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# Neutral *p*-cymene ruthenium complexes with *P*-stereogenic monophosphines. New catalytic precursors in enantioselective transfer hydrogenation and cyclopropanation

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ABSTRACT

A family of eight neutral, pseudotetrahedral piano-stool ruthenium complexes **C**, of the type [$RuCl_2$(*p*-cymene)(PArPhR)] (Ar = 1-naphthyl, 9-phenanthryl and 2-biphenylyl; R = Me, *i*-Pr, OMe, $-CH_2SiMe_3$ and $-CH_2SiPh_3$) have been prepared and characterised, including the X-ray crystal structure for **C6** (Ar = 2-biphenylyl; R = *i*-Pr). These complexes catalyse the asymmetric hydrogen transfer reaction of acetophenone in refluxing 2-propanol in the presence of potassium *tert*-butoxyde, reaching full conversions and up to 45% ee after 24 h towards the *S* enantiomer of 1-phenylethanol. Cationic complexes formed upon treatment of **C** with one equivalent of $AgSbF_6$ or $(Et_3O)PF_6$ are active in the cyclopropanation reaction of styrene and α-methylstyrene by ethyl diazoacetate. Low to moderate conversions (up to 58%), diastereoselectivities (up to 40% de), and moderate enantioselectivities (up to 69% ee) have been found. For both reactions, bulky complexes and **C6** in particular lead to the best results.



## 1. Introduction

Ruthenium is nowadays one of the most intensively used metals in homogeneous catalysis [1–4], due in part to cheaper price compared to other noble metals such as rhodium and palladium and to the wide span of reactions catalysed by Ru(II) complexes, many of them in enantioselective fashion. The most important example is arguably the reduction of ketones by Ru/BINAP and Ru/BINAP/diamine systems, via hydrogenation or transfer hydrogenation [5–7]. Another important transformation is the cyclopropanation reaction [8,9], catalysed by Ru(II) complexes mainly of nitrogen ligands. A common feature of the ligands used in both transformations is that they are either bi- or polydentate [10]. In contrast, monodentate ligands [11–13] are still infrequent in stereoselective ruthenium catalysis. In this work we explore the potential of simple [$RuCl_2$(*p*-cymene)(P*)] complexes in enantioselective hydrogen transfer and cyclopropanation, using a set of monodentate *P*-stereogenic ligands, previously described to be active in both Pd-catalysed hydrovinylation [14] and allylic alkylation [15] and less prone to secondary interactions such as those found in supposedly monodentate phosphoramidites [16,17].

## 2. Synthesis

The required *P*-stereogenic ligands **1**–**8** (Scheme 1) were prepared following the Jugé-Stephan method [18] as described previously [14,15,19] and obtained as optically pure white solids or colourless oils. Free phosphinites **3** and **5** were also obtained by standard deboronation of the corresponding phosphinite–boranes [20] and their characterisation is given in the experimental part.

Following the usual method [21–23], neutral ruthenium *p*-cymene complexes **C1**–**C8** were easily prepared in moderate to good yields by splitting the ruthenium *p*-cymene chloride dimer [24], dissolved in dichloromethane, with two equivalents of the monophosphorus ligand (Scheme 2).

The reactions were essentially complete after 1 h, as judged by $^{31}P$ NMR spectroscopy. The isolated compounds **C** were red to brown air-stable solids, soluble in dichloromethane but not in hexane or pentane, whose full characterisation was in agreement with the expected structures. $^{31}P$ NMR spectra (see experimental part and supplementary material) of complexes bearing phosphines presented singlets whose chemical shift was displaced downfield compared to the free ligands. In contrast, the value of the

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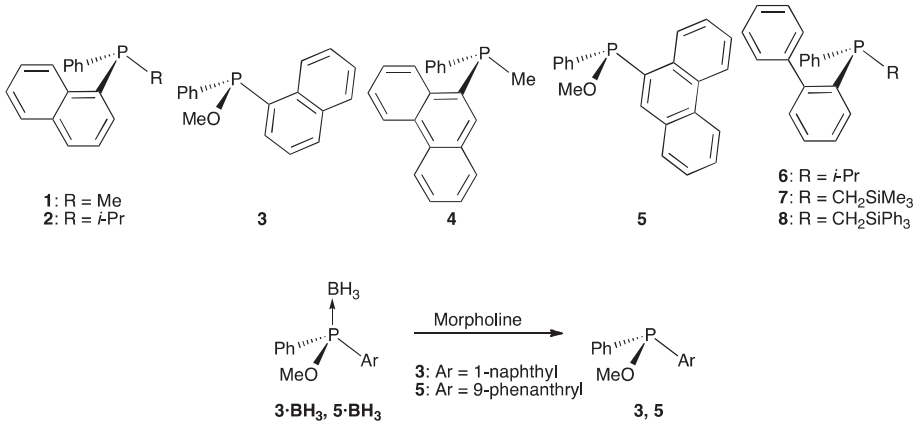
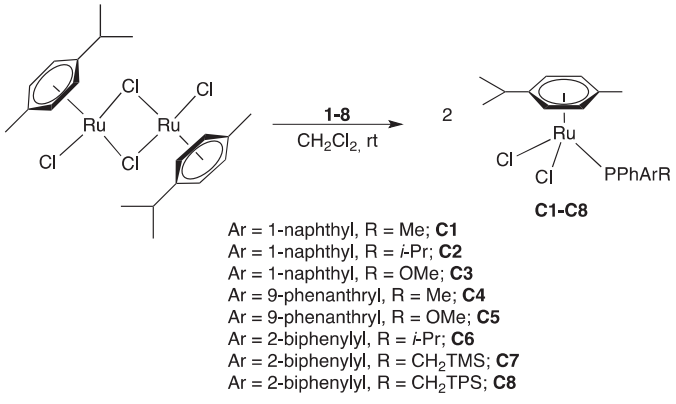



**Scheme 1.** *P*-stereogenic ligands.

chemical shift was almost unchanged in the case of complexes **C3** and **C5**, bearing phosphinite ligands. $^{1}H$ and $^{13}C$ NMR spectra presented the anticipated features (see experimental part and supplementary material). As expected due to the non-symmetric environment produced by the stereogenic phosphorus, the *p*-cymene aromatic ring presented four distinct aromatic proton resonances in the $^{1}H$ spectra and six distinct carbon resonances in the $^{13}C$ spectra for most of the complexes. Another feature is the non-equivalence of the diastereotopic methyl groups of the isopropyl fragment in the *p*-cymene, both in $^{1}H$ and $^{13}C$ NMR spectra.

A single crystal X-ray structure determination was carried out for complex **C6**. As expected, the complex has a distorted octahedral structure with the typical piano-stool pseudotetrahedral geometry around the Ru atom with the $\eta^6$ coordination of the phenyl ring of *p*-cymene. The unit cell contains two crystallographically distinct molecules of the complex (**I** and **II**), whose ORTEP view is displayed in Fig. 1. In both structures the imaginary line defined by the chloro ligands and the line passing through the substituted C carbons of the $\eta^6$-coordinated phenyl ring are approximately parallel, which is a common feature of this type of complexes. The main difference between structures **I** and **II** is simply that the $\eta^6$-coordinated *p*-cymene ring is rotated by 180°. For this reason, only some distances and angles of structure **I** will be commented.

