

# Homogeneous hydrogenation of arenes catalyzed by the bis(dihydrogen) complex $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$

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## Abstract

The reaction of benzene, naphthalene and anthracene with dihydrogen under a pressure of 3 and 20 bar at 80°C in the presence of  $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$  (**1**) leads to cyclohexane, tetralin and a mixture of 1,2,3,4-tetrahydroanthracene (4H-An) and 1,2,3,4,5,6,7,8-octahydroanthracene (8H-An), respectively. Surprisingly, the increase of dihydrogen pressure lowers the yield of hydrogenation products. Product **1** may be used directly as a catalyst precursor or may be prepared in situ from  $[\text{RuH}\{(\eta^3\text{-C}_6\text{H}_8)\text{PCy}_2\}\{(\eta^2\text{-C}_6\text{H}_9)\text{PCy}_2\}]$  (**2**) under dihydrogen at room temperature. A number of functionalized arenes (toluene, chlorobenzene, durene) as well as tetralin, phenanthrene and 9,10-dihydroanthracene are not reduced under 3 bar of dihydrogen. The reaction of **1** with arenes, either in neat benzene or in cyclohexane in the case of naphthalene and tetralin at 80°C leads to the formation of respectively,  $\eta^6$ -bound benzene (**3**), naphthalene (**4**) and tetralin (**5**) complexes that are also present in very small quantities in the final catalytic mixtures. Reaction of **1** with anthracene at room temperature yields the complex  $[\text{Ru}(\eta^4\text{-C}_{14}\text{H}_{10})(\text{PCy})_2]$  (**6**) containing an  $\eta^4$ -bound anthracene. Product **6** shows a catalytic activity for anthracene hydrogenation and can be regarded as an intermediate in the catalytic cycle. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrogenation; Arenes; Ruthenium; Dihydrogen complexes

## 1. Introduction

Hydrogenation of arenes with soluble molecular catalysts has not been studied very extensively since it generally requires rather severe conditions and because heterogeneous catalysts are remarkably active in these reactions [1–3]. Recently, several research groups have reported efficient arene hydrogenation catalytic systems based on rhodium and palladium complexes tethered to a solid support [4–6], ruthenium cluster catalyst in an ionic liquid [7], ruthenium

complexes in biphasic aqueous solutions [8–10] and colloidal rhodium as a suspension in water [11] or in aqueous/supercritical fluid biphasic media [12]. For some years, the use of molecular catalysts for arene hydrogenation was stimulated by the studies of arenes as models for products resulting from coal liquefaction [13–16]. Early works on arene hydrogenation catalysts concentrated on their activities [14–25], but in some cases the homogeneity of these systems was uncertain. However, a number of systems were proven to be homogeneous and their studies have led to a better understanding of the mechanisms of arene hydrogenation [26–37].

In the 1980s, a homogeneous process, the “Dimersol” process, developed by the Institut Français

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du Pétrole, has been applied successfully for the hydrogenation of benzene to cyclohexane [1,38]. More recently, a variety of arene substrates have been hydrogenated by hydride derivatives of niobium and tantalum [39–44]. There is, however, only one example of a dihydrogen complex quoted as an effective catalyst for hydrogenation of 9-methylanthracene [45].

Our recent observations that the bis(dihydrogen) complex  $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$  (**1**) [46,47] and some of its derivatives (e.g.  $[\text{RuH}\{(\eta^3\text{-C}_6\text{H}_8)\text{PCy}_2\}\{(\eta^2\text{-C}_6\text{H}_9)\text{PCy}_2\}]$  (**2**)) undergo H/D isotopic exchange reactions in deuterated arene solvents ( $d_6$ -benzene,  $d_8$ -toluene) are indicative of a mechanism that involves coordination of an arene ring followed by a C–H bond activation [48]. Moreover, the cyclohexyl rings of the  $\text{PCy}_3$  ligands in **1** undergo reversible, intramolecular dehydrogenation/hydrogenation reactions in the presence of a hydrogen acceptor or dihydrogen, respectively. These findings prompted us to study **1** as a potential catalyst for arene hydrogenation.

## 2. Experimental

Microanalysis were performed by The Laboratoire de Chimie de Coordination Microanalytical Service. Proton and phosphorus spectra were recorded on a Bruker AC 200 (at 200.132 and 81.015 MHz, respectively) and on an AMX 400 (at 400.133 and 161.985 MHz, respectively) while  $^{13}\text{C}$  NMR spectra were obtained by using AM 250 (50.323 MHz) and AMX 400 (100.624 MHz) spectrometers, all operating in the Fourier transform mode. All manipulations were carried out under argon using standard Schlenk-line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon prior to use.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was purchased from Johnson Matthey Ltd. and all other reagents were purchased from Aldrich and degassed before use. Reaction products were analyzed by GC on a Hewlett Packard 5890 apparatus fitted with a FID detector using a capillary column (30 mm  $\times$  0.32 mm) packed with cross-linked methyl silicone. Homogeneity of the reaction mixtures has been confirmed by the test with liquid mercury which is known to inhibit colloidal catalysis [49,50]. Products **1** and **2** have been prepared by published methods [48].

