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Cyclometallated ruthenium complexes with *P*-stereogenic monophosphines containing a polycyclic aromatic substituent

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ABSTRACT

Reactions of optically pure *P*-stereogenic *ortho*-tolyl substituted phosphines with $[RuCl_2(p\text{-cymene})]_2$ afforded the corresponding *κP*-coordinated ruthenium(II) dichlorides (**C1′**, **C2’**) even in the presence of sodium acetate. In contrast, the ruthenium cyclometallated (κ^2-*C,P*) complexes (**C3**—**C9**) were obtained with phosphines containing a polycyclic aromatic substituent (**L3-L9**), namely 1-naphthyl, 9-phenanthryl or 1-pyrenyl. Some diastereoselectivity in the cyclometallation process has been observed for the most bulky ligands. The new compounds have been used as catalytic precursors in the reduction of acetophenone to 1-phenylethanol by transfer hydrogenation.

1. Introduction

The cyclometallation reaction is a transition metal C—H activation to form a metallacyle containing a new metal-carbon σ-bond. This reaction can be split into two main processes: the coordination of the heteroatom of the ligand to the metal and, in a second step, activation of one of the C—H bonds of the ligand [1].

Cycloruthenation is an extremely versatile process and shows a broad scope [2], and cyclometallated ruthenium compounds have been used as catalysts in different reactions including reduction of ketones and aldehydes [3], olefin metathesis [4], C—C bond formation reaction [5], hydrogenation [6], and *ortho*-deuteration [7]. In addition to this, some cycloruthenated derivatives have been shown to display interesting antitumour activities [8] and also promising photophysical and electrochemical properties [9]. In recent years, the ruthenium catalyzed *ortho*- or even *meta*-C—H bond functionalizations have become a thriving research area [10].

Despite the long history of *P*-stereogenic ligands, they are relatively rare in the literature because of their cumbersome synthesis [11]. The last two decades, however, have witnessed a renaissance in the field with the appearance of new methods amenable for the synthesis of such compounds [12].

Our group has worked with several types of chiral phosphines and with the corresponding palladium and ruthenium complexes that have been used in catalytic hydrovinylation (Pd) [13], allylic substitution (Pd) [13d,14], cyclopropanation (Ru) [15] and transfer hydrogenation (Ru) [13d,15,16] reactions.

Recently, a paper of Zhu and coworkers described the synthesis, structure, reactivity and catalytic activity of cyclometallated ruthenium complexes with phosphines containing the 1-naphthyl or the 2-tolyl groups [17]. They carried out the cyclometallation reaction under very mild conditions in the presence of sodium acetate forming neutral, *Ru*-stereogenic complexes that were obtained as racemic mixtures since the phosphines used were achiral.

The aim of the present paper is to present the results obtained using Zhu's method to cyclometallate chiral optically pure *P*-stereogenic phosphines (**L1-L9)** developed previously in the group containing potentially cyclometallating groups (2-tolyl, 1-naphthyl, 9-phenanthryl and 1-pyrenyl) in a process that allows the synthesis of non-racemic *Ru*-stereogenic derivatives.

2. Results and discussion

2.1. Synthesis and characterisation of coordination compounds *C1′* and *C2’*

The *P*-stereogenic ligands (**L1**-**L9**) shown in Chart 1 were prepared via phosphine-boranes following the Jugé-Stephan

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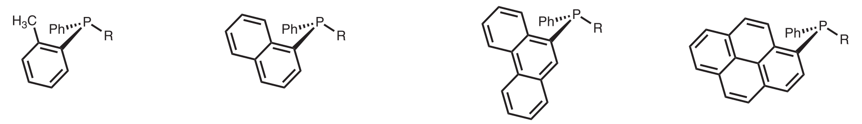


L1, R = Me; **L2**, R = iPr **L3**, R = Me; **L4**, R = iPr; **L5**, R = OMe **L6**, R = Me; **L7**, R = OMe **L8**, R = Me; **L9**, R = OMe

Chart 1. *P*-stereogenic phosphines.

methodology as we have previously reported for ligands **L3-L9** [13a,b14,16]. We here described the synthesis of phosphine **L1** by deprotection of the known phosphine-borane **L1·BH3** [18]. Phosphine **L2** was obtained in low optical purity a long time ago [19] and in racemic form very recently [20]. We here report its first enantioselective synthesis via its previously not reported borane adduct, **L2·BH3**.

P-stereogenic phosphines **L1** and **L2** could afford a five-membered cyclometallated derivative by activation of the C(sp^3)-H bond of the *ortho*-tolyl fragment. The cyclorutenation of this fragment have been described in the sterically demanding diisopropyl-(*ortho*-methylphenyl)phosphine, when this phosphine is treated with the organometallic precursor [$RuCl_2$(p-cymene)]$_2$ and sodium acetate [17]. The importance of the *ortho*-C-H bond deprotonation by carbonate [21] or carboxylate [22], as a proton shuttle to form a cyclometallated ruthenium(II) complexes has been recognised while some DFT calculations have shown that the C–H activation step involves a simultaneous metallation of the C–H bond and intramolecular deprotonation by acetate [23]. The beneficial effect of the bulkiness of phosphines in the cyclometallation process due to entropic factors has also been known for quite a long time [24].

With the idea of obtaining cyclometallated complexes **C1** and **C2**, the organometallic precursor [$RuCl_2$(*p*-cymene)]$_2$ was reacted with slightly more than 2 equivalents of the ligand **L1** or **L2** (bearing the *ortho*-tolyl group), and sodium acetate in methanol (Scheme 1). The excess of ligand ensures that no ruthenium precursor, which would be very difficult to separate from **C1** and **C2**, remained after the reaction.

Despite many efforts at different sets of conditions, only the non-cyclometallated dichlorocomplexes **C1**′ and **C2**′ were obtained, which were characterised by ^{1}H, ^{31}P-{^{1}H}, ^{13}C-{^{1}H} NMR spectra and high-resolution mass spectroscopy. ^{31}P-{^{1}H} NMR spectroscopy is a very useful tool to determine if the cyclometalated compound has been formed [25]. Only a signal at 20 ppm and 40 ppm was observed in ^{31}P-{^{1}H} NMR spectra for the reactions with **L1** and **L2** respectively. These chemical shifts are too low to correspond to the expected cyclometallated complexes **C1** and **C2** and show that dichlorocomplexes **C1**′, and **C2’** were formed [13d,15,17] instead (Scheme 1).

Suitable crystals of **C1**′ **and C2’** were obtained from a dichloromethane-hexane solution at 4 °C and were analyzed by X-ray diffraction (see Fig. 1).

Right: Ball and stick representation of **C2**′ showing the labelling scheme; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)–P(1) 2.3844(17), Ru(1)–Cl(1) 2.4287(15), Ru(1)–Cl(2) 2.4081(15), P(1)–C(11) 1.846(6); Ru(1)–P(1)–C(11) 109.27(19).P(1)-C(24) 1.870(6).