The structure confirms the expected absolute configuration of the coordinated stereogenic phosphorus atom (*R*). The average of the six Ru–$C_{p\text{-cymene}}$ distances is 2.209 Å. These distances can be divided into two groups featuring relatively short and long bonds. The first one, corresponding to the carbon atoms closer to the phosphine, has an average distance of 2.173 Å whereas for the second the value increases to 2.227 Å. Two slightly different Ru–Cl distances are also observed. The distances are in general similar to other related complexes [22,24–34] although the Ru–P distance is longer for **C6**. The average value of the P–Ru–Cl angles is 91.74° and for the Cl–Ru–Cl moiety the angle is 85.22°. The first value is larger and the second smaller compared to other [Ru(*p*-cymene)(P)$Cl_2$] complexes (P = phosphine) [24–34] and even compared to an analogous complex with a bulky phosphoramidite [22]. This data points out the rather bulky character of the phosphine ligand in **C6**.




**Scheme 2.** Synthesis of neutral Ru(*p*-cymene) complexes.

## 3. Hydrogen transfer

There is some precedent [13,35,36] that neutral [$RuCl_2(\eta^6$-arene)P] (P = monodentate phosphorus ligand) complexes are active in hydrogen transfer from alcohols to ketones. To the best of our knowledge, however, up to date only achiral phosphines have been used. Therefore the optically pure complexes **C** presented here could be interesting precatalysts in enantioselective hydrogen transfer from 2-propanol to acetophenone, which is the model substrate for this reaction (Scheme 3).

Hydrogen transfer reactions were performed in refluxing 2-propanol (82 °C), which was both the solvent and the hydrogen donor in the presence of *t*-BuOK [37]. The catalyst/*t*-BuOK/acetophenone ratio was 1/10/100. The solutions of the complexes were activated (without addition of acetophenone) for 30 min at 82 °C before the addition of acetophenone. The plot of the conversion to 1-phenylethanol vs. time for several complexes **C** is given in Fig. 2 and the plot of the ee of 1-phenylethanol vs. time is given in Fig. 3. Numerical data can be found in the supplementary material.

Fig. 2 shows that all complexes are active in reducing acetophenone, reaching almost full conversion after 24 h. In spite of that, important differences in activity are clearly observed. The activity order is **C6** ≫ **C2** > **C1** ≈ **C4** ≫ **C3** ≈ **C5**. Indeed, with **C6** full conversion is achieved after only 8 h. Surprisingly, Fig. 3 shows that the enantioselectivity follows *exactly* the same order. Although the ee value is higher and rather unreliable at low reaction times, it stabilises to a slightly lower value. Only precursor **C6** gives a moderate ee of around 45%, whereas **C2** provides 1-phenylethanol with just below 20% ee. In both cases the absolute configuration of the product is *S*. The rest of the catalysts give very poor enantioselectivities. The results described here suggest that both activity and enantioselectivity are affected by the same factors for the systems described.

Since the best results were obtained with precursor **C6**, a run at lower temperature was performed with the aim of increasing the

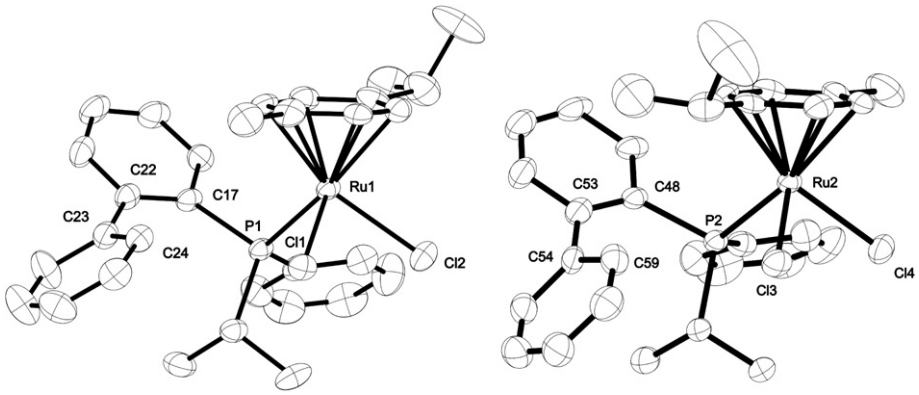



**Fig. 1.** ORTEP view (thermal ellipsoids drawn at the 30% probability level) of molecules **I** (left) and **II** (right) of complex **C6**. Hydrogen atoms have been omitted for clarity. Distances (Å) and angles (deg) for **I**: Ru(1)–Cl(1), 2.4160(19); Ru(1)–Cl(2), 2.4248(19); Ru(1)–P(1), 2.4336(19); P(1)–Ru(1)–Cl(1), 90.07(7); P(1)–Ru(1)–Cl(2), 93.41(7); Cl(1)–Ru(1)–Cl(2), 85.22(7). For **II**: Ru(2)–Cl(4), 2.413(2); Ru(2)–Cl(3), 2.4107(19); Ru(2)–P(2), 2.4180(19); P(2)–Ru(2)–Cl(4), 92.25(7); P(2)–Ru(2)–Cl(3), 91.84(7); Cl(4)–Ru(2)–Cl(3), 84.20(7).

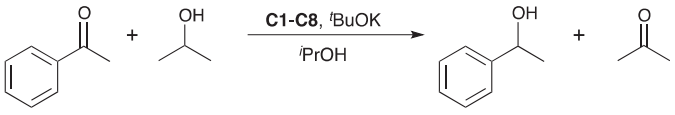
enantioselectivity. After activation of the catalytic system at 82 °C for 1 h the temperature was lowered to 40 °C and acetophenone was added. Under these conditions, the reaction was much slower, reaching only 44% conversion at 24 h and 56% at 48 h. The reaction did not reach full conversion at this temperature, indicating that the catalyst slowly deactivates over time [13]. The enantioselectivity was only marginally better at low conversions: 55% ee at 13% conversion (6 h reaction time) and 44% ee at 24 h, a result almost identical to the reaction performed at 82 °C.

Given that compounds **C** are saturated 18-electron complexes, a dissociative process has to take place in order to generate ruthenium hydride species thought to be the active catalysts [38–43]. In addition, the dependence of activity and enantioselectivity on the phosphorus ligand points out that the active species do not decoordinate the chiral ligand [42]. Considering these two facts it is possible to conceive different activation mechanisms to generate the catalytic species as depicted in Scheme 4.

A reasonable route from the starting complexes **C** to the hydride species comprises three steps: substitution of one of the chloride ligands by the in situ generated isopropoxyde anion (**I**), β-hydride elimination (**II**) and acetophenone coordination (**III**). Mechanistically, each of these steps must involve an unsaturated intermediate, which can be generated either by direct chloride decoordinations (path **A**) [35,40,41,43] or by hapticity reduction (from $\eta^6$ to $\eta^4$ or from $\eta^6$ to $\eta^2$) [43] of the *p*-cymene fragment as suggested for other systems (path **B**) [13,38,39,43].

