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 [RuCl2(p-cymene)]2 afforded the corresponding kP-coordinated ruthenium(II) dichlorides (C1′, C2’) even in the presence of sodium acetate. In contrast, the ruthenium cyclometallated (k2-C,P) complexes (C3eC9) 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 CeH activation to form a metallacyle containing a new metal-carbon s-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 CeH 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], CeC 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-sterereogenic 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 C10 and C2’

T he P-stereogenic ligands (L1-L9) shown in Chart 1 were prepared via phosphine-boranes following the Jug e-Stephan 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 L2was 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 fivemembered cyclometallated derivative by activation of the C(sp3)-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 [RuCl2(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 CeH activation step involves a simultaneous metallation of the CeH 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 [RuCl2(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 1H, 31P-{1H}, 13C-{1H} NMR spectra and high-resolution mass spectroscopy. 31P-{1H} NMR spectroscopy is a very useful tool to determine if the cyclometallated compound has been formed [25]. Only a signal at 20 ppm and 40 ppm was observed in 31P-{1H} 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 Xray 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)eP(1) 2.3844(17), Ru(1)e Cl(1) 2.4287(15), Ru(1)eCl(2) 2.4081(15), P(1)eC(11) 1.846(6); Ru(1)eP(1)eC(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 h6-p-cymene ring in the classical three-legged piano stool geometry, as commonly found for complexes of the type [Ru(h6-arene)Cl2(monophosphine)] [13d,15,17]. The phosphorus atomof 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 Jug e-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 C3eC5

After the unsuccessful preparation of C1 and C2, containing the cyclometallated ortho-tolyl group, our attention was shifted towards the synthesis of complexes C3eC5, 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(sp2)-H bond, an easier process than the activation of a C(sp3)-H bond of an ortho-methyl group.

The organometallic precursor [RuCl2(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 31P-{1H} NMR spectra of the reaction mixtures (peaks at around 55, 75 and 160 ppm for the reactions with L1, L2 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 C3eC5 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 31P-{1H} 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.

2.3. Synthesis and characterisation of cyclometallated compounds C6eC9

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(sp2)-H bond (Scheme 3).

The reactions were performed in the same conditions used for L3-L6 (see before). 31P-{1H} 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 Rucyclometallations 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 itwas not possible to study the complexes with the isopropyl phosphines with these rings since Jug e-Stephan method does not allow to obtain the corresponding ligands due to steric problems [13a].

All of the most significant peaks discussed in the previous complexes appear duplicated at the 1H NMR spectra (Fig. 2), due to the formation of two diastereomers. It is remarkable the high field shift of one of the signals (d ¼ 4.13 ppm) which suggest a proximity between this proton and the phenyl moiety. In the 31P-{1H}-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 C6eC9 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(sp2)-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 RueP 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)eP(1) 2.2825(9), Ru(1)eCl(1) 2.4197(8), Ru(1)eC(11) 2.095(3), P(1)eC(23) 1.805(3), C(23)eC(24) 1.437(5), C(24)eC(11) 1.432(5); P(1)eRu(1)eCl(1) 87.82(3), P(1)eRu(1)eC(11) 80.42(10), C(11)eRu(1)eCl(1) 85.92(9), Ru(1)eP(1)eC(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 (RRu,RP)-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 (SRu,RP)-C6 is also present in solution according to NMR. This could be due to the higher insolubility of the RRu diastereomer, or that the selected crystal contained this isomer while others contain the SRu 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 (RRu,RP)-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.

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′, C3eC6, C8) and 5% of potassium tertbutoxide 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 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 3e6 with 8e11) 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, C3eC5, 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-BH3 and H3BeP(Ph)(MeO)(2-tolyl) were prepared according previously reported methods [18,27]. Ligands L3-L9 were prepared via phosphine-boranes following the Jug e-Stephan methodology as we have previously reported [13a,b,14,16].

NMR spectra were recorded in CDCl3 at 298 K with Mercury 400 (1H, 13C-{1H}) and Bruker 400 Avance III HD (31P-{1H}) spectrometers. Chemical shifts are given in d values (ppm) relative to SiMe4 (1H and 13C-{1H}), and to 85% H3PO4 (31P-{1H}). 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. Highresolution mass spectrometry analyses were performed with electrospray ionisation. ESI (þ) spectra were acquired either on an LC/MSD-TOF instrument or on a ZQ mass spectrometer, utilizing a mixture of H2O:CH3CN (1:1, v/v) as the eluent. The GC analyses were performed on a FID-detector gas chromatograph equipped with a 30m b-Dex 225 column.

4.2. Synthesis of the ligands

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

The phosphine-borane L1-BH3 (0.34 g, 1.08 mmol) was dissolved in 10 mL of morpholine and stirred overnight under inert atmosphere. The solventwas 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, 120mL of anhydrous toluene). The toluene was removed under vacuum and the final product was a colourless oil. Yield: 88% (0.17 g).

