Catalytic hydrogenation of benzene derivatives under biphasic conditions

Laurent Plasseraud, Georg Süss-Fink *

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Abstract

The catalytic hydrogenation of various benzene derivatives was studied, using the salt $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$ in aqueous solution as the catalyst precursor. Under these biphasic conditions, the corresponding cyclohexane derivatives are obtained with catalytic turnover rates of more than 100 cycles per hour. In the case of the hydrogenation of the parent benzene, the NMR analysis of the aqueous phase revealed the presence of the hexahydrido species $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ together with the tetrahydrido species $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ under hydrogen pressure. An exchange study of the reaction of the para-cymene analogue $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4Ru_4H_4]^{2+}$ with benzene showed the four arene ligands in the tetrahydrido cluster to be successively replaced by other aromatic ligands under catalytic conditions. © 1997 Elsevier Science S.A.

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1. Introduction

The past decade has witnessed an increasing interest in water-soluble catalysts and catalytic reactions under biphasic conditions, water being a cheap and environmentally friendly solvent [1–3]. Biphasic catalytic processes also allow the facile separation of the catalyst remaining in the aqueous phase from product and substrate in the organic phase. In most cases the water-soluble catalysts used contain sulfonated phosphine ligands which make the catalytically active complexes anionic [4,5], in some cases cationic water-soluble complexes have also been used for biphasic catalytic reactions [6,7].

Recently we described the water-soluble tetranuclear ruthenium cluster cations $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ **(1)** and $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ **(2)** which represent an interesting redox couple. The electron-deficient tetrahydrido species **1** (58e) takes up molecular hydrogen to give the electron-precise hexahydrido species **2** (60e), which reacts in turn with molecular oxygen to go back to **1** with elimination of water (Scheme 1) [8]. The redox equilibrium between **1** and **2** makes this system interesting for hydrogenation reactions in aqueous solution or under

biphasic conditions. Since **1** and **2** contain benzene ligands, they are suitable candidates for catalytic reactions involving aromatics.

The hydrogenation of arenes is an important industrial process, in particular with the increasing demand for low-aromatic diesel fuels [9]. While the industrial hydrogenation of aromatics is carried out exclusively with heterogeneous catalysts, there are only a few reports of homogeneous catalysts for the hydrogenation of arenes: $(\eta^3\text{-}C_3H_5)Co(PMe_3)_3$ was found to be moderately active in organic solution (neat) [10,11], $(\eta^5\text{-}C_5Me_5)_2Rh_2Cl_4$ is active in isopropanol solution with triethylamine as a co-catalyst [12], while $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}Cl)]Cl_2$ seems to be the most active homogeneous catalyst in isopropanol even without co-catalyst [13].

In this paper, we report the use of the water-soluble salt $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$ as a catalyst for the hydrogenation of various benzene derivatives to give the corresponding cyclohexanes under biphasic (water/substrate) conditions.

2. Results

Benzene and its derivatives are hydrogenated with molecular hydrogen (60bar) at 90 °C by an aqueous

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* Corresponding author.
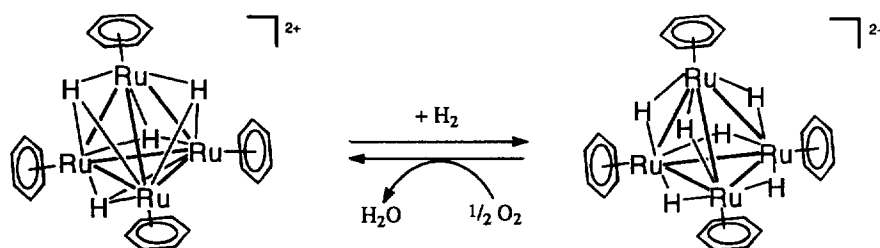
Scheme 1. Interconversion of the tetranuclear clusters $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (1) and $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ (2) by H_2 and O_2 respectively.

solution of $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$ (0.003 M) with vigorous stirring of the biphasic mixture.