Both complexes form crystals that contain individual molecules separated by Van der Waal contacts. The molecules contain a pseudotetrahedral ruthenium centre coordinated to two chloride atoms, the phosphorus atom and the η^{6}-*p*-cymene ring in the classical three-legged piano stool geometry, as commonly found for complexes of the type [Ru(η^{6}-arene)Cl_2(monophosphine)] [13d,15,17]. The phosphorus atom of the free phosphine would have the absolute configuration *S* in both molecules, according to the Cahn-Ingold-Prelog nomenclature system, as expected from the stereochemistry of the Jugé-Stephan method and the enantiomer of ephedrine used [26]. The distances and angles of **C1**′ and **C2’** are very similar and in the range for similar complexes.

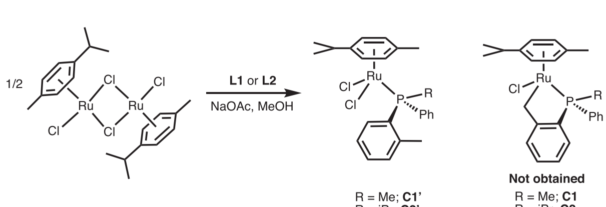
2.2. Synthesis and characterisation of cyclometallated compounds C3–C5

After the unsuccessful preparation of **C1** and **C2**, containing the cyclometallated *ortho*-tolyl group, our attention was shifted towards the synthesis of complexes **C3**–**C5**, containing the 1-naphthyl group. It has to be noted that the non-cyclometallated dichlorocomplexes **C3**′-**C5**′ have been reported in previous studies of our group [15]. The cyclometallation of these phosphines seems to be easier than the metallation of **L1** or **L2** since **L3-L5** are more sterically demanding and because the metallacycle, in this case, would be formed by activation of a C(sp^2)-H bond, an easier process than the activation of a C(sp^3)-H bond of an *ortho*-methyl group.

The organometallic precursor [$RuCl_2$(*p*-cymene)]$_2$ was reacted with slightly more than 2 equivalents of the ligands **L3-L5** and with sodium acetate in methanol (Scheme 2). The signals observed in the ^{31}P-{^{1}H} NMR spectra of the reaction mixtures (peaks at around 55, 75 and 160 ppm for the reactions with **L1**, L**2** and **L3** respectively) were strongly deshielded in relation to the signals of the corresponding previously reported dichlorocomplexes **C3**′**-C5'** (14.5, 30.3 and 166.6 ppm, respectively), pointing out that the cyclometallation reaction had taken place [15,25].

Complexes **C3**–**C5** were indeed obtained pure as brown solids in around 15% yield, after purification by column chromatography. The low yields are probably due to partial decomposition of the complexes during the purification step since the analysis at short reaction times indicates that no other major species were present. NMR spectra and high-resolution mass spectroscopy of the complexes confirmed that the cyclometallation had taken place.

The ^{31}P-{^{1}H} NMR spectrum consisted in two singlets in the case of **C3**′ and **C5**′ because of the formation of two diastereomers with different absolute configuration at the ruthenium atom. The diastereomeric ratios are 1:2.4 and 1:1.6 for **C3** and **C5** respectively. Interestingly, for complex **C4**, bearing the bulkiest phosphine **L4**, only one singlet was observed, indicating that the cyclometallation reaction had taken place diastereoselectively.



Scheme 1. Synthesis of coordination compounds **C1**′ and **C2**′.

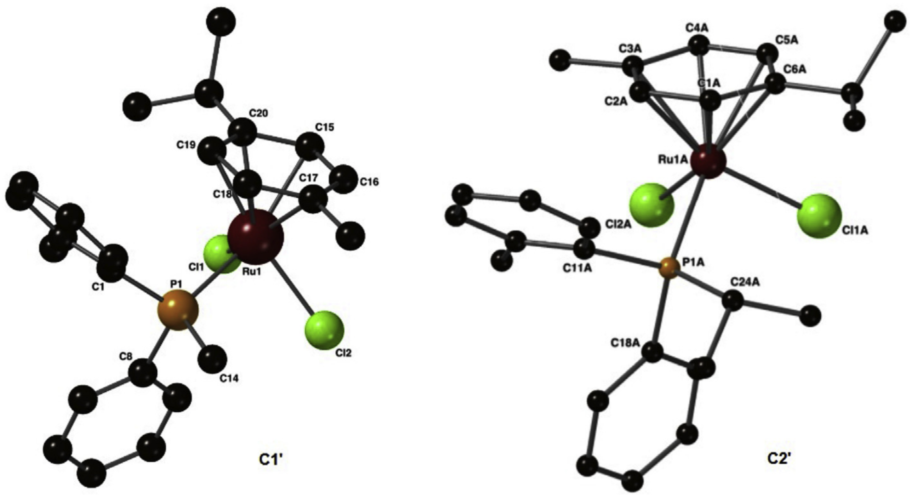
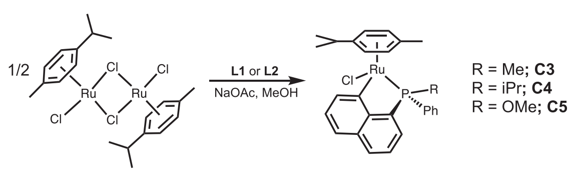


Fig. 1. Left: Ball and stick representation of **C1**′ showing the labelling scheme; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)–P(1) 2.3640(6), Ru(1)–Cl(1) 2.4103(6), Ru(1)–Cl(2) 2.4180(6), P(1)–C(1) 1.829(2); Ru(1)–P(1)–C(1) 111.13(7); P(1)-C(14) 1.820(2).



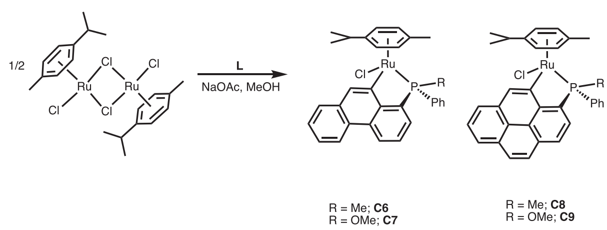
Scheme 2. Cyclometallation of **L3-L5**.

2.3. Synthesis and characterisation of cyclometallated compounds C6–C9

We subsequently explored the cyclometallation of phosphines **L6-L9**, containing a 9-phenanthryl or 1-pyrenyl groups, which could afford a five-membered metallacycle by activation of a C(sp^2)-H bond (Scheme 3).

The reactions were performed in the same conditions used for **L3**-**L6** (see before). ^{31}P-{^{1}H} NMR spectra showed two peaks at low fields with respect of dichlorocomplexes, after 2 h of reaction, suggesting that the cyclometallations had taken place for all the phosphines. It should be noted that there is no precedent of Ru-cyclometallations with phosphines bearing those groups.

