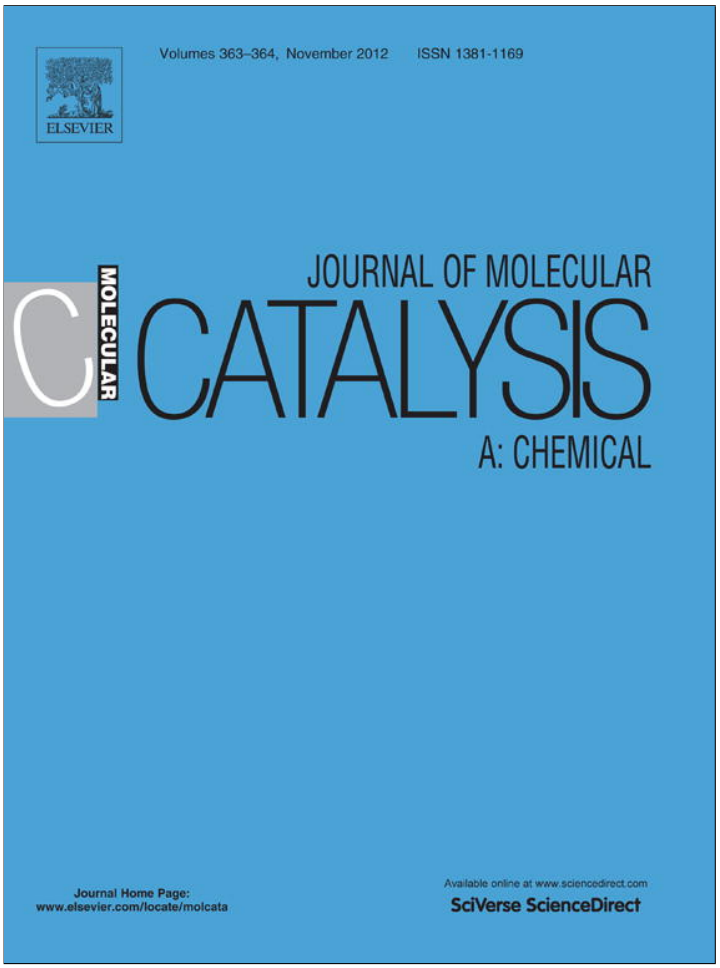

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Neutral η^6-arene ruthenium complexes with monodentate P-donor ligands Activation in the transfer hydrogenation reaction

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ABSTRACT

Five Ru(II) neutral complexes **C** of the type [$RuCl_2(\eta^6$-arene)(**P**)] (**P** = monodentate phosphorus ligand) have been prepared: **C1** (arene = *p*-cymene, **P** = PPh_3); **C2** (arene = *p*-cymene, **P** = (*R*)-Monophos); **C3** (arene = *p*-cymene, **P** = (*S*)-Ph-Binepine); **C4** (arene = benzene, **P** = PPh_3); and **C5** (arene = benzene, **P** = (*S*)-Ph-Binepine). These complexes have been screened as catalytic precursors in the transfer hydrogenation of acetophenone with 2-propanol. Under optimised conditions at 82 °C complexes **C1** and **C4** provide full conversion in less than 20 min at a [Ru]:substrate ratio of 1:200. With the chiral complexes **C2** and **C3** good TOF values have been reached but with low enantioselectivities. The activation of the catalytic precursor has been studied. Based on NMR evidence, a mechanism in which the catalytically active species is a Ru monohydride complex arising from the reaction of the catalyst precursor **C** with 2-propanol in the presence of a base is suggested. The reaction shows different sensitivity towards excess of phosphine: whereas excess of PPh_3 slows down the reaction severely, excess of (*S*)-Ph-Binepine does not cause such a sharp effect. An excess of chloride ion affects the activation of the precursor **C**.

1. Introduction

Reduction of ketones to the parent alcohols is a classic transformation of organic chemistry, traditionally carried out by metallic hydrides or molecular hydrogen in the presence of heterogeneous catalysts [1]. Albeit effective, these strategies have severe disadvantages. The former involves the manipulation of pyrophoric hydrides and the generation of stoichiometric amounts of metallic salts as waste whereas the latter usually requires elevated temperatures and high pressures of hydrogen gas with the inherent risks associated with the manipulation of a highly flammable reagent. A much safer and simple alternative is the formal transfer of two H atoms from a hydrogen donor to the carbonyl group in the presence of a suitable homogeneous catalyst, a process known as transfer hydrogenation (TH) [2]. This process is a key transformation in homogenous catalysis, especially in the asymmetric version, because it frequently ensures quantitative conversions and high enantioselectivities in a short reaction time. Ruthenium precursors bearing chiral diamines and/or diphosphines such as BINAP, developed by Noyori and coworkers [3–5], "reverse tethered" precursors, described by Wills and coworkers [6], systems that contain cyclometallated terdentate ligands, described by Baratta et al. [7] and cycloruthenated complexes such as the ones recently reported by de Vries and coworkers [8] stand out within the most successful systems. In all these systems, the presence of at least one amine unit in the ligand structure seems to be pivotal for reaching very high TOF values and elevated enantioselectivities.

Ruthenium complexes of the type [$RuCl_2(\eta^6$-arene)(**P**)] with **P** as a monodentate phosphorus ligand [9] despite being stable and easy to prepare have seldom been used in TH. Rossell and coworkers [10] reported the use of [$RuCl_2(\eta^6$-*p*-cymene)(PPh_3)] and [$RuCl_2(\eta^6$-*p*-cymene)($PMePh_2$)] in the reduction of cyclohexanone, whereas Carriedo and coworkers [11] also used [$RuCl_2(\eta^6$-*p*-cymene)(PPh_3)] but in the reduction of acetophenone. Li and coworkers [12] have recently reported very good activities of [$RuCl_2(\eta^6$-benzene)(PAr_3)] complexes (Ar = Ph, *p*-An and *p*-CF_3Ph) in the reduction of the same substrate. Almost at the same time, some of us [13] reported the successful enantioselective reduction of acetophenone using several [$RuCl_2(\eta^6$-*p*-cymene)(**P***)] containing optically pure diarylic *P*-stereogenic phosphines **P***. Some of these complexes showed good activities and moderate enantioselectivities.

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In this paper the results obtained in H-transfer reduction of acetophenone by complexes of the same family with a broader selection of both chiral and achiral monophosphorus ligands are reported. A series of experiments have been carried out with precursors **C1** and **C3** in order to shed some light on the mechanism of the catalytic reaction promoted by such complexes.

2. Results and discussion

2.1. Synthesis of Ru complexes

Complexes **C1**–**C5** were easily prepared as air-stable solids following a known procedure [14–16], by treating one equivalent of the well-known dimers $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**D1**) or $[RuCl_2(\eta^6\text{-benzene})]_2$ (**D2**) with two equivalents of the monophosphorus ligand in dichloromethane (Scheme 1).