1H NMR (CDCl3, 400 MHz): d 7.40e7.14 (m, 9H, aromatic), 2.39 (s, 3H, Me), 1.58 (d, J ¼ 4.0 Hz, 3H, Me).

13C-{1H} NMR (CDCl3, 101 MHz): d 137.5 (s), 132.2 (d, J ¼ 18.8 Hz, aromatic), 130.2 (d, J ¼ 14.2 Hz, aromatic), 128.4 (dd, J ¼ 14.6, 7.9 Hz, aromatic), 126.0 (s, aromatic), 21.2 (d, J ¼ 20.9 Hz, Me), 12.2 (d, J ¼ 13.4 Hz, Me). 31P-{1H} NMR (CDCl3, 162 MHz): d 36.3 (s).

4.2.2. Synthesis L2·BH3 (S)-isopropylphenyl(2-tolyl)phosphineborane

The phosphinite-borane H3BeP(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 iPrLi 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]þ), 279.1448 ([MþNa]þ), 535.2981 ([2 M þ Na]þ).
1H NMR (CDCl3, 400 MHz): d 7.75 (ddd, J ¼ 10.6, 7.7, 1.4 Hz, 1H, aromatic), 7.66e7.54 (m, 2H, aromatic), 7.49e7.28 (m, 4H, aromatic), 7.23e7.08 (m, 2H, aromatic), 2.78 (m, 1H, CHMe2), 2.18 (s, 3H, Me), 1.24 (dd, J ¼ 16.4, 7.0 Hz, 3H, Me2CH), 1.15 (dd, J ¼ 15.1, 6.9 Hz, 3H, Me2CH), 1.85e0.40 (q, br, 3H, BH3).
31P-{1H} NMR (CDCl3, 162 MHz): d þ25.9 (d, J ¼ 65.9 Hz).

4.2.3. Synthesis of L2 (S)-isopropylphenyl(2-tolyl)phosphine
The phosphine-borane L2·BH3 (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, 120mL of anhydrous toluene). The toluene was removed under vacuum and the final product was colourless oil. Yield: 80% (0.15 g).
1H NMR (CDCl3, 400 MHz): d 7.47 (m, 1H), 7.44e7.38 (m, 2H, aromatic), 7.31e7.13 (m, 6H, aromatic), 2.86 (m, 1H, CHMe2), 2.40 (s, 3H, Me), 1.15 (dd, J ¼ 16.2, 6.9 Hz, 3H,CHMe2), 1.03 (dd, J ¼ 15.2, 6.9 Hz, 3H, CHMe2).
13C-{1H} (CDCl3, 101 MHz): d 143.1 (d, J ¼ 24.3 Hz, aromatic), 137.4 (d, J ¼ 13.9 Hz, aromatic), 136.0 (s, aromatic), 133.7 (d, J ¼ 19.1 Hz, aromatic), 130.9 (s, aromatic), 130.3 (d, J ¼ 4.8 Hz, aromatic), 128.5 (d, J ¼ 11.3 Hz, aromatic), 128.2 (s, aromatic), 128.1 (s, aromatic), 24.7 (d, J ¼ 8.1 Hz), 21.5 (d, J ¼ 22.2 Hz), 20.0 (d, J ¼ 19.9 Hz), 19.6 (d, J ¼ 18.2 Hz).
31P-{1H} NMR (CDCl3, 162 MHz): d 11.3 (s).

4.3. Synthesis of complexes
4.3.1. Synthesis of C1’
Ligand L1 (162.6 mg, 0.76 mmol), [RuCl2(p-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 CH2Cl2, later with CH2Cl2/Et2O and finally with methanol. The title product was obtained as an orange solid. Yield 85 mg (20%).
1H NMR (CDCl3, 400 MHz): d 7.95 (ddd, J ¼ 12.8, 7.6, 1.2 Hz, 1H, aromatic), 7.71e7.66 (m, 2H, aromatic), 7.44e7.32 (m, 5H, aromatic), 7.27e7.24 (m, 1H, aromatic), 5.33 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.25 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.21 (d, J ¼ 5.6 Hz, 1H, h6-C6H4), 5.10 (d, J ¼ 6 Hz, 1H, h6-

C6H4), 2.61 (sept., J ¼ 7.2 Hz, 1H, CHMe2), 2.14 (s, 3H, Me), 2.02 (d, J ¼ 10.8 Hz, 3H, MeP), 1.95 (s, 3H, Me), 0.98 (d, J ¼ 7.2 Hz, 3H, CHMe2), 0.91 (d, J ¼ 7.2 Hz, 3H, CHMe2).
13C-{1H} NMR (CDCl3, 101 MHz): phenyl carbon signals d ¼ 141.36 (d, J ¼ 4.2 Hz, 135.94, 135.50, 135.35, 133.30, 132.89, 132.17 (d, J ¼ 7.0 Hz), 131.58 (d, J ¼ 9.1 Hz), 130.81 (d, J ¼ 2.4 Hz), 129.95 (d, J ¼ 2.4 Hz), 128.40 (d, J ¼ 9.7 Hz), 125.54 (d, J ¼ 11.4 Hz); h6-C6H4 carbon signals d ¼ 107.96, 94.86, 89.97 (d, J ¼ 4.6 Hz), 89.61 (d, J ¼ 4.5 Hz), 86.51 (d, J ¼ 5.9 Hz), 84.96 (d, J ¼ 5.5 Hz); alkyl carbon signals d ¼ 29.95, 23.10 (d, J ¼ 3.9 Hz), 21.58, 21.43, 17.32, 13.65 (d, J ¼ 35.2 Hz).
31P-{1H} NMR (CDCl3, 162 MHz): d 19.9 ppm.