The products were purified by column chromatography. The yields were very low (<8%), except for the **C6**, which was surprisingly obtained in 71% yield. The low yields are due, as previously mentioned, to decomposition during purification. It should also be noted that cyclometallated complexes with the phosphinites (**C7** and **C9**) were especially prone to decomposition and for this reason they could not be fully characterised or used in catalysis. Unfortunately it was not possible to study the complexes with the isopropyl phosphines with these rings since Jugé-Stephan method does not allow to obtain the corresponding ligands due to steric problems [13a].



Scheme 3. Cyclometallation of **L6-L9**.

All of the most significant peaks discussed in the previous complexes appear duplicated at the ^{1}H NMR spectra (Fig. 2), due to the formation of two diastereomers. It is remarkable the high field shift of one of the signals ($\delta = 4.13$ ppm) which suggest a proximity between this proton and the phenyl moiety. In the ^{31}P-{^{1}H}-NMR spectra the two expected peaks appeared, corresponding to the two diastereomeric species. The isomeric ratios were 1:3.2, 1:2.3, 1:2.6 and 1:2.8 for complexes **C6**–**C9** respectively.

From these results, it can be concluded that polycylic rings of the type 1-naphtyl, 9-phenantryl and 1-pyrenyl are adequate to form cyclometallated ruthenium complexes.

We were able to grow crystals suitable for X-ray measurements of **C6**, whose molecular structure is shown in Fig. 3. The structure confirms that the cyclometallation reaction had taken place by a C(sp^2)-H activation of the 9-phenanthryl substituent of the phosphine. The molecules of the complex also exhibit the three-legged piano stool geometry, being the ruthenium atom coordinated to chloride, phosphorus and to the C11 of the 9-phenanthryl group atoms, forming a five membered metallacycle. Remarkably, the Ru–P bond distance [2.2825(9) Å] is much shorter than in **C1**′ and **C2'** [2.3640(6) and 2.3844(17) Å respectively] suggesting that the cyclometallation probably contributes to release the tension of the molecular structure. A very short Ru(1)-C(11) bond length [2.095(3) Å] is also present. This structure is very similar to others recently described with 1-naphthylphosphines, demonstrating that phosphines with fused aromatic polycyclic substituents are particularly prone to cyclometallation [17].

Ru(1)–P(1) 2.2825(9), Ru(1)–Cl(1) 2.4197(8), Ru(1)–C(11) 2.095(3), P(1)–C(23) 1.805(3), C(23)–C(24) 1.437(5), C(24)–C(11) 1.432(5); P(1)–Ru(1)–Cl(1) 87.82(3), P(1)–Ru(1)–C(11)

80.42(10), C(11)–Ru(1)–Cl(1) 85.92(9), Ru(1)–P(1)–C(23) 105.26 (11).

The free phosphine ligand has *S* absolute configuration, as expected and, remarkably, only one diastereomer of the complex is present in the crystal, with *R* absolute configuration at the ruthenium atom. Therefore, the crystal exclusively contains the **(*R*$_{Ru}$,*R*$_P$)-C6** isomer of the complex (the descriptor of the absolute configuration of the phosphorus atom changes due to coordination with respect to the free ligand), despite the fact that **(*S*$_{Ru}$,*R*$_P$)-C6** is also present in solution according to NMR. This could be due to the

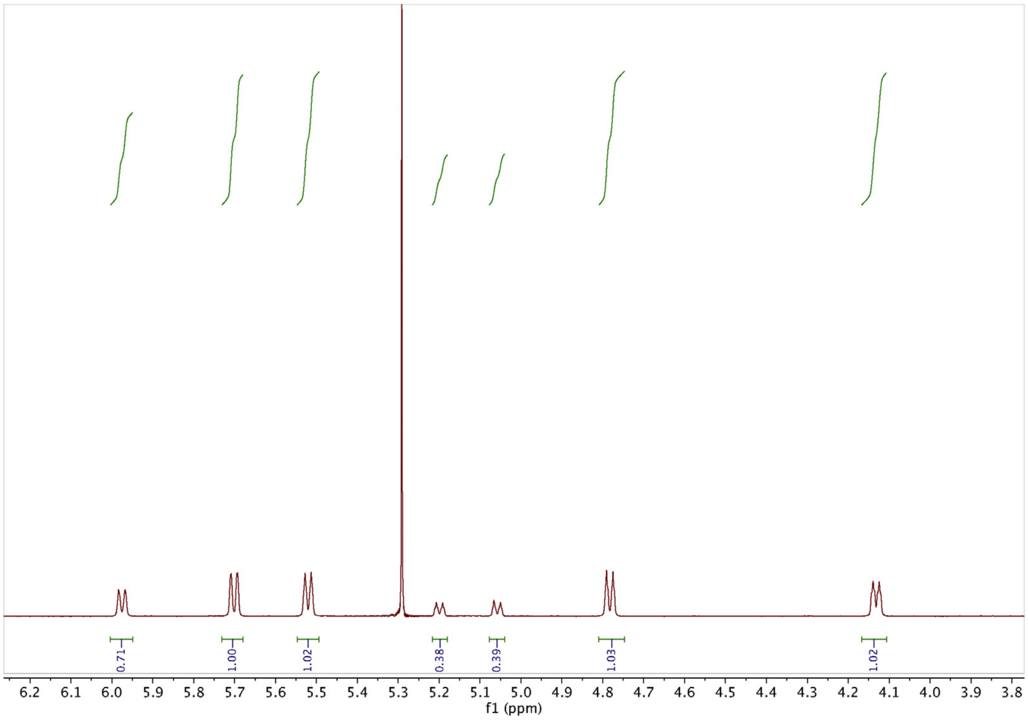


Fig. 2. NMR aromatic proton signals of η^6-C_6H_4 fragment ($\delta = 6.4$–3.8) of **C6** and singlet at $\delta = 5.30$ corresponding to dichloromethane.

higher insolubility of the R_{Ru} diastereomer, or that the selected crystal contained this isomer while others contain the S_{Ru} or finally, although unlikely, it can not be excluded that the two diastereomers are in equilibrium and that there is a dynamic resolution process producing only the **(R_{Ru},R_P)-C6** in the solid state. It has to be pointed out that the crystal was very difficult to obtain due to the instability and low crystallinity of **C6** and for this reason the analysed crystal could not be recovered and redissolved at low temperature to study if the diastereomeric mixture was formed again or only one diastereomer was present in solution.

