CYCLOOCTADIENE (vertical axis)

TIME (MINUTES) (horizontal axis)

Fig. 1. Isomerization of 1,5-cyclooctadiene catalyzed by $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}COD)/CH_3CN$ (molar ratio 1/20) at 20°C in tetrahydrofuran.

Figure 2a shows the ^1H NMR spectrum of **1** in THF-d_8 at −20°C, showing resonances due to the coordinated 1,5-COD at 1.79 ppm and 3.50 ppm and those of the coordinated naphthalene at 4.86 ppm, 6.22 pmm, 7.51 ppm and 7.61 ppm. The addition of acetonitrile-d_3 to this solution liberates some free naphthalene which gives rise to the signals at 7.62 ppm and 7.99 ppm in the ^1H NMR spectrum (Fig. 2b). When the substrate is added slow isomerization takes place at −20°C to give 1,3-COD, whose presence is indicated by the appearance in the ^1H NMR spectrum of signals at 1.61 ppm and 2.31 ppm (methylene absorptions) and 5.72 ppm and 5.90 ppm (olefinic absorptions) (Fig. 2c). The strong signals at 2.47 ppm and 5.58 ppm are due to the added 1,5-COD. When the temperature is raised to 30°C complete isomerization occurs; the signals due to **1** completely disappear and the signals of free naphthalene are observed between 7 and 8 ppm (Fig. 2d), indicating that the naphthalene ligand is displaced during the isomerization.

Some evidence for coordination of acetonitrile to ruthenium was obtained from ^2H NMR studies. Figure 3a shows the signal at 2.05 ppm of CD_3CN in THF. When

Table 2

Isomerization of 1-hexene with $Ru(\eta^6\text{-arene})$ $(\eta^4\text{-}1,5\text{-COD})$ complexes **1–3** at room temperature [a]

Run	Catalyst	CH_3CN (mmol)	$\dfrac{CH_3CN}{Catalyst}$ (mol/mol)	Time (min)	(E)- and (Z)- -2-hexene [b] (%)	Number of cycles $\left(\dfrac{\text{mol substrate}}{\text{mol catalyst min}}\right)$
17	**1**	2.8	20	120	100	0.6
18	**1**	–	–	1440	10	0.005
19	**2**	2.8	20	1440	–	–
20	**2**	–	–	1440	–	–
21	**3**	2.8	20	1440	–	–
22	**3**	–	–	1440	–	–