### 2.1. Hydrogenation under 3 bar $\text{H}_2$

$[\text{RuH}\{(\eta^3\text{-C}_6\text{H}_8)\text{PCy}_2\}\{(\eta^2\text{-C}_6\text{H}_9)\text{PCy}_2\}]$  (**2**) (0.02 g, 0.03 mmol) was placed into a Fisher–Porter flask under argon atmosphere. The system was evacuated and flushed with dihydrogen. A required amount (normally 10 ml) of a degassed solvent was then introduced. The reactor was pressurized to 3 bars of dihydrogen and stirred at room temperature for 0.5–1 h, depending on the solvent, to allow total conversion of **2** to **1**, visualized by complete dissolution and formation of a colorless homogeneous solution. The reactor was then depressurized and a suitable amount (normally, 1.5 mmol) of a degassed substrate was introduced under a dihydrogen stream. The reaction mixture was again pressurized to 3 bar of  $\text{H}_2$  and stirred at room temperature until all substrate dissolved (anthracene dissolves only partly under these conditions). Then the reactor was placed into an oil bath and heated at 80°C while stirring magnetically for the required amount of time. The Fisher–Porter flask was then cooled down to room temperature, depressurized and the hydrogenation products were analyzed by GC.

### 2.2. Hydrogenation under 20 bar $\text{H}_2$

#### 2.2.1. Hydrogenation of neat benzene

A catalyst precursor (**1**) (0.075 g, 0.112 mmol) was placed into a stainless steel autoclave (50 ml volume) fitted with gas inlet and outlet tubings, externally driven stir bar, manometer and a heating mantle. The system was evacuated and flushed with argon. This procedure was repeated three times using dihydrogen in the place of argon. A total of 20 ml degassed benzene was then introduced via a PTFE transfer tubing. The system was then pressurized to 20 bar at 20°C with vigorous stirring and the reactor was heated up to 80°C within 15 min, after which the internal pressure in the reactor reached 24 bars. On termination of tests, the reactor was cooled down to room temperature and the products were analyzed by GC.

#### 2.2.2. Hydrogenation of naphthalene and anthracene

Product **1** (0.02 g, 0.03 mmol) and a solid substrate (1.5 mmol) were placed into the autoclave and the same procedure was used as above but using cyclohexane (20 ml) in place of benzene as solvent.

### 2.3. Preparation of the complexes

$[RuH_2(\eta^6-C_6H_6)PCy_3]$  (**3**): An amount of 0.085 g (0.13 mmol) of **1** was dissolved in benzene (4 ml) and refluxed for 3 h. The resulting orange solution was evaporated to dryness giving a pale yellow solid very soluble in most common solvents. The solid was characterized as  $[RuH_2(\eta^6-C_6H_6)PCy_3]$  contaminated with free  $PCy_3$  by  $^1H$ ,  $^{31}P$  and  $^{13}C$  NMR spectra in  $C_6D_6$ .

$[(PCy_3)_2H_2Ru(\mu-\eta,\eta-C_{10}H_8)RuH_2(PCy_3)]$  (**4**): To a suspension of **1** (0.140 g, 0.21 mmol) in cyclohexane (5 ml) an excess of naphthalene (0.08 g, 0.63 mmol) was added and the mixture was stirred for ca. 3 min before heating at reflux temperature for 2 h. On cooling, the solvent was removed under vacuum resulting in a brown–red sticky mass from which unreacted naphthalene was removed by sublimation at  $60^\circ C$ . To the remaining brown solid, pentane (6 ml) was added and the yellow precipitate formed was filtered off, washed with pentane (2 ml  $\times$  1.5 ml) and dried in vacuo. Yield: ca. 0.055 g (59%). Recrystallization from benzene/pentane gave yellow, air sensitive crystals. Anal. Calcd. for  $C_{46}H_{78}P_2Ru_2$ : C, 61.72; H, 8.78. Found: C, 61.81; H, 8.58.

$[RuH_2(\eta^6-C_{10}H_{12})PCy_3]$  (**5**): To a suspension of **1** (0.100 g, 0.15 mmol) in cyclohexane (6 ml) degassed tetralin (61  $\mu$ l, 0.45 mmol) was added and refluxed for 5 h. The resulting red solution was filtered off and kept overnight under vacuum to give a red–brown sticky mass. Pentane (8 ml) was added and the mixture was filtered off and passed through a chromatographic column filled with  $Al_2O_3$ . The orange phase was eluted using benzene followed by evaporation under vacuum to form a film on the surface of the flask. Since we were unable to obtain the product in another form,  $^1H$  and  $^{31}P$  NMR spectra were run after dissolution of the yellow film in  $C_6D_6$ . The product is contaminated with large amount of  $PCy_3$  and is free of tetralin.

$[RuH_2(\eta^4-C_{14}H_{10})(PCy_3)_2]$  (**6**): A suspension of **1** (0.100 g, 0.15 mmol) and anthracene (0.0535 g, 0.3 mmol) in diethyl ether (8 ml) was stirred overnight yielding a fine yellow precipitate that was collected, washed with  $Et_2O$  (3 ml  $\times$  5 ml) and vacuum dried. Yield ca. 0.075 g (60%). Anal. Calcd. for  $C_{50}H_{78}P_2Ru$ : C, 71.31; H, 9.33. Found: C, 71.18; H, 9.2. IR  $\nu(Ru-H)$ , 2013 and  $1975\text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Hydrogenation of benzene

Under mild conditions ( $80^\circ C$ , 3 bar  $H_2$ ) methylcyclohexane solutions of **1** catalyze the hydrogenation of benzene to cyclohexane with a low turnover number of 2.8 in 24 h (Table 1). After increasing the reaction time to 45 h, no sign of metal precipitation is observed. When similar experiments are carried out in neat benzene, in which the substrate to catalyst ratio increased ca. 15 times as compared with the reaction performed in a methylcyclohexane solution, the turnover number increased to 32 after 20 h, hence revealing a significant increase in the turnover frequency. This activity seems comparable to that of  $[\eta^6-C_6(CH_3)_6Ru-\eta^4-C_6(CH_3)_6]$  under comparable reaction conditions ( $90^\circ C$ , 2–3 bar  $H_2$ ); however, the substrate to Ru ratio has not been specified in that work [30]. However, when the reaction in neat benzene was carried out in the presence of mercury as an homogeneity test, no conversion was observed [49,50]. This result might be due to the formation of colloids in this case and will be further investigated.

