Structure and Reactivity of Aromatic Polymers/Ruthenium Catalysts

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Dedicated to Professor Dr. Dr. h. c. mult. Günther Wilke on the occasion of his 60th birthday

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Hydrogenations, Heterogeneous Catalysts, Ruthenium/Aromatic Vinyl Polymer Systems, Ruthenium/Arene Systems

Previously prepared (J. Mol. Catalysis 11, 353 (1981)) polystyrene/ruthenium systems have been examined by EXAFS, TEM, IR and Raman spectroscopy. A structure based on small metal clusters bound to the polymer by single ruthenium-arene binding is proposed. The general validity of the approach has been confirmed by preparing a similar product when starting with poly-1-vinylnaphthalene in the place of polystyrene.

Both systems are active for the hydrogenation of a large variety of unsaturated groups such as olefinic double bonds, mononuclear aromatic hydrocarbons, ketones, nitriles, nitroaromatic compounds and oximes. Catalytic activity, chemio- and stereoselectivity are discussed in terms of the proposed structure.

Introduction

In a previous paper it was reported that the polystyrene/ruthenium system, obtained according to scheme 1 with Ar=Phenyl, is an active heterogeneous catalyst for the hydrogenation of a wide range of substrates such as olefins, aromatic hydrocarbons, ketones, oximes, nitroderivatives and nitriles [1, 2].

Lacking adequate structural characterization by conventional spectroscopy because of the insolubility in organic solvents of the polystyrene/ruthenium system, the formation of clusters of ruthenium (or ruthenium hydrides) was tentatively postulated in order to explain their catalytic behaviour.

In the present paper a more advanced structural characterization, based on vibrational spectroscopy (IR and Raman), Transmission Electron Microscopy (TEM), and particularly Extended X-ray Absorption Fine Structure (EXAFS) data, is reported which substantiates the previous hypothesis. Also, the general validity of the synthetic method has been confirmed by preparing quite similar complexes from poly-1-vinylnaphthalene (Scheme 1, Ar=1-naphthyl).

Moreover, on the basis of additional hydrogenation experiments carried out with different substrates containing the above-mentioned unsaturated groups as well as with carboxylic acids and esters, the general trend of the catalytic process has been examined in more detail and some relations between catalyst structure, substrate nature and catalytic activity are reported.

Structural Investigation of Polystyrene/Ruthenium System

EXAFS analysis (Fig. 1a–b) performed on the complex [-CH$_2$CH(Ph)$_n$]$_n$Ru, ($n=2$) [3], shows the presence of ruthenium atoms each bonded to a single phenyl ring of the polystyrene side chains excluding the formation of a bis-arene complex. The Ru–C distance (from six carbon atoms) of 2.05 Å is in good agreement with the typical Ru–C distance detected in homogeneous monomeric Ru/arene complexes [4].

In addition, EXAFS data indicate that ruthenium atoms can be found in the second shell of the coordination sphere. Indeed the observed Ru–Ru distances are 3.5 Å.

![Fig. 1. Fourier transform of EXAFS spectra for:](image)

- Metallic ruthenium (a) and [-CH$_2$CH(Ph)$_n$]$_n$Ru, $n=2$ (b) [3];
- Metallic ruthenium (c) and [-CH$_2$CH(Ph)$_n$]$_n$Ru, $n=1$ (d).

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tance (2.88 Å) is similar to that found for small ruthenium clusters [5]. These results suggest for the [-CH$_2$–CH(Ph)–]$_n$Ru ($n = 2$) complex a structure in which small ruthenium clusters are bonded to the aromatic rings of polystyrene through Ru/arene bonds. Such a structure could also explain the formation of an insoluble polymeric complex during the reaction between Ru(η$^5$-COT)(η$^4$-COD), (COT=1,3,5-cyclooctatriene; COD=1,5-cyclooctadiene) and 1,3-diphenylpropane (DPP) in the presence of hydrogen, together with the expected soluble complex Ru(η$^6$-DPP) (η$^4$-COD) [2]. Indeed the former insoluble product has a composition corresponding to (DPP)Ru$_2$ and shows very similar catalytic behaviour as the polystyrene/ruthenium systems [2]. Very similar indications have been obtained for the polystyrene/ruthenium system containing a double amount of Ru, {[[-CH$_2$–CH(Ph)–]Ru, $n = 1$}, (Fig. 1 c–d), thus indicating that the structure is substantially the same, independent of metal loading.