[a] Reaction conditions: $Ru(\eta^6\text{-arene})$ $(\eta^4\text{-}1,5\text{-COD})$, 0.14 mmol; 1-hexene, 1.25 ml (10^{-2} mol); THF, 20 ml. [b] $E/Z = 75/25$.
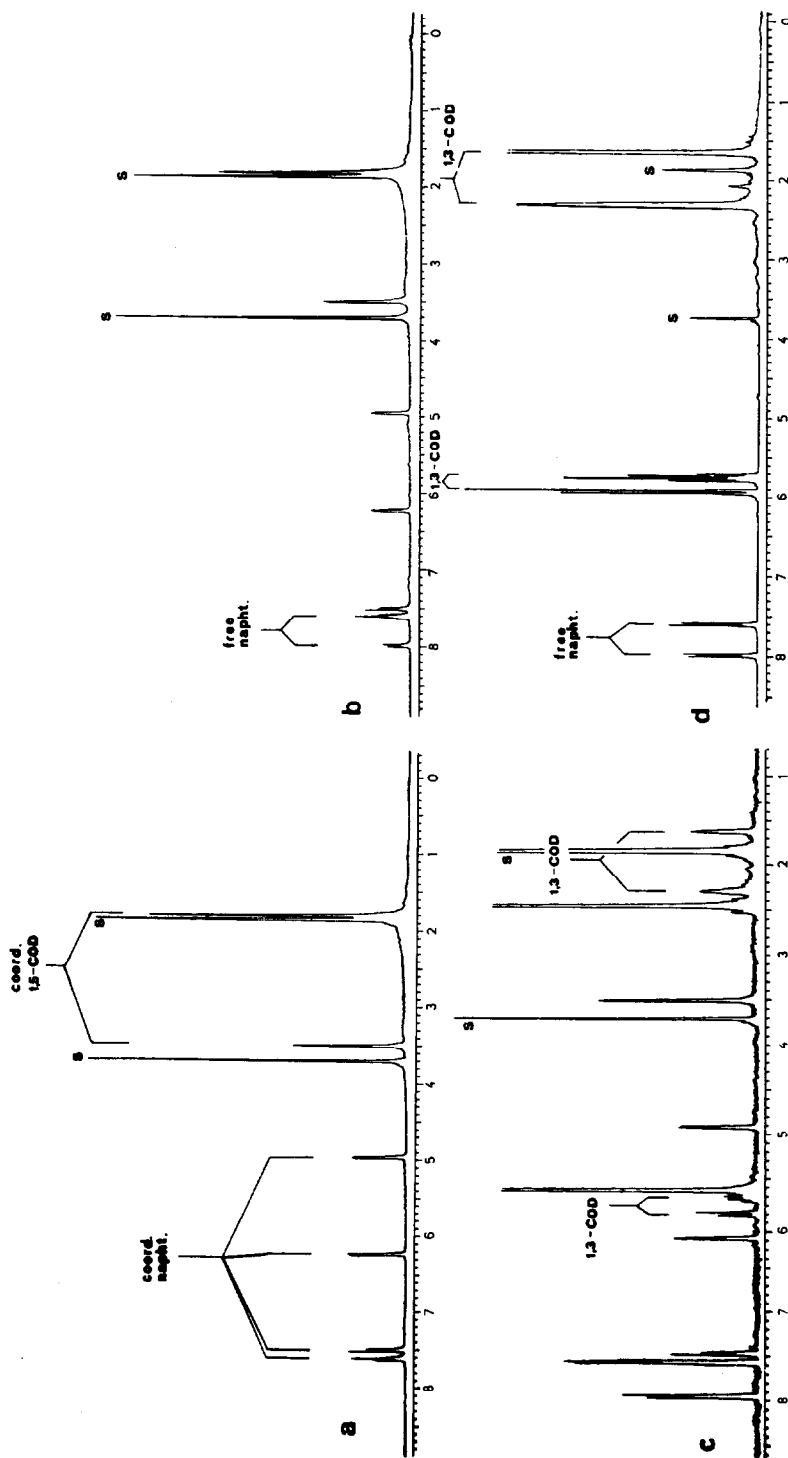
Fig. 2. ^{1}H NMR spectra (300 MHz, THF-d_8, $-20\,^\circ$C) relative to the isomerization of 1,5- to 1,3-cyclooctadiene: (a) Ru(η^6-C$_{10}$H$_8$)(η^4-1,5-COD), 1; (b) Complex 1+CD$_3$CN; (c) Complex 1+CD$_3$CN+1,5-COD, initial step; (d) End of the isomerization (30 $^\circ$C).
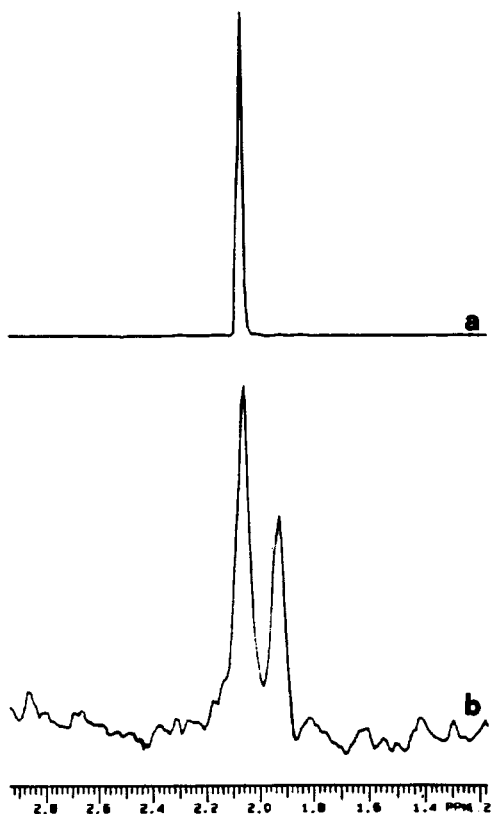
Fig. 3. ^{2}H NMR spectra (46 MHz, THF) of: (a) CD_3CN; (b) $CD_3CN + Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}COD)$.

1 is added to this solution two signals appear (Fig. 2b), at 2.05 ppm and 1.92 ppm, and these are attributed to free and bound CD_3CN, respectively.

Preliminary studies on the effect of ligands such as dimethylphenylphosphine (PMe_2Ph) and pyridine (Py) on the isomerization of 1,5-COD in the presence of $1/CH_3CN$ were carried out. Addition of PMe_2Ph ($PMe_2Ph/1 = 1$ or 2) causes only a small decrease in the rate of isomerization, and, when the ratio $PMe_2Ph/1$ is 4, the isomerization is completely inhibited (Fig. 4a). In contrast, addition of pyridine causes a slow fall in the isomerization rate as the molar ratio $Py/1$ is increased; the isomerization is completely suppressed only in the presence of a large excess of pyridine ($Py/1 = 40$) (Fig. 4b).