When toluene has been used as a substrate in cyclohexane, only traces of methylcyclohexane have been found in the reaction mixture after 24 h. Other functionalized arenes such as 1,2,4,5-tetramethylbenzene (durene) and chlorobenzene do not undergo reduction in the same conditions.

#### 3.1.1. Synthesis of $[RuH_2(\eta^6-C_6H_6)PCy_3]$ (**3**)

NMR spectra recorded after a 45 h reaction of hydrogenation of  $d_6$ -benzene used as solvent, display almost exclusively signals characteristic of **1** (e.g.  $\delta -7.83$  (Ru–H) and  $\delta 76.2$  ( $PCy_3$ ) for  $^1H$  and  $^{31}P$  NMR, respectively) which suggests the constant presence of this compound during the course of the catalytic reaction. However, a very small doublet ( $\delta -10.5$ ,  $J = 42.3$  Hz) and two weak signals of equal intensity at ca. 78 and 10 ppm can also be found in the  $^1H$  and  $^{31}P$  NMR spectra, respectively.

The reaction of **1** in refluxing benzene under an argon atmosphere leads to a new product that we were unable to isolate in pure form due to its high solubility in most commonly used solvents. Nevertheless, a  $^1H$  NMR spectrum (Table 2) of the pale yellow solid obtained by evaporation to dryness of the reaction mix-

Table 1  
Hydrogenation of arenes at 80°C under 3 bar H<sub>2</sub><sup>a</sup>

Substrate	Time (h)	Conversion (%)	Products (%)	TON <sup>b</sup>
Benzene (neat) <sup>c</sup>	20	4.3	Cyclohexane (100)	32.1
Benzene <sup>d</sup>	24	5.6	Cyclohexane (100)	2.8
Toluene	24	<0.1	Methylcyclohexane (traces)	
Chlorobenzene	15	None		
Durene	24	None		
Naphthalene	24	25	Tetralin (100)	13
Tetralin	24	<0.1	<i>Cis</i> - and <i>trans</i> -decalin (traces)	
Anthracene	4	100	4H-An <sup>e</sup> (93)	50 <sup>f</sup>
			8H-An <sup>g</sup> (7)	3.5 <sup>f</sup>
Anthracene	20	100	4H-An <sup>e</sup> (84)	50 <sup>f</sup>
			8H-An <sup>g</sup> (16)	8 <sup>f</sup>
Anthracene	24	100	4H-An <sup>e</sup> (73)	50 <sup>f</sup>
			8H-An <sup>g</sup> (27)	13.5 <sup>f</sup>
Anthracene <sup>h</sup>	24	100	4H-An <sup>e</sup> (90)	50 <sup>f</sup>
			8H-An <sup>g</sup> (10)	5 <sup>f</sup>
Phenanthrene	17	None		
9,10-2H-An <sup>i</sup>	4	None		

<sup>a</sup> Unless stated otherwise, **2** is the catalyst precursor, solvent: cyclohexane (10 ml), [Ru] = 3 × 10<sup>-3</sup> M, [arene] = 0.15 M, arene/Ru = 50, products were analyzed by GC.

<sup>b</sup> TON is defined as mole of product formed per mole of Ru.

<sup>c</sup> [Ru] = 15 × 10<sup>-3</sup> M, benzene/Ru = 750.

<sup>d</sup> Solvent: methylcyclohexane (10 ml).

<sup>e</sup> 4H-An: 1,2,3,4-tetrahydroanthracene.

<sup>f</sup> Calculations based on the assumption that 8H-An is formed in a two stage reaction. It involves hydrogenation of anthracene to 4H-An (stage 1) followed by its hydrogenation to 8H-An (stage 2).

<sup>g</sup> 8H-An: 1,2,3,4,5,6,7,8-octahydroanthracene.

<sup>h</sup> [RuH<sub>2</sub>(η<sup>4</sup>-C<sub>14</sub>H<sub>10</sub>)(PCy<sub>3</sub>)<sub>2</sub>] used as a catalyst precursor.

<sup>i</sup> 9,10-2H-An: 9,10-dihydroanthracene.

ture shows (in C<sub>6</sub>D<sub>6</sub>) a sharp singlet at δ 5.25 assigned to η<sup>6</sup>-bound benzene and a doublet in the hydride resonance region at δ -10.50 (*J*<sub>P-H</sub> = 42.5 Hz). In <sup>31</sup>P{<sup>1</sup>H} NMR, a singlet at δ 78.3 transforms into a triplet upon selective decoupling of the PCy<sub>3</sub> protons. A loss of one phosphine ligand in the reaction of **1** with benzene is confirmed by the presence of a sharp singlet for free PCy<sub>3</sub> at δ 10.0 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.