Synthesis of complexes **C1**–**C4** was achieved at room temperature whereas the preparation of **C5** required slightly higher temperature due to the poor solubility of **D2** in dichloromethane. All complexes were isolated in moderate to good yields as spectroscopically pure solids. Complexes **C1** [9,17], **C2** [18] and **C4** [12] are known compounds while (*S*)-Ph-Binepine [19,20] complexes **C3** and **C5** have not been reported previously. Complex **C3** is a dark orange solid featuring a singlet at 48.3 ppm in the ^{31}P NMR spectrum in CD_2Cl_2 with a coordination induced shift to lower field of almost 40 ppm compared to the free ligand (7.43 ppm). As a consequence of the coordination of the chiral Ph-Binepine ligand, the two methyl groups of the *i*-Pr moiety become diastereotopic and give rise to separate peaks in the ^1H NMR spectrum. For the same reason, all four arylic protons of the coordinated *p*-cymene substituent are distinguishable. In contrast, the six protons of the coordinated benzene of **C5** give rise to a single resonance at 5.40 ppm, indicative of a free rotation around the Ph–Ru axis.

2.2. Catalytic hydrogen transfer

2.2.1. Influence of the different parameters on the catalytic outcome

Optimisation of the reaction conditions for transfer hydrogenation of acetophenone was carried out using complex **C1**, already known to be active in TH (Scheme 2) [10,11].

In order to generate the catalytic active species, complex **C1** and potassium *tert*-butoxide were dissolved in 2-propanol and heated to reflux. After the allotted time (activation period), acetophenone was added. As shown in Table 1, the efficiency of the transfer hydrogenation reaction (yield and TOF value) turned out to be critically dependent on the activation period.

When catalytic precursor, base and substrate were mixed together, the conversion at 10 min (Table 1, entry 1) was much lower than when acetophenone was added later (Table 1, *cf.* entry 1 with entries 5 and 8). This suggests that some time is necessary in order to generate a steady concentration of the catalytically active species in solution. The activation process demands the presence of ^{t}BuOK since practically no conversion was observed without base (Table 1, entry 14). Further experiments at shorter activation times (not listed in the table) were carried out while sampling at every 5 min. Despite a very careful and quick sampling, erratic conversion values were obtained, suggesting that the process of formation of the active species is very sensitive. On the other hand, long induction periods (Table 1, entry 11) were detrimental for the conversion, probably due to catalyst decomposition in the absence of substrate. Therefore, an activation time of 15 min was judged to be optimal under the actual conditions, leading to the highest conversion possible (around 98%) in 20 min (Table 1, entry 6).

Table 1
Effect of the activation period on the TH of acetophenone using precursor **C1**.

Entry[a]	Activation period (min)	Time (min)[b]	Yield (%)[c] [TOF][d]
1	0	10	30.3[363]
2	0	20	48.2
3	0	30	66.7
4	0	40	81.2
5	15	10	93.1[1117]
6	15	20	97.7
7	15	30	98.1
8	30	10	84.6[1015]
9	30	20	95.3
10	30	30	97.6
11	60	10	67.5[810]
12	60	20	90.6
13	60	30	95.8
14[e]	15	0	1.3
15[e]	15	10	36.2[434]
16[e]	15	20	64.9
17[e]	15	30	83.9

[a] Conditions: 0.02 mmol of **C1** and 0.1 mmol of ^{t}BuOK were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After the allotted time, 4 mmol of acetophenone were added [Ru/^{t}BuOK/acetophenone = 1:5:200].
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).
[e] The order of addition of ^{t}BuOK and acetophenone was reversed; the reaction time is counted after addition of ^{t}BuOK.

The next round of experiments was designed to analyse the effect of the amount of potassium *tert*-butoxide on the catalytic outcome (Table 2).

Although one equivalent of potassium *tert*-butoxide was sufficient to initiate the reaction, the latter did progress very slowly (Table 2, entries 1–3), 5 or more equivalents of base (Table 2, entries 4–9) instead ensured elevated conversions at shorter reaction times.

We next turned our attention to the effect of the temperature both on the activation time and catalysis efficiency (Table 3).

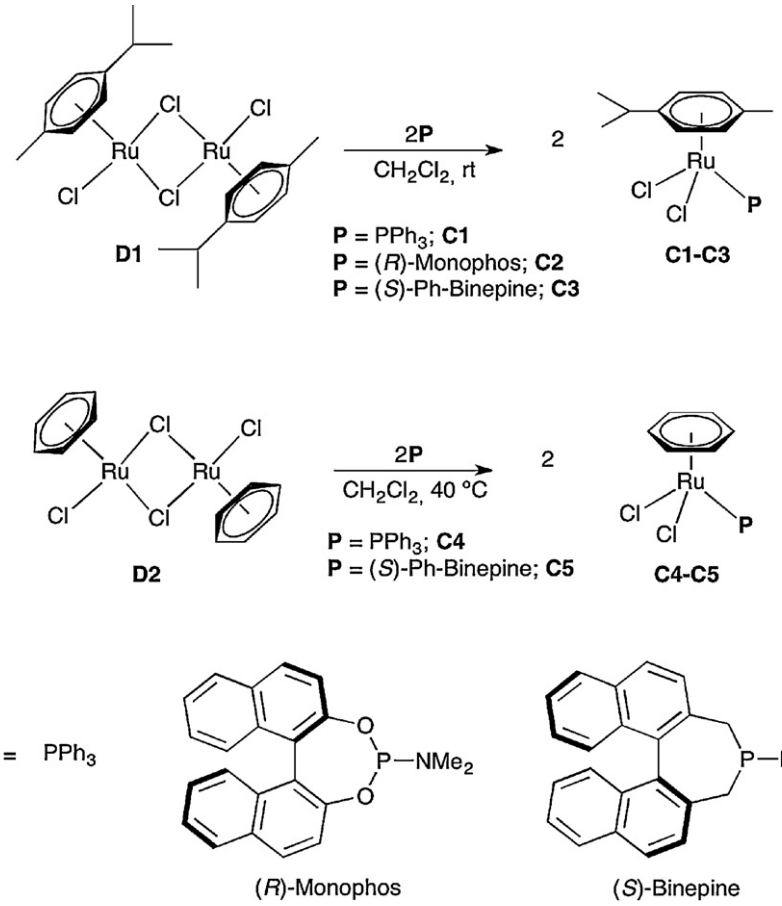
High temperatures were required for the catalytically active species to be formed since very low conversions at 10 min were recorded even in refluxing 2-propanol when the activation process was performed at room temperature (Table 3, entry 4). At 40 °C the catalyst apparently deactivates after about 10% of conversion (Table 3, entries 7–9). The reaction did not proceed at room temperature regardless of the activation temperature (Table 3, entries 10–12).

Having established the best conditions to generate the active catalytic species, other catalysts, either prepared *in situ* or

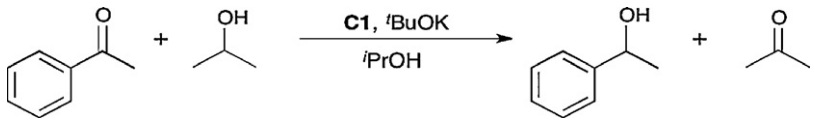
Table 2
Effect of the amount of ^{t}BuOK on the TH of acetophenone using precursor **C1**.

