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Mechanism of the hydrogenation of 2,5-norbornadiene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ in dichloromethane: a kinetic and spectroscopic investigation

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Abstract

A kinetic investigation of the selective hydrogenation of 2,5-norbornadiene to norbornene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ (**1**) has been carried out in dichloromethane at room temperature. The reaction is independent of the substrate concentration, while it is first order in catalyst and hydrogen pressure. Furthermore, the addition of triphenylphosphine inhibits the reduction. Moreover, it has been observed that under hydrogen atmosphere and at low temperature, complex **1** is in equilibrium with the dihydrido *cis–trans*-$[RhH_2(NBD)(PPh_3)_2]BF_4$, and that the addition of one equivalent of $[Rh(NBD)\{P(p\text{-Tol})_3\}_2]BF_4$ to a chloroform-d_1 solution of **1** affords $[Rh(NBD)(PPh_3)\{P(p\text{-Tol})_3\}]BF_4$ in 54% yield. On the basis of these observations and other spectroscopic results, we propose that the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by **1** proceeds by the five-coordinate dihydrido $[RhH_2(NBD)(PPh_3)]^+$, which is formed by oxidative addition of molecular hydrogen to both **1** and a tricoordinate species $[Rh(NBD)(PPh_3)]^+$, depending on the concentration of free phosphine in the catalytic solution. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Catalysis; Hydrogenation; Kinetics

1. Introduction

The discovery of the existence of the cationic rhodium complexes with the general formula $[Rh(diene)L_a]^+$ ($a = 2$ or 3) by Shapley, Schrock and Osborn [1,2] was fundamental to the development of homogeneous hydrogenation catalyzed by transition-metal compounds [3].

These complexes have been found to be active catalysts for the hydrogenation of olefins [4–9], dienes [10–12], alkynes [13,14], ketones [15], polynuclear heteroaromatic compounds [16–21] and carbon dioxide [22]. In solvents such as acetone, ethanol or acetonitrile, they react with molecular hydrogen to give dihydrido–metal complexes $[RhH_2S_xL_a]^+$ (S = solvent), which under catalytic conditions are in equilibrium with the corresponding monohydridos MHS_yL_a. Both the dihydrido and monohydrido species are active catalysts [4].

As a part of our work on the mechanism of the homogeneous hydrogenation of unsaturated organic substrates catalyzed by transition-metal complexes [23–29], we have previously reported on the mechanism of the hydrogenation of alkynes catalyzed by complexes of the type $[M(diene)L_a]^+$ (M = Rh, Ir) in dichloromethane [30,31]. In this solvent, the reactions do not imply the reduction of the dienes of the catalyst precursors, which remain coordinated during the processes, in contrast to that previously reported for the related systems in coordinating solvents [3].

Following our interest in this subject, we have now carried out kinetic and spectroscopic studies in dichloromethane on the hydrogenation of 2,5-norbornadiene (NBD) to norbornene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$. In this paper, we report the results from these studies, showing that under these conditions the reduction takes place via a five-coordinative dihydrido intermediate $[RhH_2(NBD)(PPh_3)]^+$.

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2. Results and discussion

2.1. Kinetic studies

The hydrogenation of 2,5-norbornadiene catalyzed by the complex $[Rh(NBD)(PPh_3)_2]BF_4$ (**1**) was studied at constant pressure and at 25°C. In agreement with the early results [10], the selective reduction of the diene to norbornene was observed.

Table 1
Kinetic data for the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ (**1**) in dichloromethane at 25°C

[Catalyst] (10^4 M)	[NBD] (M)	$P(H_2)$ (atm)	$[PPh_3]$ (10^5 M)	r (10^5 M s^{-1})
5.0	0.14	0.44	–	1.41
6.4	0.14	0.44	–	1.79
6.9	0.14	0.44	–	2.00
7.9	0.14	0.44	–	2.18
8.9	0.14	0.44	–	2.36
6.9	0.09	0.44	–	2.09
6.9	0.10	0.44	–	1.95
6.9	0.18	0.44	–	2.00
6.9	0.22	0.44	–	1.95
6.9	0.25	0.44	–	2.18
6.9	0.14	0.23	–	1.14
6.9	0.14	0.24	–	1.18
6.9	0.14	0.34	–	1.64
6.9	0.14	0.44	1.38	1.82
6.9	0.14	0.44	2.76	1.43
6.9	0.14	0.44	2.76	1.56
6.9	0.14	0.44	4.14	1.45
6.9	0.14	0.44	4.83	1.21
6.9	0.14	0.44	5.52	1.15
6.9	0.14	0.44	6.21	0.91
6.9	0.14	0.44	6.90	0.79