The best catalytic turnover frequency is obtained with benzene, substituted benzenes react somewhat slower (Table 1). The increasing steric hindrance of the

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

Substrate	Product (% yield) [b]	Time (h)	CT number [c]
Benzene	Cyclohexane (94)	2.5	940
Toluene	Methylcyclohexane (88)	3.5	878
Cumene	iso-Propylcyclohexane (90)	7.0	889
tert-Butylbenzene	tert-Butylcyclohexane (50)	2.0	500
Propylbenzene	Propylcyclohexane (73)	5.0	730
Biphenyl [d]	Cyclohexylbenzene (18) Bicyclohexyl (18)	24.0	360

[a] Conditions: catalyst (0.015 mmol), water (5 ml), catalyst/substrate ratio 1/1000, temperature 90 °C, hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Measured by gas chromatography.
[c] Catalytic turnover: mole substrate transformed per mole catalyst.
[d] Substrate dissolved in cyclohexane (10 ml).

Table 2
Hydrogenation of di- and trisubstituted benzene derivatives under biphasic conditions [a]

Substrate	Product (% yield) [b]	Time (h)	CT number [c]
o-Xylene	1,2-Dimethylcyclohexane (10)	10.0	100
m-Xylene	1,3-Dimethylcyclohexane (9)	10.0	90
p-Xylene	1,4-Dimethylcyclohexane (14)	10.0	140
1,2,3-Trimethylbenzene	1,2,3-Trimethylcyclohexane (41)	5.0	410

[a] Conditions: catalyst (0.015 mmol), water (5 ml), catalyst/substrate ratio 1/1000, temperature 90 °C; hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Measured by gas chromatography.
[c] Catalytic turnover: mole substrate transformed per mole catalyst.

alkyl substituents in the series benzene, toluene, cumene is clearly reflected in the decrease of the catalytic turnover frequency; the somewhat higher turnover frequency of tert-butylbenzene may be explained by a better miscibility with the aqueous phase. Disubstituted benzene derivatives react even slower, 1,2,3-trimethylbenzene being an exception (Table 2). Functionalised benzene derivatives are more difficult to hydrogenate than the corresponding alkyl derivatives. Whereas toluene is hydrogenated with a turnover frequency of 251 h^{-1}, the turnover frequency of the hydrogenation of anisole is only 15 h^{-1} (Table 3).

The hydrogenation of benzene derivatives, using $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]Cl_2$ in aqueous solution under biphasic conditions, is not very selective. Biphenyl is hydrogenated to give a 1:1 mixture of cyclohexylbenzene and bicyclohexane (Table 1). In addition to the hydrogenation of the aromatic ring, reducible functions of the substituents are also hydrogenated. Thus, acetophenone is hydrogenated to give a mixture of methylcyclohexylketone, 1-phenylethanol and 1-cyclohexylethanol (Table 3). Styrene reacts to give predominantly ethylbenzene and a small amount of ethylcyclohexane; vinylcyclohexane is not even detected (Table 4). In the case of phenylacetylene, the triple bond is preferentially hydrogenated, giving mainly styrene with some ethylbenzene and only traces of ethylcyclohexane (Table 4). Nitrobenzene is reduced to give exclusively aniline, the

Table 3
Hydrogenation of functionalised benzene derivatives under biphasic conditions [a]

Substrate	Product (% yield) [b]	Time (h)	CT number [c]
Acetophenone	Methylcyclohexylketone (38) 1-Phenylethanol (13.5) 1-Cyclohexylethanol (12)	14.0	635
Anisole	Methoxycyclohexane (22)	14.0	220
Methyl benzoate	Methyl cyclohexanoate (66)	20.0	660
Nitrobenzene	Aniline (23) [d]	24.0	230

[a] Conditions: catalyst (0.015 mmol), water (5 ml), catalyst/substrate ratio 1/1000, temperature 90 °C; hydrogen pressure 60 bar, stirred at 900 min^{-1}.
[b] Measured by gas chromatography.
[c] Catalytic turnover: mole substrate transformed per mole catalyst.
[d] Determined by ^1H NMR spectroscopy.