Entry[a]	Equivalents of ^{t}BuOK	Time (min)[b]	Yield (%)[c] [TOF][d]
1	1	10	9.0[108]
2	1	20	13.0
3	1	30	17.2
4	5	10	93.1[1117]
5	5	20	97.7
6	5	30	98.1
7	20	10	86.0[1032]
8	20	20	96.5
9	20	30	98.0

[a] Conditions: 0.02 mmol of **C1** and the allotted amount of ^{t}BuOK were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After 15 min, 4 mmol of acetophenone were added [Ru/acetophenone = 1:200].
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).



Scheme 1. Preparation of complexes **C1**–**C5**.



Scheme 2. TH of acetophenone.

Table 3
Effect of temperature on the TH of acetophenone using precursor **C1**.

Entry[a]	Temperature (°C)	Time (min)[b]	Yield (%)[c] [TOF][d]
1	82	10	93.1[1117]
2	82	20	97.7
3	82	30	98.1
4[e]	82	10	4.8[58]
5[e]	82	20	19.0
6[e]	82	30	54.9
7	40	10	11.6[139]
8	40	20	11.7
9	40	30	11.7
10	Rt	10	<1
11	Rt	20	<1
12	Rt	30	<1
13[e]	Rt	10	<1
14[e]	Rt	20	<1
15[e]	Rt	30	<1

[a] Conditions: 0.02 mmol of **C1** and 0.1 mmol of ^{t}BuOK were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After 15 min the reaction was rapidly heated to the desired temperature and 4 mmol of acetophenone were added [Ru/^{t}BuOK/acetophenone = 1:5:200].
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).
[e] The activation time was 1 h and it was carried out at room temperature.

preformed, were tested in the transfer hydrogenation of acetophenone (Table 4).

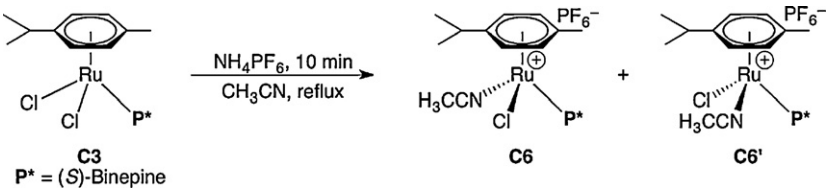
Preformed **C1** is a better catalyst than the one formed *in situ* during the activation period (Table 4, compare entries 1–3 with 4–6). This might be due to the very low solubility of **D1** in 2-propanol, thus precluding the formation of **C1**. Probably due to the same reason, dimer **D2** and triphenylphosphine also led to mediocre results (Table 4, entries 19–21). Complex **C2** with the well-known ligand (*R*)-Monophos is a very poor precursor. Under the same conditions, complex **C3** with (*S*)-Ph-Binepine led to slightly better results in terms of yield, but with very poor stereoselectivities (Table 4, entries 13–15). As expected after the experiments with **C1**, complex **C4** was also very active (Table 4, entries 16–18), a fact recently reported [12].

We finally carried out some more catalytic runs with **C1** with a higher substrate/catalyst ratio (Table 5).

Results in Table 5 show that at 500:1 acetophenone:catalyst ratio the reaction proceeded more slowly. Furthermore, deactivation of the catalytic species derived from **C1** could be observed.

2.2.2. Cationic derivatives of *C3*

The reaction of **C3** with NH_4PF_6 in acetonitrile at reflux for 20 min gave rise to the cationic complex **C6**/**C6′** as an air-stable



Scheme 3. Synthesis of cationic complexes **C6** (S_{Ru}) and **C6′** (R_{Ru}).

Table 4
Effect of the catalytic precursor on the TH of acetophenone.

Entry[a]	Precursor	Time (min)[b]	Yield (%)[c] [TOF][d]	Ee (%)[e]
1	**C1**	10	93.1[1117]	–
2	**C1**	20	97.7	–
3	**C1**	30	98.1	–
4	**D1** + PPh_3	10	24.1[289]	–
5	**D1** + PPh_3	20	43.2	–
6	**D1** + PPh_3	30	57.5	–
7	**C2**	10	5.7[68]	<1
8	**C2**	20	10.5	<1
9	**C2**	30	17.6	<1
10	**D1** + (R)-Monophos	10	3.4[41]	7 (S)
11	**D1** + (R)-Monophos	20	5.9	7 (S)
12	**D1** + (R)-Monophos	30	9.6	5 (S)
13	**C3**	10	23.8[286]	10 (S)
14	**C3**	20	35.4	10 (S)
15	**C3**	30	43.5	9 (S)
16	**C4**	10	93.1[1117]	–
17	**C4**	20	94.1	–
18	**C4**	30	96.3	–
19	**D2** + PPh_3	10	21.4[257]	–
20	**D2** + PPh_3	20	45.0	–
21	**D2** + PPh_3	30	59.3	–

[a] Conditions (entries 1–3, 7–9 and 13–18): 0.02 mmol of **C1**–**C4** and 0.1 mmol of ^{t}BuOK were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After 15 min, 4 mmol of acetophenone were added [Ru/^{t}BuOK/acetophenone = 1:5:200]; for entries 4–6, 10–12 and 19–21, 0.01 mmol of **D1** or **D2** and 0.02 mmol of PPh_3 or (*R*)-Monophos were used instead of **C1** or **C2**.
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).
[e] Enantiomeric excess of 1-phenylethanol, determined by GC.

yellow solid in moderate yield (Scheme 3). Coordination of an acetonitrile molecule renders the Ru atom a stereogenic centre and two diastereomeric complexes with opposite absolute configuration at the Ru atom were formed. In the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 the two diastereomers are identified by two singlets at 48.1 ppm and 53.9 ppm for the more and less abundant diastereomers respectively and a septet at −144.3 ppm for the hexafluorophosphate counterion. The ratio of the two diastereomers in the NMR sample changed upon standing, going from 1:4 to 1:5 after three days. This indicates that the complexes are configurationally labile at ruthenium. The clearly unequal isomeric ratio contrasts with monohydrides **C7**/**C7′** discussed below and could be rationalised through semiempirical calculations (at PM6 level, see supplementary content). In this case the difference between the enthalpies of formation was around 10 kJ mol^{-1}, favouring the S_{Ru} isomer (**C6**).

Table 5
Effect of the catalytic precursor:substrate ratio on the TH of acetophenone with **C1**.

Entry[a]	[Ru]:acetophenone ratio	Time (min)[b]	Yield (%)[c]	TOF (h^{-1})[d]
1	1:200	10	93.1	1117
2	1:200	20	97.7	586
3	1:200	30	98.1	392
4	1:500	10	27.8	834
5	1:500	20	46.7	701
6	1:500	30	60.2	602

[a] Conditions: the appropriate amounts of **C1** and of ^{t}BuOK were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After 15 min, 4 mmol of acetophenone were added [Ru/^{t}BuOK = 1:5].
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).