The contemporary presence of amorphous and diffracting domains in a sample of [-CH$_2$–CH(Ph)–]$_n$Ru, $n = 2$, has been detected by TEM. While the presence of amorphous regions is typical in polymeric materials (the polystyrene ligand was atactic), the presence of domains able to diffract the electron beam is an evident indication of a substantial degree of organization which must involve ruthenium species. Diffraction parameters moreover differ markedly from those observed for mechanical mixtures of atactic polystyrene and metallic ruthenium (Figs. 2, 3).

![Fig. 2. a) Bright field TEM image of [-CH$_2$–CH(Ph)–]$_n$Ru, $n = 2$. b) Selected area electron diffraction pattern.](image1)

![Fig. 3. a) Bright field TEM image of mechanical mixture atactic polystyrene and metallic ruthenium. Small particles are metallic ruthenium, the arrowed particle is amorphous polystyrene. b) Bright field TEM image of metallic ruthenium.](image2)
Additional information arises from IR spectra carried out on samples with different metal loading. Indeed vibrational bands related to the C–H out of plane deformations of polystyrene at 645 cm\(^{-1}\) and 698 cm\(^{-1}\) decrease in intensity with increasing ruthenium content, while the background changes progressively showing the particular spectroscopic features of semiconductors, whose spectra are mainly characterized by a broad vibronic absorption band [6]. This typical behaviour was not observed for the mechanical mixture polystyrene/metallic ruthenium (Fig. 4). Further, the permanence of the typical absorptions of the monosubstituted phenyl ring at 660 and 800 cm\(^{-1}\), which are not observed in the arene-ruthenium complexes [7], is a clear evidence that a certain fraction of the aromatic side chains of the polystyrene are not involved in the coordination of ruthenium, independent of the loading.

Preliminary examination by Raman-Laser spectroscopy does not show any evidence of ruthenium-hydride bonds [8]; however, reticular bands present in the metallic ruthenium spectrum are found both in the mixture and in the complex, suggesting the presence of crystalline agglomerates in the latter (Fig. 5).

All these evidence can be reasonably explained on the basis of the structure proposed from EXAFS data, and suggest the presence of small ruthenium clusters coordinated to the phenyl rings. The variable stoichiometry can also explain the presence of free phenyl rings even at relatively high metal loadings \((n=1/4)\) (Fig. 4, curve d).

**Preparation of Poly-1-vinylnaphthalene/Ruthenium Complexes**

The reaction described in Scheme 1 has also been carried out starting with poly-1-vinylnaphthalene as the macromolecular arene ligand (Scheme 1; \(Ar=1\)-naphthyl). The \([\text{-CH}_2\text{-CH}(1\text{-naph})\text{-}]_n\text{Ru com-}\)

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**Fig. 4.** IR spectra of:
- \([\text{-CH}_2\text{-CH} \text{(Ph)}\text{-}]_n\text{Ru, n = 4 (a), n = 2 (b), n = 1 (c), n = 1/4 (d) (solid lines).}
- Mechanical mixture of polystyrene with ruthenium (molar ratio phenyl/Ru = 1 (e) and 1/3 (f); broken lines).

**Fig. 5.** Raman-Laser spectra of:
- a) Mechanical mixture of polystyrene with ruthenium.
- b) \([\text{-CH}_2\text{-CH(Ph)}\text{-}]_2\text{Ru, n = 2.}
- c) Metallic ruthenium.

pounds are brown solids, insoluble in common organic solvents, and do not contain cycloolefins as shown by elemental analysis and by the absence of fragments, derived from COT and COD, in the mass spectra up to 250 °C. The IR spectra present the same bands as poly-1-vinyl naphthalene and, with the increase of the ruthenium content, are characterized by a reduction of the intensity of the bands of poly-1-vinyl naphthalene and the appearance of the vibronic structure [6] also observed for the corresponding polystyrene system.