The presence of an η<sup>6</sup>-coordinated benzene molecule in this compound is further supported by its <sup>13</sup>C NMR spectrum showing a doublet at δ 83.4 (*J*<sub>C-H</sub> = 170.4 Hz) coupled to phosphorus (*J*<sub>C-P</sub> = 2.5 Hz).

The <sup>1</sup>H and <sup>31</sup>P NMR resonances assigned to the minor product observed in the reaction of **1** with benzene under hydrogenation conditions and the respective data obtained for the reaction product

of **1** in the presence of boiling benzene are identical, hence indicating the formation of the same product (**3**), a η<sup>6</sup>-bound benzene ruthenium dihydride containing one tricyclohexylphosphine ligand: [RuH<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)PCy<sub>3</sub>] (**3**) (Scheme 1). The <sup>1</sup>H and <sup>31</sup>P NMR data for **3** are very close to those reported earlier for the triisopropyl phosphine analogue [51].

### 3.2. Hydrogenation of naphthalene

As expected, in the same reaction conditions, naphthalene, a condensed arene, is easier to hydrogenate than monoaromatic hydrocarbons. Hydrogenation of the first double bond in naphthalene is thermodynamically more favorable than the addition of the first dihydrogen molecule to benzene [52]. It produces 1,2,3,4-tetrahydronaphthalene (tetralin) in 25% yield

Table 2  
Selected NMR data (ppm) for compounds **3–6**, anthracene, 4H-anthracene and 8H-anthracene

Compound	<sup>1</sup> H NMR <sup>a</sup>	<sup>31</sup> P NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>a</sup>
[RuH <sub>2</sub> (η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> )PCy <sub>3</sub> ] ( <b>3</b> )	5.25 (s, 6H, η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sup>6</sup>	78.3 (s) <sup>b</sup>	83.4 (d, J <sub>C-H</sub> = 170.4 Hz; d, J <sub>C-P</sub> = 2.5 Hz, C <sup>1-6</sup> ) <sup>c</sup>
[(PCy <sub>3</sub> )RuH <sub>2</sub> ] <sub>2</sub> (μ:η:η-C <sub>10</sub> H <sub>8</sub> ) ( <b>4</b> )	-10.4 (d, 2H, J <sub>P-H</sub> = 42.3 Hz, Ru-H) 5.03 (brm, η <sup>6</sup> -C <sub>10</sub> H <sub>8</sub> <sup>1,4,5,8</sup> ) <sup>d</sup> 4.19 (brm, 4H, η <sup>6</sup> -C <sub>10</sub> H <sub>8</sub> <sup>2,3,6,7</sup> )	68.9 (s) <sup>b</sup>	95.8 (s, C <sup>9,10</sup> ) <sup>e</sup> 78.0 (d, J <sub>C-H</sub> = 169.2 Hz, C <sup>1,4,5,8</sup> ) 64.7 (brd, J <sub>C-H</sub> = 158 Hz, C <sup>2,3,6,7</sup> )
[RuH <sub>2</sub> (η <sup>6</sup> -C <sub>10</sub> H <sub>12</sub> )PCy <sub>3</sub> ] ( <b>5</b> )	-10.18 (d, 4H, J <sub>P-H</sub> = 29.3 Hz, Ru-H) 5.35 (brm, 2H, η <sup>6</sup> -C <sub>10</sub> H <sub>12</sub> <sup>1,4</sup> ) <sup>d</sup> 5.20 (brm, 2H, η <sup>6</sup> -C <sub>10</sub> H <sub>12</sub> <sup>2,3</sup> )	78.6 (s) <sup>b</sup>	
[RuH <sub>2</sub> (η <sup>4</sup> -C <sub>14</sub> H <sub>10</sub> )(PCy <sub>3</sub> ) <sub>2</sub> ] ( <b>6</b> )	-10.45 (d, 2H, J <sub>P-H</sub> = 42.3 Hz, Ru-H) 7.54 (dd, 2H, H <sup>5,8</sup> , J <sub>vic</sub> = 6.0 Hz, J <sub>all</sub> = 3.3 Hz) <sup>f,g</sup> 7.23 (dd, 2H, H <sup>6,7</sup> , J <sub>vic</sub> = 6.1 Hz, J <sub>all</sub> = 3.2 Hz) 6.99 (s, 2H, H <sup>9,10</sup> ) 5.63 (m, 2H, H <sup>1,4</sup> ) 4.20 (m, 2H, H <sup>2,3</sup> )	67.9 (s) <sup>h</sup>	79.6 (d, J <sub>C-H</sub> = 166 Hz, C <sup>2,3</sup> ) <sup>e</sup> 60.8 (C <sup>1,4</sup> ) <sup>i</sup>
Anthracene	-11.25 (t, 2H, J <sub>P-H</sub> = 28.5 Hz, Ru-H) 8.15 (s, 2H, H <sup>9,10</sup> ) <sup>d</sup> 7.80 (dd, 4H, H <sup>1,4,5,8</sup> , J <sub>vic</sub> = 6.5 Hz, J <sub>all</sub> = 3.3 Hz) <sup>g</sup> 7.25 (dd, 4H, H <sup>2,3,6,7</sup> , J <sub>vic</sub> = 6.6 Hz, J <sub>all</sub> = 3.2 Hz)		
4H-anthracene <sup>j</sup>	7.66 (dd, 2H, H <sup>5,8</sup> , J <sub>vic</sub> = 6.2 Hz, J <sub>all</sub> = 3.3 Hz) <sup>d,g</sup> 7.40 (s, 2H, H <sup>9,10</sup> ) 7.28 (dd, 2H, H <sup>6,7</sup> , J <sub>vic</sub> = 6.3 Hz, J <sub>all</sub> = 3.2 Hz) 2.74 (m, 4H, H <sup>1,4</sup> ) ca. 1.62 (m, 4H, H <sup>2,3</sup> and 8H, H <sup>2,3,6,7</sup> for 8H-An)		
8H-anthracene <sup>k</sup>	6.74 (s, 2H, H <sup>9,10</sup> ) <sup>d</sup> 2.63 (m, 8H, H <sup>1,4,5,8</sup> ) ca. 1.62 (m, 8H, H <sup>2,3,6,7</sup> and 4H, H <sup>2,3</sup> for 4H-An)		