4.3.2. Synthesis of C20
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 C26H33PClRuþ [M-Cl]þ 513.1046; found 513.1047. 1H NMR (CDCl3, 400 MHz): d 8.10 (br, 1H, aromatic); 7.60 (br, 1H, aromatic), 7.50e7.29 (m, 7H, aromatic), 5.22 (br., 1H, h6-C6H4), 5.01 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.81 (br., 1H, h6-C6H4), 4.69 (br., 1H, h6-C6H4), 3.39e3.52 (m, 1H, PCHMe2), 2.81 (sept., J ¼ 14 Hz, 1H, CHMe2), 2.57 (br., 3H, Me), 1.92 (s, 3H, Me), 1.14e1.05 (m, 9H, CHMe2), 0.95e0.85 (br m, 3H, CHMe2).
31P-{1H} NMR (CDCl3, 162 MHz): d 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 C27H28PRuþ [M-Cl]þ 485.0966; found 485.0977.
Major isomer: 1H NMR (CDCl3, 400 MHz): d 8.28e8.24 (m, 1H, aromatic), 7.80 (m, 1H, aromatic), 7.52e7.24 (m, 9H, aromatic), 5.71 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.53 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.77 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 4.04 (d, J ¼ 5.6 Hz, 1H, h6-C6H4), 2.45 (sept., J ¼ 14 Hz, CHMe2), 2.17 (d, J ¼ 10.8 Hz, 3H, MeP), 1.73 (s, 3H, Me), 1.09 (d, J ¼ 6.8. Hz, 3H, CHMe2), 0.86 (d, J ¼ 6.8. Hz, 3H, CHMe2).
13C-{1H} NMR (CDCl3, 101 MHz): phenyl carbon signals d ¼ 170.54 (d, J ¼ 13.1 Hz), 140.02, 139.45, 138.86, 138.36, 133.24 (d, J ¼ 15.7 Hz), 130.77 (d, J ¼ 2.5 Hz), 130.10 (d, J ¼ 9.2 Hz), 129.77 (d, J ¼ 2.5 Hz), 128.51 (d, J ¼ 9.5 Hz), 127.7e127.3 (multiplet), 124.58 (d, J ¼ 8.3 Hz), 121.48, h6-C6H4 carbon signals d ¼ 108.6, 97.8, 95.4 (d, J ¼ 5.6 Hz), 91.7 (d, J ¼ 3.4 Hz, major), 90.8 (d, J ¼ 6.1 Hz), 86.7 (d, J ¼ 3.6 Hz); alkyl carbon signals d ¼ 30.2, 23.1, 21.6, 18.42, 13.1 (d, J ¼ 32.0 Hz).
31P-{1H} NMR (CDCl3, 162 MHz): d 56.4.