The following conclusions may be drawn from the above results:

1. Complex **1** in the presence of acetonitrile is the precursor of a very active catalyst for the isomerization of 1,5-COD and 1-hexene to 1,3-COD and (E)-$/(Z)$-2-hexene, respectively. Free naphthalene is generated when acetonitrile is added to **1**, in THF-d_8. The acetonitrile displaces η^6-bonded naphthalene, probably via η^4- and η^2-naphthalene-ruthenium intermediates [6], binding to the metal and forming a new species that catalyzes the fast isomerization of the substrate. Moreover, the stability of the mononuclear arene–ruthenium bond [6] accounts for the failure of the $2/CH_3CN$ and $3/CH_3CN$ systems to bring about isomerization at room temperature; no displacement of the bonded arene by acetonitrile is observed under
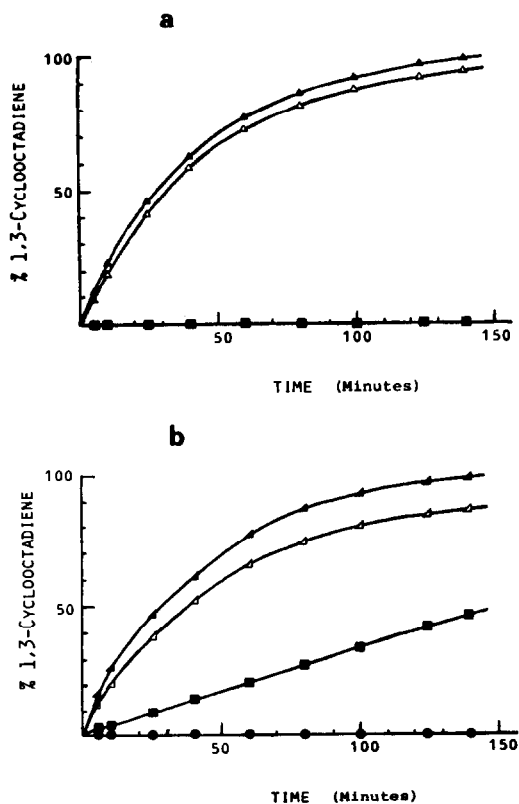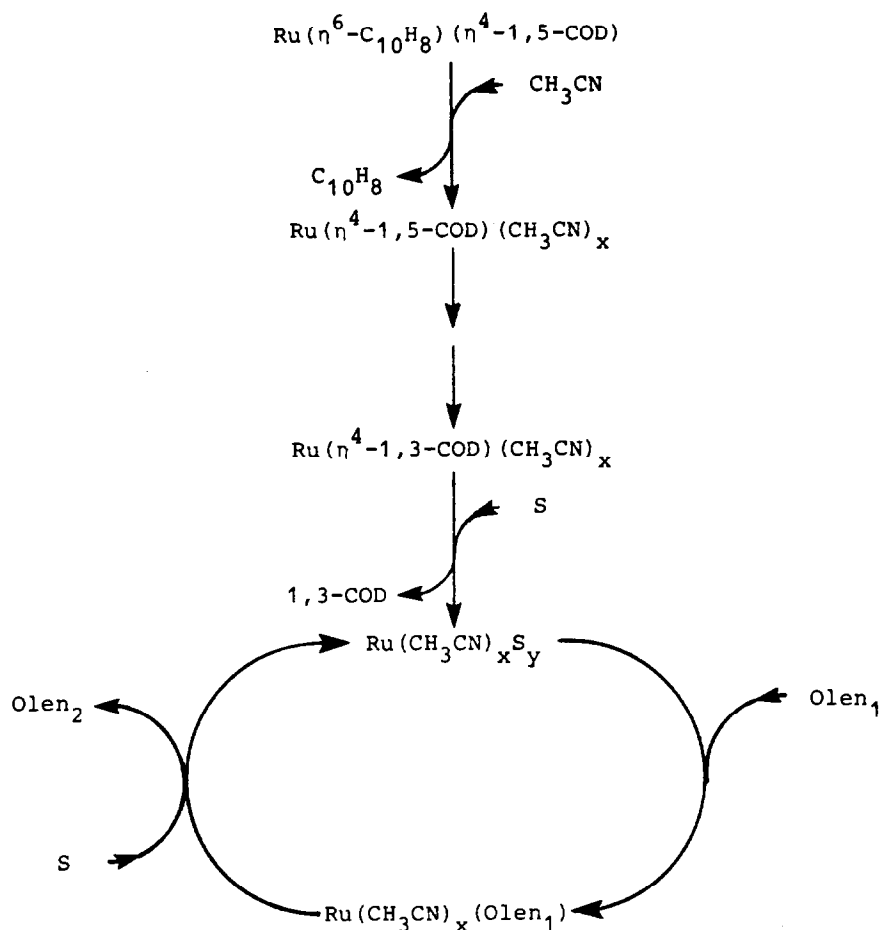
Fig. 4. Isomerization of 1,5-cyclooctadiene catalyzed by $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-COD})/CH_3CN$ (molar ratio 1/20) at 20°C in tetrahydrofuran; the effects of addition of molar equivalent of ligands L on the catalytic activity. (a) L = PMe$_2$Ph: closed triangles, 1.0; open triangles, 2.0; closed squares, 4.0; (b) L = Py: closed triangles, 1.0; open triangles, 4.0; closed squares, 10.0; closed circles, 40.0.