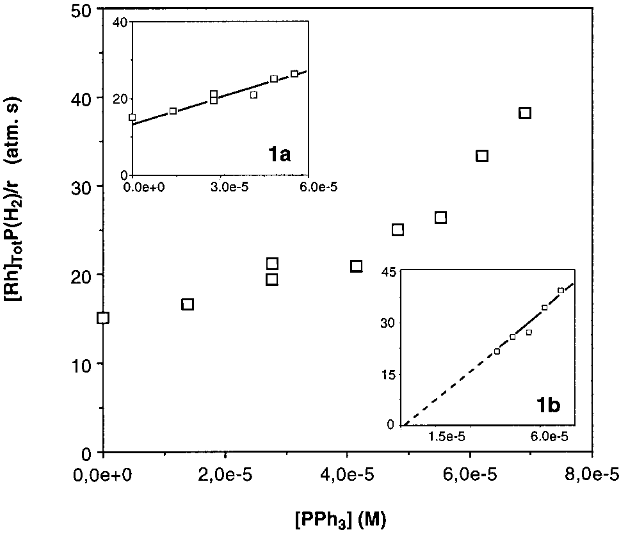


Fig. 1. Plot of $[Rh]_{Tot}P(H_2)/r$ vs. $[PPh_3]$ for the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by $[Rh(NBD)(PPh_3)_2]BF_4$ (**1**) in dichloromethane at 25°C (6.9×10^{-4} M **1**, and 0.14 M 2,5-norbornadiene): (a) the concentration of the added phosphine is lower than 6.00×10^{-5} M. (b) the concentration of the added phosphine is higher than 4.00×10^{-5} M.

In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst and 2,5-norbornadiene concentrations and at different hydrogen pressures. The reactions were followed by measuring the hydrogen consumption as a function of time, and the initial rates (r in Table 1) were calculated by using Eq. (1), where $-dV/dt$ is the initial rate measured from the experiments, P is the reaction pressure (atm), R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume (L) of the reacting solution.

$$r = -\frac{d[H_2]}{dt} = -\frac{(dV/dt)P}{RTV_{sol}} \tag{1}$$

For the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by $[Rh(NBD)L_a]^+$ precursors in acetone as solvent, Schrock and Osborn have previously observed that the rate of the diene reduction is independent of 2,5-norbornadiene concentration, and that the rate at which the molecular hydrogen reacts with $[Rh(NBD)L_a]^+$ is qualitatively parallel to the hydrogenation rate of the diene [10]. In agreement with this, the data collected in Table 1 indicate that in dichloromethane the reduction of 2,5-norbornadiene catalyzed by **1** is practically independent of the substrate concentration, while a plot of $\log r$ versus $\log (P(H_2))$ yields a straight line of slope 0.9, suggesting that the reduction is first order in hydrogen pressure. The plot of $\log r$ versus $\log ([Rh]_{Tot})$ yields a straight line of slope 0.9, indicating that the reaction is also first order in catalyst precursor concentration.

In the presence of **1**, it has been found that the reduction of phenylacetylene is inhibited by addition of triphenylphosphine [31]. The effect of the addition of this phosphine to the catalytic solutions of 2,5-norbornadiene is shown in Fig. 1. The initial reduction rate decreases by addition of phosphine to the reaction system. For lower concentrations of added phosphine than 6.00×10^{-5} M, the plot of $[Rh]_{Tot}P(H_2)/r$ versus $[PPh_3]$ (Fig. 1(a)) is a linear with a positive interception on the y axis. The relation is expressed in the form

$$r = \frac{a[RH]_{Tot}P(H_2)}{b[PPh_3]+1} \tag{2}$$

where $[PPh_3]$ is the concentration of added phosphine, and ***a*** and ***b*** are constants.