<sup>a</sup> C<sub>6</sub>D<sub>6</sub>, 293 K.

<sup>b</sup> 81.015 MHz.

<sup>c</sup> 50.323 MHz.

<sup>d</sup> 200.132 MHz.

<sup>e</sup> 100.624 MHz.

<sup>f</sup> 400.133 MHz.

<sup>g</sup> vic = vicinal, all = allylic.

<sup>h</sup> 161.985 MHz.

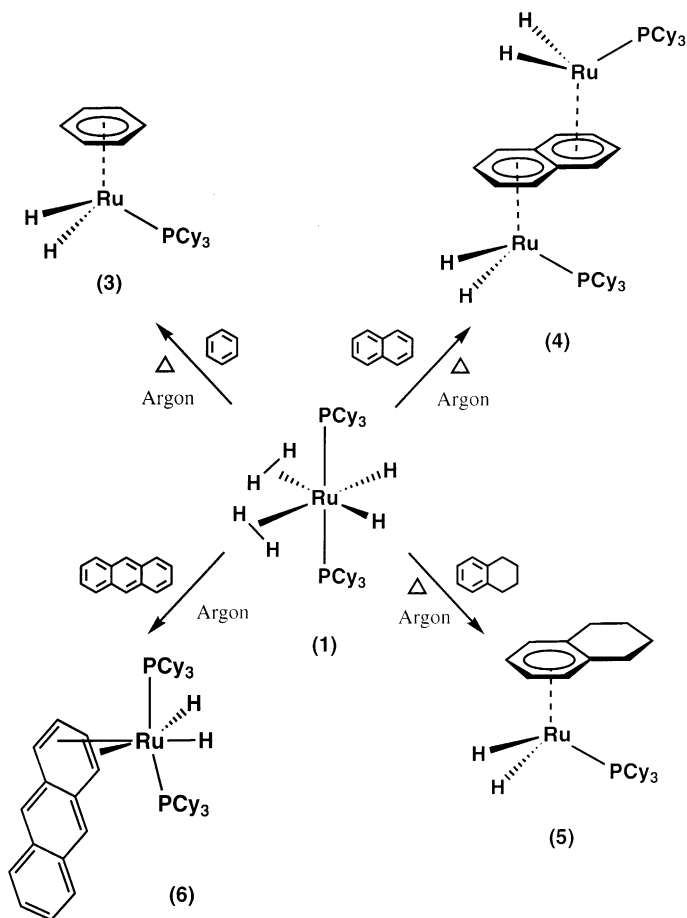
<sup>i</sup> Only <sup>13</sup>C{<sup>1</sup>H} NMR.

<sup>j</sup> 4H-anthracene: 1,2,3,4-tetrahydroanthracene.

<sup>k</sup> 8H-anthracene: 1,2,3,4,5,6,7,8-octahydroanthracene.

after 24 h and no evidence for a further hydrogenated product has been found (turnover number: ca. 13). Tetralin has also been found (GC and <sup>1</sup>H NMR) to be the sole product of the hydrogenation of naph-

thalene in C<sub>6</sub>D<sub>6</sub>, in agreement with the much higher reactivity of naphthalene compared to benzene. An attempted hydrogenation of tetralin in cyclohexane revealed only traces of *cis*- and *trans*-decalin after



Scheme 1.

a comparable reaction time. The hydrogenation of naphthalene is, however, catalyzed much faster by niobium complexes, as described by Rothwell. In that case, tetralin has been obtained in >95% yield after 24 h, but under a much higher pressure [40].

The bis(dihydrogen) complex **1** has been characterized as the main complex present in  $d_6$ -benzene solution after 20 h naphthalene hydrogenation. The  $^1H$  NMR spectra of this reaction mixture reveal the presence of two additional complexes in very small quantities. One is the complex characterized above as **3** while the other shows two multiplets at  $\delta$  5.35 and 5.20 and a doublet at  $\delta$  ca.  $-10.5$  ( $J = 42.4$  Hz) in the  $^1H$  NMR spectrum and a single peak at  $\delta$  78.6 in the  $^{31}P$  NMR spectrum.

