Ruthenium complexes of P-stereogenic phosphines with a heterocyclic substituent†

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ABSTRACT:

The synthesis via phosphine-boranes of 13 new optically pure P-stereogenic diarylphosphines P(Het)PhR (Het = 4-dibenzofuranyl (DBF), 4-dibenzothiophenyl (DBT), 4-dibenzothiophenyl-S,S-dioxide (DBTO2) and 1-thianthrenyl (TA); R = OMe, Me, i-Pr, Fc (ferrocenyl)) following the Jugé–Stephan method is described. The ligands were designed with the aim of having a heteroatom in a position capable of interacting with a metal upon coordination. The ligands and their precursors have been fully characterised, including the determination of two crystal structures of phosphine-boranes. Ru neutral complexes of the type [RuCl2(η6-arene)(κP-P)] (arene = p-cymene and methyl benzoate) have been prepared and characterised, including three crystal structure determinations. Treatment of solutions of the complexes with TlPF6 allowed the preparation of well-defined cationic complexes [RuCl(η6-arene)(κ2P,S-P)]PF6 for DBTand TA-based phosphines. The complexes possess a stereogenic Ru atom and in most of the cases they are present as a single isomer in solution. All the Ru complexes have been used in the asymmetric transfer hydrogenation of acetophenone in refluxing 2-propanol, with good activities and up to 70% ee.

INTRODUCITON

The preparation of optically pure P-stereogenic compounds is still a considerable challenge despite their long history, stretching for more than a century,[1,2] and their importance as ligands for transition metal-based homogeneous catalysis.[3–5] The lack of generality of most of the known synthetic methods and the long and tedious steps required to prepare such compounds can be blamed for the sluggish development of this area. This makes that even today the preparation of new ligands of this kind can be considered a valuable achievement. During the last twenty years, however, several very promising advances have been made,[4] which have allowed the synthesis of new families of ligands with superior performance in Rhcatalysed hydrogenation and other reactions, and the pace of these advances has been increasing lately.[6–17] At present, most of the ligands of this kind are prepared using phosphineboranes[18–20] as intermediates and by asymmetric synthesis methods relying on chiral auxiliaries. Two of the most important routes are that developed by Jugé, Stephan and coworkers[21,22] furnishing diarylphosphines and that firstly devised by Evans and coworkers[23] and much expanded by Imamoto and coworkers[24,25] to give trialkylphosphines. Both methods are based on phosphine-boranes and employ organolithium reagents as nucleophiles or bases in at least one step.

Joining these efforts, we have described several kinds of P-stereogenic monophosphines, initially prepared by resolution of the racemic ligands[26–28] and more recently by the Jugé–Stephan[29–35] or Evans[32,36,37] method. They were initially employed in Pd-catalysed hydrovinylation[29,32,34] and later in allylic substitution reactions[31,34] and Ru-catalysed cyclopropanation[33] and transfer hydrogenation[33–35,37] reactions.

We reasoned that it would be interesting to design families of new P-stereogenic monophosphines containing heteroatoms adequately located in the ligand in order to interact with the metal with a coordination bond or by a weaker secondary (hemilabile) interaction and study their performance in catalysis. With these ideas in mind, a recent paper by Hayes and coworkers[38] describing the synthesis of P-stereogenic monophosphinimine ligands for Zn-catalysed ring-opening polymerisation of lactide caught our attention. In this paper the synthesis of P(4-dibenzofuranyl) MePh was described, albeit in the racemic form. This phosphine was prepared using 4-lithiodibenzofuran,[39] easily prepared by direct o-lithiation of dibenzofuran (Scheme 1).

This ligand has the heteroatom at the γ position with respect to the P atom, a feature that would create a favoured 5-membered ring upon interaction with a transition metal. Therefore, we started a study aiming to prepare P-stereogenic phosphines bearing a heterocyclic substituent with the following requirements: (i) the ligands should have the heteroatom of the heterocycle at the γ or δ position relative to the phosphorus atom, (ii) the heterocycle should be selectively lithiated at the β position, so it can be installed at the P atom by the Jugé–Stephan method and (iii) the heterocycle should be commercially available. After analysis of the literature, we concluded that dibenzofuran (DBF), dibenzothiophene (DBT) and thianthrene (TA) met these requirements (Scheme 2).

The number of monophosphorus ligands or precursors bearing any of these substituents is very limited. With DBF, Haenel and coworkers39 first reported the preparation of 4-diphenylphosphinodibenzofuran in the course of their studies on lithiation of DBF and DBT. Much more recently several 4-diphenylphosphinodibenzofuran oxides, substituted with different moieties at the dibenzofuran fragment, have been reported because they have interesting photochemical applications.40–43 Wills and coworkers44,45 prepared 4-bis(dimethylamino) phosphinodibenzofuran and condensed it at high temperature with a chiral diamine to obtain an optically pure diazaphospholidine, a ligand that was used in Pd-catalysed allylic substitution reactions. This is the only reported example of an optically pure monophosphorus ligand based on the DBF skeleton. Finally, Hayes and coworkers38 recently reported the synthesis of racemic (4-dibenzofuranyl)methylphenylphosphine as mentioned before, by deprotection of its phosphine-borane, previously obtained by reaction of methyllithium with (4-dibenzofuranyl)methylphenylphosphineborane. With DBT, Rauchfuss, Rheingold and coworkers46 reported the synthesis of 4-diphenylphosphino- and 4-di(p-tolyl)phosphinodibenzothiophene and some derived Ru complexes. The crystal structures of the former phosphine and a derived Fe complex were also described a few years later.47 4-Diphenylphosphinodibenzothiophene was also reported by Haenel and coworkers soon afterwards.39 The only optically pure monophosphorus ligand precursor with the DBT moiety was reported by Fiaud and coworkers,48 who attached an enantiomerically pure 2,5-diphenylphospholane oxide moiety to the 4 position of DBT by Pd-catalysed C–P bond formation. Finally, no phosphines with the TA substituents have been described to the best of our knowledge. In addition, there are no examples of optically pure P-stereogenic phosphines bearing any of those heterocyclic substituents.

In this paper we describe the synthesis of a series of new P-stereogenic phosphine-boranes containing a DBF, DBT or TA substituent employing the Jugé–Stephan method, the preparation of several types of complexes containing [Ru(η6-arene)] moieties and their application as precatalysts in the asymmetric transfer hydrogenation of acetophenone.

RESULTS AND DISCUSSION

Ligand synthesis

The desired ligands were designed to be obtainable by the Jugé–Stephan method,21,22 in which the groups are sequentially introduced at the phosphorus atom via organolithium reagents. Therefore, following slightly modified literature procedures, the selective monometallation of DBF,38 DBT49 and TA50 was successfully accomplished by ortholithiation with n-butyllithium under different conditions (Scheme 3).

The solutions of the organolithiums were reacted with Jugé–Stephan's oxazaphospholidine-borane 1 at low temperature giving aminophosphine-boranes 2-Het in good yields as white solids (Scheme 4).

The acidic methanolysis of 2-Het proceeded smoothly, affording phosphinite-boranes 3-Het as pure pasty solids or oils after column chromatography purification. Treatment of these compounds with an excess of RLi (R = Me, i-Pr, t-Bu and Fc) at low temperatures was carried out to obtain a series of phosphine-boranes as resins or oils. It is known that this step is very sensitive to the bulkiness of the incoming organolithium reagent.29,51 Therefore, it is not surprising that in the case of methyllithium the reactions were successful for all the substrates, giving the methylphosphine-boranes 4-Het-Me in good yields. Isopropyllithium reacted well with 3-DBF and 3-DBT giving the desired 4-Het-iPr phosphine-boranes but reaction with 3-TA at −30 °C produced a compound containing two isopropyl groups. According to 1H and 13C NMR spectroscopy, one of them was bound to the P atom whereas the other was not. No further aliphatic hydrogen or carbon atoms could be detected. Addition of less than one equivalent of isopropyllithium led to the same product with two isopropyl groups along with incomplete conversion of the starting phosphinite-borane 3-TA. This fact indicates that isopropyllithium is not able to directly attack the phosphorus atom, so it probably reacts first with the thianthrene ring and opens it, releasing steric encumbrance at the P atom and allowing a rapid attack of a second equivalent of isopropyllithium. Although NMR suggested that only a single diastereomerically pure product was formed, we have been unable to clarify either its identity or its optical purity. Interestingly, the addition of isopropyllithium to a diethyl ether solution of thianthrene at −30 °C did not lead to any opened product but to the full recovery of unchanged thianthrene. Reaction of 3-Het with monolithiated ferrocene worked well for Het = DBF and DBT but not for TA, since unchanged 3-TA was isolated after workup.