Table 4

Hydrogenation of benzene derivatives containing substituents with C=C and C≡C bonds under biphasic conditions [a]

Substrate	Product (% yield) [b]	Time (h)	CT number [c]
Styrene	Ethylbenzene (83)	8.0	965
	Ethylcyclohexane (13.5)		
α-Methylstyrene	Cumene (73.5)	8.0	850
	iso-Propylcyclohexane (11.5)		
Allylbenzene	Propylbenzene (56)	8.0	680
	β-Methylstyrene (10)		
	α-Methystyrene (2)		
Phenylacetylene	Styrene (50)	18.0	580
	Ethylbenzene (7)		
	Ethylcyclohexane (1)		

[a] Conditions: catalyst (0.015 mmol), water (5 ml), catalyst/substrate ratio 1/1000, temperature 90 °C; hydrogen pressure 60 bar, stirred at 900 min⁻¹.

[b] Measured by gas chromatography.

[c] Catalytic turnover: mole substrate transformed per mole catalyst.

aromatic nucleus being completely retained (Table 3). With allylbenzene, hydrogenation of the olefinic side-chain is observed, along with isomerisation of the double bond, but no hydrogenation of the aromatic ring (Table 4).

3. Discussion

The catalytic hydrogenation of benzene was monitored by ^{1}H NMR spectroscopy of the aqueous phase containing the catalyst using D_2O as the solvent. In the beginning only the two singlets of the cation [(η^6-

$C_6H_6)_4Ru_4H_4]^{2+}$ (1) [$\delta(C_6H_6)$ = 5.97(24), δ(H) = 17.42(4)] are detected in the D_2O phase. During the hydrogenation process the signals of the hexahydrido cation [(η^6-$C_6H_6)_4Ru_4H_6]^{2+}$ (2) [$\delta(C_6H_6)$ = 6.02(24), δ(H) = − 15.08(6)] grow in; after 2 h both species are present in an approximately 1:1 ratio. In the ^{1}H NMR spectrum, there is no indication of another hydrido species (Fig. 1). After total conversion of benzene, degradation of 1 and 2 to metallic ruthenium is observed, but 1 and 2 stay intact as long as there is an excess of benzene or another aromatic substrate present.

