

Catalysis in aqueous solution: Hydrogenation of benzene derivatives catalysed by $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$

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Abstract

The catalytic hydrogenation of various benzene derivatives was studied, using $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ in aqueous solution as the catalyst precursor. Under biphasic conditions, the corresponding cyclohexane derivatives are obtained with catalytic turnover rates which vary, depending on the substrate, from 20 to 2000 cycles per h. After a catalytic run, the aqueous solution contains the two tetranuclear cations $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ and $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]^{2+}$ which are known to catalyse the hydrogenation of aromatic compounds, but the activity of which is considerably lower than that of the $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ precursor. An intermediate, presumably the more active species, was detected by $^1\text{H-NMR}$ spectroscopy under catalytic conditions and identified as the trinuclear cluster cation $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of water as a solvent for catalytic transformations has become more and more important, water being a cheap and environmentally friendly solvent. The past decade has witnessed an increasing interest in water-soluble catalysts and catalytic reactions under biphasic conditions [1]. Biphasic catalytic processes allow the facile separation of the catalyst remaining in the aqueous phase from the products and the substrate being in the organic phase. Recently we studied the catalytic potential of the

water-soluble tetranuclear cluster dication $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**) for the hydrogenation of benzene derivatives in biphasic conditions [2]. The tetrahydrido cluster **1** is easily accessible from the reaction of the hydrolysis mixture of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ with molecular hydrogen at 20°C, 1.5 bar, while more forcing conditions give the hexahydrido cluster $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]^{2+}$ (**2**) [3]. Both species **1** and **2** were found to be present in equilibrium in the reaction mixture of the hydrogenation of benzene to cyclohexane using the chloride salt of **1** in aqueous solution as the catalyst. Mechanistic studies showed the catalytic process to involve the coordination of the substrate by arene substitution at the Ru_4 cluster, the interplay of tetrahydrido and hexahydrido species by uptake

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of H₂ and transfer of hydrido ligands from the ruthenium framework onto the coordinated aromatic ligands [2].

In this paper we report the direct use of the dinuclear parent compound ($\eta^6\text{-C}_6\text{H}_6$)₂Ru₂Cl₄ as the catalyst precursor for the hydrogenation of various benzene derivatives to the corresponding cyclohexane under biphasic conditions.

2. Results

Benzene and a large number of mono-, di- and trisubstituted derivatives have been hydrogenated to give the corresponding cyclohexane derivatives in the presence of an aqueous solution of ($\eta^6\text{-C}_6\text{H}_6$)₂Ru₂Cl₄ under a pressure of 60 bar of H₂ and a temperature of 90°C (Tables 1–3). With most of the aromatic substrates, the reaction takes place under biphasic conditions, in the case of the water-soluble aromatics phenol, benzoic acid and aniline, the hydrogenation occurs in a homogeneous aqueous phase.

With benzene, the reaction is completed within 30 min, showing a catalytic activity of almost 2000 cycles per h. The catalytic turnover frequency drops considerably in the case of

substituted derivatives. The increasing steric hindrance of the alkyl substituents in the series toluene, propylbenzene, *tert*-butylbenzene, cyclohexylbenzene is responsible for the decrease of the catalytic turnover frequency, the case of ethylbenzene being an exception (Table 1). This tendency is reflected in the increase of the overall reaction time for the hydrogenation of the more hindered aromatics (Fig. 1). An increasing number of methyl substituents on the aromatic nucleus also leads to a decrease of the catalytic turnover frequency (Table 2) and to an increase of the reaction time (Fig. 2).

Functionalized benzene derivatives are more difficult to hydrogenate than the corresponding alkyl derivatives: whereas toluene is hydrogenated with a turnover frequency 900 h⁻¹, the turnover frequency of the hydrogenation of anisole is only 217 h⁻¹. Unfortunately the hydrogenation of functionalised benzene derivatives is not very selective. Biphenyl is hydrogenated to give a mixture of cyclohexylbenzene and bicyclohexane (Table 1). In addition to the hydrogenation of the aromatic ring, reducible functions of the substituent are also hydrogenated. Thus, acetophenone reacts to give a mixture of 1-cyclohexylethanol, ethylcyclohexane, methyl cyclohexylketone and ethylbenzene.