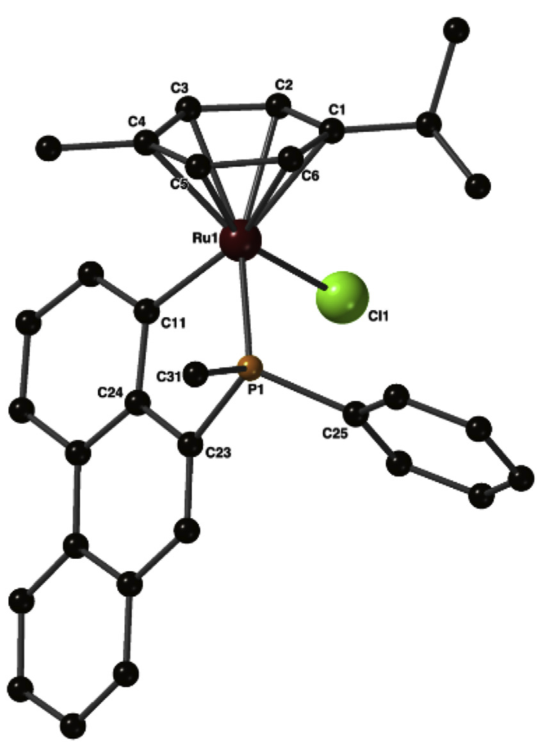


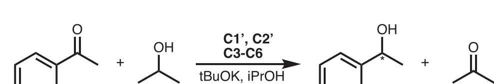
Fig. 3. Ball and stick representation of **C6** showing the labelling scheme; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°].

2.4. Ruthenium-catalysed asymmetric transfer hydrogenation

The ruthenium complexes described in the preceding sections were used as catalytic precursors in the asymmetric reduction of acetophenone by transfer hydrogenation to the chiral alcohol 1-phenylethanol. The catalytic runs were carried out using a 1% ruthenium complex (**C1′**, **C2′**, **C3**–**C6, C8**) and 5% of potassium *tert*-butoxide as base, in isopropanol as solvent (Scheme 4).

The reactions were carried out under nitrogen atmosphere in refluxing isopropanol (82 °C). This solvent also plays the role of hydrogen donor, being oxidized to acetone. The catalytic precursor was initially dissolved in the basic isopropanol solution and stirred for 15 min to form the catalytic Ru-hydride species and then acetophenone was added. At regular intervals (usually 1, 3, 5 and 7 h), aliquots were extracted and analyzed by gas chromatography, using a chiral column. This allowed the separation of the starting acetophenone and the two enantiomers of 1-phenylethanol and therefore for each injection the conversion and enantioselectivity could be immediately determined. For the sake of reproducibility, for each precursor two catalytic runs were routinely carried out in parallel.

The results of conversion and enantioselectivity obtained with cyclometallated precursors **C**, along with those with **C'** [15,16] for



Scheme 4. Reaction of ruthenium complexes in asymmetric hydrogenation catalysis.

Table 1
Catalytic results in the asymmetric hydrogenation.

Entry	Precursor	Conversion (%) at 1/3/5/7 h	*ee*(%) 5 h
1	**C1'**	23/46/64/>99	7
2	**C2'**	13/27/39/50	16
3	**C3**	25/54/70/76	<5
4	**C4**	48/83/96/>99	<5
5	**C5**	70/99/>99/>99	<5
6	**C6**	20/48/63/73	8
7	**C8**	8/27/40/53	5
8	**C3'**	<5/20/50/75	<5
9	**C4'**	10/52/75/85	13
10	**C5'**	5/22/35/45	<5
11	**C6'**	<5/9/60/80	5
12	**C8'**	8/24/39/-	6 (24 h)

comparison are given in Table 1.

It has to be pointed out that the reactions were very clean since only the peaks of starting acetophenone and its reduction products were detected in the GC traces. The table shows that all the precursors were active in the reaction, leading to full or high conversions at 7 h for most of the cases.

The different activity of coordination compounds **C'**, in relation to cyclometallated complexes **C**, show that the cyclometallation reaction does not occur during the catalytic process.

It can be seen that for the 1-naphthyl- and 9-phenanthrylphosphines, some of the cyclometallated complexes are more active than the dichloro complexes (*cf.* entries 3–6 with 8–11) while there is almost no difference in the case of the complexes with ligand **L8** (*cf.* entries 7 and 12). This effect is especially relevant for phosphinite **L5** because complex **C5** is the only one to gives full conversion already in 2 h (entry 5) while complex **C5'** is one of the less active precursors, yielding only 45% conversion at 7 h (entry 10). It would have been very interesting to explore if the other two cyclometallated complexes with phosphinite ligands, **C7** and **C9**, give also very active precursors, but unfortunately they could not be obtained in enough quantity to perform catalysis. Further studies will be directed to obtain those complexes in better yield and study their catalytic properties.

It should be noted that the enantioselectivity does not improve due to the cyclometallation. Despite the creation of a new stereocentre at the ruthenium atom most of the systems are completely unselective, giving racemic 1-phenylethanol. Only precursors **C2'** and **C4'**, containing the bulkiest ligands bearing the *i*-Pr group produced some *ee*, although still very low (entries 2 and 9).

From data obtained so far, it is clear that the cyclometallated complexes containing the 1-naphthyl group, **C3**–**C5**, are the fastest precursors of all the compounds studied. Perhaps the formation of these metallacycle facilitates the formation of the hydride ruthenium catalyst because it possibly modifies the reactivity of the metal-chloro bond and/or stabilizes to some extent the hydride derivative.

3. Conclusions

In this paper some subtleties of the cycloruthenation reaction have been uncovered. Firstly, the unsuccessful cyclometallation of *ortho*-tolyl ligands **L1** and **L2** contrasts with Zhu's ~~successful~~ cyclometallation of diisopropyl(*ortho*-tolyl)phosphine [17]. The fact that the structure of **L2** is similar to Zhu's ligand (the latter has a second isopropyl group and the former a phenyl) highlights the importance of stereoelectronic effects in the cycloruthenation reaction. Secondly, we have shown that monophosphines with a polycyclic aromatic substituent are prone to cyclometallate and that the reaction can be stereoselective, which may be interesting for applications in asymmetric catalysis. We are currently working to improve the synthesis of the cycloruthenated complexes and study their organometallic chemistry and catalytic applications.

4. Experimental section

4.1. General considerations

All compounds were prepared under a purified nitrogen atmosphere by standard Schlenk and vacuum-line techniques. The solvents were obtained from solvent-purification system or purified by standard procedures and kept under nitrogen.

L1-BH$_3$ and H_3B–P(Ph)(MeO)(2-tolyl) were prepared according previously reported methods [18,27]. Ligands **L3**-**L9** were prepared via phosphine-boranes following the Jugé-Stephan methodology as we have previously reported [13a,b,14,16].