The introduction of the t-Bu group is (usually)51,52 impossible using the Jugé–Stephan method due to steric reasons.29 In line with this finding, reaction of 3-DBT and 3-TA with t-BuLi was unsuccessful since complex mixtures of products were obtained according to 31P NMR spectroscopy. In contrast, under carefully controlled conditions, 3-DBF reacted with t-BuLi to afford the phosphine 4-DBF-tBu, which could be isolated as an oil in 60% yield. It is possible that the hard oxygen atom of DBF assists the nucleophilic attack of t-BuLi by coordination of the Li cation.52 To take advantage of this reactivity, the triarylphosphine-borane 4-DBF-DBT was successfully prepared by reaction of 3-DBF with DBTLi.

A peculiarity of this phosphine is that it suffers partial spontaneous deboronation and therefore the work-up had to be carried out under a nitrogen atmosphere to minimise the oxidation of the free phosphine. Due to this fact, the phosphine-borane was not isolated but fully deprotected with morpholine (see later) to yield the completely free phosphine, which was subsequently coordinated to ruthenium.

All the intermediates have been fully characterised by the usual techniques and the details can be found in the Experimental section. Phosphine-boranes 4-DBF-Fc and 4-DBT-Fc were also characterised in the solid state by determination of their X-ray crystal structures (Fig. 1).

The crystals contain discrete molecules having the expected S absolute configuration at the P atom. The distances and angles are in the range expected for similar compounds29,35,53 and are very similar for both structures. The only noticeable differences between the two structures are in the parameters around the heteroatom: for DBF, the two O–C distances are much shorter compared to the two S–C distances in DBT and the angle C–O–C is much wider than the angle C–S–C in DBT. In both structures, the heterocyclic substituent is essentially planar and the two Cp rings of the ferrocene are almost eclipsed, as observed in other ferrocenylphosphineboranes. 32,54,55

It is well known that the sulfur atoms of DBT and TA can be oxidised to sulfoxides (SO)50,56–60 or sulfones (SO2).56,57,60–68 For this reason it was considered worth exploring the oxidation of the ligands containing these heterocycles because the sulfoxy group of the new ligands could interact with the metal during catalysis. Phosphine-borane 4-DBT-Me was therefore treated with a variety of oxidants such as MCPBA,58 H2O2/ HAcO,60,64–67 and CrO3/H5IO6 (Scheme 5).63

With the treatment with MCPBA and H2O2/HAcO it was found that partial deprotection and oxidation of the P atom of the phosphine as well as formation of byproducts had taken place according to 31P NMR spectroscopy. In contrast, with CrO3/H5IO6 in acetonitrile63 a single product corresponding to the complete deprotection and oxidation, namely the trioxide 4-DBTO3-Me, could be isolated. It seems therefore that the borane protecting group cannot withstand the strongly oxidant conditions of the reaction. It was then reasoned that if oxidation of DBT was not possible once installed at the P atom, maybe the DBTO2 fragment could be introduced in the first step of the Jugé–Stephan method. To this end, DBT was oxidised with hydrogen peroxide66,67 and lithiated with n-BuLi (Scheme 6).

The lithiation of DBTO2 has not been reported. After a series of experiments it was found that the best conditions consisted of adding n-BuLi to a solution of DBTO2 precooled at −78 °C, removing the cold bath immediately and stirring the mixture for 3 h at room temperature. Even under these conditions, however, the lithiation was incomplete and not always reproducible. Despite the rather unsatisfactory lithiation, it allowed the introduction of the oxidised heterocycle at the P atom and following the standard method compounds 2-DBTO2 and 3-DBTO2 could be prepared. The latter compound was treated with an excess of MeLi under usual conditions but did not give the expected 4-DBTO2-Me but dimethylphenylphosphine- borane.69,70 It is possible that the strongly electron-withdrawing sulfone group weakens the P–C bond to such an extent that it can be cleaved by methyllithium even at low

temperature.71 Therefore no other phosphines with DBTO2 were prepared. Finally, the obtained phosphine-boranes were deprotected with morpholine under standard conditions29,53 to give the free phosphinites and phosphines L1–13 (Scheme 7).

The free phosphines were all air-sensitive, especially the t-Bu-containing ligand L7 and hence after deprotection the 13 ligands were immediately coordinated to Ru moieties.

Ru complexes

Neutral complexes. The ligands were used to obtain the ruthenium neutral complexes of the type [RuCl2(η6-arene)(P)], with the arene being p-cymene or methyl benzoate (Scheme 8).34,35

The complexes were easily prepared by splitting the usually employed ruthenium p-cymene dimer (D1) and for some of the ligands the much lesser used35 ruthenium methyl benzoate dimer (D2), in dichloromethane at room temperature as previously reported for analogous compounds.35 The products were obtained as red or brown solids that were characterised by IR, chemical microanalysis or MS and by multinuclear NMR in solution. The data confirmed the identity of the proposed structures and the purity of the products. Hence, single 31P resonances were found for all the complexes and due to the chirality of the phosphorus ligand, all the H and C atoms were potentially different. Accordingly, apart from the peaks corresponding to the phosphorus ligand, 4 distinct H (4.0–6.5 ppm region) and 6 C (80–110 ppm) peaks appeared, respectively, in the 1H and 13C{1H} NMR spectra of the p-cymene complexes whereas 5 H resonances could be found for the methyl benzoate complexes. As expected, the latter complexes also featured a singlet at approximately 3.9 ppm in the 1H NMR spectra, corresponding to the COOMe group. Unexpectedly, for most of the methyl benzoate complexes a pair of peaks around 53 ppm and another pair around 167 ppm can be seen in the 13C{1H} NMR spectra, corresponding to the methylic and carbonylic carbon atoms of the COOMe group. The observation of the two peaks is probably due to the presence of the two rotamers represented in Scheme 9 in the solution.

Finally, a sharp band in the IR spectra of methyl benzoate complexes close to 1728 cm−1 confirms the presence of the carbonyl of the ester group. The complex Ru7 could not be obtained satisfactorily since an extremely broad 31P{1H} NMR spectrum resulted and multiple peaks in the 1H NMR spectrum could be observed. This can be due to the bulkiness of L7 precluding efficient coordination to the Ru unit.

Single crystals, suitable for X-ray crystallography, could be obtained for complexes Ru5, Ru6 and Ru10 by slow diffusion of hexane into saturated solutions of the complexes in dichloromethane. The representation of their molecular structures is given in Fig. 2.

All the complexes adopt the typical pseudotetrahedral, “three-legged piano stool” geometry, with the Ru atom located in the centre of a distorted octahedron. The structures allow the confirmation of the expected absolute configurations of the P atoms (S for the free ligands). The crystals of complex Ru5 contain two molecules in the unit cell, whose main difference is that the p-cymene is rotated 180°

around the Ru–arene central axis. The most relevant metric parameters of the structures are given in Table 1.