These activation mechanisms, although speculative, can explain some of the experimental observations. Basic phosphines would stabilise the cationic unsaturated complexes better, whereas bulky ligands would favour the decoordination of the first and second chloride anions and the change of the hapticity of the *p*-cymene fragment. That would explain why catalysts **C2** and **C6**, both bearing a phosphine with the basic and relatively bulky isopropyl group, give the more active catalysts whereas **C3** and **C5**, with less basic and not so bulky phosphinite ligands provide more sluggish catalysts.

Regardless of the mechanism, the almost perfect linearity of the plots of the reduction process at moderate conversions of acetophenone (Fig. 4) suggests the presence of a very well-defined catalytic mechanism.




**Scheme 3.** Catalytic hydrogen transfer.

## 4. Cyclopropanation

Following previous studies with Ru/phosphoramidite ligands [16,17,22] the performance of complexes **C** as precatalysts in cyclopropanation of styrene and α-methylstyrene by controlled decomposition of ethyl diazoacetate was explored (Scheme 5).

Ethyl diazoacetate (EDA) slowly decomposes transferring a carbene unit to the chiral Ru complex, forming a metallic carbene [44], which cyclopropanates the substrate. The formation of such metallic carbenes from saturated 18-electron precursors **C** requires the decoordination of one or more ligands. Although thermal decoordination of the *p*-cymene unit has been suggested for similar complexes [45], the most common method is the formation of cationic unsaturated 16 electron species by abstracting one of the chloride ligands [17,22]. Therefore, the conditions to generate active species in the cyclopropanation of styrene were screened with complex **C6** and several halide abstractors (Table 1).

Entries 1 and 2 show that neutral complexes **C** are almost catalytically inactive, a fact that was expected since they are saturated 18 $e^-$ compounds bearing no labile ligands. Upon activation by halide scavenger salts with uncoordinating anions, catalytic activity

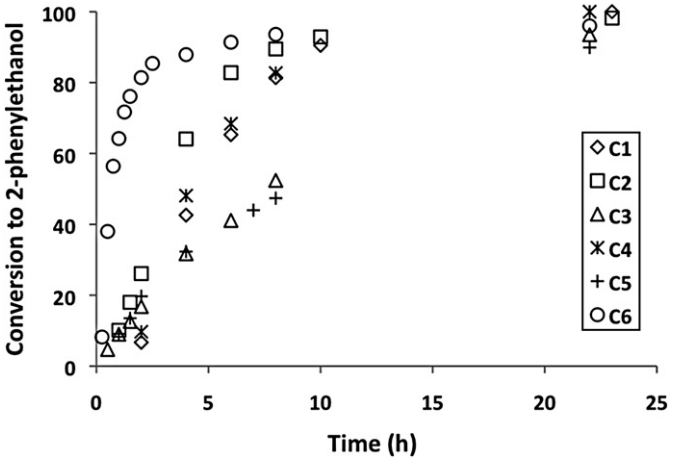



**Fig. 2.** Conversion of acetophenone vs. time in hydrogen transfer. Complex **C** ($6 \times 10^{-3}$ mmol) was dissolved in 3 ml of a 0.02 M solution of potassium *tert*-butoxyde in 2-propanol. After stirring for 30 min at 82 °C a solution of acetophenone (0.06 M, 10 ml) in 2-propanol was added.

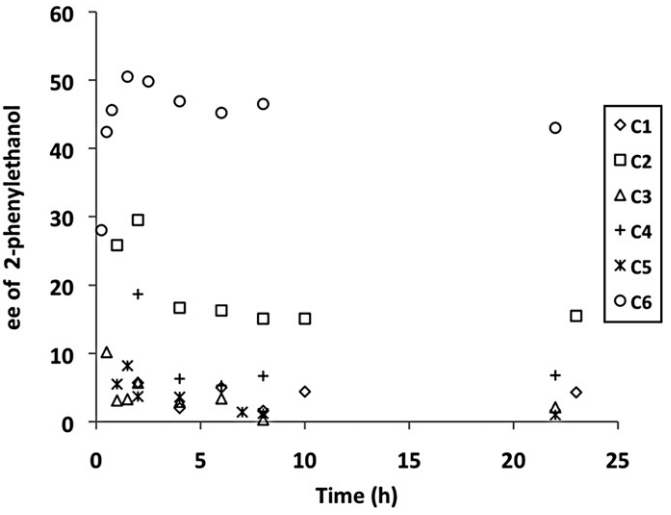



**Fig. 3.** Enantiomeric excess of 1-phenylethanol vs. time in hydrogen transfer of acetophenone.

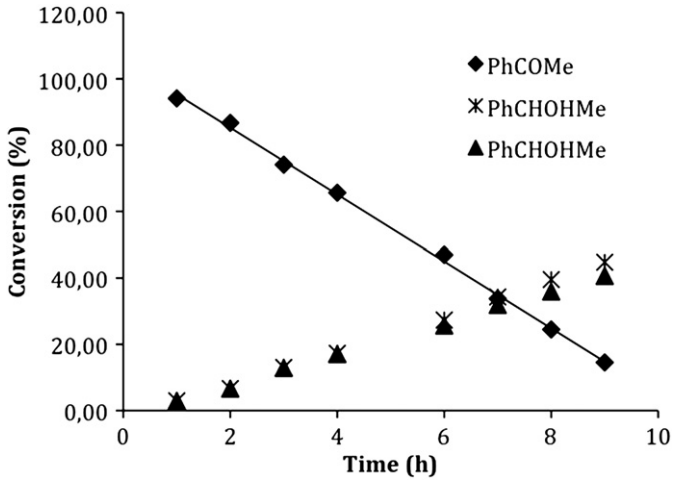
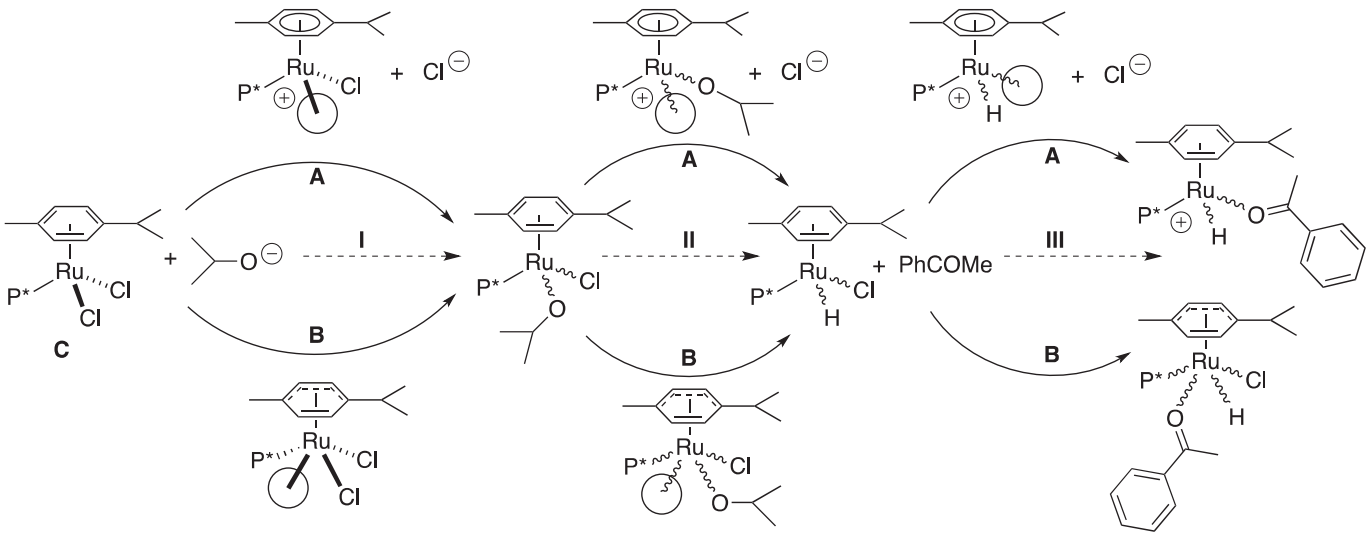



**Fig. 4.** Conversion of species vs. time in hydrogen transfer of acetophenone in the presence of complex **C1**. The crosses and the triangles represent each of the enantiomers of 1-phenylethanol.