NMR spectra were recorded in $CDCl_3$ at 298 K with Mercury 400 (^{1}H, ^{13}C-{^{1}H}) and Bruker 400 Avance III HD (^{31}P-{^{1}H}) spectrometers. Chemical shifts are given in δ values (ppm) relative to $SiMe_4$ (^{1}H and ^{13}C-{^{1}H}), and to 85% H_3PO_4 (^{31}P-{^{1}H}). Coupling constants are given in Hz and multiplicity is expressed as: s (singlet), d (doublet), t (triplet), sept (septuplet) and m (multiplet). The IR spectra were recorded in a Nicolet iS5 spectrophotometer in KBr, and the main absorption bands are expressed in cm^{-1}. High-resolution mass spectrometry analyses were performed with electrospray ionisation. ESI (+) spectra were acquired either on an LC/MSD-TOF instrument or on a ZQ mass spectrometer, utilizing a mixture of H_2O:CH_3CN (1:1, v/v) as the eluent. The GC analyses were performed on a FID-detector gas chromatograph equipped with a 30 m β-Dex 225 column.

4.2. Synthesis of the ligands

4.2.1. Synthesis of **L1,** (S)-methylphenyl(2-tolyl)phosphine

The phosphine-borane **L1-BH$_3$** (0.34 g, 1.08 mmol) was dissolved in 10 mL of morpholine and stirred overnight under inert atmosphere. The solvent was removed to dryness leading to a crude brown-yellow solid, which was redissolved in the minimum volume of anhydrous toluene and purified by column chromatography (alumina, 120 mL of anhydrous toluene). The toluene was removed under vacuum and the final product was a colourless oil. Yield: 88% (0.17 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.14 (m, 9H, *aromatic*), 2.39 (s, 3H, *Me*), 1.58 (d, J = 4.0 Hz, 3H, *Me*).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 137.5 (s), 132.2 (d, J = 18.8 Hz, *aromatic*), 130.2 (d, J = 14.2 Hz, *aromatic*), 128.4 (dd, J = 14.6, 7.9 Hz, *aromatic*), 126.0 (s, *aromatic*), 21.2 (d, J = 20.9 Hz, *Me*), 12.2 (d, J = 13.4 Hz, *Me*).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −36.3 (s).

4.2.2. Synthesis **L2·BH$_3$** (S)-isopropylphenyl(2-tolyl)phosphine-borane

The phosphinite-borane H_3B–P(Ph)(MeO)(2-tolyl) (0.68 g, 2.8 mmol) was dissolved in 20 mL of anhydrous diethyl ether and the solution was cooled to −25 °C. 3 equivalents of a solution of *i*PrLi in pentane (8.5 mL, 5.92 mmol) were added. Starting at −20 °C, the temperature was sequentially increased (10 °C every 30 min) to room temperature and the solution was stirred for 1 h. Carefully, around 20 mL of water were added to the pink solution, which turned white. The suspension was extracted with diethyl ether (3 x 30 mL) and the combined organic phases were washed with water and dried with anhydrous sodium sulphate. The suspension was filtered and the solvents were evaporated to dryness, leading to a colourless oil. Yield: 91% (0.46 g).

MS(EI) m/e: 253.1318 ([M-3H]+), 279.1448 ($[M+Na]^+$), 535.2981 ($[2M+Na]^+$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (ddd, $J = 10.6$, 7.7, 1.4 Hz, 1H, *aromatic*), 7.66–7.54 (m, 2H, *aromatic*), 7.49–7.28 (m, 4H, *aromatic*), 7.23–7.08 (m, 2H, *aromatic*), 2.78 (m, 1H, C*H*Me$_2$), 2.18 (s, 3H, *Me*), 1.24 (dd, $J = 16.4$, 7.0 Hz, 3H, *Me$_2$*CH), 1.15 (dd, $J = 15.1$, 6.9 Hz, 3H, *Me$_2$*CH), 1.85–0.40 (q, br, 3H, *BH$_3$*).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ +25.9 (d, $J = 65.9$ Hz).

4.2.3. Synthesis of **L2** (S)-isopropylphenyl(2-tolyl)phosphine

The phosphine-borane **L2·BH$_3$** (0.20 g, 0.79 mmol) was dissolved in 10 mL of morpholine and stirred overnight under inert atmosphere. The solvent was evaporated to dryness leading to a crude brown-yellow solid, which was redissolved in the minimum volume of anhydrous toluene and purified by column chromatography (alumina, 120 mL of anhydrous toluene). The toluene was removed under vacuum and the final product was colourless oil. Yield: 80% (0.15 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (m, 1H), 7.44–7.38 (m, 2H, *aromatic*), 7.31–7.13 (m, 6H, *aromatic*), 2.86 (m, 1H, C*H*Me$_2$), 2.40 (s, 3H, *Me*), 1.15 (dd, $J = 16.2$, 6.9 Hz, 3H,CH*Me$_2$*), 1.03 (dd, $J = 15.2$, 6.9 Hz, 3H, CH*Me$_2$*).

^{13}C-{^{1}H} ($CDCl_3$, 101 MHz): δ 143.1 (d, $J = 24.3$ Hz, *aromatic*), 137.4 (d, $J = 13.9$ Hz, *aromatic*), 136.0 (s, *aromatic*), 133.7 (d, $J = 19.1$ Hz, *aromatic*), 130.9 (s, *aromatic*), 130.3 (d, $J = 4.8$ Hz, *aromatic*), 128.5 (d, $J = 11.3$ Hz, *aromatic*), 128.2 (s, *aromatic*), 128.1 (s, *aromatic*), 24.7 (d, $J = 8.1$ Hz), 21.5 (d, $J = 22.2$ Hz), 20.0 (d, $J = 19.9$ Hz), 19.6 (d, $J = 18.2$ Hz).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −11.3 (s).

4.3. Synthesis of complexes

4.3.1. Synthesis of **C1'**

Ligand **L1** (162.6 mg, 0.76 mmol), $[RuCl_2(p\text{-cymene})]_2$ (214.3 mg, 0.35 mmol) and sodium acetate (164.1 mg, 2 mmol) were dissolved in 80 mL of methanol and the solution was stirred at room temperature for 4 h. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with first CH_2Cl_2, later with CH_2Cl_2/Et_2O and finally with methanol. The title product was obtained as an orange solid. Yield 85 mg (20%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (ddd, $J = 12.8$, 7.6, 1.2 Hz, 1H, *aromatic*), 7.71–7.66 (m, 2H, *aromatic*), 7.44–7.32 (m, 5H, *aromatic*), 7.27–7.24 (m, 1H, *aromatic*), 5.33 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.25 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.21 (d, $J = 5.6$ Hz, 1H, η^6-C_6H_4), 5.10 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 2.61 (sept., $J = 7.2$ Hz, 1H, C*H*Me$_2$), 2.14 (s, 3H, Me), 2.02 (d, $J = 10.8$ Hz, 3H, *Me*P), 1.95 (s, 3H, *Me*), 0.98 (d, $J = 7.2$ Hz, 3H, CH*Me$_2$*), 0.91 (d, $J = 7.2$ Hz, 3H, CH*Me$_2$*).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): phenyl carbon signals $\delta = 141.36$ (d, $J = 4.2$ Hz, 135.94, 135.50, 135.35, 133.30, 132.89, 132.17 (d, $J = 7.0$ Hz), 131.58 (d, $J = 9.1$ Hz), 130.81 (d, $J = 2.4$ Hz), 129.95 (d, $J = 2.4$ Hz), 128.40 (d, $J = 9.7$ Hz), 125.54 (d, $J = 11.4$ Hz); η^6-C_6H_4 carbon signals $\delta = 107.96$, 94.86, 89.97 (d, $J = 4.6$ Hz), 89.61 (d, $J = 4.5$ Hz), 86.51 (d, $J = 5.9$ Hz), 84.96 (d, $J = 5.5$ Hz); alkyl carbon signals $\delta = 29.95$, 23.10 (d, $J = 3.9$ Hz), 21.58, 21.43, 17.32, 13.65 (d, $J = 35.2$ Hz).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 19.9 ppm.