Ru–Binepine complexes, either as preformed species **C3** and **C6** or as catalysts generated *in situ* from (*S*)-Ph-Binepine and the relevant arene dimer **D1** or **D2**, were tested in the transfer hydrogenation of acetophenone (Table 6).

In general, activity and selectivity were modest, regardless of the catalyst precursor used. The best enantioselectivity was obtained when [Ru(*p*-cymene)Cl_2]$_2$ (**D1**) was used in the presence of 4 equivalents of (*S*)-Ph-Binepine at 40 °C (Table 6, entry 2). Use of a larger excess of the chiral ligand did not improve selectivity and slowed down the reaction (Table 6, entry 3). The reaction could be brought to completeness in 3 h by operating at 82 °C but at the expense of enantioselectivity, which dropped considerably (Table 6, *cf.* entries 2 and 8). The use of dimer **D2**, bearing a less electron-rich η^6-benzene instead of *p*-cymene, did not improve the rate of the reaction (Table 6, entries 9 and 10). The activity was not boosted either when the cationic complex **C6**/**C6′** (1:4 mixture) and one equivalent of free (*S*)-Ph-Binepine were used (Table 6, entries 11 and 12). Interestingly, a slight excess of (*S*)-Ph-Binepine seems to stabilise the catalytically active species and a large excess does not seem to decrease dramatically the rate of the catalytic process (Table 6, entries 1–3), a fact that contrasts to the effect of the excess of PPh_3 (see Table 7).

2.2.3. The mechanism of TH

In contrast to the extensive literature regarding the mechanism of TH with Ru complexes bearing chiral diamines and/or diphosphines [4,5,21–25], there are only a handful of reports [10,12,13] with hints about the mechanism of TH with precursors of the type **C**. Taking into account the mechanism of TH with bidentate ligands and the strong tendency of ruthenium to form compounds with Ru—H bonds, it seems reasonable to assume that the catalytically active species are ruthenium hydride complexes formed under catalytic conditions [7,8,26]. The absence of any X–H (X = N, O, S) fragment in the complex suggests that the H transfer from the donor (2-propanol) to the acceptor (acetophenone) is promoted by the metal through stepwise coordination of both donor and acceptor to the metal centre through an inner-sphere mechanism [22].

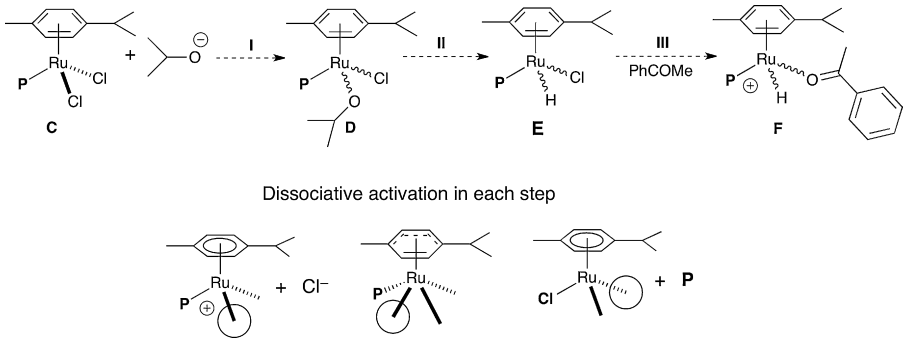
Because the starting complexes **C** are saturated 18-electron species, a dissociative process is expected to precede the formation of Ru-hydride species. An overview of possible pathways leading to formation of such species is depicted in Scheme 4 [13].

Step **I** is the substitution of the one coordinated chloride in **C** by the isopropoxide anion generated *in situ* by deprotonation of 2-propanol by potassium *tert*-butoxide. The neutral intermediate **D** undergoes β-hydride elimination (step **II**) to generate the neutral monohydride complex **E**, which binds acetophenone to give **F** and starts the catalytic cycle (Scheme 7). As depicted at the bottom part of the scheme, each of these steps should require a vacant

Table 6
TH of acetophenone with precursors containing (*S*)-Ph-Binepine.

Entry[a]	Precursor	M/L[b]	Temperature (°C)	Time (h)[c]	Yield (%)[d]	Ee (%)[e]
1	**C3**	1/1	40	22	10	14
2	**D1** + (S)-Ph-Binepine	1/2	40	22	45	19
3	**D1** + (S)-Ph-Binepine	1/5	40	22	24	17
4	**C3**	1/1	82	0.16	24	10
5	**C3**	1/1	82	0.33	35	10
6	**C3**	1/1	82	0.5	44	9
7	**D1** + (S)-Ph-Binepine	1/2	82	1	63	11
8	**D1** + (S)-Ph-Binepine	1/2	82	3	98	6
9	**D2** + (S)-Ph-Binepine	1/2	40	1	12	14
10	**D2** + (S)-Ph-Binepine	1/2	40	22	28	9
11	**C6/C6′** + (S)-Ph-Binepine	1/2	40	1	13	16
12	**C6/C6′** + (S)-Ph-Binepine	1/2	40	22	29	15

[a] Conditions: a solution of the Ru precursor and the ligand in 25 ml of 2-propanol was refluxed for 1 h. The solution was cooled down to room temperature and solid ^{t}BuOK was added. After total dissolution, the solution was heated to the desired temperature and acetophenone was added. The final [Ru]:[base]:[acetophenone] was set to 1:10:200.
[b] Ru:(*S*)-Ph-Binepine ratio.
[c] Time after addition of acetophenone.
[d] Yield in 1-phenylethanol, determined by GC.
[e] Enantiomeric excess of 1-phenylethanol, determined by GC; with (*S*)-Ph-Binepine (*S*)-1-phenylethanol was the major enantiomer.



Scheme 4. Possible routes to Ru hydride species from precursors **C**. The circle represents a vacant coordination site.

coordination site at the metal, which could be formed by dissociation of the Cl or the phosphine ligands [10,27–30] or by reduction of the hapticity (from η^6 to η^4 or to η^2) of the *p*-cymene ring through ring slippage [29,31].

In order to explore whether the activation of the catalyst precursors **C** implies a dissociation of Cl or phosphine, some experiments were performed in the presence of KCl or PPh_3. The results are listed in Table 7.

Table 7
Effect of the addition of KCl and PPh_3 on the TH of acetophenone with **C1**.