Table 1
Hydrogenation of benzene and monosubstituted derivatives under biphasic conditions^a

R	Substrates	Products	Conversion ^b	Time (h)	TOF ^c
-H	benzene	cyclohexane	99.9	0.50	1998
-CH ₃	toluene	methylcyclohexane	99.0	1.10	900
-CH ₂ CH ₃	ethylbenzene	ethylcyclohexane	83.2	8.10	103
-CH ₂ CH ₂ CH ₃	propylbenzene	propylcyclohexane	96.2	1.35	713
-CH(CH ₃) ₂	<i>iso</i> -propylbenzene	<i>iso</i> -propylcyclohexane	99.3	1.50	662
-C(CH ₃) ₃	<i>tert</i> -butylbenzene	<i>tert</i> -butylcyclohexane	98.0	1.45	676
-C ₆ H ₁₁	cyclohexylbenzene	bicyclohexyl	98.4	3.00	328
-C ₆ H ₅	biphenyl ^d	bicyclohexyl	35.0	2.20	396
		cyclohexylbenzene	63.0		
-OCH ₃	anisole	methoxycyclohexane	95.3	4.40	217

^a Conditions: catalyst (0.04 mmol), water (5 ml), catalyst/substrate ratio = 1/1000, temperature: 90°C, hydrogen pressure: 60 bar, stirred: 900 min⁻¹.

^b Measured by gas chromatography.

^c Turnover frequency: mol substrate transformed per mol catalyst per time unit (h⁻¹).

^d Substrate dissolved in cyclohexane (10 ml).

Table 2
Hydrogenation of di-, tri- and polysubstituted benzene derivatives under biphasic conditions^a

Substrates	Products	Conversion ^b	Time (h)	TOF ^c
<i>o</i> -Xylene	<i>trans</i> -1,2-dimethylcyclohexane	2	1.50	640
	<i>cis</i> -1,2-dimethylcyclohexane	94		
<i>m</i> -Xylene	<i>trans</i> -1,3-dimethylcyclohexane	15	2.00	490
	<i>cis</i> -1,3-dimethylcyclohexane	83		
<i>p</i> -Xylene	<i>trans</i> -1,4-dimethylcyclohexane	25	2.30	404
	<i>cis</i> -1,4-dimethylcyclohexane	68		
1,2,3-Trimethylbenzene	<i>trans,trans</i> -1,3,5-trimethylcyclohexane	51	3.20	159
1,2,4,5-Tetramethylbenzene ^d	<i>cis,cis,cis</i> -1,2,4,5-tetramethylcyclohexane	61	22.00	14

^aConditions: catalyst (0.04 mmol), water (5 ml), catalyst/substrate ratio = 1/1000, temperature: 90°C, hydrogen pressure: 60 bar, stirred: 900 min⁻¹.

^bMeasured by gas chromatography.

^cTurnover frequency: mol substrate transformed per mol catalyst per time unit (h⁻¹).

^dSubstrate dissolved in cyclohexane (10 ml), catalyst/substrate ratio = 1/500.

Surprisingly, styrene reacts to give only ethylbenzene. With allylbenzene, hydrogenation of the olefinic side-chain is observed, along with isomerisation of the double bond, but not the hydrogenation of the aromatic ring (Table 3).

The water-soluble substrates phenol and aniline react in homogeneous aqueous phase. In the

case of phenol, cyclohexanol is produced qualitatively, however the turnover frequency (42 h⁻¹) is low. Aniline is not converted at all under the same conditions, however reacts in acidic solution (pH = 2) to give cyclohexylamine with a yield of 53% and a turnover frequency of 44 h⁻¹. Benzoic acid was hydro-

Table 3
Hydrogenation of functionalised benzene derivatives under biphasic conditions^a

Substrates	Products	Conversion ^b	Time (h)	TOF ^c
Styrene	ethylbenzene	57.0	21.40	27
α -Methylstyrene	<i>iso</i> -propylcyclohexane	95.0	3.30	288
Allylbenzene	propylbenzene	53.0	23.30	39
	β -methylstyrene	33.0		
	α -methylstyrene	5.0		
	cyclohexanol	100.0		
Phenol ^d	1-cyclohexylethanol	74.5	24.00	40
	ethylcyclohexane	11.0		
	methylcyclohexylketone	8.0		
	ethylbenzene	3.5		
Methyl benzoate	methylcyclohexanoate	88.0	21.00	42
Ethyl benzoate	ethylcyclohexanoate	100.0	8.10	123
Benzoic acid ^e	cyclohexanecarboxylic acid	63.0	5.50	91
	ethylcyclohexanoate	37.0		
Aniline ^f	cyclohexylamine	53.0	12.00	44
α -Methylbenzylamine	α -methylcyclohexylamine	44.0	9.45	46
<i>N,N</i> -Dimethylaniline	<i>N,N</i> -dimethylcyclohexylamine	70.0	9.30	75

^aConditions: catalyst (0.04 mmol), water (5 ml), catalyst/substrate ratio = 1/1000, temperature: 90°C, hydrogen pressure: 60 bar, stirred: 900 min⁻¹.