As commonly found for this type of compound, the η6-coordinated p-cymene ring is located in such a way that the imaginary line defined by the two Cl atoms is approximately parallel to the line passing through the substituted C atoms of the p-cymene group. It can also be seen that the heterocyclic substituent is almost completely flat. In general, the distances and angles are in the range expected for previously reported similar compounds.33,34,37,72,73

Cationic complexes

Neutral p-cymene Ru complexes were treated with thallium hexafluorophosphate (or tetrafluoroborate in the case of Ru10) in order to abstract the chloride ligand and force the coordination of the heteroatom of the heterocycle to the metal (Scheme 10).74–76

Treatment of dichloromethane solutions of complexes Ru1 (δP,Ru1 = +112.7 ppm) and Ru6 (δP,Ru6 = +21.5 ppm), bearing a phosphine with the DBF group, with TlPF6 caused a rapid precipitation of TlCl that was filtered, the solvent removed and the crude product analysed by NMR. In both experiments, a singlet at +113.8 and +24.0 ppm respectively in the 31P{1H} spectra of the isolated product was observed. Since the values are almost unchanged from Ru1 and Ru6, it can be concluded that the desired complex with a five-membered chelate ring with the κ2P,O-coordinated phosphine did not form because a large downfield shift would be expected.77 1H NMR spectra, however, revealed that the products were not the starting complexes and that they contained the p-cymene and the phosphine moieties in a 1 : 1 ratio. They could correspond to dimeric species although their constitution was not further investigated. In the case of Ru4 (δP,Ru4 = 117.0 ppm), after treatment with TlPF6, 31P{1H} NMR showed that 30% of the starting material was still present but another species slightly shifted upfield (δP = 112.0 ppm) had also formed. This species could indeed correspond to the desired κ2P,O-chelate since it is known that the ring contribution to the 31P shift is small and negative in six-membered rings.77 Despite this, given that only partial conversion could be achieved, its synthesis was not pursued further.

In contrast to the unsuccessful coordination of the O atom, the coordination of the S atom of the dibenzothiophenyl and thianthryl groups could be achieved, yielding cationic complexes Ru2′, Ru3′ and Ru9′-13′. A strong deshielding of the 31P signals (Δδ(Ru′–Ru) = 20–43 ppm) occurred upon formation of the 5-membered ring via coordination of the S atom, as expected.77 Similarly, in the 1H NMR the peaks of the H atoms of the coordinated arene ring shifted downfield approximately 1 ppm and in the 13C{1H} the six C resonances also shifted roughly 5 ppm downfield. These downfield shifts possibly reflect the decreased electron density of the η6-coordinated arene ring due to the presence of a positive charge compared to the neutral Ru complexes. The identity of the complexes was also verified by elemental analyses or high resolution mass spectrometry as detailed in the Experimental section. The complex Ru11*′, bearing the methyl benzoate as coordinated arene, was also obtained by treating Ru11* with thallium hexafluorophosphate.

An interesting aspect of the cationic Ru complexes described here is the possible formation of two diastereomeric complexes due to the presence of a stereogenic Ru atom (Scheme 10). NMR analysis showed a single 31P signal and a unique set of C and H signals for complexes Ru2′, Ru3′, Ru11′ and Ru11*′, suggesting that they are present as an optically pure species. In contrast, the two isomers could be detected for the rest of the complexes, since two 31P peaks and two sets of C and H signals were found as detailed in the Experimental section. The ratio between isomers was approximately 1 : 4 for complexes Ru9′ and Ru10′ and 1 : 2 for Ru12′ and Ru13′. It seems that there is no simple correlation between the structure of the ligand and the isomeric ratio. Despite many attempts we were unable to obtain crystals suitable to perform X-ray diffraction studies of any of the complexes in order to ascertain the absolute configuration of the main isomer.

Ru-catalysed transfer hydrogenation

The reduction of ketones to alcohols is an extremely important transformation in organic chemistry that can be catalytically performed by hydrogenation using hydrogen gas, or in a safer way, by transfer hydrogenation, using a hydrogen donor.78,79 The latter reaction has been studied with a large number of soluble Ru(II) systems, very often chiral, to obtain enantioenriched alcohols.80–82 The model substrate for the asymmetric transfer hydrogenation is acetophenone and the typical conditions involve carrying out the reaction in refluxing 2-propanol in the presence of a base (Scheme 11).

Although not the most typical precursors, Ru complexes of the type [RuCl2(η6-arene)(P)] are easy to prepare and they are active in the reaction, as shown by us33–35,37 and other groups.74,83–86 The enantioselectivities of our systems with P-stereogenic phosphines are, however, rather low (up to 50% ee),33,35,37 so the performance of neutral and cationic Ru complexes with the new heterocyclic phosphines was studied (Table 2).

The precursors were activated for 15 min in the presence of t-BuOK before the addition of acetophenone to form the catalytically active ruthenium–hydride species.87 All were active in the reaction, resulting in full conversion at 24 h. At shorter reaction times, however, notable differences in activity can be seen depending on the structure of the precursor. In most of the cases, neutral κP-coordinated complexes lead to more active precursors compared to cationic κ2P,S-coordinated counterparts (cf. for example entries 15 and 17 or 21 and 23). The complexes with methyl benzoate give more active systems than those with p-cymene (cf. for example entries 8 and 9 or 15 and 16), in line with previously published results for similar systems.35 These findings suggest that η6-arene decoordination or slippage (hapticity reduction) probably occurs during the catalytic cycle. Such a process is easier for electron poor methyl benzoate complexes compared to p-cymene analogues and also for neutral complexes compared to cationic counterparts.

Finally, the enantioselection is very low for most of the precursors, as usually found with similar monophosphorus ligands.33,35 The precursors with L11 (entries 15–18) are moderately enantioselective, except Ru11′ (entry 17). Interestingly, the same value of 70% ee was obtained with

complexes Ru11* and Ru11*′ (entries 16 and 18 respectively), pointing to the formation of a common intermediate under catalytic conditions. It is worth noting that Ru11 and Ru11* both form single cationic species in solution, a fact that could be beneficial for the enantioselectivity.

CONCLUSIONS

In this paper the Jugé–Stephan method has allowed the preparation of 13 optically pure P-stereogenic diaryl monophosphinites and monophosphines of the type PPh(Het)R (Het = 4-DBF, 4-DBT, 1-TA and 4-DBTO2; R = OMe, Me, i-Pr, t-Bu, Fc) by direct lithiation of the heterocycle. The ligands are a valuable addition to the small number of optically pure P-stereogenic ligands with a heterocyclic substituent.

The ligands had been designed with the idea of introducing the heteroatom (A) at a position capable of interacting with the ruthenium centre via the formation of a favoured five-membered κ2P,A-chelate. This coordination has been achieved for DBT- and TA-containing phosphines but not for the DBFbased ligands. This is possibly due to the hard character of the oxygen atom, showing less tendency to coordinate to the Ru atom compared to sulfur. An important stereoselection in the formation of the stereogenic Ru atom has been observed for most of the ligands.

The obtained complexes have been used in catalytic transfer hydrogenation of acetophenone with the aim of comparing the performance of the new ligands with previously reported systems based in P-stereogenic PArPhR ligands (Ar = polycyclic aromatic group).33–35,37,87 It has been found that the activities are similar to some of the previous generation precursors but one of the ligands, L11, gives a considerably higher enantioselectivity.

EXPERIMENTAL SECTION

General data

All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified using a solvent purification system or by standard procedures88 and kept under nitrogen. 1H, 13C{1H}, and 31P{1H} and HSQC 1H-13C NMR spectra were recorded using 300 and 400 MHz spectrometers using CDCl3 as a solvent unless otherwise specified. Chemical shifts are reported downfield from standards. The protons of BH3 of the phosphine-boranes group appeared in the aliphatic region of the spectra as very broad bands and have not been assigned. IR spectra were recorded in KBr and the main absorption bands are expressed in cm−1. High-resolution mass analyses (HRMS) were carried out on a time-of-flight instrument using electrospray ionisation. Optical rotations were measured at rt using a sodium lamp at the sodium D-line wavelength (589.592 nm). For all the determinations, the solvent was CH2Cl2 and the concentration was 1 g per 100 mL. Transfer hydrogenation reactions were analysed by GC with He as a carrier gas. Oxazaphospholidine-borane 1 (prepared from (1R,2S)-(−)-ephedrine),21 dibenzothiophene dioxide,66,67 and Ru dimer D289 were prepared using literature procedures whereas other reagents were used as received from commercial suppliers.