Entry[a]	KCl:**C1**	PPh_3:**C1**	Time (min)[b]	Yield (%)[c]	TOF (h^{-1})[d]
1	0:1	0:1	10	93.1	1117
2	0:1	0:1	20	97.7	586
3	0:1	0:1	30	98.1	392
4	5:1	0:1	10	82.8	994
5	5:1	0:1	20	96.1	577
6	5:1	0:1	30	97.7	391
7[e]	5:1	0:1	10	91.2	1094
8[e]	5:1	0:1	20	97.1	583
9[e]	5:1	0:1	30	98.0	392
10	0:1	5:1	10	5.5	66
11	0:1	5:1	20	12.9	77
12	0:1	5:1	30	20.3	81
13[e]	0:1	5:1	10	3.8	46
14[e]	0:1	5:1	20	11.9	71
15[e]	0:1	5:1	30	22.7	91

[a] Conditions: 0.02 mmol of **C1**, 0.1 mmol of ^{t}BuOK and the appropriate amount of KCl or PPh_3 were dissolved in 25 ml of ^{i}PrOH and heated to 82 °C. After the allotted time, 4 mmol of acetophenone were added [Ru/^{t}BuOK/acetophenone = 1:5:200].
[b] Time after addition of acetophenone.
[c] Yield in 1-phenylethanol, determined by GC.
[d] Turnover frequency, TOF = [mmol of 1-phenylethanol/mmol of **C1**]/time (h).
[e] KCl or PPh_3 was added after the activation time, along with acetophenone.

A small, but not negligible, inhibitory effect was observed when 5 equivalents of KCl were added *before* the activation time (Table 7, *cf.* entries 1 and 4). In contrast, no such effect was observed when the same amount of KCl is added along with acetophenone *after* the activation time (Table 7, *cf.* entries 1 and 7). This suggests that chloride dissociation may be involved in an early step of the activation process on the way to the active catalytic species [30], presumably complex **E** (Scheme 4). In contrast, the addition of 5 equivalents of PPh_3 slows down the reaction severely regardless of whether the excess of phosphine is added before or after the activation period (Table 7, entries 10–15). The intense inhibition of triphenylphosphine is likely to be due merely to its ability to block coordination positions at the Ru atom, and prevent decoordination of PPh_3. Additionally, we have recently reported chirality transfer to 1-phenylethanol from neutral complexes of the type **C** bearing *P*-stereogenic monophosphines [13], showing that the chiral phosphine remains coordinated to the Ru centre, at least throughout the catalytic cycle.

2.2.4. NMR experiments

To gain further insight into the mechanism, NMR experiments with **C1** were carried out with the objective of detecting possible intermediates, particularly Ru-H species (more details can be found in the experimental part and in the supplementary information). Thus one equivalent of complex **C1** and 5 equivalents of ^{t}BuOK were stirred in 2-propanol both at room temperature and at reflux. ^{31}P and ^{1}H spectra were recorded at different times. The starting complex **C1** is barely soluble in 2-propanol at room temperature therefore only an ill-defined singlet at +23 ppm in the $^{31}P\{^{1}H\}$ spectrum could be observed. After addition of 5 equivalents of ^{t}BuOK and stirring for 15 min at room temperature, two singlets

at +53.3 and +58.9 ppm in approximate 3:1 ratio were observed. A small resonance at around −6 ppm ascribable to PPh_3 was also present. The spectrum did not change after 1 h whereas after another extra hour we could not observe the PPh_3 peak. The peaks at +53.3 and +58.9 ppm give rise to broad doublets ($J \sim 54$ and 60 Hz respectively) in the H-coupled ^{31}P spectra. In the hydride region of the ^1H NMR spectra, two almost overlapped doublets at −7.28 and −7.34 ppm ($J = 60$ and 57 Hz respectively) could be observed whose intensities roughly fit with the 1:3 ratio of the ^{31}P spectra. These data fits well with Ru-H species, indeed [RuClH(η^6-*p*-cymene)(PPh_3)] (**E** in Scheme 4) is a known compound [32] ($\delta(^{31}P) = 52.5$ ppm, $J = 54$ Hz; $\delta(^1H) = -7.44$ ppm, $J = 53$ Hz). This suggests that after the activation at room temperature this species is formed along with a similar one, possibly bearing a coordinated isopropoxide group instead of a Cl.

When the same experiment was carried out at reflux temperature for 15 min, the ^{31}P NMR spectrum showed two major singlets at +58.8 and −14.2 ppm (roughly 1:1 ratio) and one minor resonance at +53.3 ppm. In the hydride region of the ^1H NMR spectrum, an apparent major doublet at −7.40 ppm ($J = 39$ Hz) was accompanied by two minor doublets at −7.33 and −7.48 ppm ($J = 57$ and 60 Hz respectively). Similarly to the experiment at room temperature, the peak at +58.8 ppm can be assigned to [Ru(O*i*-Pr)H(η^6-*p*-cymene)(PPh_3)] while the signal at −14.2 ppm could correspond to Ph_2P–PPh_2 [33]. The hydride peaks centred at −7.40 ppm could belong to a Ru hydridic species probably lacking a coordinated phosphine, formed upon decomposition of the complex. After refluxing for 2 h, only the singlet at −14.2 ppm could be observed in the ^{31}P NMR spectrum. Such decomposition may explain the detrimental effect of long activation times on catalyst activity (Table 1). In the third experiment, a catalytic run was started by addition of 200 equivalents of acetophenone after having activated the complex at reflux for 15 min with 5 equivalents of ^{t}BuOK. After 30 min, no peaks were observed neither in the $^{31}P\{^1H\}$ spectrum nor in the hydridic region of the ^1H spectrum.

Finally, **C1** was reacted with 5 equivalents of ^{t}BuOK in perdeuterated 2-propanol at room temperature for 1 h. The $^{31}P\{^1H\}$ spectrum was identical to the first experiment carried out with undeuterated 2-propanol. The ^1H spectrum showed some peaks belonging to the coordinated *p*-cymene unit. Two resonances at 2.00 and 2.14 ppm (in 1:3 ratio) can be assigned to the Me group of the *p*-cymene ring. The region of the aromatic protons of the *p*-cymene ring contained a group of four intense signals mixed with several other less intense peaks. The four intense signals is composed of two clear doublets at 4.17 and 5.03 ppm, which fit well with those reported for complex [RuClH(η^6-*p*-cymene)(PPh_3)] [32], and two broad signals at 4.43 and 5.25 ppm, which do not fit the mentioned complex.

The detection of PPh_3 and Ph_2P–PPh_2 and the observation of differentiated behaviour of the aromatic protons of the coordinated *p*-cymene ring are in agreement with a dissociative activation of complexes **C** to form the catalytically active species.

2.3. Preparation of hydride complexes derived from *C3*

Analogous hydride species have been detected by NMR when complex **C3**, containing the chiral ligand (*S*)-Ph-Binepine, was treated with a suitable hydrogen donor in the presence of base. Upon replacement of one of the chloride ligands with a hydride, the metal centre in **C3** becomes stereogenic and therefore two diastereomeric monohydride species can be formed. Replacement of both chlorides gives rise to a dihydride species. The conversion of the starting complex and the relative amounts of the possible hydride species turned out to be critically dependent on hydride donor, base strength and reaction temperature.