In order to find out how the catalyst acts on the substrate, we studied the exchange reaction of the aromatic ligands in the tetranuclear cluster cations. Neither 1 nor 2 undergo arene substitution under reflux conditions, but under hydrogen pressure the benzene ligands in both 1 and 2 can be replaced by other aromatic ligands. In the tetrahydrido species [(η^6-$C_6H_6)_4Ru_4H_4]^{2+}$ (1), reacted as chloride salt in aqueous solution at 90 °C under H_2 (60 bar), with p-xylene, the four benzene ligands are successively replaced by p-xylene ligands; at the same time the corresponding hexahydrido species are formed. The tetrasubstituted species [(η^6-$C_6H_6)_4Ru_4H_4]^{2+}$ and [(η^6-$C_6H_6)_4Ru_4H_6]^{2+}$ are observed only after 40 h. In order to identify the mixed species unambiguously, the substitution reaction was carried out starting from the known p-cymene analogues of 1 and 2, [(η^6-$C_6H_6MePr^i$-$p)_4Ru_4H_4]^{2+}$ [14] and [(η^6-$C_6H_4MePr^i$-$p)_4Ru_4H_6]^{2+}$ [8] with benzene as the incoming ligand. An aqueous solution of [(η^6-$C_6H_4MePr^i$-$p)_4Ru_4H_4]Cl_2$ was mixed with benzene, pressurized with hydrogen (60 bar) and
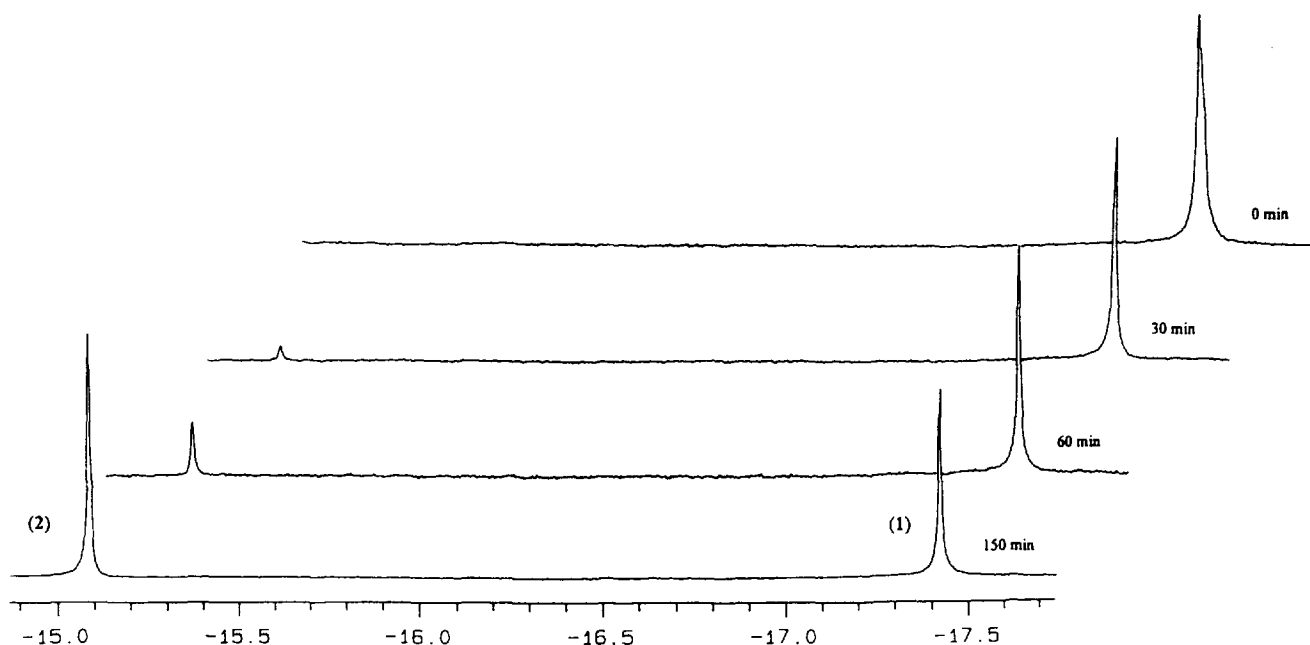