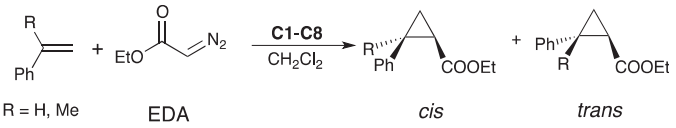
was observed, following the order $(Et_3O)PF_6 > AgSF_6 > TlPF_6$. As $(Et_3O)PF_6$ (Meerwein's salt) provides both the higher activity and enantioselectivity, it was selected as a reagent of choice to activate the precursors. Under the same conditions, the other complexes **C** were tested in the cyclopropanation of styrene and α-methylstyrene. The results obtained for these two substrates are listed in Table 2 and Table 3 respectively.

In general, conversions and yields remain low for styrene, reaching the maximum value of 29% in entry 14 at 20 h. The comparison between the values at 3 and 20 h indicates that the catalysts decompose over the time to inactive species. Entries 1–10 show that the diastereoselectivity is approximately 2:3 in favour of the *trans* diastereomers regardless of the catalyst and on the time. For the bulky silylated phosphines of complexes **C7** and **C8** (entries 11–14) the *cis*:*trans* ratio increases slightly to approximately 1:2. Enantioselectivity ranges from low to moderate. The best results are obtained with complexes **C2** and **C6** bearing phosphines with an isopropyl group (entries 3, 4, 9 and 10) and with **C8**, containing a very bulky silylated phosphine (entries 13 and 14). The best result is obtained with complex **C6** at 3 h, although a severe decrease in enantioselectivity is observed at 20 h (entry 9 vs. entry 10). This fact, observed previously in other systems [22], can be due to unselective catalysis by achiral Ru species originated by degradation of the catalyst. Most of the catalysts give better enantioselectivity results for the *cis* diastereomers, but this is not general (entries 1, 2 and 9). A remarkable feature is that complexes bearing phosphines with the 2-biphenylyl group (entries 9–14) favour the (*R*,*R*) enantiomer of the *trans* diastereomers but the contrary happens for the other catalysts. A surprising fact is the very low enantioselectivity of complex **C7** (entries 11 and 12), bearing a phosphine with the 2-biphenylyl group compared to **C6** and **C8** (entries 8, 9, 13 and 14).

It is known that α-methylstyrene often gives better results in cyclopropanation compared to unsubstituted styrene due to the more electron rich nature of the former [17]. The data from the table confirm this expectation. Conversions and yields are higher, reaching or surpassing the 50% mark (entries 2, 4, 6, 8 and 10). The different steric requirements of α-methylstyrene causes that in this case the *cis* diastereomers of the cyclopropanated products are favoured. Like for styrene, though, the diastereoselectivity is only modest, reaching a 7:3 ratio for catalyst **C6** (entry 5). The enantioselectivity also




**Scheme 4.** Generation of Ru–H catalysts from precursors **C**.




**Scheme 5.** Catalytic cyclopropanation.

improves compared to styrene, reaching a value close to 70% at low conversion for **C6** (entry 5). The more enantioselective catalysts, in parallel to styrene cyclopropanation, are **C6** and **C8**, bearing 2-biphenylyl groups (entries 5, 6, 9 and 10). In contrast, **C2** (entries 3 and 4) is very unselective. Like in the case of styrene, a degradation of stereoselectivity as the reaction progresses is observed.

**Table 1**
Catalytic cyclopropanation of styrene by ethyl diazoacetate in the presence of **C6** and several halide abstractors.

| Entry | Abstractor | Time h | Conversion[a]% | Yield[a]% | cis:trans[a] | e.e. (%)[a] | |
|---|---|---|---|---|---|---|---|
| | | | | | | cis | trans |
| 1[b] | – | 3 | 1 | 0.6 | 37:63 | – | – |
| 2[b] | – | 20 | 2 | 0.7 | 43:57 | – | – |
| 3 | $AgSbF_6$ | 3 | 7 | 6.0 | 40:60 | 27.8 (1*S*,2*R*) | 21.8 (1*R*,2*R*) |
| 4 | $AgSbF_6$ | 20 | 21 | 18.3 | 38:62 | 8.8 (1*S*,2*R*) | 5.5 (1*R*,2*R*) |
| 5 | $TlPF_6$ | 3 | 5 | 3.0 | 38:62 | – | – |
| 6 | $TlPF_6$ | 20 | 19 | 9.7 | 32:68 | ≈0 | ≈0 |
| 7 | $(Et_3O)PF_6$ | 3 | 12 | 10.6 | 46:54 | 57.8 (1*S*,2*R*) | 58.9 (1*R*,2*R*) |
| 8 | $(Et_3O)PF_6$ | 20 | **26** | **21.7** | 42:48 | 37.0 (1*S*,2*R*) | 31.2 (1*R*,2*R*) |

Catalyst preparation: complex **C6** (24 μmol) and the halide abstractor (24–26 μmol) were dissolved in 1 ml of $CH_2Cl_2$ and stirred at room temperature for 14 h and filtered. Catalytic runs: the internal standard and styrene (0.48 mmol) were added to the flask containing the catalyst solution. Ethyl diazoacetate (0.48 mmol), dissolved in 1 ml of $CH_2Cl_2$, was added over a period of 6 h by an automatic syringe pump. The results are the average of at least two runs.
[a] Results from GC analysis.
[b] The precatalyst was **C1**.