Minor isomer 1H NMR (CDCl3, 400 MHz): d 8.28e8.24 (m, 1H, aromatic), 7.80 (m, 1H, aromatic), 7.52e7.24 (m, 9H minor, aromatic), 5.97 (d, J ¼ 6 Hz, 2H, h6-C6H4), 5.16 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.03 (d, J ¼ 5.6 Hz, 1H, h6-C6H4), 2.45 (sept., J ¼ 14 Hz, 1H, CHMe2), 2.16 (d, J ¼ 9.2 Hz, 3H, MeP), 1.87 (s, 3H, Me), 0.95 (d, J ¼ 6.8. Hz, 3H, CHMe2), 0.80 (d, J ¼ 6.8 Hz, 3H, CHMe2).
13C-{1H} NMR (CDCl3, 101 MHz): phenyl carbon signals d ¼ 170.54 (d, J ¼ 13.1 Hz), 139.45, 138.03, 137.52, 134.85, 134.37, 133.30 (d, J ¼ 15.7 Hz), 131.18 (d, J ¼ 9.1 Hz), 130.93 (d, J ¼ 2.5 Hz), 129.40 (d, J ¼ 3.0 Hz, minor), 128.51 (d, J ¼ 9.5 Hz), 127.7e127.3 (multiplet), 124.33 (d, J ¼ 8.3 Hz), 121.37 minor; h6-C6H4 carbon signals d ¼ 107.1, 99.1, 94.6 (d, J ¼ 4.8 Hz), 92.8 (d, J ¼ 4.3 Hz), 87.8 (d, J ¼ 4.8 Hz), 87.2 (d, J ¼ 4.8 Hz) alkyl carbon signals d ¼ 30.41, 22.3, 21.9, 19.4 (d, J ¼ 32.1 Hz), 18.46, 15.25.
31P-{1H} NMR (CDCl3, 162 MHz): d 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%).
1H NMR (CDCl3, 400 MHz): d 8.26 (d, J ¼ 6.8 Hz, 1H, aromatic), 7.83 (d, J ¼ 6.4 Hz, 1H, aromatic), 7.78e7.29 (m, 9H, aromatic), 5.66 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.64 (d, J ¼ 7.6 Hz, 1H, h6-C6H4), 4.58 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 4.08 (d, J ¼ 6 Hz, 1H, h6-C6H4), 2.81 (sept., J ¼ 7.6 Hz, 1H, CHMe2), 2.32e2.16 (m, 1H, PCHMe2), 1.81 (s, 3H), 1.55 (dd, J ¼ 16.8, 7.2 Hz, 3H, PCHMe2), 1.25 (dd, J ¼ 14.4, 7.2 Hz, 3H, PCHMe2), 0.94 (d, J ¼ 7.0, 3H, CHMe2), 0.52 (d, J ¼ 6.8, 3H, CHMe2).
13C-{1H} NMR (CDCl3, 101 MHz): phenyl carbon signals d ¼ 170.04 (d, J ¼ 12.8 Hz), 149.10 (d, J ¼ 35.2 Hz), 138.95, 135.75 (d, J ¼ 12.3 Hz), 132.53 (d, J ¼ 15.2 Hz), 130.40 (d, J ¼ 8.0 Hz), 129.82 (d, J ¼ 2.6 Hz), 128.66 (d, J ¼ 2.4 Hz), 128.32, 127.31 (d, J ¼ 8.9 Hz), 126.14, 122.75 (d, J ¼ 7.6 Hz), 120.43; h6-C6H4 carbon signals d ¼ 105.3, 98.8, 93.9 (d, J ¼ 3 Hz), 93.4 (d, J ¼ 5.1 Hz), 90.9 (d, J ¼ 5.8 Hz), 83.7 (d, J ¼ 2.9 Hz); alkyl carbon signals d ¼ 29.1, 26.37 (d, J ¼ 25.5 Hz), 21.6, 20.7, 17.7 (d, J ¼ 3.9 Hz), 17.1.
31P-{1H} NMR (CDCl3, 162 MHz): d 76.6 ppm.
IR: 3039, 2957, 2857,1561,1435,1378,1265,1096,1043, 813, 778, 704, 635, 530.
HRMS (ESI): m/z calc. for C29H32PRuþ [M-Cl]þ 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 C27H28OPRuþ [M-Cl]þ 501.0915; found 501.0923.
Major: 1H NMR (CDCl3, 400 MHz): d 8.32 (dd, J ¼ 7.0, 1.1 Hz, 1H, aromatic), 7.89e7.83 (m, 1H, aromatic), 7.75e7.32 (m, 9H, aromatic), 5.96 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.94 (d, J ¼ 6.4 Hz, 1H, h6-

C6H4), 5.49 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.12 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 3.47 (d, J ¼ 10.8 Hz, 3H, MeO), 2.45 (m, 1H, CHMe2), 1.96 (s, 3H, Me), 1.13 (d, J ¼ 7.1 Hz, 3H, CHMe2), 0.96 (d, J ¼ 7.2 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 162.6.

Minor: 1H NMR (CDCl3, 400 MHz): d 8.29 (dd, J ¼ 7.0, 1.0 Hz, 1H, aromatic), 7.89e7.83 (m, 1H, aromatic), 7.75e7.32 (m, 9H, aromatic), 5.86 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.74 (d, J ¼ 6.0 Hz, 1H, h6-C6H4), 4.83 (d, J ¼ 6.8 Hz, 1H, h6-C6H4), 4.05 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 3.76 (d, J ¼ 11.6 Hz, 3H, MeO), 2.45 (m, 1H, CHMe2), 1.72 (s, 3H, Me), 1.10 (d, J ¼ 7.2 Hz, 3H, CHMe2), 1.01 (d, J ¼ 6.8 Hz, 3H CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 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 C31H30PRuþ [M-Cl]þ 535.1123; found 535.1132.

Major: 1H NMR (CDCl3, 400 MHz): d 8.71 (d, J ¼ 8.3 Hz, 1H, aromatic), 8.40 (d, J ¼ 7.2, 1H, aromatic), 8.26, (m,1H, aromatic), 7.80e7.30 (m, 10H, aromatic), 5.71 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.53 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.77 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 4.13 (d, J ¼ 6 Hz, 1H, h6-C6H4), 2.40e2.50 (m, 1H, CHMe2), 2.22 (d, J ¼ 10.8 Hz, 3H, MeP), 1.73 (s, 3H, Me), 1.08 (d, J ¼ 7.2 Hz, 3H, CHMe2), 0.86 (d, J ¼ 6.8. Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 56.4.