4.3.2. Synthesis of **C2**′

The procedure was the same as the one followed to prepare **C1**. Starting from **L2** (182.2 mg, 0.75 mmol). The title product was obtained as an orange solid. Yield 289.3 mg (66%).

IR: 3043, 2957, 2917, 2861, 1630, 1465, 1430, 1378, 1261, 1022, 796, 743, 696, 552, 530.478.

HRMS (ESI): *m/z* calc. for $C_{26}H_{33}PClRu^+$ $[M\text{-}Cl]^+$ 513.1046; found 513.1047.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (br, 1H, aromatic); 7.60 (br, 1H, aromatic), 7.50–7.29 (m, 7H, aromatic), 5.22 (br., 1H, η^6-C_6H_4), 5.01 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 4.81 (br., 1H, η^6-C_6H_4), 4.69 (br., 1H, η^6-C_6H_4), 3.39–3.52 (m, 1H, PC*H*Me$_2$), 2.81 (sept., $J = 14$ Hz, 1H, C*H*Me$_2$), 2.57 (br., 3H, *Me*), 1.92 (s, 3H, *Me*), 1.14–1.05 (m, 9H, CH*Me$_2$*), 0.95–0.85 (br m, 3H, CH*Me$_2$*).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 40.0.

4.3.3. Synthesis of **C3**

The procedure was the same as the one followed to prepare **C1**. Starting from ligand **L3** (200 mg, 0.8 mmol), the title product was obtained as a brown solid. Yield 70.1 mg (17%).

IR: 1630, 1543, 1482, 1467, 1434, 1384, 1340, 1193, 1099, 1036, 987, 888, 812, 775, 746, 729, 700, 500, 481, 472.

HRMS (ESI): *m/z* calc. for $C_{27}H_{28}PRu^+$ $[M\text{-}Cl]^+$ 485.0966; found 485.0977.

Major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28–8.24 (m, 1H, *aromatic*), 7.80 (m, 1H, *aromatic*), 7.52–7.24 (m, 9H, *aromatic*), 5.71 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.53 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 4.77 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 4.04 (d, $J = 5.6$ Hz, 1H, η^6-C_6H_4), 2.45 (sept., $J = 14$ Hz, C*H*Me$_2$), 2.17 (d, $J = 10.8$ Hz, 3H, *Me*P), 1.73 (s, 3H, Me), 1.09 (d, J = 6.8. Hz, 3H, CH*Me$_2$*), 0.86 (d, J = 6.8. Hz, 3H, CH*Me$_2$*).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): phenyl carbon signals $\delta = 170.54$ (d, $J = 13.1$ Hz), 140.02, 139.45, 138.86, 138.36, 133.24 (d, $J = 15.7$ Hz), 130.77 (d, $J = 2.5$ Hz), 130.10 (d, $J = 9.2$ Hz), 129.77 (d, $J = 2.5$ Hz), 128.51 (d, $J = 9.5$ Hz), 127.7–127.3 (multiplet), 124.58 (d, $J = 8.3$ Hz), 121.48, η^6-C_6H_4 carbon signals $\delta = 108.6$, 97.8, 95.4 (d, $J = 5.6$ Hz), 91.7 (d, $J = 3.4$ Hz, major), 90.8 (d, $J = 6.1$ Hz), 86.7 (d, $J = 3.6$ Hz); alkyl carbon signals $\delta = 30.2$, 23.1, 21.6, 18.42, 13.1 (d, $J = 32.0$ Hz).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 56.4.

Minor isomer ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28–8.24 (m, 1H, *aromatic*), 7.80 (m, 1H, *aromatic*), 7.52–7.24 (m, 9H minor, *aromatic*), 5.97 (d, $J = 6$ Hz, 2H, η^6-C_6H_4), 5.16 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.03 (d, $J = 5.6$ Hz, 1H, η^6-C_6H_4), 2.45 (sept., $J = 14$ Hz, 1H, C*H*Me$_2$), 2.16 (d, $J = 9.2$ Hz, 3H, *Me*P), 1.87 (s, 3H, *Me*), 0.95 (d, J = 6.8. Hz, 3H, CH*Me$_2$*), 0.80 (d, $J = 6.8$ Hz, 3H, CH*Me$_2$*).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): phenyl carbon signals $\delta = 170.54$ (d, $J = 13.1$ Hz), 139.45, 138.03, 137.52, 134.85, 134.37, 133.30 (d, $J = 15.7$ Hz), 131.18 (d, $J = 9.1$ Hz), 130.93 (d, $J = 2.5$ Hz), 129.40 (d, $J = 3.0$ Hz, minor), 128.51 (d, $J = 9.5$ Hz), 127.7–127.3 (multiplet), 124.33 (d, $J = 8.3$ Hz), 121.37 minor; η^6-C_6H_4 carbon signals $\delta = 107.1$, 99.1, 94.6 (d, $J = 4.8$ Hz), 92.8 (d, $J = 4.3$ Hz), 87.8 (d, $J = 4.8$ Hz), 87.2 (d, $J = 4.8$ Hz) alkyl carbon signals $\delta = 30.41$, 22.3, 21.9, 19.4 (d, $J = 32.1$ Hz), 18.46, 15.25.

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 51.9.