**Table 2**
Catalytic cyclopropanation of styrene.

| Entry | Precursor | Time h | Conversion[a] % | Yield[a] % | cis:trans[a] | e.e. (%)[a] | |
|---|---|---|---|---|---|---|---|
| | | | | | | cis | trans |
| 1 | **C1** | 3 | 11 | 7.4 | 43:57 | 4.6 (1*S*,2*R*) | 12.4 (1*S*,2*S*) |
| 2 | **C1** | 20 | 23 | 15.1 | 43:57 | 6.5 (1*S*,2*R*) | 11.1 (1*S*,2*S*) |
| 3 | **C2** | 3 | 16 | 11.7 | 43:57 | 38.4 (1*S*,2*R*) | 22.6 (1*S*,2*S*) |
| 4 | **C2** | 20 | 32 | 26.1 | 41:59 | 22.2 (1*S*,2*R*) | 22.0 (1*S*,2*S*) |
| 5 | **C3** | 3 | 20 | 5.8 | 46:54 | 9.7 (1*S*,2*R*) | 2.9 (1*S*,2*S*) |
| 6 | **C3** | 20 | 38 | 19.5 | 44:56 | 10.8 (1*S*,2*R*) | 5.4 (1*S*,2*S*) |
| 7 | **C4** | 3 | 8 | 5.4 | 43:57 | 7.4 (1*S*,2*R*) | 7.2 (1*S*,2*S*) |
| 8 | **C4** | 20 | 18 | 12.6 | 43:57 | 8.3 (1*S*,2*R*) | 6.9 (1*S*,2*S*) |
| 9 | **C6** | 3 | 12 | 10.6 | 42:58 | 57.8 (1*S*,2*R*) | 58.9 (1*R*,2*R*) |
| 10 | **C6** | 20 | 26 | 21.7 | 42:58 | 37.0 (1*S*,2*R*) | 31.2 (1*R*,2*R*) |
| 11 | **C7** | 3 | 9 | 7.4 | 35:65 | 8.2 (1*S*,2*R*) | 5.7 (1*R*,2*R*) |
| 12 | **C7** | 20 | 23 | 21.0 | 35:65 | 3.8 (1*S*,2*R*) | ≈0 |
| 13 | **C8** | 3 | 9 | 8.6 | 35:65 | 24.4 (1*S*,2*R*) | 8.6 (1*R*,2*R*) |
| 14 | **C8** | 20 | 29 | 29.0 | 33:67 | 25.4 (1*S*,2*R*) | 8.5 (1*R*,2*R*) |

Catalyst preparation: complex **C** (24 μmol) and $Et_3OPF_6$ (26 μmol) were dissolved in 1 ml of $CH_2Cl_2$ and stirred at room temperature for 14 h and filtered. Typical catalytic run: The internal standard (*n*-decane) and styrene (0.48 mmol) were added to the flask containing the catalyst solution. Ethyl diazoacetate (0.48 mmol), dissolved in 1 ml of $CH_2Cl_2$, was added over a period of 6 h by an automatic syringe pump. The results are the average of at least two runs.
[a] Results from GC analysis.

**Table 3**
Catalytic cyclopropanation of α-methylstyrene.

| Entry | Precursor | Time h | Conversion[a] % | Yield[a] % | cis:trans[a] | e.e. (%)[a] | |
|---|---|---|---|---|---|---|---|
| | | | | | | cis | trans |
| 1 | **C1** | 3 | 18 | 15.2 | 69:31 | 3.7 (*cis*-I) | 10.4 (*trans*-I) |
| 2 | **C1** | 20 | 52 | 49.3 | 67:33 | 3.4 (*cis*-I) | 10.2 (*trans*-I) |
| 3 | **C2** | 3 | 25 | 24.6 | 64:36 | 13.7 (*cis*-II) | 14.8 (*trans*-I) |
| 4 | **C2** | 20 | 56 | 55.7 | 62:38 | 21.1 (*cis*-II) | 20.8 (*trans*-I) |
| 5 | **C6** | 3 | 33 | 33.0 | 71:29 | 66.5 (*cis*-I) | 68.6 (*trans*-II) |
| 6 | **C6** | 20 | 58 | 58.0 | 68:32 | 58.7 (*cis*-I) | 52.9 (*trans*-II) |
| 7 | **C7** | 3 | 19 | 18.0 | 63:37 | 37.5 (*cis*-I) | 23.1 (*trans*-II) |
| 8 | **C7** | 20 | 50 | 46.6 | 59:41 | 24.8 (*cis*-I) | 11.7 (*trans*-II) |
| 9 | **C8** | 3 | 14 | 14.0 | 69:31 | 60.8 (*cis*-I) | 60.9 (*trans*-II) |
| 10 | **C8** | 20 | 41 | 41.0 | 62:38 | 40.7 (*cis*-I) | 28.0 (*trans*-II) |

Catalyst preparation: complex **C** (24 μmol) and $Et_3OPF_6$ (26 μmol) were dissolved in 1 ml of $CH_2Cl_2$ and stirred at room temperature for 14 h and filtered. Typical catalytic run: The internal standard (*n*-dodecane) and α-methylstyrene (0.48 mmol) were added to the flask containing the catalyst solution. Ethyl diazoacetate (0.48 mmol), dissolved in 1 ml of $CH_2Cl_2$, was added over a period of 6 h by an automatic syringe pump. The results are the average of at least two runs.
[a] Results from GC analysis, **I** and **II** simply refer to the order of elution of each enantiomer in the chromatographic analysis.

## 5. Conclusions

Ruthenium complexes with monodentate phosphorus ligands are competent systems for hydrogen transfer and cyclopropanation. Good activities, leading to full conversions, are obtained in hydrogen transfer of acetophenone whereas the enantioselectivity is moderate at best. The active catalyst seems a well-defined single species whose discrimination ability does not appear to change with the temperature. In cyclopropanation, the complexes show low activity and low to moderate stereoselectivity.

It seems that for both reactions the phosphines must have a relatively bulky alkyl group since those with methyl or methoxy give very low enantioselectivities. For the systems examined the best catalysts, both in activity and stereoselectivity, contain the 2-biphenylyl group in the phosphine [46], in parallel to previous results in Pd-catalysed hydrovinylation [14] and allylic alkylation [15]. The optical induction, although far from satisfactory with the phosphines used, stems only from a single stereogenic phosphorus atom of a simple Horner phosphine [47]. These results show that it is possible to generate interesting new catalytic systems with a ratio Ru/*P*-stereogenic phosphine = 1/1. Therefore it seems plausible to obtain good results with other bulky phosphines bearing *P*-stereogenic atoms, a chiral motif hardly ever used in ruthenium-catalysed reactions [47–51].

## 6. Experimental section

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. 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.

Achiral GC analyses for cyclopropanation of styrene and α-methylstyrene were performed with an instrument equipped with an Optima column, 25 m long with He as a carrier gas (100 kPa). Conditions: 50 °C isotherm for 5 min, then to 200 °C at 5 °C/min. Data for styrene cyclopropanation: $t_R$ (min) styrene, 8.5; *n*-decane (internal standard), 12.8; ethyl-*cis*-2-phenylcyclopropane carboxylate, 26.5; ethyl-*trans*-2-phenylcyclopropane carboxylate, 27.9. Data for α-methylstyrene cyclopropanation: $t_R$ (min) α-methylstyrene, 12.0; *n*-dodecane (internal standard), 19.6; ethyl-*cis*-2-methyl-phenylcyclopropane-1-carboxylate, 26.3; ethyl-*trans*-2-methyl-phenylcyclopropane-1-1-carboxylate, 27.6. Chiral GC analyses were carried out in a Supelco Beta Dex 120 column with He as a carrier gas (1.4 mL/min). Conditions: 120 °C isotherm. Data for styrene cyclopropanation: $t_R$ (min), *cis*-(1*R*, 2*S*), 52.8; *cis*-(1*S*,2*R*), 55.5; *trans*-(1*R*,2*R*), 62.7; *trans*-(1*S*,2*S*), 64.6. Data for α-methylstyrene cyclopropanation: $t_R$ (min), *cis*-isomers, 39.3 and 41.3; *trans*-isomers, 49.7 and 50.9.