### 3.3. Synthesis of $[(PCy_3)_2Ru(\mu-\eta,\eta-C_{10}H_8)-RuH_2(PCy_3)]$ (**4**) and $[RuH_2(\eta^6-C_{10}H_{12})PCy_3]$ (**5**)

In order to get more information concerning the course of naphthalene hydrogenation, we have performed several reactions with **1** and naphthalene in a 1:3 molar ratio, using  $d_{12}$ -cyclohexane as solvent. The progress of the reaction was followed by  $^1H$  NMR. Two products were observed with relative ratios depending on the reaction duration. Shorter reaction times (several hours) favored the formation of a complex **4** (see below) showing two multiplets at  $\delta$  ca. 4.7 and 3.8 and a doublet at  $\delta$   $-10.6$  ( $J_{P-H} = 29$  Hz). Longer reaction times (above 10 h) revealed the predominant formation of a compound

(5) (see below) displaying two multiplets at  $\delta$  ca. 5 and 4.9 and a doublet at  $\delta$  ca.  $-11$  ( $J_{P-H} = 43$  Hz). Additionally, in all these experiments, we have observed the formation of a small amount of the complex  $[\text{RuH}\{\{\eta^3\text{-C}_6\text{H}_8\}\text{PCy}_2\}\{\{\eta^2\text{-C}_6\text{H}_9\}\text{PCy}_2\}]$  (2) in which both phosphine ligands contain a dehydrogenated cyclohexyl ring bound to the metal in an  $\eta^3$ - and  $\eta^2$ -mode, respectively [48]. As reported previously, this complex may be formed upon reaction of **1** with functionalized alkenes serving as hydrogen acceptors [48] or as a product of thermal decomposition of **1** under an helium atmosphere [53].

The synthesis of  $[(\text{PCy}_3)_2\text{H}_2\text{Ru}(\mu\text{-}\eta\text{-}\eta\text{-C}_{10}\text{H}_8)\text{RuH}_2(\text{PCy}_3)]$  (**4**) was achieved by reacting **1** with naphthalene in boiling cyclohexane for 2 h (Scheme 1). Product **4** was isolated as yellow crystals in 59% yield. The  $^1\text{H}$  NMR spectrum of **4** (Table 2) shows two broad multiplets at  $\delta$  4.19 and 5.03 characteristic of the presence of a  $\pi$ -bonded naphthalene ring. The two hydride ligands resonate at  $\delta$   $-10.18$  as a doublet due to coupling with one phosphorus atom ( $J_{P-H} = 29.3$  Hz). The ratio of two hydrides per one phosphorus is confirmed by a  $^{31}\text{P}$  NMR spectrum where the singlet at  $\delta$  68.9 splits into a triplet upon selective decoupling of  $\text{PCy}_3$  protons. Finally, the arene protons to hydride integration ratio of 2:1 is in agreement with a dinuclear formulation involving one naphthalene ligand for four hydrides. The  $^{13}\text{C}$  NMR spectrum confirms the presence of coordinated naphthalene. A singlet at  $\delta$  95.8 has been assigned to the  $\text{C}^{9,10}$  carbons, while two doublets at  $\delta$  78.0 and at  $\delta$  64.7 have been assigned to the  $\text{C}^{1,4,5,8}$  and  $\text{C}^{2,3,6,7}$  carbons, respectively, of an  $\eta^6$ -coordinated naphthalene molecule. Bubbling dihydrogen through a  $d_6$ -benzene solution of **4** did not lead to any changes in the  $^1\text{H}$  NMR spectrum. This may suggest the absence of involvement of **4** in the hydrogenation catalytic cycle.

The second compound  $[\text{RuH}_2(\eta^6\text{-C}_{10}\text{H}_{12})\text{PCy}_3]$  (**5**), was produced in a 5 h reaction of (**1**) with tetralin in boiling cyclohexane but could not be isolated in a pure form due to its contamination by  $\text{PCy}_3$ . The  $^1\text{H}$  NMR spectrum of **5** in  $\text{C}_6\text{D}_6$  shows two multiplets centered at  $\delta$  5.35 and 5.20 assignable to the  $\eta^6$ -bound arene ring of tetralin. The presence of two hydrides coupled to one phosphorus atom is evidenced by a doublet at  $\delta$   $-10.45$  ( $J_{P-H} = 42.3$  Hz) and this finding is supported by the transformation of the sharp

singlet at  $\delta$  78.6 in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum into a triplet ( $J_{P-H} = 42$  Hz) upon selective decoupling of  $\text{PCy}_3$  protons. The signals of the  $\text{H}^{1,4}$  protons of the saturated ring of tetralin appear as a multiplet at  $\delta$  ca. 2.60, while the signals of the  $\text{H}^{2,3}$  protons are probably hidden under the resonances of the  $\text{PCy}_3$  protons between 1.9 and 1.0 ppm. Finally, integration of the hydrides against the arene ring protons indicate a 1:2 ratio, in agreement with the proposed structure. Product **5** is therefore, a ruthenium(II) complex in which the metal atom coordinates one tetralin ligand through an  $\eta^6$ -bound arene ring along with two hydrides and one tricyclohexylphosphine ligand. The same product has been found in small quantities on termination of the hydrogenation tests of naphthalene.

### 3.4. Hydrogenation of anthracene

Anthracene is reduced in the standard conditions in less than 4 h into a mixture of 1,2,3,4-tetrahydroanthracene (4H-An) (93%) and 1,2,3,4,5,6,7,8-octahydroanthracene (8H-An) (7%) (Table 1). The total conversion of anthracene and the presence of these two products suggest that after hydrogenation of the first ring, the reaction proceeds on prolonged reaction time to the hydrogenation of the second ring but with a much slower rate. Interestingly, no 9,10-dihydroanthracene was detected. This compound is the typical product of catalysis proceeding through a radical mechanism [54]. The mixture of hydrogenation products of anthracene has been isolated as a white product after a 24 h reaction and analyzed by GC and  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_6$ . The assignments for 4H-An and 8H-An are given in Table 2.