When complex **C3** was refluxed in MeOH in the presence of 1 equivalent of sodium formate, a maximum conversion of 73% was observed after 1 h, which could not be improved by extending the reaction time (see Scheme 5 and supplementary content) [34]. In the ^1H NMR spectrum the diastereomeric (with different absolute configuration at the Ru atom) monohydrides derivatives **C7** (S_{Ru}) and **C7′** (R_{Ru}) give rise to two doublets with chemical shifts of −8.42 ppm ($J_{H-P} = 55.7$ Hz) and −8.61 ppm ($J_{H-P} = 56.6$ Hz). The $^{31}P\{^1H\}$ NMR spectrum shows, beside the signal relative to unreacted **C3**, those corresponding to the two hydrides, at 71.5 ppm, relative to the more abundant diastereomer (60%), and at 75.5 ppm, relative to the less abundant one (40%). As expected, these signals are shifted of about 30 ppm to lower field compared to the starting complex **C3** (48.3 ppm) [35].

The relative amounts of the two hydrides is time-dependent: it varies from 1:1, after 1 h at reflux, to a 1:1.5 ratio, after three hours, in favour of the most stable diastereomer (71.5 ppm). Unfortunately all the attempts to isolate complexes **C7** in pure form were unsuccessful. The almost 1:1 isomeric ratio was rationalised through semiempirical calculations (at PM6 level, see supplementary content) of the formation enthalpies of both isomers, which showed that difference between the two values was less than 1 kJ mol^{-1}.

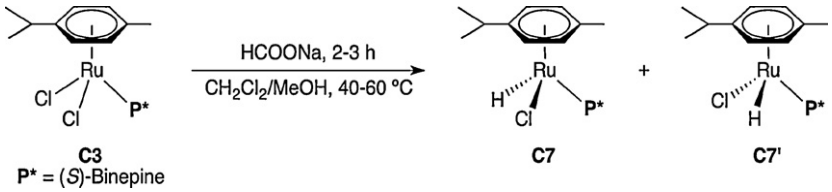
The same monohydrides **C7** and **C7′** were formed in a 1:1 ratio, although in lower yield (30%), by reacting **C3** with a stoichiometric amount of K_2CO_3 in MeOH for 24 h at room temperature [36]. When the same reaction was performed at reflux for 1 h, no starting material could be detected. Approximately 50% of the products corresponded to **C7**/**C7′** monohydrides (1:1 ratio) whereas the remaining 50% was the dihydride complex **C8** (see Scheme 6 and supplementary content). In the latter, the two hydrides are diastereotopic giving rise to partially superimposed doublets of doublets: H_a −11.32 ppm ($J_{H-P} = 56.4$ Hz, $J_{H-H} = 7.3$ Hz); H_b −11.12 ppm ($J_{H-P} = 56.4$ Hz, $J_{H-H} = 7.3$ Hz). The $^{31}P\{^1H\}$ chemical shift of **C8** was 79.5 ppm.

In order to prepare pure dihydride complex **C8**, **C3** was reacted with 2 equivalents of sodium methoxide. ^1H NMR spectrum showed 75% conversion to the monohydrides **C7**/**C7′** (1:1 ratio), and 25% of a different species, whose resonances could not be ascribed to the desired dihydride. It featured a doublet of quartets centred at −11.32 ppm (apparent $J_{H-P} = 55.4$ Hz, $J_{H-H} = 7.3$ Hz; see supplementary content). The hydride signal of this unexpected new species appears in the typical range of dihydrides but its identity remains unclear. The two apparent quartets might arise from the two diastereotopic protons of a dihydride complex coupled to each other and with a phosphorous atom with similar coupling constants. Alternatively, the coupling pattern could also fit with a monohydridic species arising from displacement of a chloride from the metal coordination sphere in either **C7** or **C7′** by a methoxide ion, in which case the hydride would couple not only with phosphorus but also with the hydrogen atoms of the methyl group of the methoxide. In this case, NMR data would suggest that the formation of this species is highly selective, as only one of the two possible diastereomers would be observed.

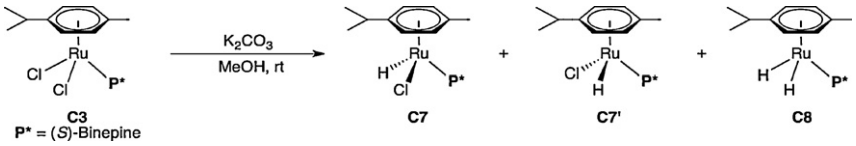
In order to reproduce the reaction conditions of the transfer hydrogenation promoted by an *in situ* delivered catalyst, the preparation of the hydridic species was also attempted starting from the dimer [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ in the presence of equivalent amounts of (*S*)-Ph-Binepine and K_2CO_3 in refluxing 2-propanol [37]. The reaction was followed by ^{31}P NMR spectroscopy. The intermediate formation of **C3** was observed, but the latter did not evolve into hydride species **C7** because it decomposed into unidentified species.

In order to rationalise the results with neutral complexes **C** the following catalytic cycle (Scheme 7) is suggested.

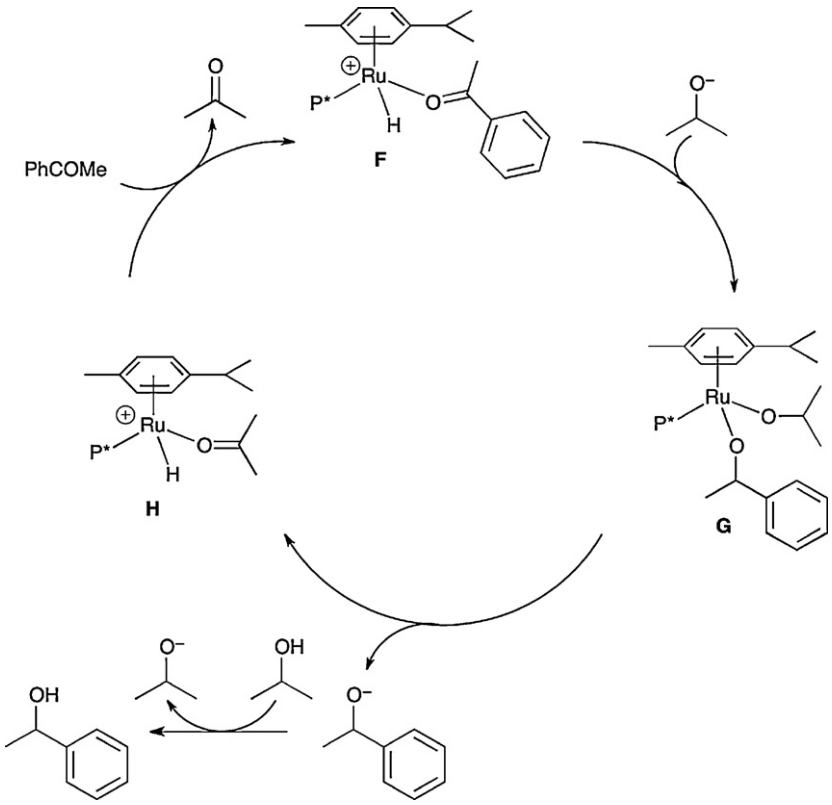
The catalytic cycle would start with migratory insertion of acetophenone into the Ru—H bond [7] of **F**. Coordination of an



Scheme 5. Synthesis of monohydride complexes **C7** and **C7′**.