GC analyses of transfer hydrogenation of acetophenone were performed with an instrument equipped with a chiral FS cyclodex β column, 30 m long with He as a carrier gas (100 kPa). Conditions: 120 °C isotherm. Data: $t_R$ (min), acetophenone, 7.0; 1-phenylethanol, 11.1 (*R*) and 11.8 (*S*).

### 6.1. (R)-methoxy(1-naphthyl)phenylphosphine, 3

(*R*)-methoxy(1-napthyl)phenylphosphine-borane [20] (0.70 g, 2.5 mmol) was dissolved in morpholine (30 ml) and stirred for 14 h at room temperature. After concentration to dryness, the gummy residue was purified by column chromatography (alumina, toluene) to yield the title product as colourless oil. Yield: 0.60 g (90%).

**$^{1}H$ NMR** (300.1 MHz, $CDCl_3$), δ(ppm): 3.78 (*d*, 3H, $J$ = 14.1 Hz), 7.35–8.32 (*m*, 12H, Ar). **$^{13}C\{^{1}H\}$ NMR** (62.9 MHz, $CDCl_3$), δ(ppm): 57.3 (*d*, $CH_3$, $J_{CP}$ = 20.7 Hz), 125.1–141.0 (*m*, C, CH, Ar). **$^{31}P\{^{1}H\}$ NMR** (101.1 MHz, $CDCl_3$), δ(ppm): +113.4.

### 6.2. (R)-methoxy(9-phenanthryl)phenylphosphine, 5

The same procedure used to prepare **3** was followed. Starting from (*R*)-methoxy(9-phenanthryl)phenylphosphine-borane [20] (0.66 g, 2.0 mmol), the title product was obtained as a colourless oil. Yield: 0.23 g (37%).

**$^{1}H$ NMR** (250.1 MHz), δ(ppm): 3.79 (*d*, 3H, $J$ = 14.2 Hz), 7.29–8.69 (*m*, 14H, Ar). **$^{13}C\{^{1}H\}$ NMR** (100.0 MHz), δ(ppm): 57.6 (*d*, $CH_3$, $J_{CP}$ = 21.4 Hz), 122.8–140.7 (*m*, C, CH, Ar). **$^{31}P\{^{1}H\}$ NMR** (101.1 MHz), δ(ppm): +114.4.

### 6.3. Dichloro(η⁶-p-cymene)[(R)-methyl(1-naphthyl) phenylphosphine]ruthenium(II), C1

Ruthenium *p*-cymene dimer (0.490 g, 0.8 mmol) and phosphine **1** (0.400 g, 1.6 mmol) were dissolved in 10 ml of dichloromethane and left stirring for 1 h. The solvent was removed and the brownish found was suspended in diethyl ether. The solid was filtrated and washed with diethyl ether and pentane. Yield: 0.490 g (60%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3061 ν(C–H), 3044 ν(C–H), 2964 ν(C–H), 2952 ν(C–H), 2940 ν(C–H), 2924 ν(C–H), 2871 ν(C–H), 1503, 1489, 1470, 1435, 1387, 1280, 893, 804, 799, 780, 750, 689, 453. **$^{1}H$ NMR** (250.1 MHz), δ(ppm): 0.71 (*d*, 3H, $J$ = 6.9 Hz), 0.89 (*d*, 3H, $J$ = 7.0 Hz), 1.91 (*s*, 3H), 2.12 (*d*, 3H, $J$ = 10.7 Hz), 2.52–2.61 (*m*, 1H), 4.97–5.05 (*m*, 2H), 5.18 (*d*, 1H, $J$ = 6.3 Hz), 5.36 (*d*, 1H, $J$ = 6.2 Hz), 7.29–8.21 (*m*, 12H, Ar). **$^{13}C\{^{1}H\}$ NMR** (50.0 MHz), δ(ppm): 14.8 (*d*, $CH_3$, $J_{CP}$ = 35.5 Hz), 17.6 (*s*, $CH_3$), 20.4 (*s*, $CH_3$), 22.4 (*s*, $CH_3$), 30.0 (*s*, CH), 82.8 (*d*, CH, $J_{CP}$ = 4.6 Hz), 87.7 (*d*, CH, $J_{CP}$ = 2.7 Hz), 88.6 (*d*, CH, $J_{CP}$ = 7.3 Hz), 91.8 (*d*, CH, $J_{CP}$ = 5.9 Hz), 95.0 (*s*, C) 107.5 (*s*, C), 124.6–135.4 (*m*, C, CH, Ar). **$^{31}P\{^{1}H\}$ NMR** (101.1 MHz), δ(ppm): +14.5. **EA**: Calcd. for $C_{27}H_{29}Cl_2PRu$: C 58.28%, H 5.25%. Found: C 58.15%, H 5.69%. **MS**(**MALDI**) *m*/*e*: 485, $[M-Cl-HCl]^+$

### 6.4. Dichloro(η⁶-p-cymene)[(R)-(isopropyl)(1-naphthyl) phenylphosphine] ruthenium(II), C2

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.300 g, 0.49 mmol) and phosphine **2** (0.289 g, 1.04 mmol), the title product was obtained as a brown solid. Yield: 0.236 g (41%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3047 ν(C–H), 2962 ν(C–H), 2927 ν(C–H), 2870 ν(C–H), 1507, 1469, 1435, 1387, 1094, 809, 780, 702, 513, 479. **$^{1}H$ NMR** (300.1 MHz), δ(ppm): 1.03–1.10 (*m*, 12H), 1.69 (*s*, 3H), 2.55–2.64 (*m*, 1H), 3.65 (*s*, 1H), 4.74 (*d*, 2H, $J$ = 5.7 Hz), 4.92 (*s*, 1H), 5.10 (*s*, 1H), 7.42–8.50 (*m*, 12H, Ar). **$^{31}P\{^{1}H\}$ NMR** (121.5 MHz), δ(ppm): +30.3. **EA**: Calcd. for $C_{29}H_{33}Cl_2PRu$: C 59.59%, H 5.69%. Found: C 59.78%, H 5.34%.