The observation that 4H-An is an intermediate in the formation of 8H-An contrasts to the results reported by Crabtree et al. [55], Caulton et al. [56], and Halpern and Linn [45] for polyhydrido triphenylphosphine complexes of Ir, Re and Ru, respectively. However, the almost exclusive production of 4H-An prior to the formation of 8H-An, without detectable 9,10-dihydroanthracene, has also been observed by Rothwell et al. for  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_3]$  and  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Cy}_2\text{-2,6})_2(\text{H})_3(\text{PMe}_2\text{Ph})_2]$  under comparable conditions except for the considerably higher pressure (83 bar  $\text{H}_2$ ) [40–44].

Finally, we have checked that 9,10-dihydroanthracene is not hydrogenated under our standard conditions.

### 3.4.1. Synthesis of $[RuH_2(\eta^4-C_{14}H_{10})(PCy_3)_2]$ (**6**)

Reaction of **1** with a small excess of anthracene in cyclohexane or diethyl ether under argon yields a yellow product analyzed as  $[RuH_2(\eta^4-C_{14}H_{10})(PCy_3)_2]$  (**6**). The  $^1H$  NMR spectrum of **6** (Table 2) shows two resonances for the  $H^{1,4}$  and  $H^{2,3}$  protons of the coordinated anthracene ring as multiplets at  $\delta$  5.62 and 4.20, respectively. The hydrides resonate as a triplet at  $\delta$  -11.25 ( $J_{P-H} = 28.5$  Hz) due to coupling with two equivalent *trans*-phosphorus atoms which display a singlet at  $\delta$  67.9 in  $^{31}P$  NMR. The proton signal transforms into a singlet upon phosphorus decoupling. The relatively low value of proton–phosphorus coupling found for **6** (28.5 Hz) suggests an  $\eta^4$ -coordination mode for anthracene since previous data concerning comparable hydrido phosphino arene ruthenium complexes report values below 30 Hz [57], whereas the coupling constant  $J_{P-H}$  is found above 40 Hz for complexes accommodating  $\eta^6$ -coordinated arenes [51,58].

The  $H^{1,4}$  and  $H^{2,3}$  proton resonances are considerably shifted upfield as compared with the analogous signals for free anthracene (cf. Table 2). The resonances of the  $H^{5,8}$  and  $H^{6,7}$  protons appear as doublets of doublets and are only slightly shifted. The integration ratio between the hydride signal and the signals for protons  $H^{1,4}$ ,  $H^{2,3}$ ,  $H^{5,8}$ ,  $H^{6,7}$  and  $H^{9,10}$  is 1:1:1:1:1. The pattern found for **6** resembles that of  $[Fe(CO)_3(\eta^4-C_{14}H_{10})]$  [59].  $\eta^4$ -Anthracene coordination rather than  $\eta^6$  [60] is additionally supported by the  $^{13}C$  NMR spectra of **6** in which the  $C^{2,3}$  and  $C^{1,4}$  carbon resonances are shifted upfield to  $\delta$  79.6 and 60.8, respectively. Finally,  $\eta^4$ -coordination ensures an 18-valence-electron configuration for this complex.

### 3.4.2. Hydrogenation of anthracene with **6** used as a catalyst precursor

Product **6** also acts as a hydrogenation catalyst leading to a total conversion of anthracene into a mixture of 4H-An (90%) and 8H-An (10%) after 24 h (80°C, 3 bar  $H_2$ , see Table 1). Since **6** readily forms from **1** by substitution of two dihydrogen molecules, it is very likely that **6** may be involved, as a transient form, in a catalytic cycle for anthracene hydrogenation. Another

observation supports this hypothesis. Bubbling dihydrogen through a  $C_6D_6$  solution of **6** in an NMR tube leads to rapid and total restoration of **1** along with the liberation of anthracene and formation of some amounts of 4H-An and 8H-An.

When considering these findings, we can propose a very simple catalytic cycle for the hydrogenation of anthracene to 4H-An (Scheme 1) which starts with the dissociation of two  $H_2$  molecules creating a vacancy allowing anthracene coordination in an  $\eta^4$ -mode. The rest of the catalytic cycle, although not investigated is presumably straightforward. At the end of the catalytic reaction, either a new anthracene molecule may coordinate to Ru forming **6** and starting a new catalytic cycle or the bis(dihydrogen) complex **1** regenerates upon coordination of two  $H_2$  molecules. Reduction of the second external ring of 4H-An begins presumably when most (or all) of the anthracene is consumed.

### 3.5. Hydrogenation of naphthalene and anthracene under 20 bar $H_2$

The results of naphthalene and anthracene hydrogenation performed under a pressure of 20 bar of dihydrogen (Table 3) cannot be compared directly with those obtained under a lower pressure (3 bar, Table 1) since the volumes of the reaction mixtures and the catalyst concentrations differ considerably. A general trend can nevertheless be assessed. Naphthalene has been hydrogenated to tetralin at considerably slower rate in the presence of 20 bar of dihydrogen leading to a turnover number of only 1.5 after 24 h. The hydrogenation of anthracene has been less affected by the

Table 3  
Hydrogenation of arenes at 80°C under 20 bar  $H_2^a$

Substrate	Time (h)	Conversion (%)	Products (%)	TON <sup>b</sup>
Naphthalene	24	3	Tetralin (100)	1.5
Anthracene	4	47	4H-An <sup>c</sup> (100)	23.5
Anthracene	24	93	4H-An <sup>c</sup> (91) 8H-An <sup>d</sup> (2)	46.5 1

<sup>a</sup> Catalyst precursor:  $[RuH_2(H_2)_2(PCy_3)_2]$  (**1**) in 20 ml cyclohexane solvent  $[Ru] = 1.5 \times 10^{-3}$  M,  $[arene] = 0.075$  M, arene/Ru = 50.