For higher concentrations of added phosphine than 4.00×10^{-5} M, the plot of $[Rh]_{Tot}P(H_2)/r$ versus $[PPh_3]$ (Fig. 1(b)) is also linear. However, in this case, the relation is expressed in the form

$$r = \frac{c[Rh]_{Tot}P(H_2)}{[PPh_3]} \tag{3}$$

The above-mentioned data suggest that in dichloromethane as solvent the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by **1** goes by two different pathways, which have different rate laws. Depending upon the phosphine added to the catalytic solution, one of them is favored with regard to the other one.

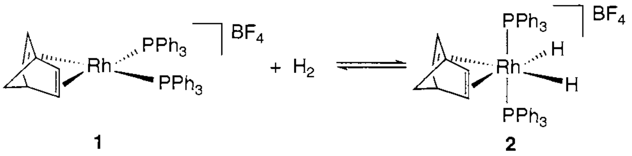
2.2. Spectroscopic studies

Under argon atmosphere, the ^{1}H-NMR spectrum of **1** in dichloromethane-d_2 shows, along with the signals corresponding to the phenyl protons of the phosphine ligands, three broad resonances at 4.5, 4.0 and 1.6 ppm, the first of them corresponding to the =CH protons of the diene and the other two due to the aliphatic –CH and –CH_2 protons of the 2,5-norbornadiene ligand. The $^{31}P\{^1H\}$-NMR spectrum contains at 29.8 ppm a doublet with a P–Rh coupling constant of 155.5 Hz. These spectra are temperature invariant between − 80 and 40°C.

The addition of 32 equivalents of 2,5-norbornadiene to the dichloromethane-d_2 solution of **1** does not produce any changes in the ^{1}H and $^{31}P\{^1H\}$-NMR spectra of **1**, between the above-mentioned temperatures. This excludes the formation, under catalytic conditions, of the five-coordinate species $[Rh(NBD)_2L]^+$ ($L = PPh_3$), which have been previously observed when the ancillary ligands L are nitriles, arsines and stibines [32,33].

Under hydrogen atmosphere, the ^{1}H-NMR spectrum of the solution resulting from the addition of 32 equivalents of 2,5-norbornadiene to **1** in dichloromethane-d_2 shows the resonances of norbornene, unreacted 2,5-norbornadiene and **1**, and the $^{31}P\{^1H\}$-NMR spectrum only contains the doublet at 29.8 ppm. These observations suggest that under catalytic conditions the main organometallic species is **1**. Furthermore, since complex **1** does not interact with 2,5-norbornadiene, they also indicate that the hydrogenation takes place by reaction of **1** with molecular hydrogen.

In order to obtain information about the reaction of **1** with molecular hydrogen, we carried out the ^{1}H- and $^{31}P\{^1H\}$-NMR spectra of **1** under hydrogen atmosphere between − 80 and − 20°C. In this range of temperatures the reduction of the coordinated diene is very slow and the formation of norbornene is not practically observed during the experiments. The most accurate ^{1}H-NMR spectrum was obtained at − 60°C. In the low-field region, the spectrum shows the resonances of **1** along with three broad resonances at 4.73 (2H), 2.13 (4H) and 1.42 (2H) ppm, and in the high-field region a double triplet at − 21.73 (2H) ppm, with H–Rh and H–P coupling constants of 27.0 and 12.0 Hz, respectively. A variable-temperature 300 MHz T_1 study of this resonance gives a T_1(min) of 318 ($\pm$10) ms at − 20°C, indicating that it corresponds to a hydrido resonance. At − 60°C, the $^{31}P\{^1H\}$-NMR spectrum contains the doublet of **1** at 29.8 ppm, and a new doublet at 44.5 ppm with a P–Rh coupling constant of 119.0 Hz. Under off-resonance conditions, the latter doublet is converted into a double triplet as a result of the coupling with two equivalent hydrido ligands. The equivalence of the phosphine and hydrido ligands and the vinylic protons of the coordinated 2,5-norbornadiene diolefin indicates that the new compound is *cis–trans*-$[RhH_2(NBD)(PPh_3)_2]BF_4$ (**2**) which is formed by oxidative addition of molecular hydrogen to **1** (Eq. (4)). At − 60°C, the yield of the addition is about 5%.