Reactivity of \([-\text{CH}_2-\text{CH(Ph)}-\text{]}_n\text{Ru}\) Catalysts

a) Hydrogenation of aromatic hydrocarbons

It has been previously [2] shown that the \([-\text{CH}_2-\text{CH(Ph)}-\text{]}_n\text{Ru}\) acts as a catalyst for the hydrogenation of benzene to cyclohexane both in the presence of THF and in the absence of solvent. Also, alkyl substituted benzene derivatives such as toluene, \(o\)-xylene, and \(t\)-butylbenzene can be converted into the corresponding alkyl substituted cycloalkanes (runs 1–6, Table I). The increase of number and bulkiness of substituents is accompanied by a decrease of reaction rate and number of cycles; comparable reaction rates as for benzene can be achieved by progressive increase of the temperature (runs 5 and 6, Table I). However, no hydrogenation at all was observed for hexamethylbenzene and poly styrene even up to 150 °C and 70 atm of hydrogen for 10 and 17 h, respectively (runs 7 and 8, Table I). Condensation of the aromatic rings, as in naphthalene, inhibits the hydrogenation even under rather drastic conditions, whereas tetrahydro naphthalene is converted into a mixture of \(trans\)- and \(cis\)-decalin already at 80 °C (runs 9 and 10, Table I). It is of interest to point out that in the case of \(1\)-vinyl naphthalene the selective hydrogenation of the aliphatic double bond is observed at 25 °C (run 11, Table I), the reaction rate being substantially the same as for the vinyl double bond in aliphatic olefins (run 1, Table II).

This proves that while the condensed aromatic nuclei of naphthalene are not hydrogenated, they do not act as a poison for the catalyst. Steric effects do not seem to account entirely for the behaviour of naphthalene, as even larger steric effects should exist for \(t\)-butylbenzene and tetrahydro naphthalene. Thus electronic factors, connected with the hydrogenation mechanism, should probably play an important role in determining the low reactivity of naphthalene which is a weak \(\eta^6\)-coordinating ligand towards transition metals [9]. Indeed, the displacement of the aromatic hydrocarbon ligand in the complex Ru(\(\eta^6\)-naphthalene)(\(\eta^4\)-COD) occurs quite

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\text{Table I. Hydrogenation of aromatic hydrocarbons in the presence of aromatic polymers/ruthenium catalysts.}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Run</th>
<th>Substrate (mmoles)</th>
<th>Substrate/Ru (mmoles/mg-atoms)</th>
<th>(P_{H_2}\ast) (Atm)</th>
<th>(T) (°C)</th>
<th>(t) (h)</th>
<th>Products (%yield)</th>
<th>Number of cycle mmoles substrate mg-atoms Ru (=)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([-\text{CH}_2-\text{CH(C}_6\text{H}_5\text{)}-\text{]}_n\text{Ru}) ((n = 2))</td>
<td>1</td>
<td>Benzene (56.3)</td>
<td>135</td>
<td>50</td>
<td>25</td>
<td>6</td>
<td>Cyclohexane (100)</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>2*</td>
<td>Benzene (56.3)</td>
<td>135</td>
<td>50</td>
<td>25</td>
<td>6</td>
<td>Cyclohexane (100)</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Toluene (47.1)</td>
<td>90</td>
<td>50</td>
<td>25</td>
<td>6.5</td>
<td>Methylcyclohexane (100)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>(o)-Xylene (42.2)</td>
<td>135</td>
<td>50</td>
<td>25</td>
<td>6.5</td>
<td>Methylcyclohexane (100)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>(t)-Butylbenzene (32.3)</td>
<td>135</td>
<td>50</td>
<td>25</td>
<td>6.5</td>
<td>Methylcyclohexane (100)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>(t)-Butylbenzene (32.3)</td>
<td>135</td>
<td>50</td>
<td>60</td>
<td>24</td>
<td>(cis)-Dimethylcyclohexane (90)</td>
<td>6</td>
</tr>
<tr>
<td>([-\text{CH}_2-\text{CH(1-C}_6\text{H}_7\text{)}-\text{]}_n\text{Ru}) ((n = 1))</td>
<td>7***</td>
<td>Hexamethylbenzene (6.2)</td>
<td>37</td>
<td>70</td>
<td>150</td>
<td>10</td>
<td>No hydrogenation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8***</td>
<td>Polystyrene (9.6)*c</td>
<td>135</td>
<td>70</td>
<td>150</td>
<td>10</td>
<td>No hydrogenation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9***</td>
<td>Naphthalene (16.4)</td>
<td>81</td>
<td>70</td>
<td>150</td>
<td>10</td>
<td>No hydrogenation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Tetrahydro naphthalene (22.7)</td>
<td>135</td>
<td>50</td>
<td>80</td>
<td>9</td>
<td>(cis)-Decahydronaphthalene (80)</td>
<td>15</td>
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<tr>
<td></td>
<td>11</td>
<td>1-Vinyl naphthalene (25.3)</td>
<td>140</td>
<td>50</td>
<td>25</td>
<td>8</td>
<td>(trans)-Decahydronaphthalene (20)</td>
<td>15</td>
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<tr>
<td></td>
<td>12</td>
<td>Benzene (56.3)</td>
<td>135</td>
<td>50</td>
<td>25</td>
<td>7.5</td>
<td>Cyclohexane (100)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>13***</td>
<td>Benzene (56.3)</td>
<td>135</td>
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<td>25</td>
<td>7.5</td>
<td>Cyclohexane (100)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>14****</td>
<td>Naphthalene (16.4)</td>
<td>80</td>
<td>70</td>
<td>150</td>
<td>24</td>
<td>No hydrogenation</td>
<td>18</td>
</tr>
</tbody>
</table>