SYNTHESIS OF THE LIGANDS

2-DBF, (1R,2S)-2-{[(S)-(4-dibenzofuranyl)phenylphosphanyl] methylamino}-1-phenylpropan-1-ol-borane. Dibenzofuran (1.85 g, 11.0 mmol) was dissolved in 30 mL of THF in a Schlenk flask. The solution was cooled to −78 °C and then 1.6 M n-BuLi solution in hexanes (6.9 mL, 11.0 mmol) was added using a syringe. The resulting brown solution was removed from the cold bath, left stirring for 30 min at room temperature and then recooled to −78 °C. At the same time oxazaphospholidine-borane 1 (2.85 g, 10.0 mmol) was dissolved in 40 mL of THF and the solution was cooled down to −78 °C. The content of the first flask was slowly transferred to the second Schlenk flask via cannula and the resulting mixture was stirred for 14 h. Around 30 mL of water were added to the orange solution and THF was evaporated. The dark-brown residue was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with water and dried with anhydrous sodium sulfate. The suspension was filtered and the solvents were evaporated to dryness, leaving a yellowish pasty solid that was purified by column chromatography (flash SiO2, from 95 : 5 to 80 : 20 of hexane/ethyl acetate). The title product was obtained as a whitish solid. Yield: 3.52 g (77%).

1H NMR (300 MHz): 8.11 (dt, J = 7.8, 1.2, 1H), 7.96 (dm, J = 6.6, 1H), 7.78 (ddd, J = 12.3, 7.5, 1.2, 1H), 7.58 (dm, J = 8.1, 1H), 7.51–7.18 (m, Ar, 13H), 4.90 (d, 3JHH = 6.0, 1H), 4.45 (m, 1H), 2.63 (d, 3JHP = 8.1, 3H), 1.29 (d, 3JHH = 6.6, 3H). 13C{1H} NMR (101 MHz): 156.3–111.6 (C, CH, Ar), 78.6 (d, 3JCP = 6.2, CH), 58.2 (d, 2JCP = 11.0, CH), 30.9 (d, 2JCP = 4.4, CH3), 13.0 (s, CH3). 31P{1H} NMR (121 MHz): +67.5 (br, s). HRMS: calcd for C28H27NO2P ([M] + H − BH3), 440.1779; found, 440.1771. [α]D = +66.2°.

2-DBT, (1R,2S)-2-{[(S)-(4-dibenzothiophenyl)phenylphosphanyl] methylamino}-1-phenylpropan-1-ol-borane. Dibenzothiophene (2.03 g, 11.0 mmol) was dissolved in 30 mL of THF in a Schlenk flask. The solution was cooled to −78 °C and then 1.6 M n-BuLi solution in hexanes (6.9 mL, 11.0 mmol) was added using a syringe. The resulting brown solution was removed from the cold bath, left stirring at 0 °C for 5 h and recooled to −78 °C. At the same time oxazaphospholidineborane 1 (2.85 g, 10.0 mmol) was dissolved in 40 mL of THF and the solution was cooled down to −78 °C. The content of the first flask was slowly transferred to the second Schlenk flask via cannula and the resulting mixture was stirred for 14 h. Around 30 mL of water were added to the brownyellow solution and THF was evaporated. The white residue was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with water and dried with anhydrous sodium sulfate. The suspension was filtered and the solvents were evaporated to dryness, leaving a white pasty solid, which was purified by column chromatography (flash SiO2, from 95 : 5 to 80 : 20 of hexane/ethyl acetate). The title product was obtained as a white solid. Yield: 4.11 g (87%).

1H NMR (400 MHz): 8.29 (m, 1H), 8.18 (m, 1H), 7.84 (m, 1H), 7.73 (m, 1H), 7.58–7.42 (m, Ar, 9H), 7.34 (t, J = 7.6, 2H), 7.27 (t, J = 6.4, 1H), 4.96 (s, br, 1H), 4.47 (m, 1H), 2.75 (d, 3JHP = 7.6, 3H), 1.36

(d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 142.4–121.4 (C, CH, Ar), 78.9 (d, 3JCP = 2.7, CH), 58.5 (d, 2JCP = 10.4, CH), 31.6 (d, 2JCP = 4.3, CH3), 11.3 (d, 3JCP = 5.4, CH3). 31P{1H} NMR (121 MHz): +70.1 (br, s). HRMS: calcd for C28H27NOPS ([M] + H − BH3), 456.1551; found, 456.1540. [α]D = +52.2°.

2-TA, (1R,2S)-2-{[(S)-(1-thianthrenyl)phenylphosphanyl] methylamino}-1-phenylpropan-1-ol-borane. Thianthrene (600 mg, 2.8 mmol) was dissolved in 40 mL of THF in a Schlenk flask. The solution was cooled to −78 °C and then 1.6 M n-BuLi solution in hexanes (2.3 mL, 3.7 mmol) was added using a syringe. The resulting brown solution was allowed to reach room temperature and then was refluxed for 1 h, cooled to room temperature and then to −78 °C. At the same time oxazaphospholidine-borane 1 (720 mg, 2.5 mmol) was dissolved in 40 mL of THF and the solution was cooled down to −78 °C. The content of the first flask was slowly transferred to the second Schlenk flask via cannula and the resulting mixture was stirred for 14 h. Around 30 mL of water were added to the brown-yellow solution and THF was evaporated. The white residue was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with water and dried with anhydrous sodium sulfate. The suspension was filtered and the solvents were evaporated to dryness, leaving a white pasty solid, which was purified by column chromatography (flash SiO2, from 95 : 5 to 80 : 20 of hexane/ethyl acetate). The title product was obtained as a white solid. Yield: 1.15 g (91%).

1H NMR (400 MHz): 7.67 (dt, J = 7.6, 1.2, 1H), 7.52–7.43 (m, Ar, 7H), 7.39–7.27 (m, Ar, 6H), 7.22 (td, J = 7.6, 1.6, 1H), 7.15 (td, J = 7.6, 1.6, 1H), 7.02 (dd, J = 7.6, 1.6, 1H), 4.98 (d, J = 4.4, 1H), 4.45 (m, 1H), 2.63 (d, 3JHP = 7.2, 3H), 1.32 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 142.4–126.2 (C, CH, Ar), 79.0 (d, 3JCP = 2.8, CH), 58.4 (d, 2JCP = 10.7, CH), 31.4 (d, 2JCP = 4.1, CH3), 12.0 (d, 3JCP = 4.1, CH3). 31P{1H} NMR (162 MHz): +71.9 (br, s). HRMS: calcd for C28H27NOPS2 ([M] + H − BH3), 488.1272; found, 488.1267. [α]D = +40.4°.

2-DBTO2, (1R,2S)-2-{[(S)-(4-dibenzothiophenyldioxide)phenylphosphanyl] methylamino}-1-phenylpropan-1-ol-borane. Dibenzothiophene- S,S-dioxide (1.19 g, 5.5 mmol) was dissolved in 40 mL of THF in a Schlenk flask. The solution was cooled to −78 °C and then 1.6 M n-BuLi solution in hexanes (3.4 mL, 5.5 mmol) was added using a syringe. The resulting brown solution was removed from the cold bath, left stirring at room temperature for 3 h and recooled to −78 °C. At the same time oxazaphospholidine-borane 1 (1.43 g, 5.5 mmol) was dissolved in 35 mL of THF and the solution was cooled down to −78 °C. The content of the first flask was slowly transferred to the second Schlenk flask via cannula and the resulting mixture was stirred for 14 h. Around 30 mL of water were added to the brown-yellow solution and THF was evaporated. The white residue was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with water and dried with anhydrous sodium sulfate. The suspension was filtered and the solvents were evaporated to dryness, leaving a white solid. Yield: 1.25 g (45%).