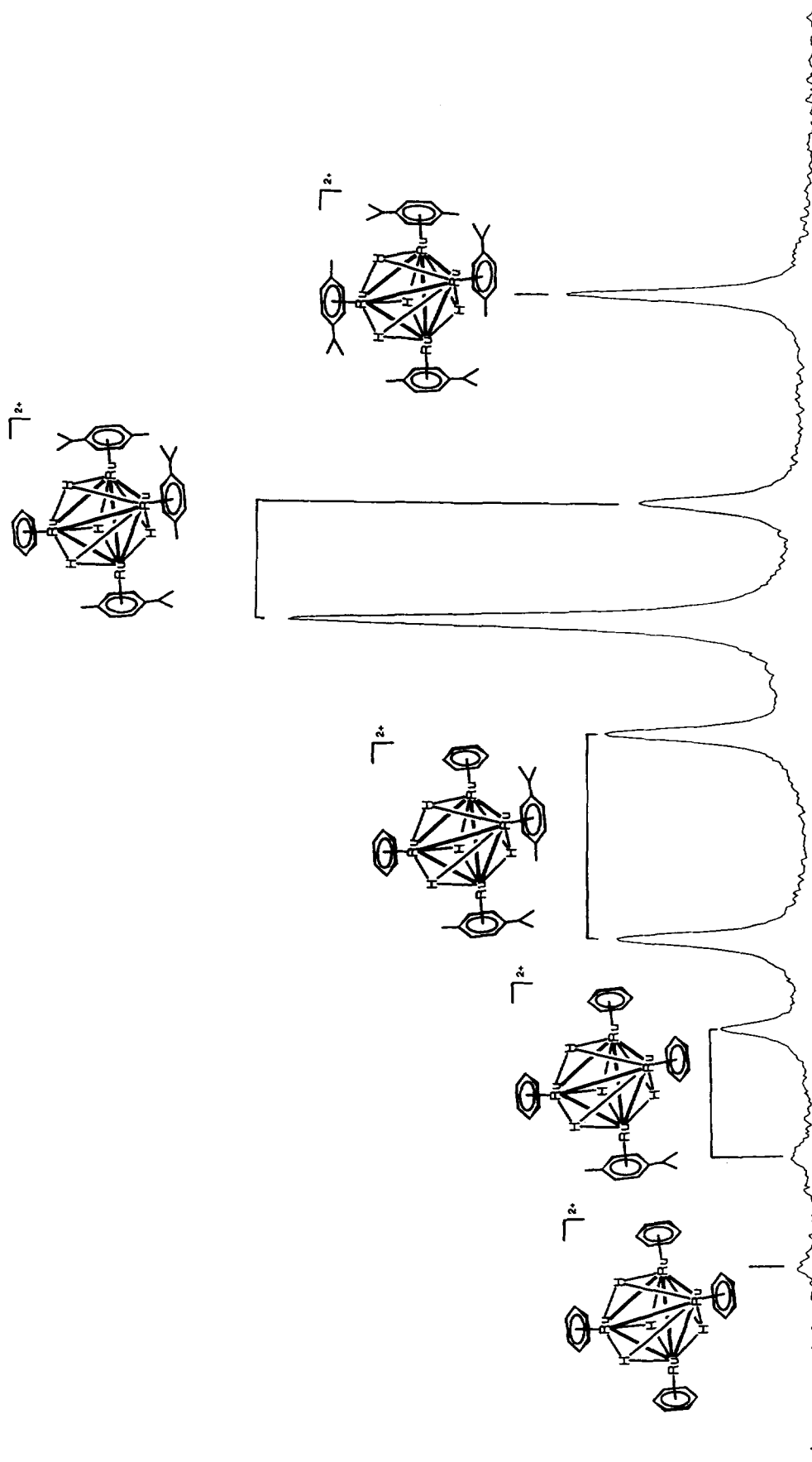Fig. 1. ^{1}H NMR study of the D_2O phase during the catalytic biphasic hydrogenation of benzene.