* Starting pressure at 25 °C; ** Catalyst recycled from run 1; *** Carried out in THF (5 ml); **** Catalyst recycled from run 12; * Mmoles of monomeric unity; the atactic polymer with \(M_w = 86,000\) was used.
Table II. Hydrogenation of substrates containing functional groups (Hydrogen starting pressure at 25 °C = 50 atm).

| Substrate | Substrate/Ru T t Products Number of cycles |
|-----------|------------------------------------------|------------------------------------------|
|           | Run (mmoles) | (mmoles/mg-atoms) | (°C) | (h) | (%yield) | mmoles substrate | catalyst | mg-atoms Ru x h |
| 15        | 1-Pentene (55.2) | 140 | 25 | 5 | n-Pentane (100) | 28 | (C=C) |
| 16        | 3-Pentanone (27.4) | 135 | 25 | 10 | 3-Pentanol (100) | 13.5 | (C=O) |
| 17        | Propionitrile (71) | 290 | 120 | 8 | n-Propylamine (70) | 25 | (C=N) |
| 18        | Acetophenone (47.5) | 135 | 80 | 10 | 1-Cyclohexylethanol (100) | 13.5 | |
| 19*       | Acetophenoxime (10) | 75 | 80 | 8 | 1-Phenylethylamine (100) | 9.5 | (C=NOH) |
| 20*       | Phenol (37) | 135 | 25 | 20 | Cyclohexanol (50) | 3.4 | (Ph) |
| 21*       | Phenol (37) | 135 | 80 | 7 | Cyclohexanol (100) | 20 | (Ph) |
| 22        | Nitrobenzene (48) | 135 | 80 | 10 | Cyclohexylamine (100) | 13.5 | |
| 23        | Benzonitrile (49) | 230 | 140 | 8 | Benzylamine (100) | 29 | (C=N) |
| 24        | Ethylacetate (31) | 135 | 140 | 48 | No hydrogenation | 26 | (Ph) |
| 25*       | Benzoic acid (16.4) | 135 | 25 | 26 | Cyclohexane carboxylic acid (25) | 1.3 | (Ph) |
| 26        | Ethyl acetoacetate (23.5) | 36 | 25 | 18 | Ethyl 3-hydroxybutyrate (100) | 2 | (C=O) |
| 27*       | Cinnamic acid (13.5) | 100 | 25 | 65 | 3-Cyclohexylpropanoic acid (80) | 1.2 | |
| 28*       | o-Acetamidocinnamic acid (9.7) | 32 | 100 | 24 | N-Acetocyclohexylalanine (100) | 1.3 | |
| 29        | 1-Pentene (60) | 140 | 25 | 6 | n-Pentane (100) | 23 | (C=C) |
| 30        | 3-Pentanone (27.4) | 135 | 20 | 25 | 3-Pentanol (100) | 7 | (C=O) |
| 31*       | Phenol (37) | 135 | 80 | 9 | Cyclohexanol (100) | 15 | (Ph) |