4.3.4. Synthesis of **C4**

The procedure was the same as the one followed to prepare **C1**. Starting from **L4** (164.3 mg, 0.59 mmol), the title product was obtained as a brown solid. Yield 52.8 mg (12%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, $J = 6.8$ Hz, 1H, *aromatic*), 7.83 (d, $J = 6.4$ Hz, 1H, *aromatic*), 7.78–7.29 (m, 9H, *aromatic*), 5.66 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.64 (d, $J = 7.6$ Hz, 1H, η^6-C_6H_4), 4.58 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 4.08 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 2.81 (sept., $J = 7.6$ Hz, 1H, C*H*Me$_2$), 2.32–2.16 (m, 1H, PC*H*Me$_2$), 1.81 (s, 3H), 1.55 (dd, $J = 16.8$, 7.2 Hz, 3H, PCH*Me$_2$*), 1.25 (dd, $J = 14.4$, 7.2 Hz, 3H, PCH*Me$_2$*), 0.94 (d, J = 7.0, 3H, CH*Me$_2$*), 0.52 (d, J = 6.8, 3H, CH*Me$_2$*).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): phenyl carbon signals $\delta = 170.04$ (d, $J = 12.8$ Hz), 149.10 (d, $J = 35.2$ Hz), 138.95, 135.75 (d, $J = 12.3$ Hz), 132.53 (d, $J = 15.2$ Hz), 130.40 (d, $J = 8.0$ Hz), 129.82 (d, $J = 2.6$ Hz), 128.66 (d, $J = 2.4$ Hz), 128.32, 127.31 (d, $J = 8.9$ Hz), 126.14, 122.75 (d, $J = 7.6$ Hz), 120.43; η^6-C_6H_4 carbon signals $\delta = 105.3$, 98.8, 93.9 (d, $J = 3$ Hz), 93.4 (d, $J = 5.1$ Hz), 90.9 (d, $J = 5.8$ Hz), 83.7 (d, $J = 2.9$ Hz); alkyl carbon signals $\delta = 29.1$, 26.37

(d, $J = 25.5$ Hz), 21.6, 20.7, 17.7 (d, $J = 3.9$ Hz), 17.1.

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 76.6 ppm.

IR: 3039, 2957, 2857, 1561, 1435, 1378, 1265, 1096, 1043, 813, 778, 704, 635, 530.

HRMS (ESI): *m/z* calc. for $C_{29}H_{32}PRu^+$ [M-Cl]$^+$ 513.1279; found 513.1297.

4.3.5. Synthesis of **C5**

The procedure was the same as the one followed to prepare **C1**. Starting from **L5** (226.1 mg, 0.85 mmol), the title product was obtained as a brown solid. Yield 54.3 mg (13%).

IR: 3039, 2922, 2848, 2357, 2335, 1026, 809, 770, 696, 665, 565, 530.

HRMS (ESI): *m/z* calc. for $C_{27}H_{28}OPRu^+$ [M-Cl]$^+$ 501.0915; found 501.0923.

Major: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (dd, $J = 7.0$, 1.1 Hz, 1H, *aromatic*), 7.89–7.83 (m, 1H, *aromatic*), 7.75–7.32 (m, 9H, *aromatic*), 5.96 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.94 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.49 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.12 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 3.47 (d, $J = 10.8$ Hz, 3H, MeO), 2.45 (m, 1H, C*H*Me$_2$), 1.96 (s, 3H, Me), 1.13 (d, $J = 7.1$ Hz, 3H, CH*Me*$_2$), 0.96 (d, $J = 7.2$ Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 162.6.

Minor: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (dd, $J = 7.0$, 1.0 Hz, 1H, *aromatic*), 7.89–7.83 (m, 1H, *aromatic*), 7.75–7.32 (m, 9H, *aromatic*), 5.86 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.74 (d, $J = 6.0$ Hz, 1H, η^6-C_6H_4), 4.83 (d, $J = 6.8$ Hz, 1H, η^6-C_6H_4), 4.05 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 3.76 (d, $J = 11.6$ Hz, 3H, MeO), 2.45 (m, 1H, C*H*Me$_2$), 1.72 (s, 3H, Me), 1.10 (d, $J = 7.2$ Hz, 3H, CH*Me*$_2$), 1.01 (d, $J = 6.8$ Hz, 3H CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 154.2.

4.3.6. Synthesis of **C6**

The procedure was the same as the one followed to prepare **C1**. Starting from ligand **L6** (240.1 mg, 0.8 mmol), the title product was obtained as a brown solid. Yield 324.1 mg (71%).

IR: 3430, 3039, 2957, 2917, 2852, 2356, 1709, 1622, 1557, 1465, 1422, 1383, 1326, 1274, 1187, 1100, 1030, 948, 883, 843, 748, 722, 691, 622, 600, 491, 422.

HRMS (ESI): *m/z* calc. for $C_{31}H_{30}PRu^+$ [M-Cl]$^+$ 535.1123; found 535.1132.

Major: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, $J = 8.3$ Hz, 1H, *aromatic*), 8.40 (d, J = 7.2, 1H, *aromatic*), 8.26, (m,1H, *aromatic*), 7.80–7.30 (m, 10H, *aromatic*), 5.71 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.53 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 4.77 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 4.13 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 2.40–2.50 (m, 1H, C*H*Me$_2$), 2.22 (d, $J = 10.8$ Hz, 3H, MeP), 1.73 (s, 3H, Me), 1.08 (d, $J = 7.2$ Hz, 3H, CH*Me*$_2$), 0.86 (d, J = 6.8. Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 56.4.

Minor: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, $J = 8.2$ Hz, 1H, *aromatic*), 8.38 (d, J = 7.2, 1H, *aromatic*), 8.26, (m,1H, *aromatic*), 7.80–7.30 (m, 10H, *aromatic*), 5.97 (d, $J = 6$ Hz, 2H, η^6-C_6H_4), 5.20 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.06 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 2.40–2.50 (m, 1H, C*H*Me$_2$), 2.25 (d, $J = 9.6$ Hz, 3H, MeP), 1.87 (s, 3H, Me), 0.96 (d, J = 6.8. Hz, 3H, CH*Me*$_2$), 0.83 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$).

^{13}C-{^{1}H} NMR ($CDCl_3$, 101 MHz): selected phenyl carbon signals, major and minor derivatives $\delta = 172.15$ (d, $J = 14.0$ Hz), 145.75 (d, $J = 36.3$ Hz), 141.38, 130.26 (d, $J = 9.1$ Hz), 129.87 (d, $J = 2.5$ Hz), 127.41 (d, $J = 25.9$ Hz), 125.95, 123.25, 116.68; η^6-C_6H_4 carbon signals $\delta = 108.5$ (s, major), 107.1 (s, minor), 99.4 (s, minor), 98.3 (s, major), 95.6 (d, $J = 5.6$ Hz, major), 94.8 (d, $J = 4.8$ Hz, minor), 93.2 (d, $J = 4.4$ Hz, minor), 92.2 (d, $J = 3.6$ Hz, major), 90.9 (d, $J = 5.9$ Hz, major), 87.9 (d, $J = 4.9$ Hz, minor), 87.6 (d, $J = 4.4$ Hz, minor), 87.0 (d, $J = 3.8$ Hz, major); alkyl carbon signals $\delta = 30.4$ (s, minor), 30.3 (s, major), 23.2 (s, major), 22.5 (s, minor), 22.1 (s, minor), 21.6 (s, major), 19.2 (d, J = 32.2, minor), 18.5 (minor), 18.4 (major), 13.6 (d, J = 32.0, major).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 51.2.