^bMeasured by gas chromatography.

^cTurnover frequency: mol substrate transformed per mol catalyst per time unit (h⁻¹).

^dCatalyst/substrate ratio = 1/500 (homogeneous phase).

^eCatalyst/substrate ratio = 1/500, substrate dissolved in H₂O/ethanol.

^fHomogeneous aqueous phase (pH = 2).

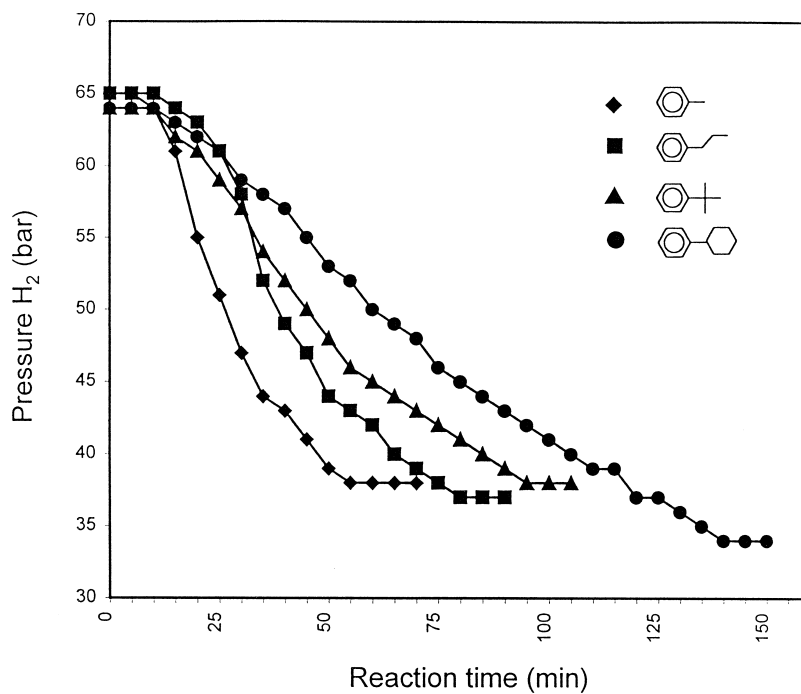


Fig. 1. Effect of substituent on rate of hydrogenation.

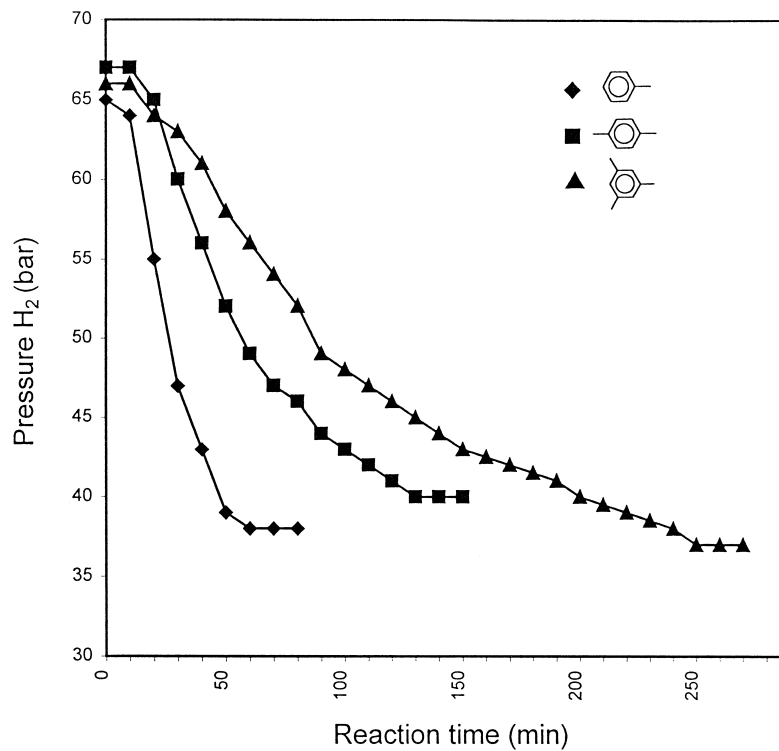


Fig. 2. Effect of number of methyl groups on rate of hydrogenation.

genated in a homogeneous water/ethanol mixture (1:1), it gives not only cyclohexanecarboxylic acid, but also its ethylester (Table 3).