Carried out in THF (5 ml).

easily [10], whereas in the analogous complex Ru(η²-benzene)(η⁴-COD) the displacement does not take place [11].

This particular behaviour of naphthalene suggested the investigation of the catalytic properties of the analogous system prepared from poly-l-vinyl-naphthalene, where, according to the proposed structure, some ruthenium atoms are bound each to a single naphthalene side-chain.

This last system is able to catalyze the hydrogenation of benzene under the same conditions as [-CH₂-CH(Ph)-]ₙRu, but with a slightly lower activity, thus indicating that the nature of the aromatic polymer can appreciably affect the catalytic properties of the system (runs 12—14, Table I).

Runs 2 and 13 (Table I) have both been performed with recycled catalyst, based on polystyrene and poly-l-vinyl-naphthalene, respectively. Both these experiments show that these catalysts maintain their stability with time, probably thanks to the fact that the aromatic polymer ligand is not hydrogenated at all during the reaction (see also run 8 with polystyrene as the substrate). Kinetic control of stereoselectivity of the hydrogenation is observed both in case of o-xylene and tetrahydronaphthalene (runs 4 and 10, Table I). Indeed in both cases the thermodynamically less stable cis isomer is obtained [12]. The ratio cis to trans being 9/1 in the former case carried out at room temperature, and 4/1 in the latter case where the reaction temperature was 80 °C, all other conditions being the same. No cis to trans isomerization has been observed by heating the above mixture at 100 °C in the presence of the [-CH₂-CH(Ph)-]ₙRu catalyst under nitrogen atmosphere.

b) Hydrogenation of molecules containing functional groups

[-CH₂-CH(Ph)-]ₙRu is able also to hydrogenate [2] functional groups such as double bonds, keto and nitro groups, oximes and nitriles. Moreover, the hydrogenation of the aromatic ring is possible also when substituents such as –OH in phenol, –CN in benzonitrile, –NO₂ in nitrobenzene, –COCH₃ in CH₃-acetophenone, and –C=NOH in its oxime were originally present (Runs 18—23, Table II). The presence of two unsaturated functions in the same substrate arises the problem of selectivity and competitive reactivity. Further experiments have now been performed to have a more complete picture of the features of this particular heterogeneous hydrogena-
tion catalyst and its sensitivity to the molecular structure of the substrate.

It is known that esters and carboxylic acids are reduced to the corresponding alcohols by oxides of transition metals [13]. More recently these substrates have been hydrogenated under mild conditions \((P_H_2 = 5-10 \text{ atm}, T = 80 \text{ °C})\) in the presence of phosphine-hydride ruthenium complexes [14]. The complex \([-\text{CH}_2-\text{CH}(\text{Ph})_2]_n\text{Ru}, n = 2\), is not active in the reduction of ethyl acetate up to 140 °C and 50 atm of hydrogen (run 24, Table II). In the case of benzoic acid the free carboxylic group is also not affected at room temperature but the hydrogenation of the aromatic ring takes place with the formation of cyclohexane carboxylic acid (run 25, Table II). The inactivity for the reduction of the carboxylic or ester groups, which on the other side do not act as poison, allows to hydrogenate selectively other functional groups. Thus in the case of ethylacetocetate the carbonyl group is selectively converted into the corresponding alcohols while the ester is not affected; cinnamic acid is converted into 3-cyclohexylpropanoic acid and \(\alpha\)-acetamidocinnamic acid into N-acetylcyclohexylalanine (runs 26–28, Table II). During the reaction the aromatic groups when present are also hydrogenated as already observed in previous cases which are also reported in Table II.