1H NMR (400 MHz): 7.97 (m, 2H), 7.91. (dt, J = 7.6, 1.2, 1H), 7.79 (d, J = 8.0, 1H), 7.75 (d, J = 7.6, 1H), 7.62 (td, J = 7.6, 1.2, 1H), 7.57 (m, 1H), 7.55–7.50 (m, 4H), 7.45 (m, 1H), 7.39 (d, J = 7.6, 2H),

7.29 (td, J = 7.6, 2.0, 2H), 7.20 (tt, J = 7.2, 1.2, 1H), 5.11 (d, J = 2.8, 1H), 4.30 (m, 1H), 2.84 (d, 3JHP = 8.4, 3H), 1.24 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 142.4–121.2 (C, CH, Ar), 78.7 (d, 3JCP = 1.5, CH), 59.3 (d, 2JCP = 9.9, CH), 33.9 (d, 2JCP = 3.9, CH3), 9.6 (d, 3JCP = 7.2, CH3). 31P{1H} NMR (162 MHz): +73.4 (br, s). HRMS: calcd for C28H27NO3PS ([M] + H − BH3), 488.1449; found, 488.1457. [α]D = +66.1°.

3-DBF, (R)-(4-dibenzofuranyl)methoxyphenylphosphineborane. Aminophosphine-borane 2-DBF (3.52 g, 7.7 mmol) was dissolved in 200 mL of freshly distilled methanol, concentrated H2SO4 (0.84 mL, 1.51 g, 15.4 mmol) was carefully added and the solution was stirred for 14 h. The solvent was removed in vacuo and the crude was purified by column chromatography (flash SiO2, 95 : 5 hexane/ethyl acetate). The title product was obtained as a pale brown oil. Yield: 1.67 g (67%).

1H NMR (400 MHz): 8.13 (dt, J = 7.6, 1.2, 1H), 7.98–7.91 (m, 4H), 7.58 (d, J = 12.0, 1H), 7.56 (d, J = 12.0, 1H), 7.51–7.43 (m, 4H), 7.36 (m, 1H), 3.85 (d, 3JHP = 12.4, 3H). 13C{1H} NMR (101 MHz): 156.1–111.6 (C, CH, Ar), 54.3 (d, 2JCP = 2.7, CH3). 31P{1H} NMR (121 MHz): +106.6 (d, br, J ≈ 88). HRMS: calcd for C19H22BNO2P ([M] + NH4), 338.1481; found, 338.1472. [α]D = –81.9°.

3-DBT, (R)-(4-dibenzothiophenyl)methoxyphenylphosphineborane. The procedure was the same as that used to prepare 3-DBF but starting from precursor 2-DBT (2.06 g, 4.4 mmol). The desired phosphinite-borane was obtained as a colourless oil. Yield: 1.19 g (81%).

1H NMR (400 MHz): 8.32 (d, J = 8.0, 1H), 8.17 (m, 1H), 8.09 (dd, J = 13.2, 7.6, 1H), 7.82–7.76 (m, 3H), 7.60 (td, J = 7.2, 2.0, 1H), 7.53–7.40 (m, 5H), 3.86 (d, 3JHP = 12.4, 3H). 13C{1H} NMR (101 MHz): 141.1–121.5 (C, CH, Ar), 54.2 (d, 2JCP = 2.3, CH3). 31P{1H} NMR (121 MHz): +110.6 (d, br, J ≈ 89). HRMS: calcd for C19H22BNOPS ([M] + NH4), 354.1253; found, 354.1252. [α]D = –78.0°.

3-TA, (R)-methoxyphenyl(1-thianthrenyl)phosphine-borane. The procedure was similar to that used to prepare 3-DBF but starting from precursor 2-TA (1.15 g, 2.3 mmol) and stirring for 3 days. The desired phosphinite-borane was obtained as a white pasty solid. Yield: 447 mg (53%).

1H NMR (400 MHz): 7.91 (ddd, J = 11.2, 7.6, 1.2, 1H), 7.74–7.69 (m, 3H), 7.52 (td, J = 7.2, 1.2, 1H), 7.46–7.37 (m, 4H), 7.21 (td, J = 7.6, 1.6, 1H), 7.12 (td, J = 7.6, 1.2, 1H), 6.96 (dd, J = 7.6, 1.2, 1H), 3.80 (d, 3JHP = 12.4, 3H). 13C{1H} NMR (101 MHz): 140.0–127.0 (C, CH, Ar), 54.1 (d, 2JCP = 2.5, CH3). 31P{1H} NMR (162 MHz): +109.3 (d, br, J ≈ 83). HRMS: calcd for C19H22BNOPS2 ([M] + NH4), 386.0973; found, 386.0976. [α]D = –10.5°.

3-DBTO2, (R)-(4-dibenzothiophenyl dioxide)methoxyphenylphosphine- borane. The procedure was the same as that used to prepare 3-DBF but starting from precursor 2-DBTO2 (1.00 g, 3.0 mmol). The desired phosphinite-borane was obtained as a white solid. Yield: 433 mg (59%).

1H NMR (400 MHz): 7.93–7.78 (m, 6H), 7.68–7.62 (m, 2H), 7.56 (td, J = 7.6, 0.8, 1H), 7.52–7.42 (m, 3H), 3.99 (d, 3JHP = 12.0, 3H). 13C{1H} NMR (101 MHz): 139.4–121.3 (C, CH, Ar), 55.4 (d, 2JCP = 2.0, CH3). 31P{1H} NMR (162 MHz): +112.0 (d, br, J ≈ 73). HRMS: calcd for C19H22BNO3PS ([M] + NH4), 386.1151; found, 386.1156. [α]D = –291.1°.