<sup>b</sup> TON is defined as mole of product formed per mole of Ru.

<sup>c</sup> 4H-An: 1,2,3,4-tetrahydroanthracene.

<sup>d</sup> 8H-An: 1,2,3,4,5,6,7,8-octahydroanthracene.



increase of hydrogen pressure. After 4 h of reaction, 47% conversion of anthracene into exclusively 4H-An was observed which corresponds to a turnover number of 23.5. After 24 h, anthracene conversion to 4H-An reached 91% and only 2% 8H-An could be found in the reaction mixture.

In these arene hydrogenation reactions catalyzed by **1**, we have observed that the increase of dihydrogen pressure from 3 to 20 bar reduces the reaction rates. This trend is rather exceptional in hydrogenation reactions. In general, an increase of dihydrogen pressure results in an increase of the reaction rate or has no influence on it. The results of our studies allow us to propose that similarly to many other catalytic systems involving dihydrogen complexes [61], it is the dissociation of dihydrogen molecules that provides free coordination sites for substrate coordination. This dissociation is disfavored at high pressure of dihydrogen. As a result, a considerably lower conversion of arenes to hydrogenation products is observed when increasing dihydrogen pressure.

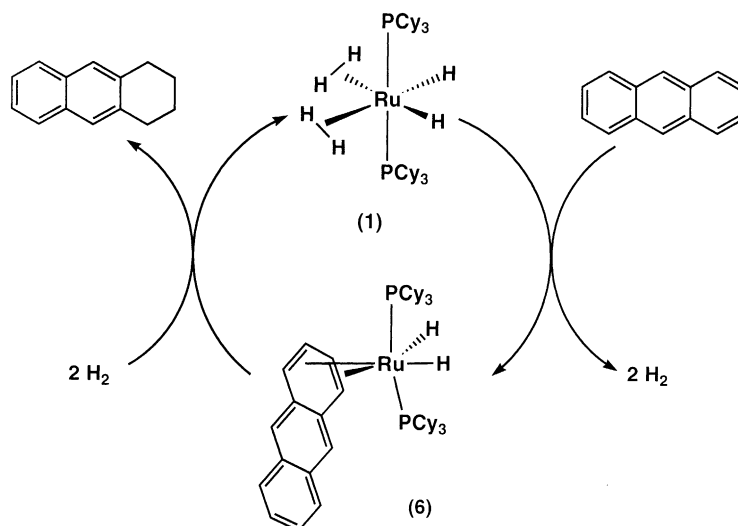
#### 4. Conclusions

We have described in this paper the catalytic activity of  $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$  (**1**) for arene hydrogenation. In methylcyclohexane solution, **1** is

considerably less active for benzene hydrogenation than  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-H})_2(\mu\text{-Cl})\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]\text{Cl}$  in neat benzene [21] or  $[\text{H}_4\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4][\text{BF}_4]$  in the ionic liquid [7] ( $0.11 \text{ mol mol}^{-1} \text{ h}^{-1}$  against 246 and  $364 \text{ mol mol}^{-1} \text{ h}^{-1}$ , respectively). Furthermore, the absence of hydrogenation products in reactions performed in neat benzene in the presence of mercury may suggest the involvement of metal particles.

A better conversion has, however, been achieved for naphthalene which has been reduced re-gioselectively to tetralin, and for anthracene which is hydrogenated even more readily into tetrahydro- and octahydro-anthracene in consecutive reactions. Functionalized arenes (toluene, chlorobenzene, durene), tetralin, phenanthrene and 9,10-dihydroanthracene have not been reduced in these reactions. In the latter case, the reason may be steric ( $\text{sp}^3$  hybridisation of  $\text{C}^9$  and  $\text{C}^{10}$  carbons cause that this three-ring molecule is not planar); the high resonance energy of the isolated external aromatic ring may also account for these observations. However, **1** is almost as efficient as a catalyst precursor for hydrogenation of naphthalene and anthracene as Nb and Ta complexes incorporating aryloxy ligands [40,44].

Complex **1** can be used directly for hydrogenation reactions or can be generated in situ from **2**. Product **1** is the major species detected all along the catalytic reaction. After termination of the hydrogenation



Scheme 2.

reactions of benzene and naphthalene, **1** has been found by NMR to be virtually the only complex present in the reaction solution. A very small amount of other complexes (**3** in the case of benzene hydrogenation, or **4** and **5** in the case of hydrogenation of naphthalene) have been found in the reaction mixtures. They seem to be the products of side reactions. These complexes have been isolated in separate experiments by direct reaction of **1** with the corresponding arene in a dihydrogen free atmosphere (Schemes 1 and 2). The isolated complex **6** shows a catalytic activity for anthracene hydrogenation which suggests its intermediary role in the catalytic cycle.

Somewhat surprisingly, the increase of hydrogen pressure up to 20 bar, lowers conversion to the expected hydrogenation products in all the cases. This can be best explained by the reduced accessibility of free coordination sites for large arene molecules due to an increased stabilization of the bis(dihydrogen) complex **1**.

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