3. Discussion

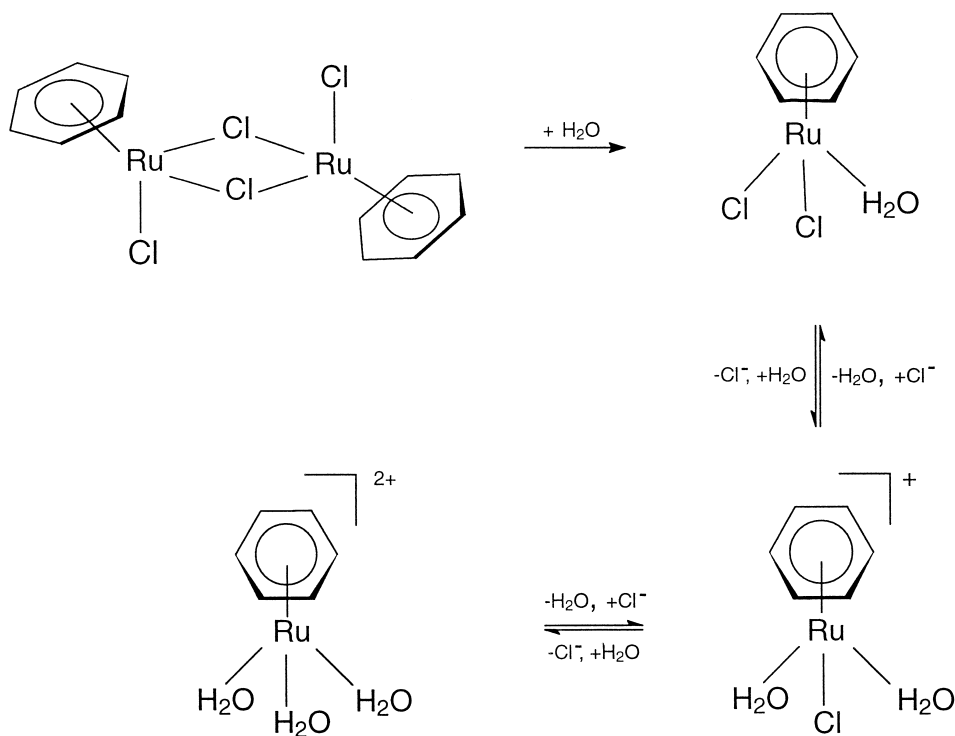
The dinuclear complex bis(benzene)tetrachlorodiruthenium(II), $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$, dissolves in water with degradation to give the mononuclear complexes $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})\text{Cl}_2$, $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_2\text{Cl}]^+$ and $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$, which are in equilibrium with each other (Scheme 1) [4].

The low-pressure hydrogenation (1.5 atm, 20°C) of this hydrolysis mixture in water leads, in the presence of NaBF_4 , to the tetranuclear tetrahydrido cluster cation $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**). The reaction of the hydrolysis mixture of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ in water with molecular hydrogen under forcing condi-