As far as reactivity of a single functional group is concerned the following order of hydrogenation seems to be operative:

\[
\begin{align*}
\text{C}=\text{C} & \quad \text{(aliphatic)} > \text{Benzene} > \\
\text{C}=\text{O} & \quad \text{(aliphatic)} > -\text{C}=\text{N}
\end{align*}
\]

The effect of the substituent on the hydrogenation of the phenyl group is more complex to detect quantitatively as some substituents are hydrogenated themselves. However, the available data allow to propose this tentative order of ability to assist hydrogenation of the phenyl ring:

\[
-\text{OH} > -\text{COOH} > -\text{NO}_2 > -\text{C}_3\text{-CH}_3 > -\text{C}=\text{N}
\]

As already mentioned, the analogous complex from poly-1-vinylnaphthalene shows slightly lower reactivity than the polystyrene-based catalyst (runs 29–31, Table II), but the relative reactivity of the various unsaturated group are the same, thus confirming a similar structure and mechanism.

**Final Remarks**

The main aim of the present work was to show that the unusual catalytic behaviour of the products obtained by reacting under hydrogen \(\text{Ru}(\eta^6\text{-COT})(\eta^4\text{-COD})\) with the polymer of an aromatic vinyl monomer, such as styrene or 1-vinylnaphthalene, had to be related to the particular molecular structure of the type arene/metal cluster. In this way it could also be shown that the reaction of a transition metal complex bearing easily displaced ligands with a ligand containing at least two aromatic rings in a proper relative position, can provide an additional way for the catalytic application of the "naked metal" concept, firstly proposed by Professor Wilke already in the early 60's [15].

Both structural properties and catalytic behaviour indicate that the above aim has been reached. Indeed the presence of small Ru-clusters attached to arene groups of the macromolecular ligand is consistent with EXAFS, TEM, IR and Raman data. Moreover, this structure allows to explain the formation of an insoluble polymeric product when reacting \(\text{Ru}(\eta^6\text{-COT})(\eta^4\text{-COD})\) with 1,3-diphenylpropane under hydrogen [2]. Finally the important role of the arene-metal interactions in the formation of the products are shown by the formation of metallic ruthenium when a non-aromatic polymer, such as polyethylene, is used in the place of polystyrene under the same conditions.

Also, the dependence of catalytic properties on the nature of the aromatic polymer ligand, metal loading, and substrate structure, as well as reaction stereochemistry, can be better explained taking into account substrate activation by coordination and steric effects at the molecular level, as observed for homogeneous ruthenium and rhodium complexes active for arene hydrogenation [16, 17].

The most typical results obtained during the catalytic hydrogenation reactions carried out in the presence of polystyrene/Ru system are:

- mononuclear aromatic compounds are promptly hydrogenated under relatively mild conditions, whereas naphthalene, a weak \(\eta^4\)-coordinating molecule, is not hydrogenated at all;
- the increased bulkiness of substituent(s) on the benzene ring is accompanied by a decrease of hydrogenation rate, but even \(\tau\)-butylbenzene and disubstituted benzene derivatives give the corresponding cycloalkanes;
– both o-xylene and tetralin give in larger amount the less thermodynamically stable cis-product;
– no intermediate hydrogenation products, cyclo-
olefins or -diolefins, are observed thus suggesting the strong binding of the substrate to the active 
site;
Finally it was observed that the metal species re-
main bonded to the aromatic polymer during all reaction time and can be recycled without substantial 
loss of catalytic activity. This stability is connected 
with the lack of hydrogenation of the aromatic side 
chains of the macromolecular ligand. Indeed, even 
linear polystyrene is not hydrogenated under the 
reaction conditions probably because of the substan-
tial heterogeneous character of the used catalyst [18].

In this connection it is of interest to note that polystyrene is also not hydrogenated in the presence of \([\text{RhCl}_2(\text{C}_6\text{H}_5\text{Me}_3)]_2\), which is a good hydrogenation catalyst for low molecular weight arenes [17, 18].