4-DBF-Me, (S)-(4-dibenzofuranyl)methylphenylphosphineborane. Methoxyphosphine-borane 3-DBF (673 mg, 2.1 mmol) was dissolved in 30 mL diethyl ether, and the solution was cooled down to −30 °C. A 1.6 M MeLi solution in diethyl ether (2.6 mL, 4.2 mmol) was added using a syringe and the mixture was stirred for 1 h before slowly warming it to room temperature. About 15 mL of water were added and the mixture was extracted with diethyl ether (3 × 10 mL), the combined organic phases were washed with 20 mL of water and dried with anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and the crude product was purified by column chromatography (flash SiO_2, 95 : 5 hexane/ethyl acetate). The title product was obtained as a colourless oil. Yield: 523 mg (82%).
1H NMR (400 MHz): 8.11 (d, J = 7.6, 1H), 8.00–7.95 (m, 2H), 7.85–7.80 (m, 2H), 7.59–7.55 (m, 2H), 7.52–7.33 (m, 5H), 2.23 (d, 2JHP = 10.8, 3H). 13C{1H} NMR (101 MHz): 156.9–111.6 (C, CH, Ar), 11.1 (d, 1JCP = 41.6, CH3). 31P{1H} NMR (121 MHz): +7.7 (d, br, J ≈ 81). HRMS: calcd for C19H22BNOP ([M] + NH4), 322.1532; found, 322.1530. [α]D = +140.8°. 4-DBF-iPr, (S)-(4-dibenzofuranyl)isopropylphenylphosphineborane. The procedure was the same as that used to prepare 4-DBF-Me. Starting from 3-DBF (1.15 g, 3.6 mmol) and 0.7 M i-PrLi solution in pentane (15.2 mL, 10.8 mmol) the desired phosphinite-borane was obtained as a colourless oil. Yield: 897 mg (75%).
1H NMR (400 MHz): 8.15–7.97 (m, 5H), 7.66 (d, J = 8.0, 1H), 7.53 (td, J = 7.6, 1.2, 1H), 7.45–7.38 (m, 5H), 3.67 (m, 1H), 1.29 (dd, 3JHP, 3JHH = 17.2, 7.2, 3H), 1.16 (dd, 3JHP, 3JHH = 17.2, 6.8, 3H). 13C{1H} NMR (101 MHz): 156.7–111.7 (C, CH, Ar), 22.6 (d, 1JCP = 37.9, CH), 17.1 (d, 2JCP = 2.8, CH3), 16.8 (d, 2JCP = 2.9, CH3). 31P{1H} NMR (121 MHz): +26.1 (d, br, J ≈ 77). HRMS: calcd for C21H26BNOP ([M] + NH4), 350.1845; found, 350.1842. [α]D = +228.9°.
4-DBF-tBu, (S)-(tert-butyl)(4-dibenzofuranyl)phenylphosphine- borane. The procedure was the same as that used to prepare 4-DBF-Me. Starting from 3-DBF (732 mg, 2.1 mmol) and 1.6 M t-BuLi solution (1.5 mL, 2.3 mmol) the desired phosphinite-borane was obtained as a colourless oil. Yield: 440 mg (60%).
1H NMR (400 MHz): 8.17–8.12 (m, 2H), 7.98 (td, J = 7.6, 0.8, 1H), 7.90–7.85 (m, 2H), 7.49–7.43 (m, 4H), 7.42–7.36 (m, 3H), 1.41 (d, 3JHP = 14.8, 9H). 13C{1H} NMR (101 MHz): 155.4–111.7 (C, CH, Ar), 31.8 (d, 1JCP = 31.3, C), 27.8 (d, 2JCP = 3.0, CH3). 31P{1H} NMR (121 MHz): +36.7 (d, br, J ≈ 70). HRMS: calcd for C22H28BNOP ([M] + NH4), 364.2002; found, 350.2014. [α]D = +82.3°.
4-DBF-Fc, (S)-(4-dibenzofuranyl)ferrocenylphenylphosphineborane. Ferrocene (2.5 g, 13.4 mmol) was dissolved in 20 Ml of THF in a Schlenk flask. The solution was cooled to 0 °C, 1.6 M t-BuLi solution in pentane (16.7 mL, 26.9 mmol) was added using a syringe and the mixture was left stirring for 2 h. At this point 40 mL of hexane were added and the solution was cooled down to −78 °C, which caused the precipitation of FcLi. The solid was filtered under nitrogen, washed with hexane and dried in vacuo. In parallel, 3-DBF (2.15 g, 6.7 mmol) was dissolved in 20 mL of THF and the solution was cooled down to −78 °C. Solid FcLi was rapidly added to that solution and the mixture was left stirring for 14 h. About 15 mL of water were added and most of the THF was removed in vacuo. The mixture was extracted with dichloromethane (3 × 10 mL), the combined organic phases were washed with 20 mL of water and

dried with anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and the red crude product was purified by column chromatography (flash SiO2, 70 : 30 hexane/dichloromethane) and recrystallized in dichloromethane/hexane. The title product was obtained as an orange solid. Yield: 1.80 g (56%).

1H NMR (400 MHz): 8.13 (d, J = 7.6, 1H), 8.04 (dd, J = 12.8, 7.6 1H), 7.96 (d, J = 6.8, 1H), 7.67–7.62 (m, 2H), 7.48 (t, J = 7.6, 1H), 7.44–7.35 (m, 6H), 4.69 (s, br, 2H), 4.53 (s, br, 1H), 4.49 (s, br, 1H), 4.00 (s, br, 5H). 13C{1H} NMR (101 MHz): 156.6–111.8 (C, CH, Ar), 74.1 (d, JCP = 13.5, CH), 73.0 (d, JCP = 7.8, CH), 71.9 (d, JCP = 7.7, CH), 71.6 (d, JCP = 8.5, CH), 69.7 (s, 5CH), 67.7 (d, JCP = 70.5, C). 31P{1H} NMR (162 MHz): +12.6 (d, br, J ≈ 43). HRMS: calcd for C28H21FeOP ([M] − BH3), 460.0679; found, 460.0663. [α]D = +65.4°.

4-DBT-Me, (S)-(4-dibenzothiophenyl)methylphenylphosphine-borane. The procedure was the same as that used to prepare 4-DBF-Me. Starting from 3-DBT (580 mg, 1.7 mmol) and 1.6 M MeLi solution (1.2 mL, 1.7 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 357 mg (70%).

1H NMR (400 MHz): 8.31 (dt, J = 8.0, 1.2, 1H), 8.16 (m, 1H), 8.08 (ddd, J = 12.8, 7.2, 1.2, 1H), 7.74 (m, 1H), 7.70–7.64 (m, 2H), 7.61 (td, J = 7.6, 1.6, 1H), 7.52–7.40 (m, 5H), 2.09 (d, 2JHP = 10.0, 3H). 13C{1H} NMR (101 MHz): 142.2–121.5 (C, CH, Ar), 10.0 (d, 1JCP = 40.2, CH3). 31P{1H} NMR (121 MHz): +13.2 (d, br, J ≈ 77). HRMS: calcd for C19H22BNPS ([M] + NH4), 338.1304; found, 338.1293. [α]D = +41.5°.

4-DBT-iPr, (S)-(4-dibenzothiophenyl)isopropylphenylphosphine-borane. The procedure was the same as that used to prepare 4-DBF-iPr. Starting from 3-DBT (1.00 g, 3.0 mmol) and 0.7 M i-PrLi solution in pentane (6.4 mL, 4.5 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 985 mg (95%).

1H NMR (400 MHz): 8.10 (dt, J = 8.0, 1.6, 1H), 8.02 (dd, J = 7.6, 1.2, 1H), 7.96 (m, 1H), 7.71–7.66 (m, 2H), 7.58 (m, 1H), 7.41 (td, J = 7.6, 2.0, 1H), 7.34–7.24 (m, 3H), 7.11 (d, J = 7.2, 1H), 7.04 (d, br, J = 8.4, 1H), 3.17 (m, 1H), 1.23 (dd, 3JHP, 3JHH = 16.0, 6.8, 3H), 1.01 (dd, 3JHP, 3JHH = 16.8, 6.8, 3H). 13C{1H} NMR (101 MHz): 142.3–121.5 (C, CH, Ar), 21.3 (d, 1JCP = 36.0, CH), 17.3 (d, 2JCP = 1.6, CH3), 17.1 (d, 2JCP = 2.5, CH3). 31P{1H} NMR (121 MHz): +29.7 (d, br, J ≈ 50). HRMS: calcd for C21H26BNPS ([M] + NH4), 366.1617; found, 366.1622. [α]D = +40.4°.

4-DBT-Fc, (S)-(4-dibenzothiophenyl)ferrocenylphenylphosphine-borane. The procedure was the same as that used to prepare 4-DBT-Fc. Starting from ferrocene (1.31 g, 7.0 mmol) and 3-DBT (1.18 g, 3.5 mmol) the desired phosphine-borane was obtained as an orange solid. Yield: 1.36 g (79%).

1H NMR (400 MHz): 8.26 (d, J = 7.6, 1H), 8.14 (dd, J = 6.4, 2.4, 1H), 7.76–7.67 (m, 4H), 7.56–7.39 (m, 6H), 4.75 (s, br, 1H), 4.56 (s, br, 2H), 4.43 (s, br, 1H), 4.08 (s, br, 5H). 13C{1H} NMR (101 MHz): 139.9–121.5 (C, CH, Ar), 74.1 (d, JCP = 12.4, CH), 72.8 (d, JCP = 7.9, CH), 72.1 (d, JCP = 7.3, CH), 71.9 (d, JCP = 8.4, CH), 69.9 (s, 5CH), 67.8 (d, JCP = 69.7, C). 31P {1H} NMR (162 MHz): +18.9 (s, br). HRMS: calcd for C28H22FePS ([M] + H − BH3), 477.0529; found, 477.0537. [α]D = –98.2°.