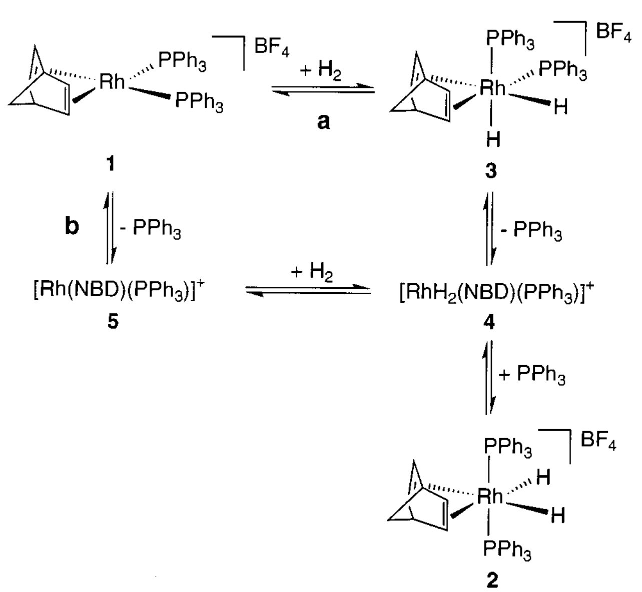
(4)

There is precedent for this reaction. Similarly to **1**, the iridium-tetrafluorobenzobarrelene complex $[Ir(TFB)(P\mathit{i}Pr_3)_2]BF_4$ reacts with molecular hydrogen to give *cis–trans*-$[IrH_2(TFB)(P\mathit{i}Pr_3)_2]BF_4$ [34]. However, under hydrogen atmosphere the related 1,5-cyclooctadiene derivatives $[Ir(COD)(PR_3)_2]PF_6$ afford *cis–cis*-$[IrH_2(COD)(PR_3)_2]PF_6$ ($PR_3 = PPh_3$, $PMePh_2$) [35,36]. Complexes $[Ir(DCT)(PR_3)_2]^+$ (DCT = dibenzo[*a*, *e*]-cyclooctatetraene) show a similar behavior to that of $[Ir(COD)(PR_3)_2]PF_6$ [37]. Cations *cis–trans*-$[IrH_2(COD)(PR_3)_2]^+$ can be prepared by reaction of $[Ir(COD)(PR_3)_2]^+$ with molecular hydrogen in the presence of 1,5-cyclooctadiene or alternatively by treatment of the solvated compounds $[IrH_2(acetone)_2(PR_3)_2]^+$ with 1,5-cyclooctadiene [35,36].

The formation of **2** by oxidative addition of molecular hydrogen to **1** is not a single reaction, since the oxidative addition of X–X or X–Y bonds of non-polar molecules to square-planar complexes is a diastereoselective concerted *cis* addition process with specific substrate orientation [38–43]. Furthermore, the only path to approach the hydrogen molecule to **1** is the olefin-Rh–P axis, which should lead to the *cis–cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$ (**3**) isomer.

Scheme 1 shows the two possible pathways for the formation of **2** according to Eq. (4). Both mechanisms have the five-coordinate dihydrido species **4** as key intermediate. Path **a** involves the oxidative addition of molecular hydrogen along one of the two P–Rh-olefin axes of **1** to give the *cis–cis*-isomer **3**, which dissociates phosphine to afford the five-coordinate dihydrido intermediate **4**. The re-coordination of the phosphine to **4** should lead to **2**.

In complex **3**, the dissociation of the phosphine *trans* disposed to the hydrido ligand should be favored due to the high *trans* effect of the hydrido, and the large steric



Scheme 1.