**Experimental**

C and H elemental analysis was performed at the Laboratorio di Microanalisi, Instituto di Chimica Or-
ganica, Facoltà di Farmacia, Università di Pisa. The ruthenium content in low and high molecular weight complexes was obtained by X-ray fluorescence analysis [19].

$^1$H NMR and mass spectra were recorded on Varian XL-100 and on Varian CH7 spectrometers, respectively. IR spectra were carried out with the Perkin-Elmer 283B and Perkin-Elmer 337 spectrometers. Raman-Laser spectra were recorded on a Ramanor Jobin Yvon HG25, using CRS Super graphite Ion-Laser coherent as laser source (Argon).

G.l.c. analyses of the catalytic hydrogenation products were carried out on Perkin-Elmer F30 and Dani 6800 apparatus equipped with columns (2 m length) packed with squalane, carbowax 20M and silicone SE 30 on chromosorb W 80/100.

TEM analysis were performed on a Philips EM400T microscope at the Dipartimento di Scienza della Terra dell’Università di Pisa. EXAFS measure-
ments have been performed at the Wiggler Facility of the National Laboratories in Frascati, as elsewhere reported [3].

**Preparation of polymers**

Polystyrene and poly-1-vinylnaphthalene were pre-
pared by radical initiation in bulk at 60 °C (8 h) with 
2,2-azobisisobutyronitrile (AIBN) (0.1% wt/wt). 
$[\eta]_{\text{PSI}} = 0.415 \text{ dL/g}, \overline{M}_n = 86,000; [\eta]_{\text{PVN}} = 0.14 \text{ dL/g}.$

**Synthesis of \(\text{Ru}(\eta^6\text{-COT})(\eta^4\text{-COD})\)**

This complex was synthesized by the reaction of 
\(\text{RuCl}_3\cdot\text{H}_2\text{O}\) with COD in the presence of zinc dust and ethanol [20].

**Synthesis of \(-\text{CH}_2\text{−CH} (\text{Ar})\text{−}_n\text{Ru} \quad (\text{Ar} = \text{Phenyl, 1-naphthyl})\)**

These compounds have been prepared by the reac-
tion of \(\text{Ru}(\eta^6\text{-COT})(\eta^4\text{-COD})\) and the polymeric ligand in the presence of hydrogen, according to the method previously reported [2]. The preparation on the compound \([-\text{CH}_2\text{−CH}(1\text{-naphthyl})\text{−}_n\text{Ru}, n = 1\) will be described in detail. In a 250 ml Schlenk tube the compound \(\text{Ru}(\eta^6\text{-COT})(\eta^4\text{-COD})\) (322 mg, 1.02 mmoles) and poly-1-vinylnaphthalene (157 mg, 1.02 mmoles of monomeric unity) were dissolved in 10 ml of anhydrous freshly distilled THF under ni-
trogen. The nitrogen was removed under vacuum and the tube was charged with hydrogen (1 atm). The yellow solution was shaken at room tempera-
ture under hydrogen atmosphere for 5 h. During this period the solution became brown with precipi-
tation of a dark-brown solid. The solid was washed with n-hexane and THF giving 255 mg of 
\([-\text{CH}_2\text{−CH}(1\text{-naphthyl})\text{−}_n\text{Ru}, n = 1\).

\(\text{C}_{12}\text{H}_{10}\text{Ru}\)

Calcd C 56.45 H 3.92 Ru 39.63,

Found C 57.02 H 3.87 Ru 37.13.

**Catalytic hydrogenation experiments**

All the hydrogenation experiments were per-
formed in a stainless steel autoclave (125 ml) and 
were carried out as elsewhere reported [2]. A glass 
vial, containing the catalyst, the substrate and the 
solvent was introduced into the autoclave under ni-
trogen. After cooling the autoclave at −78 °C, the 
nitrogen was removed under vacuum and hydrogen 
was introduced at room temperature at the appro-
priate pressure. The autoclave was stirred in a ther-
mostatic oil-bath at the fixed temperature until the 
hydrogen absorption finished. The products were 
separated from the catalyst by decantation and iden-
tified by g.l.c. and/or spectroscopic analysis.

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