Minor: 1H NMR (CDCl3, 400 MHz): d 8.69 (d, J ¼ 8.2 Hz, 1H, aromatic), 8.38 (d, J ¼ 7.2, 1H, aromatic), 8.26, (m,1H, aromatic), 7.80e7.30 (m,10H, aromatic), 5.97 (d, J ¼ 6 Hz, 2H, h6-C6H4), 5.20 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.06 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 2.40e2.50 (m, 1H, CHMe2), 2.25 (d, J ¼ 9.6 Hz, 3H, MeP), 1.87 (s, 3H, Me), 0.96 (d, J ¼ 6.8. Hz, 3H, CHMe2), 0.83 (d, J ¼ 6.8 Hz, 3H, CHMe2).

13C-{1H} NMR (CDCl3, 101 MHz): selected phenyl carbon signals, major and minor derivatives d ¼ 172.15 (d, J ¼ 14.0 Hz), 145.75 (d, J ¼ 36.3 Hz), 141.38, 130.26 (d, J ¼ 9.1 Hz), 129.87 (d, J ¼ 2.5 Hz), 127.41 (d, J ¼ 25.9 Hz), 125.95, 123.25, 116.68; h6-C6H4 carbon signals d ¼ 108.5 (s, major), 107.1 (s, minor), 99.4 (s, minor), 98.3 (s, major), 95.6 (d, J ¼ 5.6 Hz, major), 94.8 (d, J ¼ 4.8 Hz, minor), 93.2 (d, J ¼ 4.4 Hz, minor), 92.2 (d, J ¼ 3.6 Hz, major), 90.9 (d, J ¼ 5.9 Hz, major), 87.9 (d, J ¼ 4.9 Hz, minor), 87.6 (d, J ¼ 4.4 Hz, minor), 87.0 (d, J ¼ 3.8 Hz, major); alkyl carbon signals d ¼ 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 ¼ 32.2, minor), 18.5 (minor), 18.4 (major), 13.6 (d, J ¼ 32.0, major).

31P-{1H} NMR (CDCl3, 162 MHz): d 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 C31H30OPRuþ [M-Cl]þ 551.1072; found 551.1057.

Major: 1H NMR (CDCl3, 400 MHz): d 8.72 (m, 1H, aromatic), 8.62 (d, J ¼ 7.2 Hz, 1H, aromatic), 8.29 (m, 1H, aromatic), 7.85e7.40 (m, 10H, aromatic), 5.93 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.54 (d, J ¼ 6.0 Hz, 1H, h6-C6H4), 5.47 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 4.22 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 3.60 (d, J ¼ 11.2 Hz, 3H, MeO), 2.38 (sept., J ¼ 14, 1H, CHMe2), 1.68 (s, 3H, Me), 1.22 (d, J ¼ 7.2 Hz, 3H, CHMe2), 1.07 (d, J ¼ 6.8 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 158.2.

Minor: 1H NMR (CDCl3, 400 MHz): d 8.72 (m, 1H, aromatic), 8.58 (d, J ¼ 7.2 Hz, 1H, aromatic), 8.29 (m, 1H, aromatic), 7.85e7.40 (m, 10H, aromatic), 6.10 (d, J ¼ 5.2 Hz, 1H, h6-C6H4), 6.0 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.86 (d, J ¼ 5.6 Hz, 1H, h6-C6H4), 5.02 (d, J ¼ 5.2 Hz, 1H, h6-C6H4), 3.61 (d, J ¼ 11.2 Hz, 3H, MeO), 2.46 (sept., J ¼ 14, 1H, minor), 2.38 (sept., J ¼ 14, 1H, CHMe2), 1.93 (s, 3H, Me), 1.24 (d, J ¼ 6.8 Hz, 3H, CHMe2), 0.87 (d, J ¼ 6.8 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 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 C33H30PRuþ [M-Cl]þ 559.1123; found 559.1133.

Major: 1H NMR (CDCl3, 400 MHz): d 8.91 (s, 1H, aromatic), 8.20e7.30 (m, 12H, aromatic), 6.12 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.68 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.87 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.14 (d, J ¼ 6 Hz, 1H, h6-C6H4), 2.55 (sept., J ¼ 6.8 Hz, 1H, CHMe2), 2.29 (d, J ¼ 10.8 Hz, 3H, MeP), 1.80 (s, 3H, Me), 1.13 (d, J ¼ 6.8 Hz, 3H, CHMe2), 0.87 (d, J ¼ 6.8. Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 56.7.