### 6.5. Dichloro(η⁶-p-cymene)[(S)-methoxy(1-naphthyl) phenylphosphine]ruthenium(II), C3

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.345 g, 0.56 mmol) and phosphinite **3** (0.332 g, 1.24 mmol), the title product was obtained as a light red solid. Yield: 0.597 g (92%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3056 ν(C–H), 3045 ν(C–H), 2960 ν(C–H), 2938 ν(C–H), 2871 ν(C–H), 1507, 1470, 1437, 1387, 1098, 1030, 821, 807, 776, 743, 695, 538, 509, 481. **$^{1}H$ NMR** (300.1 MHz), δ(ppm): 1.03 (*d*,

3H, $J$ = 6.6 Hz), 1.12 (*d*, 3H, $J$ = 6.6 Hz), 1.75 (*s*, 3H), 2.73 (*m*, 1H), 3.56 (*d*, 3H, $J$ = 11.4 Hz), 4.43 (*s*, 1H), 5.19 (*s*, 2H), 5.31 (*s*, 1H), 7.29–8.32 (*m*, 12H, Ar). **$^{13}$C{$^{1}$H} NMR** (62.9 MHz), $\delta$(ppm): 17.6 (*s*, $CH_3$), 20.9 (*s*, $CH_3$), 22.4 (*s*, $CH_3$), 29.9 (*s*, CH), 55.9 (*d*, $CH_3$, $J_{CP}$ = 7.5 Hz), 85.4 (*d*, CH, $J_{CP}$ = 4.9 Hz), 90.4 (*d*, CH, $J_{CP}$ = 3.1 Hz), 90.9 (*d*, CH, $J_{CP}$ = 6.8 Hz), 92.6 (*d*, CH, $J_{CP}$ = 6.7 Hz), 97.5 (*s*, C), 108.9 (*s*, C), 124.2–133.9 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (121.5 MHz), $\delta$(ppm): +116.6. **EA**: Calcd. for $C_{27}H_{30}Cl_2OPRu$: C 56.55%, H 5.27%. Found: C 56.01%, H 5.52%.

### 6.6. Dichloro($\eta^6$-p-cymene)[(R)-methyl(9-phenanthryl) phenylphosphine]ruthenium(II), ***C4***

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.172 g, 0.281 mmol) and phosphine **4** (0.186 g, 0.619 mmol), the title product was obtained as a red solid. Yield: 0.279 g (87%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3053 ν(C–H), 2960 ν(C–H), 2938 ν(C–H), 2868 ν(C–H), 2839 ν(C–H), 1435, 1096, 1029, 752, 725, 694, 564, 489, 431. **$^{1}$H NMR** (300.1 MHz), $\delta$(ppm): 0.89 (*d*, 3H, $J$ = 6.9 Hz), 0.94 (*d*, 3H, $J$ = 6.9 Hz), 1.92 (*s*, 3H), 2.25 (*d*, 3H, $J$ = 10.5 Hz), 2.61–2.66 (*m*, 1H), 4.95 (*d*, 1H, $J$ = 5.4 Hz), 5.12–5.18 (*m*, 2H), 5.33 (*d*, 1H, $J$ = 6.0 Hz), 7.17–8.81 (*m*, 14H, Ar). **$^{13}$C{$^{1}$H} NMR** (62.9 MHz), $\delta$(ppm): 15.8 (*d*, $CH_3$, $J_{CP}$ = 13.3 Hz), 17.7 (*s*, $CH_3$), 20.9 (*s*, $CH_3$), 22.4 (*s*, $CH_3$), 30.1 (*s*, CH), 83.5 (*d*, CH, $J_{CP}$ = 4.9 Hz), 88.2 (*d*, CH, $J_{CP}$ = 6.4 Hz), 88.4 (*d*, CH, $J_{CP}$ = 3.4 Hz), 91.3 (*d*, CH, $J_{CP}$ = 5.5 Hz), 95.3 (*s*, C), 107.9 (*s*, C), 122.7–136.0 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (121.5 MHz), $\delta$(ppm): +16.5. **EA**: Calcd. for $C_{31}H_{31}Cl_2PRu$: C 61.39%, H 5.15%. Found: C 61.76%, H 5.79%.

### 6.7. Dichloro($\eta^6$-p-cymene)[(S)-methoxy(9-phenanthryl) phenylphosphine] ruthenium(II), ***C5***

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.203 g, 0.330 mmol) and phosphinite **5** (0.231 g, 0.720 mmol), the title product was obtained as a deep red solid. Yield: 0.149 g (36%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3056 ν(C–H), 2961 ν(C–H), 2923 ν(C–H), 2869 ν(C–H), 1436, 893, 751, 726, 696, 691, 461, 432. **$^{1}$H NMR** (400.1 MHz), $\delta$(ppm): 1.03 (*d*, 3H, $J$ = 6.8 Hz), 1.14 (*d*, 3H, $J$ = 6.4 Hz), 1.74 (*s*, 3H), 2.75–2.82 (*m*, 1H), 3.59 (*d*, 3H, $J$ = 11.6 Hz), 4.45 (*s*, 1H), 5.17 (*d*, 1H, $J$ = 6.0 Hz), 5.23 (*d*, 1H, $J$ = 5.2 Hz), 5.34 (*d*, 1H, $J$ = 6.4 Hz), 7.26–8.76 (*m*, 14H, Ar). **$^{13}$C{$^{1}$H} NMR** (100.0 MHz), $\delta$(ppm): 17.9 (*s*, $CH_3$), 21.0 (*s*, $CH_3$), 22.7 (*s*, $CH_3$), 30.1 (*s*, CH), 56.3 (*d*, $CH_3$, $J_{CP}$ = 7.7 Hz), 85.4 (*s*, CH), 90.7 (*s*, CH), 91.5 (*s*, C), 93.2 (*s*, CH), 97.5 (*s*, CH), 109.0 (*s*, C), 122.9–134.2 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (121.5 MHz), $\delta$(ppm): +114.9. **EA**: Calcd. for $C_{31}H_{31}Cl_2OPRu$: C 59.81%, H 5.02%. Found: C 59.58%, H 5.23%. **MS**(**MALDI**) *m*/*e*: 443, [M–phenanthryl–2H]$^+$; 551, [M–Cl–HCl]$^+$; 579, [M–$^i$Pr]$^+$

### 6.8. Dichloro($\eta^6$-p-cymene)[(R)-(2-biphenylyl)(isopropyl)phenyl phosphine]ruthenium(II), ***C6***

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.171 g, 0.279 mmol) and phosphine **6** (0.170 g, 0.558 mmol), the title product was obtained as a brown solid. Yield: 0.227 g (63%). Single crystals, suitable for X-ray crystallography were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane, at 4 °C.

**IR** $\bar{\nu}$ ($cm^{-1}$): 3048 ν(C–H), 2962 ν(C–H), 2925 ν(C–H), 2868 ν(C–H), 1467, 1458, 1444, 1435, 1088, 761, 755, 703, 668, 524, 465. **$^{1}$H NMR** (400.1 MHz), $\delta$(ppm): 0.66–0.70 (*m*, 6H), 1.11 (*d*, 3H, $J$ = 7.2 Hz), 1.19 (*d*, 3H, $J$ = 7.2 Hz), 2.02 (*s*, 3H), 2.50–2.60 (*m*, 1H), 2.85–2.93 (*m*, 1H), 4.74 (*d*, 1H, $J$ = 6.0 Hz), 5.13 (*d*, 1H, $J$ = 6.0 Hz), 5.43–5.47 (*m*, 2H), 7.11–7.92 (*m*, 14H, Ar). **$^{13}$C{$^{1}$H} NMR** (100.0 MHz), $\delta$(ppm): 18.1 (*s*, $CH_3$), 19.2 (*d*, $CH_3$, $J_{CP}$ = 2.3 Hz), 20.0 (*s*, $CH_3$, $J_{CP}$ = 6.9 Hz), 22.1 (*s*, $CH_3$), 22.6 (*s*, $CH_3$), 25.4 (*d*, CH, $J_{CP}$ = 22.1 Hz), 29.8 (*s*, CH), 84.9 (*d*, CH, $J_{CP}$ = 3.8 Hz), 88.6 (*d*, CH, $J_{CP}$ = 5.3 Hz), 89.8 (*d*, CH, $J_{CP}$ = 5.4 Hz), 89.9 (*d*, CH, $J_{CP}$ = 3.8 Hz), 97.5 (*s*, C), 106.9 (*s*, C), 126.3–146.1 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (101.1 MHz), $\delta$(ppm): +29.2. **EA**: Calcd. for $C_{31}H_{35}Cl_2PRu$: C 60.98%, H 5.78%. Found: C 60.46%, H 6.44%. **MS**(**MALDI**) *m*/*e*: 303, [M–Ru(*p*-cymene)Cl–HCl]$^+$; 339, [M–Ru(*p*-cymene)Cl]$^+$; 441, [M–(*p*-cymene)Cl]$^+$; 575, [M–Cl]$^+$; 580, [M–Cl–HCl]$^+$.