Fig. 2. ^{1}H NMR spectrum in D_2O, δ from -17 to -19, of the exchange reaction of $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4Ru_4H_4]^{2+}$ with benzene.
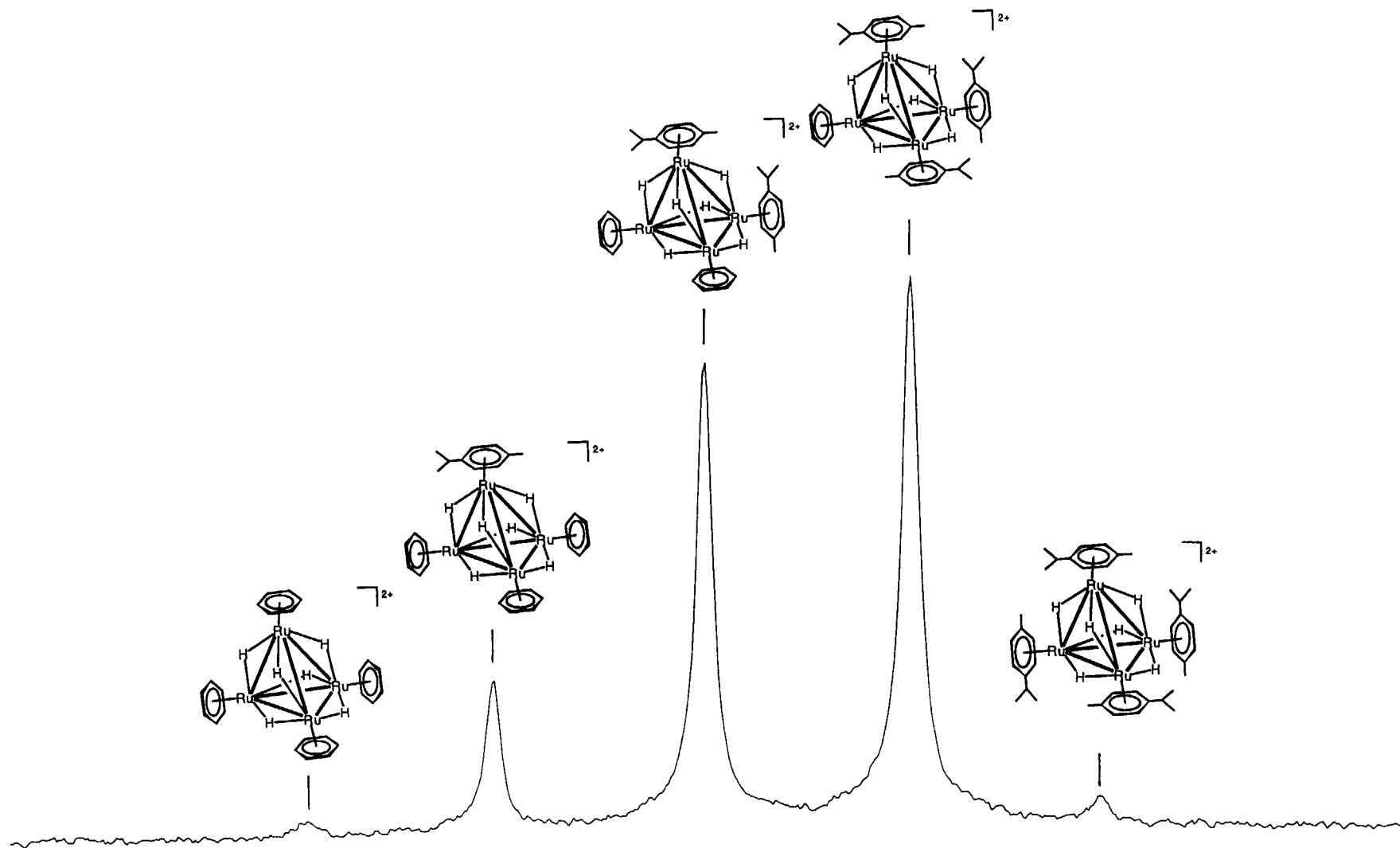
Fig. 3. ^{1}H NMR spectrum in D_2O, δ from -15 to -16, of the exchange reaction of $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4Ru_4H_4]$ with benzene.

heated to 90 °C for 42 h. The ^{1}H NMR spectrum of the aqueous phase revealed the presence of 10 cationic hydrido clusters, the five possible tetrahydrido species $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4Ru_4H_4]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_3(\eta^6\text{-}C_6H_6)Ru_4H_4]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\eta^6\text{-}C_6H_6)_2Ru_4H_4]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)(\eta^6\text{-}C_6H_6)_3Ru_4H_4]^{2+}$, $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (Fig. 2), and the five possible hexahydrido species $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4Ru_4H_6]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_3(\eta^6\text{-}C_6H_6)Ru_4H_6]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\eta^6\text{-}C_6H_6)_2Ru_4H_6]^{2+}$, $[(\eta^6\text{-}C_6H_4MePr^i\text{-}p)(\eta^6\text{-}C_6H_6)_3Ru_4H_6]^{2+}$, $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ (Fig. 3). The tetrasubstituted species 1 and 2 were identified by comparison with an authentic sample. In the region from δ −17 to −19, the hydrido resonances of the five tetrahydrido species are observed. While the tetrabenzene and the tetra-p-cymene derivatives exhibit only one resonance, the four μ_3-H ligands being equivalent, the three mixed species give rise to two signals each (ratio 1:3, 2:2, 3:1), reflecting the two types of μ_3-H ligands in the mixed clusters (Fig. 2). In contrast to the tetrahydrido species, the five hexahydrido species show up, in the region from δ −15 to −16, with only one singlet resonance each (Fig. 3), indicating the hexahydrido species to be fluxional in solution already at room temperature. As not only the tetrabenzene and tetra-p-cymene derivatives, but also the three mixed species, give rise to a singlet, the six μ_2-H ligands undergo a scrambling process on the Ru_4 framework. The integral ratio of the hydrido signals shows that in, both the

tetrahydrido and the hexahydrido series, the monosubstituted derivatives are the predominant species; di-, tri-, and tetrasubstitution occur to a much lesser extent.