Minor: 1H NMR (CDCl3, 400 MHz): d 8.89 (1H, aromatic), 8.20e7.30 (m, 12H, aromatic), 5.87 (d, J ¼ 6.4 Hz, 2H, h6-C6H4), 5.25 (d, J ¼ 6 Hz, 1H, h6-C6H4), 5.16 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 2.55 (sept., J ¼ 6.8 Hz, 1H, CHMe2), 2.29 (d, J ¼ 10.8 Hz, 3H, MeP), 1.94 (s, 3H, Me), 0.99 (d, J ¼ 6.8. Hz, 3H, CHMe2), 0.79 (d, J ¼ 6.8 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 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 C33H30OPRuþ [M-Cl]þ 575.1072; found 575.1077.Major: 1H NMR (CDCl3, 400 MHz): d 9.25 (s, 1H, aromatic), 8.13 (dd, J ¼ 6.9, 1.8 Hz, 1H, aromatic), 7.70e6.80 (m, 11H, aromatic), 5.74 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.58 (d, J ¼ 5.6 Hz, 1H, h6-C6H4), 5.14 (d, J ¼ 6 Hz, 1H, h6-C6H4), 3.62 (d, J ¼ 6.0 Hz, 1H, h6-C6H4), 3.27 (d, J ¼ 11.2 Hz, 3H, POMe), 2.43 (m, 1H, CHMe2), 1.61 (s, 3H, Me), 0.87 (d, J ¼ 7.2 Hz, 3H, CHMe2), 0.51 (d, J ¼ 6.8 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 158.4.

Minor: 1H NMR (CDCl3, 400 MHz): d 9.16 (s, 1H, aromatic), 8.08 (dd, J ¼ 7.1, 1.6 Hz, 1H, aromatic) 7.70e6.80 (m, 11H, aromatic), 5.90 (d, J ¼ 6.8 Hz, 1H, h6-C6H4), 5.83 (d, J ¼ 6.4 Hz, 1H, h6-C6H4), 5.40 (d, J ¼ 6 Hz, 1H, h6-C6H4), 4.52 (d, J ¼ 6.0 Hz, 1H, h6-C6H4), 3.27 (d, J ¼ 11.2 Hz, 3H, major), 2.84 (d, J ¼ 11.2 Hz, 3H, POMe), 2.43 (m, 1H, CHMe2), 1.86 (s, 3H, Me), 0.70 (d, J ¼ 7.2 Hz, 3H, CHMe2), 0.49 (d, J ¼ 6.8 Hz, 3H, CHMe2).

31P-{1H} NMR (CDCl3, 162 MHz): d 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 (l ¼ 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 1907310e1907312 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 100mL 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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576

577 **Legends to figures**

578 **Chart 1.** P-stereogenic phosphines**.**

579

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

581

582 **Fig. 1. Left:** Ball and stick representation of C1′ showing the labelling scheme; hydrogen atoms have
583 been omitted for clarity. Selected bond lengths [Å] and angles [ ]: Ru(1)eP(1) 2.3640(6), Ru(1)eCl(1)
584 2.4103(6), Ru(1)eCl(2) 2.4180(6), P(1)eC(1) 1.829(2); Ru(1)eP(1)eC(1) 111.13(7); P(1)-C(14) 1.820(2).

585

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

587

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

589

590 **Figure.2** NMR aromatic proton signals of h6-C6H4 fragment (d ¼ 6.4e3.8) of C6 and singlet at d ¼
591 5.30 corresponding to dichloromethane.

592

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

595

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

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605 **CHART 1**

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607

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

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610 **SCHEME 1**

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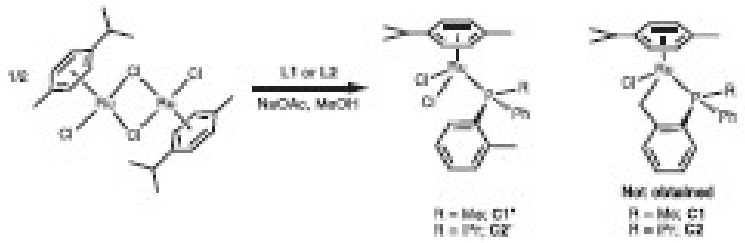
612



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615 **FIGURE 1**

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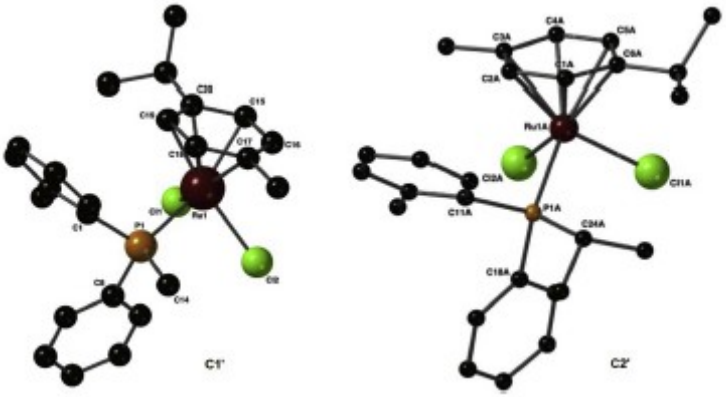