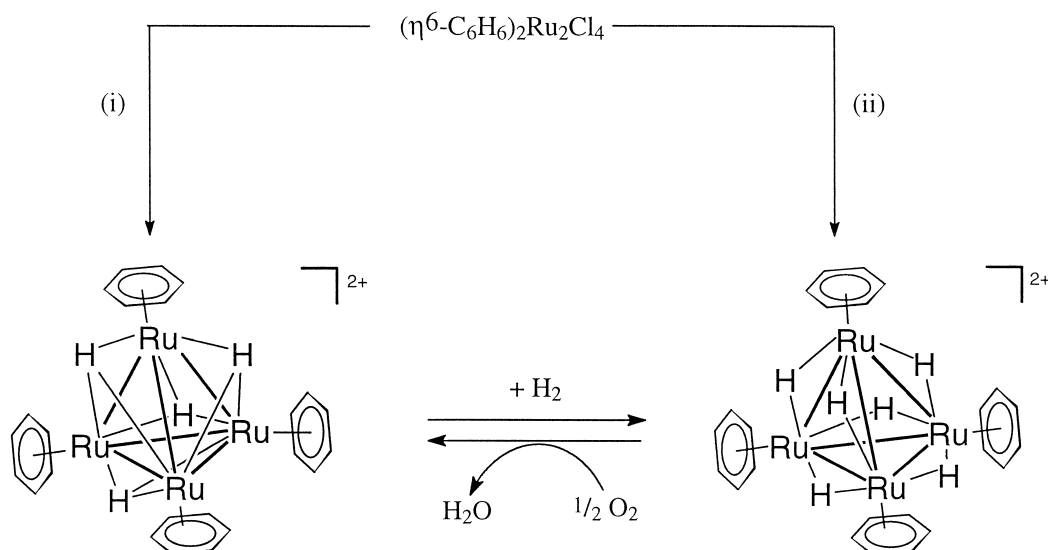
tions (60 atm, 55°C) and in the absence of an additional salt leads to the formation of the tetranuclear hexahydrido cluster $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]^{2+}$ (**2**). Cation **2** reacts readily with oxygen to give the tetrahydrido cation $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**). Under high-pressure hydrogenation conditions (60 atm H_2 , 55°C) the tetrahydrido cluster cation **1** yields the hexahydrido cluster **2** (Scheme 2) [3].

The salt $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]\text{Cl}_2$ (cation **1**) catalyses the hydrogenation of benzene derivatives under biphasic conditions [2]. The NMR analysis of the aqueous phase revealed the presence of the hexahydrido species $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]^{2+}$ (**2**) together with the tetrahydrido species $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**) under hydrogen pressure, which enabled us to propose a mechanism for the catalytic hydrogenation of benzene using the tetranuclear cation **1** as the catalyst [2].

When the dinuclear complex $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ is used as catalyst precursor,



Scheme 1. Hydrolysis of bis(benzene)tetrachlorodiruthenium (II) according to Ref. [4].

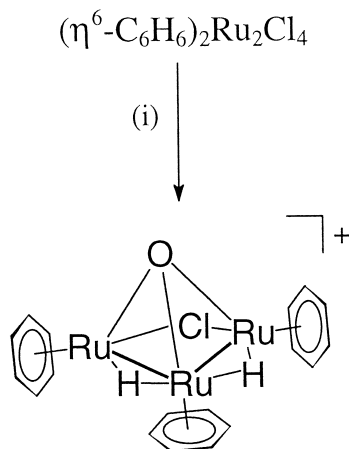


Scheme 2. Build-up of the tetranuclear benzene ruthenium cluster $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**) and $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]^{2+}$ (**2**) by hydrogenation of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ in water. (i) 1.5 atm H_2 , 20°C, NaBF_4 , H_2O ; (ii) 60 atm H_2 , 55°C, H_2O according to Ref. [3].

after a catalytic run the aqueous phase contains the tetranuclear cluster cations **1** and **2**. It is therefore reasonable to assume **1** and **2** to be the catalytically active species also in the case of the dinuclear precursor. However, the catalytic turnover frequency is much higher by using $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ instead of $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]\text{Cl}_2$ (cation **1**) in aqueous solution for the catalytic hydrogenation of aromatics. Thus, under the same conditions (60 bar, 90°C) benzene is converted to cyclohexane by **1** with a catalytic turnover frequency of 376 h^{-1} (conversion 94%, 2.5 h, TON 940) [2], but using $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ a catalytic turnover frequency of 1998 h^{-1} (conversion 99%, 0.5 h, TON 999) is observed (Table 1). This observation shows that, in addition to **1** and **2**, there must be another species **3** in the aqueous solution, which is more active than **1** and **2**. This species **3** is, however, finally converted into a mixture of **1** and **2** during the catalytic reaction, so that after the catalytic run the high catalytic activity in solution has dropped to the lower value known for **1** [2].