these conditions. The better catalytic properties of **1** than either **2** or **3** observed even in the absence of acetonitrile can also be related to the differences in the stability of the arene–ruthenium bonds [6,7].

2. Since the isomerization occurs in the absence of hydrogen in a solvent such as THF, which has low tendency to donate hydrogen atoms, the reaction probably proceeds stepwise via η^3-enyl ruthenium hydride intermediates [8]. The fact that free 1,4-COD, the thermodynamically least stable isomer, is not observed in the isomerization of 1,5-COD suggests that the diolefin is very rapidly isomerized to 1,3-COD during the catalytic cycle. The stoichiometric isomerization of 1,5- to 1,3-COD without the intermediate formation of 1,4-COD has been recently reported in the reaction of $Ru(\eta^6\text{-cycloocta-1,3,5-triene})(\eta^4\text{-1,5-COD})$ with arenes in the presence of HPF$_6$ [9]. With 1-hexene, selective isomerization to (E)-/(Z)-2-hexenes is observed, indicating that 2-hexenes are quickly displaced from the metal before they can be further isomerized to 3-hexenes.

3. The solvent plays an important role in the isomerization by stabilizing intermediate species. In THF the red-brown solution remains clear during and at the end of the reaction, and the catalyst it contains is still active. Thus when fresh olefin is added isomerization starts again at the same rate (run 7, Table 1). With

$$Ru(\eta^6-C_{10}H_8)(\eta^4-1,5-COD)$$

$$\downarrow \leftarrow CH_3CN$$

$$C_{10}H_8 \leftarrow$$

$$Ru(\eta^4-1,5-COD)(CH_3CN)_x$$

$$\downarrow$$

$$Ru(\eta^4-1,3-COD)(CH_3CN)_x$$

$$\downarrow \leftarrow S$$

$$1,3-COD \leftarrow$$

$$Ru(CH_3CN)_x S_y$$

Olen$_2$ ←   → Olen$_1$

S →

$$Ru(CH_3CN)_x(Olen_1)$$

Scheme 1. Proposed catalytic cycle for the isomerization of 1-hexene and 1,5-cyclooctadiene by Ru(η^6-C$_{10}$H$_8$) (η^4-1,5-COD). The upper part of the scheme represents the catalyst activation and the lower part represents the cycle itself. The isomerization of the double bonds via η^3-allylhydride species is not shown [8]. Olen$_1$ = (a) 1-hexene; (b) 1,5-cyclooctadiene; Olen$_2$ = (a) (E)- and (Z)-2-hexene; (b) 1,3-cyclooctadiene; S = solvent or acetonitrile.

pentane as solvent the rate of reaction is lower (run 8, Table 1) and a large amount of solid material is formed.

4. A strong donor ligand such as PMe$_2$Ph completely inhibits the isomerization of 1,5- to 1,3-COD when the molar ratio PMe$_2$Ph/$1 \geqslant 4$, probably by binding to free coordination sites on the ruthenium, thus preventing the approach of 1,5-COD and its subsequent isomerization.

Taken together these observations indicate that the catalytically active species is a labile intermediate of the type Ru(CH$_3$CN)$_x$S$_y$ (S = solvent or acetonitrile) (Scheme 1). It is generated by displacement of naphthalene from ruthenium by acetonitrile and by the removal of 1,5-COD as 1,3-COD, either by the solvent or by acetonitrile. The solvent and the acetonitrile stabilize the ruthenium and prevent the precipitation of ruthenium metal when all the substrate has undergone isomerization.

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