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621 **SCHEME 2**

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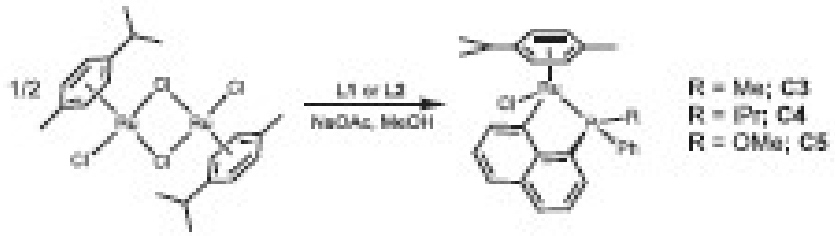

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626 **SCHEME 3**

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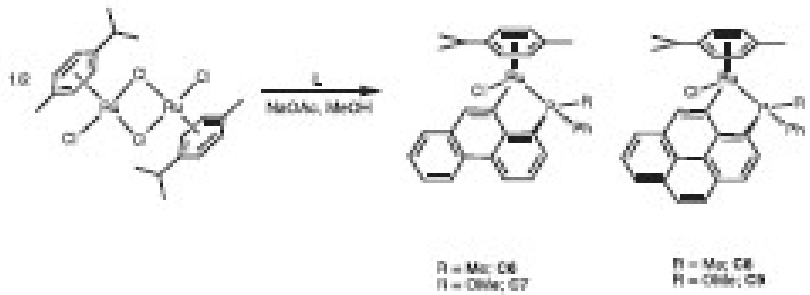
628



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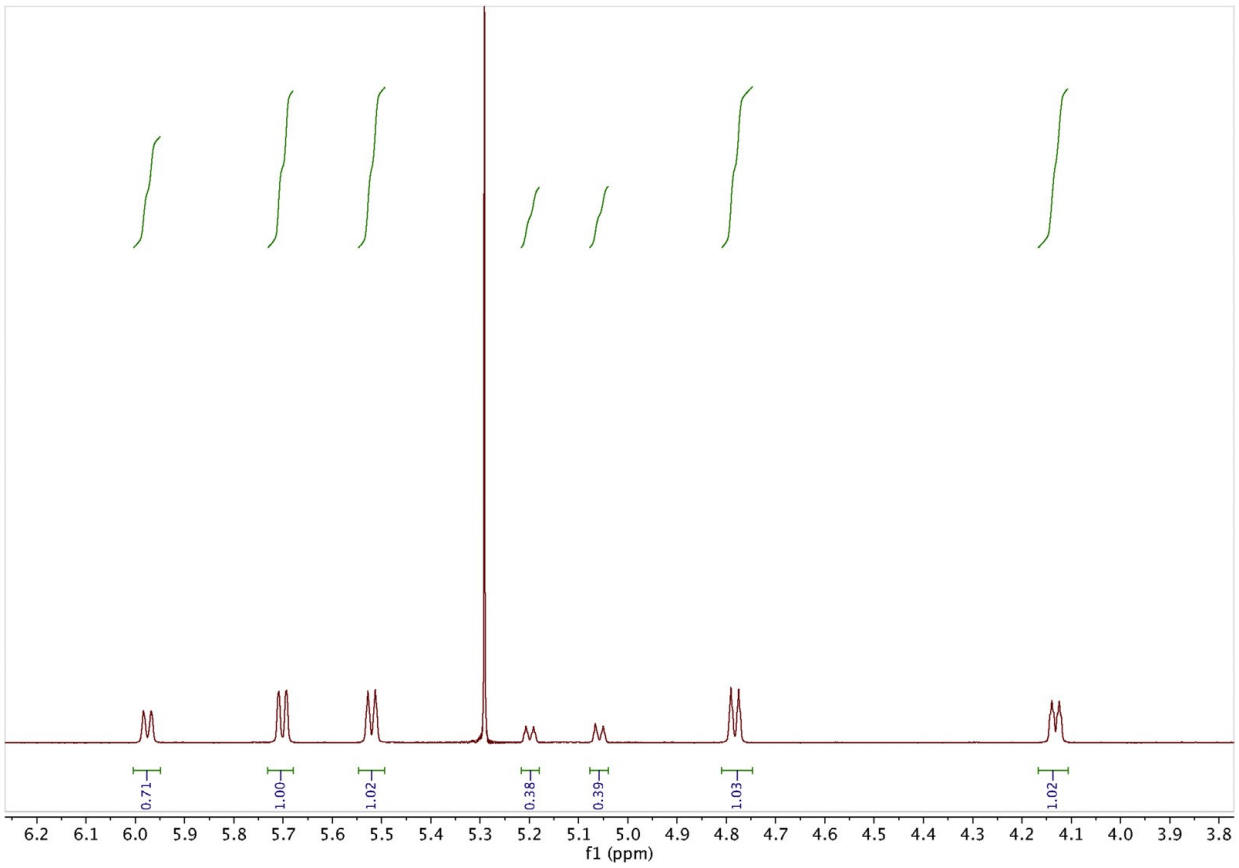
630