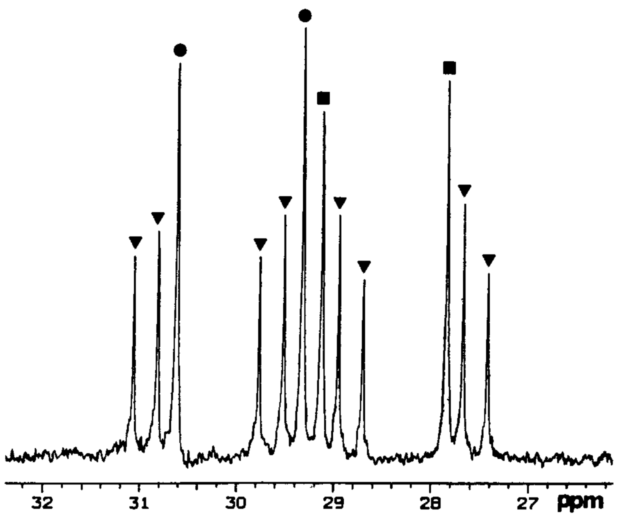


Fig. 2. $^{31}P\{^1H\}$-NMR spectrum (121.4 MHz, 20°C) of the solution resulting from the addition of one equivalent of $[Rh(NBD)\{P(p\text{-}Tol)_3\}_2]BF_4$ to a chloroform-d_1 solution of $[Rh(NBD)(PPh_3)_2]BF_4$ (■$[Rh(NBD)(PPh_3)_2]BF_4$; ●$[Rh(NBD)\{P(p\text{-}Tol)_3\}_2]BF_4$; ▼$[Rh(NBD)(PPh_3)\{P(p\text{-}Tol)_3\}]BF_4$).

hindrance experienced by the triphenylphosphine groups, which are mutually *cis* disposed.

The formation of the key intermediate **4**, according to path **b**, involves the initial dissociation of a triphenylphosphine ligand from the square-planar complex **1**, followed by the oxidative addition of molecular hydrogen to the resulting three-coordinate species **5**. The dissociation of a ligand L from square-planar complexes of the type $[Rh(NBD)L_2]^+$ has been previously observed for monodentate nitrogen donor ligands [32,33].

In order to support the dissociation of phosphine suggested in path **b**, we carried out NMR spectra of the solution resulting from the addition of one equivalent of $[Rh(NBD)\{P(p\text{-}Tol)_3\}_2]BF_4$ to a chloroform-d_1 solution of **1**. In agreement with the dissociation of phosphine from **1**, at room temperature, the $^{31}P\{^1H\}$-NMR spectrum of the mixture shows the formation of the mixed-ligand complex $[Rh(NBD)(PPh_3)\{P(p\text{-}Tol)_3\}]BF_4$ in 54% yield (Fig. 2).

2.3. Mechanism of the hydrogenation

The first-order dependence of the reduction rate with regard to the hydrogen pressure suggests that the active species for the catalysis is a dihydrido derivative, generated by oxidative addition of molecular hydrogen to the precursor **1**. Furthermore, from the results of the spectroscopic study, we conclude that the formation of this dihydrido derivative requires the dissociation of a phosphine ligand from **1** or, alternatively, from the undetectable *cis–cis*-$[RhH_2(NBD)(PPh_3)_2]BF_4$ (**3**) intermediate. The dissociation of phosphine is in agreement with the observed decreasing of the reduction rate as a result of the addition of triphenylphosphine to the catalytic solution.

In addition, it should be noted that the insertion of carbon–carbon double bonds into M–H bonds is a concerted process, which requires planar M(C=C)H groups [3,44]. So one should expect that the *cis–trans*-isomer **2** was not an active intermediate for the catalysis. This is strongly supported by the high stability of the previously mentioned *cis–trans*-$[IrH_2(diene)(PR_3)_2]^+$ cations [34–36] and the dihydrido–silyl complexes $IrH_2(SiR_3)(diene)(PR_3)$ (diene = COD, TFB), towards the reduction of the diene [45–48].

In the light of the above-mentioned considerations, and assuming that the oxidative addition of molecular hydrogen to **1** occurs via the pathway **b** of Scheme 1, the following mechanism (Eqs. (5)–(8)) can be proposed for the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by **1**:

$$\underset{\mathbf{1}}{[\mathrm{Rh(NBD)(PPh_3)_2}]^+} \overset{k_5}{\rightleftharpoons} \underset{\mathbf{5}}{[\mathrm{Rh(NBD)}]^+} + \mathrm{PPh_3} \tag{5}$$

$$\underset{\mathbf{5}}{[\mathrm{Rh(NBD)(PPh_3)}]^+} + \mathrm{H_2} \overset{k_6}{\rightleftharpoons} \underset{\mathbf{4}}{[\mathrm{RhH_2(NBD)(PPh_3)^+}]} \tag{6}$$

$$\underset{\mathbf{4}}{[\mathrm{RhH_2(NBD)(PPh_3)}]^+} \overset{k_7}{\rightarrow} \underset{\mathbf{6}}{[\mathrm{RhH(C_7H_9)(PPh_3)}]^+} \tag{7}$$

$$\underset{\mathbf{6}}{[\mathrm{RhH(C_7H_9)(PPh_3)}]^+} + \mathrm{NBD} \rightarrow \underset{\mathbf{5}}{[\mathrm{Rh(NBD)(PPh_3)}]^+} + \mathrm{C_7H_{10}} \tag{8}$$