Since Bennett has reported that the dinuclear hexamethylbenzene derivative $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-Cl})]^+$ is an active hydrogenation catalyst [5], we suspected the benzene analogue $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-Cl})]^+$, unknown hitherto, to be active in our case in aqueous solution. We therefore undertook the identification of the active species **3** by studying by NMR-spectroscopy of the reaction under milder conditions than those used for the standard catalytic process. While the aqueous phase of the toluene hydrogenation using $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ as catalyst precursor at 90°C contains only **1** and **2** as detectable organometallic species, an additional hydride resonance at $\delta(\text{D}_2\text{O}) = -13.08$ ppm could be detected when the reaction was carried out at 60°C, where the hydrogenation of the toluene takes already place. In the aromatic region of the ^1H -NMR spectrum two different signals of coordinated benzene ligand at $\delta(\text{D}_2\text{O}) = 6.18$ ppm, 5.77 ppm (intensity ratio 1:2) were observed and shown to belong to the same compound giving rise to the hydride signal at $\delta = -13.08$ ppm. Because of these characteristics we were able to identify species **3** as the known trinuclear cluster cation $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$ which we have reported

$[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$ which we have reported



Scheme 3. Build-up of the trinuclear benzene ruthenium cluster $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$ by hydrogenation of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ in water. (i) 1.5 atm H_2 , 20°C, H_2O , NaClO_4 according to Ref. [3].

from the reaction of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ with molecular hydrogen in the presence of sodium perchlorate (Scheme 3) [3].

We finally confirmed the implication of **3** by using the isolated salt $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]\text{Cl}$ as the catalyst precursor for the hydrogenation of toluene; under standard conditions (60 bar, 90°C) the catalytic turnover frequency was found to be 1485 h^{-1} , as compared to 900 h^{-1} for the use of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ and 250 h^{-1} for **1** or **2**.

4. Conclusion

The dinuclear complex $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ in aqueous solution is an efficient catalyst for the hydrogenation for benzene and alky-substituted benzene derivatives to give the corresponding cyclohexane. It is less efficient for functionalised aromatics, in particular it is not selective for substrates containing other reducible functions. The catalytic activity of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ is higher than that of $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ (**1**), which are present in the reaction mixture after a catalytic run. A more

active intermediate, has been identified NMR-spectroscopically to be the trinuclear cluster cation $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$ (**3**).

5. Experimental

Organic substrates were purchased from Fluka or Aldrich and checked for their purity by GC prior to use. Water was bidistilled, degassed and saturated with N_2 prior to use. The complex $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ was synthesised according to published methods [6]. The NMR spectra were recorded on a Varian Gemini 200 BB instrument, the treatment of the spectra being done by a Sun Varian station. GC spectra were recorded with a DANI 86.10 gas chromatograph using a Carbowax 20M capillary column.

5.1. Catalytic runs

In a typical experiment, 20 mg (0.04 mmol) $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ were dissolved in water (5 ml). To this solution, placed in a 100 ml stainless steel autoclave, 4 mmol of the organic substrate were added. After purging three times with H_2 , the autoclave was pressurised with hydrogen (60 bar) and heated to 90°C under vigorous stirring of the reaction mixture (900 rpm). After the reaction time indicated in Tables 1–3, the autoclave was cooled to room temperature and the pressure released. The two-phase system was decanted, the aqueous phase was analysed by NMR spectroscopy, the organic phase containing the products and substrate was filtered and analysed by GC and NMR spectroscopy.

5.2. Preparation of $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]\text{Cl}$

The cation $[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)_3(\mu_2\text{-Cl})(\mu_3\text{-O})(\mu_2\text{-H})_2]^+$ (**3**) was synthesised as the per-

chlorate salt according to Ref. [3]. This salt (200 mg, $0.29 \cdot 10^{-4}$ mmol) was dissolved in hot water (50 ml) and then submitted to an ion-exchange chromatography using Doewex 1×8 , 200–400 mesh (chloride form) and water as elutant. The solution containing the chloride salt of **3** was evaporated to dryness. The yield was 181 mg (100%).

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References

- [1] F. Joó, A. Kathó, *J. Mol. Catal.* 116 (1997) 3.
- [2] L. Plasseraud, G. Süss-Fink, *J. Organomet. Chem.* 539 (1997) 163.
- [3] G. Meister, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc. Dalton Trans.* (1994) 3215.
- [4] R. Robertson, T.A. Stephenson, T. Arthur, *J. Organomet. Chem.* 162 (1978) 121.
- [5] M.A. Bennett, T.N. Huang, T.W. Turney, *J. Chem. Soc. Chem. Commun.* (1979) 312.
- [6] T. Arthur, T.A. Stephenson, *J. Organomet. Chem.* 208 (1981) 369.