On the bases of the ^{1}H NMR studies during the catalytic hydrogenation and the aromatic exchange experiments we propose the mechanism depicted in Scheme 2 for the catalytic hydrogenation of benzene using the cluster cation $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (1) as the catalyst. Uptake of molecular hydrogen converts the electron-deficient tetrahydrido species 1 into the electron-precise hexahydrido species 2. Intramolecular transfer of two hydrogen atoms from the metal framework to a benzene ligand gives the tetrahydrido species 3 with one cyclohexadiene ligand, which reacts with H_2 to the corresponding hexahydrido species 4. Transfer of two hydrogen atoms from the Ru_4 skeleton to the cyclohexadiene ligand affords the tetrahydrido species 5 containing a cyclohexene ligand. Uptake of H_2 gives the corresponding hexahydrido species 6 in which again two hydrogen atoms are transferred from the metal framework to the cyclohexene ligand, the cyclohexane is eliminated, while the remaining tetrahydrido cluster fragment adds immediately benzene to give 1.

Since only 1 and 2 can be detected by ^{1}H NMR spectroscopy throughout the catalytic hydrogenation of benzene, we assume the proposed species 3 to 6 to be present in an equilibrium concentration of less then 1%. This is not surprising, given the high degree of electronic insaturation of these species. Accordingly, neither cyclohexadiene nor cyclohexene were detected as side-
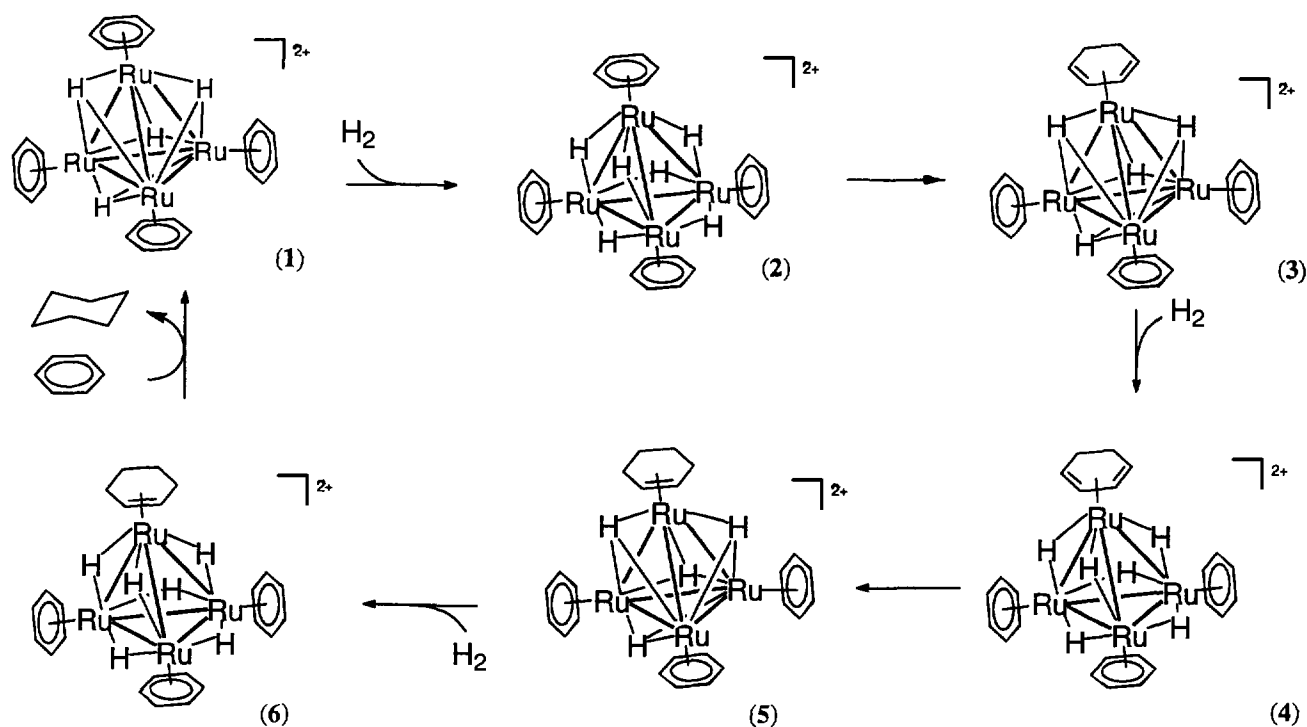
Scheme 2. Proposed mechanism for the catalytic hydrogenation of benzene.