With regard to the kinetic results, there is no doubt that the migratory insertion of one of the C–C double bonds of the diene into one of the M–H bonds of **4** (Eq. (7)) is the rate-determining step. Thus, the rate of formation of norbornene is:

$$\frac{\mathrm{d}[\mathrm{C_7H_{10}}]}{\mathrm{d}t} = k_7[\mathbf{4}] \tag{9}$$

The concentration of the key intermediate **4** can be determined as follows:

$$[\mathrm{Rh}]_{\mathrm{Tot}} = [\mathbf{1}] + [\mathbf{5}] + [\mathbf{4}] \tag{10}$$

since $k_5 = [\mathbf{5}][\mathrm{PPh_3}]/[\mathbf{1}]$ and $k_6 = [\mathbf{4}]/[\mathbf{5}]P(\mathrm{H_2})$, we have $[\mathbf{1}] = [\mathbf{4}][\mathrm{PPh_3}]/k_5k_6P(\mathrm{H_2})$ and $[\mathbf{5}] = [\mathbf{4}]/k_6P(\mathrm{H_2})$ and finally

$$[\mathbf{4}] = \frac{k_6[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]/k_5 + 1 + k_6P(\mathrm{H_2})} \tag{11}$$

Complex **1** is the main species under catalytic conditions. Thus, $[\mathrm{PPh_3}]/k_5 + 1 \gg k_6P(\mathrm{H_2})$, when $P(\mathrm{H_2}) \leq 1$ and $[\mathrm{PPh_3}]_{\mathrm{equilibrium}} \cong [\mathrm{PPh_3}]_{\mathrm{added}}$. Therefore [**4**] can be written as follow:

$$[\mathbf{4}] \cong \frac{k_6[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]/k_5 + 1} \tag{12}$$

Combining Eq. (9) and Eq. (12), we obtain Eq. (13), where $[\mathrm{Rh}]_{\mathrm{Tot}}$ and $[\mathrm{PPh_3}]$ are the concentrations of catalyst precursor and added phosphine, respectively.

$$\frac{\mathrm{d}[\mathrm{C_7H_{10}}]}{\mathrm{d}t} \cong \frac{k_7k_6[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]/k_5 + 1} \tag{13}$$

Eq. (13) agrees well with the experimental Eq. (2), where **a** is k_7k_6 and **b** is $1/k_5$. So, the Eqs. (5)–(8) are a reasonable description of the mechanism of the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by **1**, in the absence of triphenylphosphine, or when the concentration of the added phosphine is lower than 6.00×10^{-5} M.

If the formation of **4** takes place via the path **a** of Scheme 1, the mechanism of the reduction of 2,5-norbornadiene could be summarised by Eqs. (14), (15), (7) and (8).

$$\underset{\mathbf{1}}{[\mathrm{Rh(NBD)(PPh_3)_2}]^+} + \mathrm{H_2} \overset{k_{14}}{\rightleftharpoons} \underset{\mathbf{3}}{cis\text{-}cis\text{-}[\mathrm{RhH_2(NBD)(PPh_3)_2}]^+} \tag{14}$$

$$\underset{\mathbf{3}}{cis\text{-}cis\text{-}[\mathrm{RhH_2(NBD)(PPh_3)_2}]^+} \overset{k_{15}}{\rightleftharpoons} \underset{\mathbf{4}}{[\mathrm{RhH_2(NBD)(PPh_3)}]^+} + \mathrm{PPh_3} \tag{15}$$

In such a case, the concentration of **4** can be determined according to Eq. (16).

$$[\mathrm{Rh}]_{\mathrm{Tot}} = [\mathbf{1}] + [\mathbf{3}] + [\mathbf{4}] \tag{16}$$