### 6.9. Dichloro($\eta^6$-p-cymene)[(R)-(2-biphenylyl)(2,2-dimethyl-2-silapropyl)phenylphosphine] ruthenium(II), ***C7***

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.061 g, 0.099 mmol) and phosphine **7** (0.069 g, 0.198 mmol), the title product was obtained as a deep red solid. Yield: 0.060 g (47%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3054 ν(C–H), 2962 ν(C–H), 2925 ν(C–H), 2896 ν(C–H), 2885 ν(C–H), 2872 ν(C–H), 1434, 1120, 850, 842, 783, 757, 706, 695, 510. **$^{1}$H NMR** (250.1 MHz), $\delta$(ppm): −0.18 (*s*, 9H), 0.65 (*d*, 3H, $J$ = 6.8 Hz), 1.06 (*d*, 3H, $J$ = 6.8 Hz), 2.03 (*s*, 3H), 2.48–2.59 (*m*, 1H), 4.60 (*d*, 1H, $J$ = 5.5 Hz), 5.32–5.37 (*m*, 3H), 6.89–8.71 (*m*, 14H, Ar). **$^{13}$C{$^{1}$H} NMR** (62.9 MHz), $\delta$(ppm): 1.7 (*d*, $CH_3$, $J_{CP}$ = 2.5 Hz), 12.1 (*d*, $CH_2$, $J_{CP}$ = 18.4 Hz), 17.2 (*s*, $CH_3$), 20.0 (*s*, $CH_3$), 22.9 (*s*, $CH_3$), 29.7 (*s*, CH), 85.4 (*d*, CH, $J_{CP}$ = 4.2 Hz), 86.8 (*d*, CH, $J_{CP}$ = 3.4 Hz), 87.2 (*d*, CH, $J_{CP}$ = 7.5 Hz), 93.4 (*d*, CH, $J_{CP}$ = 6.0 Hz), 101.3 (*s*, C), 107.7 (*s*, C), 126.3–146.1 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (101.1 MHz), $\delta$(ppm): +24.2. **EA**: Calcd. for $C_{32}H_{39}Cl_2PRuSi$: C 58.70%, H 6.00%. Found: C 58.35%, H 6.32%. **MS**(**MALDI**) *m*/*e*: 347 (24) [M–Ru(*p*-cymene)$Cl_2$]$^+$, 577 (14) [M–Ph]$^+$.

### 6.10. Dichloro($\eta^6$-p-cymene)[(R)-(2-biphenylyl)(2,2,2-triphenyl-2-silaethyl)phenylphosphine] ruthenium(II), ***C8***

The same procedure used in the preparation of **C1** was employed. From the Ru *p*-cymene dimer (0.085 g, 0.139 mmol) and phosphine **8** (0.164 g, 0.307 mmol), the title product was obtained as a red solid. Yield: 0.169 g (66%).

**IR** $\bar{\nu}$ ($cm^{-1}$): 3047 ν(C–H), 2959 ν(C–H), 2924 ν(C–H), 2869 ν(C–H), 1466, 1427, 1107, 799, 755, 741, 717, 699, 667, 518, 499, 488. **$^{1}$H NMR** (250.1 MHz), $\delta$(ppm): 0.95 (*d*, 3H, $J$ = 6.5 Hz), 1.02 (*d*, 3H, $J$ = 6.5 Hz), 1.88 (*s*, 3H), 2.51–2.63 (*m*, 1H), 5.19 (*s*, 1H), 5.31 (*s*, 3H), 6.75–8.24 (*m*, 29H, Ar). **$^{13}$C{$^{1}$H} NMR** (62.9 MHz), $\delta$(ppm): 12.2 (d, $CH_2$, $J_{CP}$ = 24.0 Hz), 17.2 (*s*, $CH_3$), 21.5 (*s*, $CH_3$), 22.0 (*s*, $CH_3$), 29.9 (*s*, CH), 85.5 (*d*, CH, $J_{CP}$ = 6.7 Hz), 85.9 (*d*, CH, $J_{CP}$ = 4.8 Hz), 89.1 (*d*, CH, $J_{CP}$ = 5.0 Hz), 90.1 (*d*, CH, $J_{CP}$ = 4.2 Hz), 94.5 (*s*, C), 107.5 (*s*, C), 126.6–148.0 (*m*, C, CH, Ar). **$^{31}$P{$^{1}$H} NMR** (101.1 MHz), $\delta$(ppm): +27.4. **EA**: Calcd. for $C_{47}H_{45}Cl_2PRuSi$: C 67.13%, H 5.39%. Found: C 69.46%, H 5.80%. **MS**(**MALDI**) *m*/*e*: 533 (58) [M–Ru(*p*-cymene)Cl–HCl]$^+$, 569 (90) [M–$CH_2SiPh_3$]$^+$, 843 (8) [M+2H]$^+$.

### 6.11. General procedure for the enantioselective transfer hydrogenation

A typical transfer hydrogenation run was performed as follows. Under a nitrogen atmosphere in a *schlenk* flask, the ruthenium precursor **C** ($6 \times 10^{-3}$ mmol) was dissolved in 3 ml of a 0.02 M solution of potassium *tert*-butoxyde in 2-propanol and left stirring for 30 min. A solution (0.06 M, 10 ml) of acetophenone in 2-propanol was added rapidly by syringe, to give a 0.046 M solution of acetophenone in 2-propanol. The flask was heated to the desired temperature. The reaction was monitored by GC analysis.

### 6.12. General procedure for the enantioselective cyclopropanation

A typical cyclopropanation run was performed as follows. In a nitrogen-filled glovebox the ruthenium precursor **C** (0.024 mmol) and the chloride abstractor were dissolved in 1 ml of dichloromethane and stirred for 14 h protected from light. The solution was filtered through an HPLC filter and transferred to an *schlenk* flask, which was closed and taken out of the glovebox. To this flask, the olefin (0.48 mmol) and the internal standard (*n*-decane for styrene and *n*-dodecane for α-methylstyrene) were added. A solution of ethyl diazoacetate (0.48 mmol) in 1 ml of dichloromethane was slowly added over a period of 6 h by a syringe mounted into an automatic delivery system. The reaction was monitored by GC analysis.

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## Appendix A. Supplementary material

CCDC-835810 contains the supplementary data for **C6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.09.015.

## Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.09.015.

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