Scheme 6. Synthesis of monohydride complexes **C7** and **C7′** and dihydride **C8**.



Scheme 7. Mechanism of TH of acetophenone.

isopropoxide anion would generate *bis*(alkoxide) neutral complex **G** which would suffer decoordination of the deprotonated product and β-hydride elimination to furnish **H**. Exchange of acetone by incoming acetophenone would regenerate catalyst **F**.

3. Conclusions

This paper describes the synthesis of five neutral [$RuCl_2(\eta^6$-arene)(**P**)] complexes (**C**), two of them previously unreported. These systems are catalytically active (at 0.5% of **C**) in transfer hydrogenation of acetophenone in the presence of 5 equivalents of potassium *tert*-butoxide in refluxing 2-propanol with initial TOF values up to 1117 h^{-1} for **C1** and **C4**, leading to complete conversions in less than 20 min for **C1** at substrate/Pd ratio (200/1). Low activities and enantioselectivities have been observed when using chiral P-ligands such as Monophos and Ph-Binepine.

Experiments aimed at studying the effect of the different parameters on the catalytic performance have been performed with the catalytic precursor **C1**. These experiments showed that for the systems under investigation, 2-propanol reflux temperature (82 °C), excess of potassium *tert*-butoxide and a period of activation to form the catalysts are required for efficient catalysis. This activation period has been monitored by NMR, which showed the formation of ruthenium monohydride complexes with **C1**. The same sort of monohydride species were formed from **C3**. In this case, due to presence of a chiral ligand, a pair of diastereoisomeric complexes could be clearly observed by NMR. The mechanism of the reaction has also been investigated by analysing the results of the catalytic runs and by NMR experiments. After the induction period (before the addition of acetophenone) ruthenium monohydride complexes have been spectroscopically detected. The addition of KCl before the activation period slows down the reaction somewhat but this

effect is not observed when this salt is added after the activation period. This fact suggests that chloride dissociation is an important step in the formation of the hydride active species. Contrasting to the impact of Cl on the rate, PPh_3, added either before or after the activation period, produces a strong inhibitory effect.

4. Experimental

All compounds were prepared under a purified nitrogen or argon atmosphere using standard *Schlenk* and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using the following spectrometers: Varian XL-500, Mer-400 MHz, Varian Inova 300 and Bruker DRX-250, using $CDCl_3$ as a solvent unless otherwise specified. Chemical shifts were reported downfield from standards. IR spectra were recorded using Nicolet Impact 400 and Avatar 330 spectrometers. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument.

GC analyses of transfer hydrogenation of acetophenone were performed in an Agilent 6890N instrument equipped with a chiral DiEt-*t*-Bu-β-cyclodex column, 25 m long with helium as a carrier gas. Conditions: 80 °C (2 min) to 150 °C (2 °C/min). Data: t_R (min), acetophenone, 7.0; 1-phenylethanol, 11.1 (*R*) and 11.8 (*S*).

4.1. Dichloro(η^6-*p*-cymene)[(*S*)-Ph-Binepine]ruthenium(II), C3

[$RuCl_2(\eta^6$-*p*-cymene)]$_2$ (287 mg, 0.47 mmol) and (*S*)-Ph-Binepine (400 mg, 1.03 mmol) were dissolved in 20 ml of dichloromethane and the orange solution was stirred for 1 h. Addition of hexane caused the precipitation of the product as a dark orange solid, which was filtered, washed with copious amounts of hexane and dried *in vacuo*. Yield: 564 mg (79%).

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 7.93 (*d*, *J* = 8.3 Hz), 7.89 (*d*, *J* = 8.3 Hz), 7.82–7.78 (*m*, Ar), 7.68–7.62 (*m*, Ar), 7.46–7.41 (*m*, Ar), 7.37 (*bt*, *J* = 6.8 Hz), 7.18–7.13 (*m*, Ar), 7.04 (*d*, *J* = 8.3 Hz), 5.32 (*d*, 2H, η^6-*p*-cymene, *J* = 10.3 Hz), 5.18 (*d*, 2H, η^6-*p*-cymene, *J* = 9.8 Hz), 3.96 (*d*, 1H, C$\underline{H}_2$, *J* = 12.7 Hz), 3.67–3.64 (*m*, 2H, C$\underline{H}_2$), 3.41 (*dd*, 1H, C$\underline{H}_2$, *J* = 17.1 Hz), 2.44–2.37 (*m*, 1H, C$\underline{H}$(CH$_3$)$_2$), 1.84 (*s*, 3H, C$\underline{H}_3$), 1.10 (*d*, 3H, CH(C$\underline{H}_3$)$_2$, *J* = 7.3 Hz), 0.99 (*d*, 3H, CH(C$\underline{H}_3$)$_2$, *J* = 6.8 Hz). **^{13}C{^{1}H} NMR** (100.5 MHz, CD_2Cl_2): δ 136.7 (*s*), 134.0 (*bs*), 133.6 (*bs*), 132.7 (*d*, *J* = 29.9 Hz), 132.5 (*d*, *J* = 4.6 Hz), 132.1 (*s*), 131.9 (*d*, *J* = 6.1 Hz), 130.4 (*d*, *J* = 3.8 Hz), 130.2 (*d*, *J* = 6.9 Hz), 130.0 (*d*, *J* = 2.3 Hz), 128.5–128.4 (*m*), 128.0 (*d*, *J* = 8.4 Hz), 127.4 (*d*, *J* = 13.8 Hz), 126.7 (*s*), 125.5 (*d*, *J* = 19.2 Hz), 125.2 (*s*), 107.9 (*s*), 95.6 (*s*), 84.7 (*d*, *J* = 5.4 Hz), 89.4 (*d*, *J* = 3.8 Hz), 85.6 (*d*, *J* = 4.6 Hz), 84.7 (*d*, *J* = 5.4 Hz), 32.9 (*d*, C$\underline{H}_2$, *J* = 26.1 Hz), 31.6 (*s*, C$\underline{H}_2$), 30.2 (*s*, C$\underline{H}_2$), 24.5 (*d*, C$\underline{H}_2$, *J* = 26.1 Hz), 22.5 (*d*, C$\underline{H}$(CH$_3$)$_2$, *J* = 29.9 Hz), 21.7 (*d*, C$\underline{H}$(CH$_3$)$_2$, *J* = 18.4 Hz), 17.5 (*s*, C$\underline{H}_3$), 13.9 (*s*, CH(C$\underline{H}_3$)$_2$). **^{31}P{^{1}H} NMR** (161.89 MHz, CD_2Cl_2): δ +48.3 (*s*).