Since $k_{14} = [\mathbf{3}]/[\mathbf{1}]P(\mathrm{H_2})$ and $k_{15} = [\mathbf{4}][\mathrm{PPh_3}]/[\mathbf{3}]$, we have $[\mathbf{1}] = [\mathbf{4}][\mathrm{PPh_3}]/k_{14}k_{15}P(\mathrm{H_2})$ and $[\mathbf{3}] = [\mathbf{4}][\mathrm{PPh_3}]/k_{15}$ and finally

$$[\mathbf{4}] = \frac{k_{14}k_{15}[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]\{1 + k_{14}P(\mathrm{H_2})\} + k_{14}k_{15}P(\mathrm{H_2})} \tag{17}$$

As complex **1** is the main species under catalytic conditions, we can assume that $[\mathrm{PPh_3}]\{1 + k_{14}P(\mathrm{H_2})\} \geq k_{14}k_{15}P(\mathrm{H_2})$ and $k_{14}P(\mathrm{H_2}) \leq 1$, when $P(\mathrm{H_2}) \leq 1$ and $[\mathrm{PPh_3}]_{\mathrm{equilibrium}} \cong [\mathrm{PPh_3}]_{\mathrm{added}}$. Therefore [**4**] can be written as follow:

$$[\mathbf{4}] \cong \frac{k_{14}k_{15}[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]} \tag{18}$$

Combining Eq. (9) and Eq. (18), we obtain Eq. (19).

$$\frac{\mathrm{d}[\mathrm{C_7H_{10}}]}{\mathrm{d}t} \cong \frac{k_7k_{14}k_{15}[\mathrm{Rh}]_{\mathrm{Tot}}P(\mathrm{H_2})}{[\mathrm{PPh_3}]} \tag{19}$$

Eq. (19) agrees well with the experimental Eq. (3), where **c** is $k_7k_{14}k_{15}$. So, Eqs. (14), (15) and (7) and Eq. (8) are a reasonable description of the mechanism of the hydrogenation of 2,5-norbornadiene to norbornene catalyzed by **1**, when the concentration of the added phosphine is higher than 4.00×10^{-5} M.

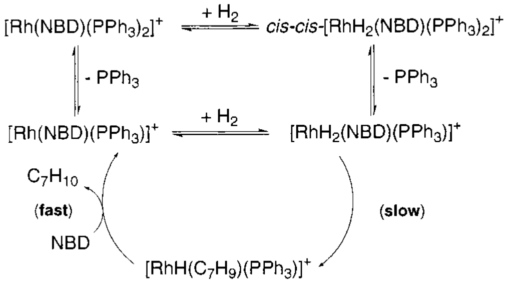
In summary, the complex $[\mathrm{Rh(NBD)(PPh_3)_2}]\mathrm{BF_4}$ catalyzes the selective hydrogenation of 2,5-norbornadiene to norbornene via the five-coordinate dihydrido intermediate $[\mathrm{RhH_2(NBD)(PPh_3)}]^+$ (Eqs. (7) and (8)). In the absence of triphenylphosphine or in the presence of low concentrations of phosphine, this dihydrido is mainly formed by dissociation of triphenylphosphine from $[\mathrm{Rh(NBD)(PPh_3)_2}]\mathrm{BF_4}$ and subsequent oxidative addition of molecular hydrogen to the resulting three-coordinate species $[\mathrm{Rh(NBD)(PPh_3)}]^+$. In the presence of moderate concentrations of phosphine, the formation of the dihydrido involves the oxidative addition of molecular hydrogen to $[\mathrm{Rh(NBD)(PPh_3)_2}]\mathrm{BF_4}$, to give *cis-cis*-$[\mathrm{RhH_2(NBD)(PPh_3)_2}]^+$, which dissociates a triphenylphosphine ligand.

3. Experimental

All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. 2,5-Norbornadiene (Merck) was purified by chromatography on $\mathrm{Al_2O_3}$ (neutral, activity grade I, column length 10 cm). The starting materials $[\mathrm{Rh(NBD)(PPh_3)_2}]\mathrm{BF_4}$ (**1**) and $[\mathrm{Rh(NBD)\{P(}p\mathrm{\text{-}Tol)_3\}_2}]\mathrm{BF_4}$ were prepared as described in the literature [2]. NMR spectra were recorded on Varian UNITY 300 and Bruker ARX 300 instruments.