4.3.7. Synthesis of **C7**

The procedure was the same as the one followed to prepare **C1**. Starting from **L7** (258.9 mg, 0.80 mmol), the title product was obtained as a brown solid. Yield 26.8 mg (6%).

IR: 3057, 2957, 2913, 2847, 2361, 2322, 1709, 1613, 1552, 1430, 1383, 1309, 1100, 1035, 948, 800, 757, 687, 609, 570, 465.

HRMS (ESI): *m/z* calc. for $C_{31}H_{30}OPRu^+$ [M-Cl]$^+$ 551.1072; found 551.1057.

Major: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (m, 1H, *aromatic*), 8.62 (d, $J = 7.2$ Hz, 1H, *aromatic*), 8.29 (m, 1H, *aromatic*), 7.85–7.40 (m, 10H, *aromatic*), 5.93 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.54 (d, $J = 6.0$ Hz, 1H, η^6-C_6H_4), 5.47 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 4.22 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 3.60 (d, $J = 11.2$ Hz, 3H, MeO), 2.38 (sept., J = 14, 1H, C*H*Me$_2$), 1.68 (s, 3H, Me), 1.22 (d, $J = 7.2$ Hz, 3H, CH*Me*$_2$), 1.07 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 158.2.

Minor: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (m, 1H, *aromatic*), 8.58 (d, $J = 7.2$ Hz, 1H, *aromatic*), 8.29 (m, 1H, *aromatic*), 7.85–7.40 (m, 10H, *aromatic*), 6.10 (d, $J = 5.2$ Hz, 1H, η^6-C_6H_4), 6.0 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.86 (d, $J = 5.6$ Hz, 1H, η^6-C_6H_4), 5.02 (d, $J = 5.2$ Hz, 1H, η^6-C_6H_4), 3.61 (d, $J = 11.2$ Hz, 3H, MeO), 2.46 (sept., J = 14, 1H, minor), 2.38 (sept., J = 14, 1H, C*H*Me$_2$), 1.93 (s, 3H, Me), 1.24 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$), 0.87 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 168.4.

4.3.8. Synthesis of **C8**

The procedure was the same as the one followed to prepare **C1**. Starting from Ligand **L8** (244.6 mg, 0.75 mmol), the title product was obtained as a brown solid. Yield 32 mg (7%).

IR: 3030, 2957, 2917, 2867, 1709, 1622, 1596, 1574, 1513, 1439, 1387, 1278, 1170, 1113, 1030, 883, 839, 800, 726, 691, 596, 491.

HRMS (ESI): *m/z* calc. per $C_{33}H_{30}PRu^+$ [M-Cl]$^+$ 559.1123; found 559.1133.

Major: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (s, 1H, *aromatic*), 8.20–7.30 (m, 12H, *aromatic*), 6.12 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.68 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 4.87 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 4.14 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 2.55 (sept., $J = 6.8$ Hz, 1H, C*H*Me$_2$), 2.29 (d, $J = 10.8$ Hz, 3H, MeP), 1.80 (s, 3H, Me), 1.13 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$), 0.87 (d, J = 6.8. Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 56.7.

Minor: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (1H, *aromatic*), 8.20–7.30 (m, 12H, *aromatic*), 5.87 (d, $J = 6.4$ Hz, 2H, η^6-C_6H_4), 5.25 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 5.16 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 2.55 (sept., $J = 6.8$ Hz, 1H, C*H*Me$_2$), 2.29 (d, $J = 10.8$ Hz, 3H, MeP), 1.94 (s, 3H, Me), 0.99 (d, J = 6.8. Hz, 3H, CH*Me*$_2$), 0.79 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 51.9.

4.3.9. Synthesis of **C9**

The procedure was the same as the one followed to prepare **C1**. Starting from **L9** (272.1 mg, 0.80 mmol), the title product was obtained as a brown solid. Yield 20 mg (4%).

IR: 3052, 2965, 2926, 2861, 2357, 2222, 1709, 1613, 1565, 1470, 1435, 1383, 1300, 1257, 1183, 1104, 1030, 843, 735, 696, 604, 574, 522, 457.

HRMS (ESI): *m/z* calc. for $C_{33}H_{30}OPRu^+$ [M-Cl]$^+$ 575.1072; found 575.1077. Major: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.25 (s, 1H, *aromatic*), 8.13 (dd, $J = 6.9$, 1.8 Hz, 1H, *aromatic*), 7.70–6.80 (m, 11H, *aromatic*), 5.74 (d, $J = 6.4$ Hz, 1H, η^6-C_6H_4), 5.58 (d, $J = 5.6$ Hz, 1H, η^6-C_6H_4), 5.14 (d, $J = 6$ Hz, 1H, η^6-C_6H_4), 3.62 (d, $J = 6.0$ Hz, 1H, η^6-C_6H_4), 3.27 (d, $J = 11.2$ Hz, 3H, POMe), 2.43 (m, 1H, C*H*Me$_2$), 1.61 (s, 3H, Me), 0.87 (d, $J = 7.2$ Hz, 3H, CH*Me*$_2$), 0.51 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 158.4.

Minor: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.16 (s, 1H, *aromatic*), 8.08 (dd, J = 7.1, 1.6 Hz, 1H, *aromatic*) 7.70–6.80 (m, 11H, *aromatic*), 5.90 (d, J = 6.8 Hz, 1H, η^6-C_6H_4), 5.83 (d, J = 6.4 Hz, 1H, η^6-C_6H_4), 5.40 (d, J = 6 Hz, 1H, η^6-C_6H_4), 4.52 (d, J = 6.0 Hz, 1H, η^6-C_6H_4), 3.27 (d, J = 11.2 Hz, 3H, major), 2.84 (d, J = 11.2 Hz, 3H, POMe), 2.43 (m, 1H, C*H*Me$_2$), 1.86 (s, 3H, Me), 0.70 (d, J = 7.2 Hz, 3H, CH*Me*$_2$), 0.49 (d, J = 6.8 Hz, 3H, CH*Me*$_2$).

^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 168.1.

4.4. X-ray crystallography

The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The structure was solved and refined using the Bruker SHELXTL Software Package [28]. CCDC 1907310–1907312 contain the supplementary data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.5. General procedure for transfer hydrogenation reactions

Transfer hydrogenation reactions of acetophenone were carried out in 100 mL Schlenk flasks and in pairs in order to improve the reproducibility of the data. Under a nitrogen atmosphere, the Schlenk flask was charged with 0.02 mmol (1%) of the ruthenium complex and 0.10 mmol of potassium tert-butoxide. The solids were dissolved in 25 mL of 2-propanol and the mixture was left stirring for 15 min at reflux to activate the catalyst. At this point, 4.0 mmol of acetophenone were added to start the reaction. At regular intervals of time (1, 3, 5 and 7 h) aliquots were extracted and analysed by gas chromatography, in order to study the conversion of the reaction and the enantioselectivity of the process.

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