products of benzene or cyclohexane, being consistent with the assumption that **3** to **6** are short-lived species.

In the case of the hydrogenation of benzene derivatives to the correponding cyclohexane catalysed by **1**, we assume aromatic ligand exchange to take place prior to the transformations outlined in Scheme 2. Since the ligand exchange studies have shown monosubstitution to prevail, whereas multiple substitution requires a long time and occurs to a lesser extent, we suppose the catalytic hydrogenation of the aromatic substrate to take place at one ruthenium centre only (monosubstitution).

This mechanism is consistent with isotope labelling studies. The hydrogenation of the deuterated substrate C_6D_6, catalysed by $[(\eta^6-C_6H_6)_4Ru_4H_4]^{2+}$ (**1**) with H_2 in H_2O, gives exclusively one isomer of $C_6D_6H_6$. The $^2D\{^1H\}$ NMR spectrum of the product (neat) shows only a single deuterium resonance presenting a width at half-height of 2.0 Hz; in the ^1H NMR spectrum the signal at $\delta = 1.39$ ppm sharpens under ^2D-decoupling, indicating that the all-cis isomer is present at $> 99\%$ (measurements by Professor Bernd Wrackmeyer, Universität Bayreuth, Germany). This result proves the high stereoselectivity of **1** in the catalytic hydrogenation of benzene derivatives.

4. Conclusion

The electron-deficient cluster cation $[(\eta^6-C_6H_6)_4Ru_4H_4]^{2+}$ (**1**) in aqueous solution is an efficient catalyst for the hydrogenation of benzene and alkyl-substituted benzene derivatives to give the corresponding cyclohexane. It is less efficient for functionalised aromatics; in particular, it is not selective if the aromatic substrate contains other reducible functions.

Aromatic ligand exchange experiments and ^1H NMR studies reveal the coordination of the aromatic substrate by ligand substitution under catalytic conditions and the formation of the electron-precise hexahydrido clusters.

5. Experimental details

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 complexes $[(\eta^6-C_6H_6)_4Ru_4H_4]Cl_2$ and $[(\eta^6-C_6H_4MePr^i-p)_4Ru_4H_4]Cl_2$ were synthesized according to published methods [8]. 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, 12 mg (0.015 mmol) $[(\eta^6-C_6H_6)_4Ru_4H_4]Cl_2$ (anion **1**) was dissolved in water (5 ml). To this solution, placed in a 100 ml stainless steel autoclave, 15 mmol of the organic substrate was added. After purging three times with H_2, the autoclave was pressurized with hydrogen (60 bar) and heated to 90 °C under vigorous stirring of the reaction mixture (900 revolutions per mix). After the reaction time indicated in Tables 1–4, the autoclave was cooled to room temperature and the pressure released. The two-phase system was decanted, the aqueous phase containing the catalyst was re-used for further runs, the organic phase containing products and substrate was filtered and analysed by GC and NMR spectroscopy.

5.2. Ligand exchange experiments

The ligand exchange experiments of $[(\eta^6-C_6H_6MePr^i-p)_4Ru_4H_4]Cl_2$ with benzene, and of $[(\eta^6-C_6H_6)_4Ru_4H_4]Cl_2$ with p-xylene, were carried out in the same way as the catalytic experiments (complex/aromatic ratio 1:1000, H_2 60 bar, 90 °C), but the reaction was prolonged for 42 h. After cooling and venting of the autoclave, the aqueous phase, after separation by decanting, was evaporated to dryness, the residue dissolved in D_2O and analysed by NMR spectroscopy.

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