3.1. Reaction of 1 with molecular hydrogen

$\mathrm{H_2}$ was bubbled through a solution of **1** in dichloromethane-d_2 (0.5 ml) previously cooled at −78°C, and contained in a 5 mm NMR tube. The reaction was monitored by ^{1}H- and ^{31}P{^{1}H}-NMR between −80 and −20°C. The most accurate spectra were obtained at −60°C. Along with unreacted complex **1** a new compound appeared in a 5% yield, which was identified as *cis–trans*-$[\mathrm{RhH_2(NBD)(PPh_3)_2}]\mathrm{BF_4}$ (**2**). ^{1}H-NMR (300 MHz, −60°C): δ 4.73 (br, 2H, –C*H* of NBD), 2.13 (br, 4H, =C*H* of NBD), 1.42 (br, 2H,



Scheme 2.

–CH_2 of NBD), −21.73 (dt, 2H, $J_{RhH} = 27.0$, $J_{PH} = 12.0$ Hz, Rh*H*), signals of phenyl-protons of **2** are overlapped by phenyl-protons of **1**. $^{31}P\{^1H\}$-NMR (121.4 MHz, −60°C): δ 44.5 (d, $J_{RhP} = 119.0$ Hz; dt *off-resonance*). T_1 (min) (ms, 'RhH_2'. 300 MHz, −20°C, dichloromethane-d_2): 318 (±10).

3.2. Reaction of 1 with [Rh(NBD){P(p-Tol)$_3$}$_2$]BF$_4$

Compound **1** (15.3 mg, 0.019 mmol) was treated, at room temperature, with one equivalent of [Rh(NBD){P(*p*-Tol)$_3$}$_2$]BF$_4$ (16.9 mg, 0.019 mmol) in chloroform-d_1 (0.5 ml) contained in a 5 mm NMR tube. The ^1H- and $^{31}P\{^1H\}$-NMR spectra of the resulting solution were measured immediately. A new compound appeared in a 54% yield, which was identified as [Rh(NBD)(PPh$_3$){P(*p*-Tol)$_3$}]BF$_4$. ^1H-NMR (300 MHz, $CDCl_3$, 20°C): δ 4.44 (br, 4H, =C*H* of NBD), 3.98 (br, 2H, –C*H* of NBD), 1.46 (br, 2H, –CH_2 of NBD), 2.32 (s, 9H, CH_3), signals of phenyl-protons of [Rh(NBD)(PPh$_3$){P(*p*-Tol)$_3$}]BF$_4$ are overlapped by phenyl-protons of **1** and [Rh(NBD){P(*p*-Tol)$_3$}$_2$]BF$_4$. $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 20°C): δ 30.3 (dd, $J_{RhP} = 157.9$, $J_{PP} = 30.1$ Hz), 28.2 (dd, $J_{RhP} = 156.0$, $J_{PP} = 30.1$ Hz).

3.3. Kinetic studies

The catalytic reactions were followed, at constant pressure[3], by measuring the hydrogen consumption as a function of time on a gas burette (Afora 516256). The analysis of the products of the catalytic reactions was carried out on a Perkin–Elmer 8500 gas chromatograph with a flame ionization detector and a β,β′-oxidipropionitrile W–HP–80/100 (4 m × 1/8) column at 60°C. In a typical procedure, the substrate was added to a solution of the catalyst in dichloromethane (15 ml), under argon atmosphere. This solution was syringed through a silicon septum into a 50 ml flask attached to a gas burette, which was in turn connected to a Schlenk manifold and had been previously evacuated and refilled with hydrogen three time. The flask was then immersed in a 25°C bath and the mixture was vigorously shaken during the run.

4. Conclusions

The kinetic and spectroscopic results of this study suggest that in dichloromethane as solvent the selective hydrogenation of 2,5-norbornadiene to norbornene catalyzed by [Rh(NBD)(PPh$_3$)$_2$]$^+$ takes place via the five-coordinate dihydrido intermediate [RhH$_2$(NBD)(PPh$_3$)]$^+$ (Scheme 2), which is formed by oxidative addition of molecular hydrogen to both [Rh(NBD)(PPh$_3$)$_2$]$^+$ and [Rh(NBD)(PPh$_3$)]$^+$ depending on the concentration of free phosphine in the catalytic solution.

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[3] $P = P(H_2) + P(CH_2Cl_2)$, where $P(CH_2Cl_2) = 0.56$ atm at 25°C.

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