4-TA-Me, (S)-methylphenyl(1-thianthrenyl)phosphineborane. The procedure was the same as that used to prepare 4-DBF-Me. Starting from 3-TA (200 mg, 0.5 mmol) and 1.6 M MeLi solution (0.7 mL, 1.1 mmol) the desired phosphineborane was obtained as a white pasty solid. Yield: 166 mg (87%).
1H NMR (400 MHz): 7.94 (ddd, J = 12.8, 8.0, 1.6, 1H), 7.71 (dt, J = 7.6, 1.6, 1H), 7.57 (dt, J = 11.2, 1.6, 1H), 7.55 (dd, J = 11.2, 1.6, 4H), 7.44–7.36 (m, 2H), 7.23 (m, 1H), 7.16 (td, J = 7.6, 1.2, 1H), 7.06 (dd, J = 7.6, 1.6, 1H), 2.09 (d, 2JHP = 10.0, 3H). 13C{1H} NMR (101 MHz): 140.7–126.3 (C, CH, Ar), 11.8 (d, 1JCP = 40.5, CH3). 31P{1H} NMR (162 MHz): +15.9 (d, br, J ≈ 51). HRMS: calcd for C19H17BPS2 ([M] − H), 351.0602; found, 351.0602. [α]D = +115.8°.
L1 (5-DBF-OMe), (R)-(4-dibenzofuranyl)methoxyphenylphosphine. Phosphinite-borane 3-DBF (240 mg, 0.72 mmol) was dissolved in 5 mL of morpholine and the solution was stirred at 40 °C for 14 h. Morpholine was removed under vacuum and the gummy residue was purified by column chromatography (Al2O3, toluene) to yield the title product as a dense, colourless oil. Yield: 190 mg (81%).
1H NMR (400 MHz): 7.98–7.93 (m, 3H), 7.64 (td, J = 8.0, 2.0, 1H), 7.58 (d, J = 8.0, 1H), 7.53 (m, 1H), 7.49–7.42 (m, 2H), 7.40–7.31 (m, 4H), 3.80 (d, 3JHP = 14.0, 3H). 13C{1H} NMR (101 MHz): 156.2–111.0 (C, CH, Ar), 57.3 (d, 2JCP = 20.6, CH3). 31P{1H} NMR (121 MHz): +106.8 (s).
L2 (5-DBT-OMe), (R)-(4-dibenzothiophenyl)methoxyphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 3-DBT (328 mg, 0.98 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 220 mg (70%).
1H NMR (400 MHz): 8.19–8.13 (m, 3H), 7.88–7.83 (m, 2H), 7.65–7.57 (m, 2H), 7.53–7.43 (m, 3H), 7.37–7.34 (m, 2H), 3.78 (d, 3JHP = 14.0, 3H). 13C{1H} NMR (101 MHz): 139.4–121.5 (C, CH, Ar), 57.2 (d, 2JCP = 20.0, CH3). 31P{1H} NMR (162 MHz): +114.2 (s).
L3 (5-TA-OMe), (R)-Methoxyphenyl(1-thianthrenyl)phosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 3-TA (630 mg, 1.71 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 510 mg (84%).
1H NMR (400 MHz): 7.61–7.41 (m, 5H), 7.38–7.30 (m, 4H), 7.26–7.17 (m, 2H), 3.71 (d, 3JHP = 14.0, 3H). 13C{1H} NMR (101 MHz): 142.3–127.4 (C, CH, Ar), 57.1 (d, 2JCP = 21.8, CH3). 31P{1H} NMR (162 MHz): +104.4 (s).
L4 (5-DBTO2-OMe), (R)-(4-dibenzothiophenyl-S,S-dioxide) methoxyphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 3-DBTO2 (200 mg, 0.54 mmol) the desired phosphine-borane was obtained as a white solid. Yield: 150 mg (78%).
1H NMR (400 MHz): 7.82 (dq, J = 7.6, 0.4, 1H), 7.75–7.63 (m, 5H), 7.59 (tt, J = 8.0, 0.8, 1H), 7.56–7.47 (m, 2H), 7.41–7.30 (m, 3H), 3.78 (d, 3JHP = 14.4, 3H). 13C{1H} NMR (101 MHz): 141.1–121.4 (C, CH, Ar), 57.2 (d, 2JCP = 21.9, CH3). 31P{1H} NMR (162 MHz): +101.4 (s).
L5 (5-DBF-Me), (S)-(4-dibenzofuranyl)methylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBF-Me (500 mg, 1.56 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 329 mg (69%).

1H NMR (300 MHz): 8.00–7.92 (m, 2H), 7.62–7.54 (m, 3H), 7.51–7.43 (m, 2H), 7.40–7.30 (m, 5H), 1.86 (d, 2JHP = 3.9, 3H). 13C{1H} NMR (101 MHz): 158.0–111.6 (C, CH, Ar), 11.1 (d, 1JCP = 12.8, CH3). 31P{1H} NMR (121 MHz): −37.0 (s)

L6 (5-DBF-iPr), (S)-(4-dibenzofuranyl)isopropylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBF-iPr (185 mg, 0.56 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 120 mg (68%).

1H NMR (300 MHz): 7.94 (d, J = 7.5, 2H), 7.67–7.52 (m, 4H), 7.45 (td, J = 7.2, 1.2, 1H), 7.37–7.29 (m, 5H), 2.91 (dd, J = 7.2, 6.9, 1H), 1.16 (dd, J = 13.2, 6.9, 3H), 1.11 (dd, J = 13.2, 6.9, 3H). 13C{1H} NMR (101 MHz): 159.7–110.0 (C, CH, Ar), 22.4 (d, 1JCP = 6.7, CH), 19.9 (d, 2JCP = 7.1, CH3), 19.7 (d, 2JCP = 8.8, CH3). 31P{1H} NMR (121 MHz): −10.7 (s).

L7 (5-DBF-tBu), (S)-(tert-butyl)(4-dibenzofuranyl)phenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBF-tBu (600 mg, 1.73 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 488 mg (85%).

1H NMR (300 MHz): 7.97 (dd, J = 7.5, 1.2, 1H), 7.95 (ddd, J = 7.8, 1.5, 0.8, 1H), 7.68–7.57 (m, 4H), 7.44 (td, J = 7.2, 1.5, 1H), 7.38–7.30 (m, 5H), 1.28 (d, 3JHP = 13.2, 9H). 31P{1H} NMR (121 MHz): +0.6 (s).

L8 (5-DBF-Fc), (S)-(4-dibenzofuranyl)ferrocenylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBF-Fc (600 mg, 1.26 mmol) the desired phosphine-borane was obtained as an orange solid. Yield: 490 mg (84%).

1H NMR (400 MHz): 7.95 (dq, J = 7.6, 0.8 1H), 7.94 (ddd, J = 7.6, 1.2, 0.4, 1H), 7.57 (d, J = 8.0, 1H), 7.48–7.41 (m, 3H), 7.35–7.29 (m, 4H), 7.27 (d, J = 7.2, 1H), 7.15 (m, 1H), 4.39 (m, 2H), 4.18 (m, 1H), 4.15 (m, 1H), 4.08 (m, 5H). 13C{1H} NMR (101 MHz): 156.0–111.6 (C, CH, Ar), 73.1 (d, JCP = 15.0, CH), 73.0 (d, JCP = 15.4, CH), 70.9 (d, JCP = 4.0, CH), 70.7 (d, JCP = 4.0, CH), 69.1 (s, 5CH), 67.9 (s, C). 31P{1H} NMR (162 MHz): −32.1 (s).