631 **FIGURE 2**

632

633



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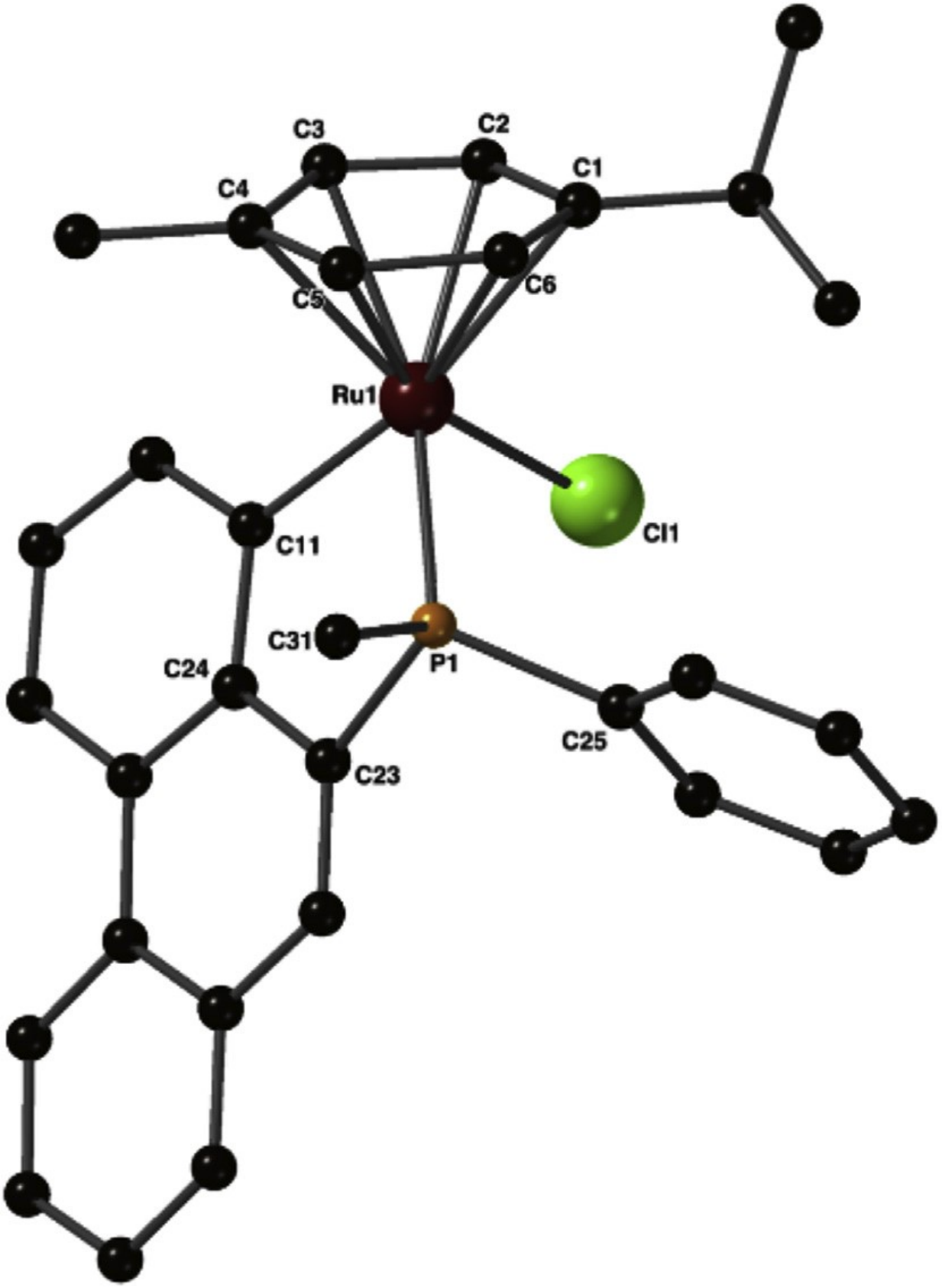
635

636 **FIGURE 3**

637



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639

SCHEME 4

645 **Table 1** Catalytic results in the asymmetric hydrogenation

646

Entry	Precursor	Conversion (%) at 1/3/5/7 h	ee(%) 5 h
1	C1[a]	23/86/94/>99	7
2	C2[a]	13/27/39/50	16
3	C3	25/54/70/76	<5
4	C4	48/83/96/>99	<5
5	C5	70/89/>99/>99	<5
6	C6	20/68/93/73	8
7	C8	8/27/40/53	5
8	C3[a]	<5/20/50/75	<5
9	C4[a]	10/52/75/85	13
10	C5[a]	5/22/35/45	<5
11	C8[a]	<5/9/50/80	5
12	C8[a]	8/24/39/-	6 (24 h)

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