4.2. Dichloro(η^6-benzene)[(*S*)-Ph-Binepine]ruthenium(II), C5

[$RuCl_2(\eta^6$-benzene)]$_2$ (100 mg, 0.19 mmol) and (*S*)-Ph-Binepine (170.8 mg, 1.03 mmol) were suspended in 20 ml of dichloromethane and the brownish mixture refluxed (40 °C) overnight. The brown precipitate was filtered, washed with copious amounts of hexane and dried *in vacuo*. Yield: 105 mg (41%).

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 7.91 (*t*, *J* = 8.8 Hz), 7.79–7.76 (*m*, Ar), 7.75–7.60 (*m*, Ar), 7.42–7.36 (*m*, Ar), 7.19–7.14 (*m*, Ar), 7.10 (*t*, *J* = 6.6 Hz), 7.02 (*d*, *J* = 8.3 Hz), 5.40 (*s*, 6H, η^6-benzene), 3.86 (*d*, C$\underline{H}_2$, *J* = 2.2 Hz), 3.82 (*d*, C$\underline{H}_2$, *J* = 1.8 Hz), 3.56–3.61 (*m*, C$\underline{H}_2$), 3.57 (*d*, C$\underline{H}_2$, *J* = 4.4 Hz), 3.53 (*s*, C$\underline{H}_2$). **^{31}P{^{1}H} NMR** (161.89 MHz, CD_2Cl_2): δ +46.5 (*s*).

4.3. Chloro(acetonitrile)(η^6-*p*-cymene)[(*S*)-Ph-Binepine] ruthenium(II) hexafluorophosphate, C6/C6′

C3 (100 mg, 0.144 mmol) and NH_4PF_6 (30.8 mg, 0.187 mmol) were suspended in 4.4 ml of acetonitrile and the orange mixture was brought to reflux (82 °C). After 10 min the solution turned dark yellow. After 30 min, the solution was cooled down to room temperature and the solvent removed *in vacuo*. The residue was dissolved with dichloromethane and filtered through a small Celite pad. Addition of hexane to the solution caused the precipitation of the title product, which was filtered and washed with hexane. Yield: 70 mg (58%).

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 8.04 (*d*, *J* = 8.8 Hz), 7.92 (*d*, *J* = 8.3 Hz), 7.85 (*s*, Ar), 7.82 (*d*, *J* = 7.8 Hz), 7.78 (*m*, Ar), 7.69 (*m*, Ar), 7.64 (*m*, Ar), 7.61 (*m*, Ar), 7.58 (*m*, Ar), 7.30 (*m*, Ar), 7.21 (*m*, Ar), 7.10 (*m*, Ar), 7.05 (*m*, Ar), 6.94 (*m*, Ar), 6.81 (*d*, *J* = 8.8 Hz), 6.74 (*s*, Ar), 5.76 (*d*, η^6-*p*-cymene, major, *J* = 5.9 Hz), 5.69, 5.59 (*dd*, η^6-*p*-cymene, minor, *J* = 47.9 Hz), 5.50 (*d*, η^6-*p*-cymene, major, *J* = 5.9 Hz), 5.47–5.23 (*m*, η^6-*p*-cymene), 5.19 (*d*, η^6-*p*-cymene, minor, *J* = 27.8 Hz), 4.86 (*d*, η^6-*p*-cymene, minor, *J* = 6.3 Hz), 4.43, 4.39 (*dd*, C$\underline{H}_2$, minor, *J* = 0.5 Hz), 3.97 (*d*, C$\underline{H}_2$, minor, *J* = 3.9 Hz), 3.93 (*d*, C$\underline{H}_2$, major, *J* = 4.4 Hz), 3.75 (*d*, C$\underline{H}_2$, major, *J* = 5.9 Hz), 3.71 (*d*, C$\underline{H}_2$, major, *J* = 5.9 Hz), 3.54, 3.47 (*m*, C$\underline{H}_2$, major), 3.29, 3.24 (*m*, C$\underline{H}_2$, minor), 2.96 (*s*, C$\underline{H}_2$, minor), 2.92 (*d*, C$\underline{H}_2$, minor, *J* = 4.4 Hz), 2.88 (*s*, C$\underline{H}_2$, minor), 2.77 (*d*, C$\underline{H}_2$, major, *J* = 8.3 Hz), 2.73 (*d*, C$\underline{H}_2$, major, *J* = 8.3 Hz), 2.34, 2.24 (*m*, C$\underline{H}$Me$_2$, minor), 2.22, 2.18 (*m*, C$\underline{H}$Me$_2$, major), 1.83 (*s*, C$\underline{H}_3$, major), 1.78 (*s*, C$\underline{H}_3$, minor), 1.60 (*s*, C$\underline{H}_3$CN, minor), 1.30 (*s*, C$\underline{H}_3$CN, major), 1.13 (*d*, CH$\underline{Me}_2$, major, *J* = 6.8 Hz), 1.04 (*d*, CH$\underline{Me}_2$, minor, *J* = 7.3 Hz), 0.97 (*d*, CH$\underline{Me}_2$, major, *J* = 6.8 Hz), 0.84 (*d*, CH$\underline{Me}_2$, major, *J* = 6.8 Hz). **^{31}P{^{1}H} NMR** (161.89 MHz, CD_2Cl_2): δ +53.9 (*s*, minor); +48.1 (*s*, major); −144.3 (*septet*, *J* = 287.4 Hz).

4.4. General procedure for the enantioselective transfer hydrogenation

A typical transfer hydrogenation run was performed as follows. A 50 ml *schlenk* flask was charged with the ruthenium precursor **C** (0.02 mmol) and potassium *tert*-butoxide (11.2 mg, 0.1 mmol) and was purged with three vacuum/argon cycles. Under a gentle flow of argon, 25 ml of degassed 2-propanol were added and the flask heated to reflux (85 °C) for 15 min. After that time acetophenone (468 μL, 4.0 mmol) was rapidly added to start the catalytic run. The reaction was monitored by GC analysis.

4.5. NMR experiments with C1

4.5.1. Experiment 1

Complex **C1** (56.8 mg, 0.1 mmol) and ^{t}BuOK (56.1 mg, 0.5 mmol) were dissolved in 10 ml of degassed 2-propanol under a N_2 atmosphere. The solution was stirred at room temperature. At the allotted times, aliquots were taken and analysed by NMR (300 MHz spectrometer).

4.5.2. Experiment 2

Complex **C1** (56.8 mg, 0.1 mmol) and ^{t}BuOK (56.1 mg, 0.5 mmol) were dissolved in 10 ml of degassed 2-propanol under a N_2 atmosphere. The stirred solution was brought to reflux (82 °C). At the allotted times, aliquots were taken and analysed by NMR (300 MHz spectrometer).

4.5.3. Experiment 3

Complex **C1** (56.8 mg, 0.1 mmol) and ^{t}BuOK (56.1 mg, 0.5 mmol) were dissolved in 10 ml of degassed 2-propanol under a N_2 atmosphere. The stirred solution was brought to reflux (82 °C). After 15 min acetophenone (20 mmol) was added and the mixture

refluxed for 30 min. An aliquot was taken and analysed by NMR (300 MHz spectrometer).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.05.015.

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