L9 (5-DBF-DBT), (S)-(4-dibenzofuranyl)(4-dibenzothiophenyl) phenylphosphine. Dibenzothiophene (210 mg, 1.1 mmol) was dissolved in 20 mL of THF in a Schlenk flask. The solution was cooled to −78 °C and then 1.6 M n-BuLi solution in hexanes (0.7 mL, 1.1 mmol) was added using a syringe. The resulting brown solution was removed from the cold bath, left stirring at 0 °C for 5 h and recooled to −78 °C. At the same time phosphinite-borane 5-DBF-OMe (350 mg, 1.1 mmol) was dissolved in 20 mL of THF and the solution was cooled down to −78 °C. The content of the first flask was slowly transferred to the second Schlenk flask via cannula and the resulting mixture was stirred for 14 h. Around 20 mL of deoxygenated water were added to the brown-yellow solution and THF was evaporated. The white residue was extracted with dichloromethane (3 × 30 mL) under a nitrogen atmosphere and the combined organic phases were washed with deoxygenated water and dried with anhydrous sodium sulfate. The suspension was filtered under nitrogen and the solvent was evaporated to dryness, leaving a white pasty solid. 10 mL of morpholine were added and the solution was stirred at

40°C for 14 h. Morpholine was removed under vacuum and the gummy residue was purified by column chromatography (Al2O3, toluene) to yield the title product as a pale brown solid. Yield: 307 mg (61%). 1H NMR (400.1 MHz): 8.17 (m, 2H), 7.96 (m, 2H), 7.86 (m, 1H), 7.58 (d, J = 8.4, 1H), 7.46 (m, 7H), 7.35 (m, 3H), 7.27 (t, J = 7.6, 1H), 7.10 (m, 1H), 7.02 (m, 1H). 31P{1H} NMR (162 MHz): −23.1 (s). HRMS: calcd for C30H20OPS ([M] + H), 459.0972; found, 459.0975.

L10 (5-DBT-Me), (S)-(4-dibenzothiophenyl)methylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBT-Me (450 mg, 1.41 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 380 mg (88%).

1H NMR (400 MHz): 8.17–8.13 (m, 2H), 7.84 (m, 1H), 7.51–7.42 (m, 6H), 7.35–7.31 (m, 3H), 1.78 (d, 2JHP = 3.2, 3H). 13C{1H} NMR (101 MHz): 145.0–121.5 (C, CH, Ar), 11.2 (d, 1JCP = 13.1, CH3). 31P{1H} NMR (162 MHz): −30.6 (s).

L11 (5-DBT-iPr), (S)-(4-dibenzothiophenyl)isopropylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBT-iPr (490 mg, 1.41 mmol) the desired phosphine-borane was obtained as a colourless oil. Yield: 400 mg (85%).

1H NMR (400 MHz): 8.19–8.10 (m, 3H), 7.85 (m, 1H), 7.61–7.55 (m, 2H), 7.52–7.41 (m, 4H), 7.33–7.29 (m, 2H), 2.70 (m, 1H), 1.18 (dd, 3JHP, 3JHH = 6.8, 2.4, 3H), 1.14 (dd, 3JHP, 3JHH = 6.8, 2.4, 3H). 13C{1H} NMR (101 MHz): 147.2–121.5 (C, CH, Ar), 25.0 (d, 1JCP = 7.7, CH), 19.8 (d, 2JCP = 6.7, CH3), 19.6 (d, 2JCP = 7.8, CH3). 31P{1H} NMR (162 MHz): −5.1 (s).

L12 (5-DBT-Fc), (S)-(4-dibenzothiophenyl)ferrocenylphenylphosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-DBT-Fc (350 mg, 0.71 mmol) the desired phosphine-borane was obtained as an orange solid. Yield: 300 mg (89%).

1H NMR (400 MHz): 8.14 (d, J = 4.4, 1H), 8.11 (d, J = 7.2, 1H), 7.80 (t, J = 4.8, 1H), 7.54–7.48 (m, 2H), 7.45–7.38 (m, 3H), 7.35–7.30 (m, 3H), 7.22 (m, 1H), 4.45 (s, br, 1H), 4.41 (s, br, 1H), 4.38 (s, br, 1H), 4.09 (s, br, 5H), 4.06 (s, br, 1H). 13C{1H} NMR (101 MHz): 144.6–121.6 (C, CH, Ar), 74.2 (d, JCP = 4.2, C), 73.9 (d, JCP = 23.2, CH), 72.4 (d, JCP = 6.8, CH), 71.2 (d, JCP = 5.9, CH), 70.7 (d, JCP = 2.4, CH), 69.2 (s, 5CH). 31P{1H} NMR (162 MHz): −20.5 (s).

L13 (5-TA-Me), (S)-methylphenyl(1-thianthrenyl)phosphine. The procedure was the same as that used to prepare 5-DBF-OMe. Starting from 4-TA-Me (350 mg, 0.99 mmol) the desired phosphine-borane was obtained as colourless, dense oil. Yield: 280 mg (83%).

1H NMR (400 MHz): 7.50–7.41 (m, 4H), 7.36–7.33 (m, 3H), 7.26–7.18 (m, 4H), 7.15 (ddd, J = 7.6, 4.4, 1.2, 1H), 1.65 (d, 2JHP = 4.8, 3H). 13C{1H} NMR (101 MHz): 140.8–126.6 (C, CH, Ar), 12.3 (d, 1JCP = 14.6, CH3). 31P{1H} NMR (162 MHz): −32.1 (s).

Synthesis of the Ru complexes

Ru1, [RuCl2(η6-p-cymene)(L1)]. Phosphinite L1 (214 mg, 0.70 mmol) was dissolved in 20 mL of dichloromethane, Ru dimer D1 (150 mg, 0.25 mmol) was added and the dark red solution was stirred for

1 h. The solvent was removed under vacuum and the residue was recrystallised in dichloromethane/hexane to furnish the title product as a dark red solid. Yield: 246 mg (80%). IR: 3051, 2958, 2869, 1580, 1469, 1450, 1400, 1185, 1109, 1032, 845, 804, 757, 696, 562. 1H NMR (400 MHz): 8.37 (ddd, J = 11.2, 7.6, 1.2, 1H), 8.05–8.00 (m, 3H), 7.93 (dt, J = 7.6, 1.2, 1H), 7.43–7.32 (m, 7H), 5.41 (d, J = 6.6, 1H), 5.37 (d, J = 6.0, 1H), 5.33 (d, J = 6.0, 1H), 5.05 (d, J = 6.0, 1H), 3.63 (d, 3JHP = 12.0, 3H), 2.72 (sept, 3JHH = 6.8, 1H), 1.97 (s, 3H), 1.01 (d, 3JHH = 6.8, 3H), 0.88 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 155.6–111.6 (C, CH, Ar), 110.9 (d, 2JCP = 1.7, C), 96.5 (s, C), 92.6 (d, 2JCP = 5.6, CH), 90.3 (d, 2JCP = 3.9, CH), 88.3 (d, 2JCP = 7.2, CH), 86.5 (d, 2JCP = 5.6, CH), 55.1 (d, 2JCP = 5.1, CH3), 30.0 (s, CH), 21.8 (s, CH3), 21.0 (s, CH3), 17.6 (s, CH3). 31P{1H} NMR (121 MHz): +112.7 (s). Anal.: calcd for C29H29Cl2O2PRu, C 56.87%, H 4.77%; found, C 57.29%, H 5.03%.

Ru2, [RuCl2(η6-p-cymene)(L2)]. The procedure was the same as that followed to prepare Ru1. Starting from L2 (220 mg, 0.68 mmol) and Ru dimer D1 (149 mg, 0.24 mmol), the desired complex was obtained as a dark red solid. Yield: 217 mg (72%). IR: 3053, 2958, 2870, 1439, 1375, 1103, 1028, 756, 695, 554.

1H NMR (300 MHz): 8.34 (ddd, J = 13.2, 7.5, 0.9, 1H), 8.23 (dt, J = 8.0, 1.5, 1H), 8.18–8.14 (m, 1H), 7.99–7.93 (m, 2H), 7.84–7.81 (m, 1H), 7.53–7.45 (m, 3H), 7.39–7.32 (m, 3H), 5.44 (d, J = 6.0, 1H), 5.36 (d, J = 6.9, 1H), 5.33 (d, J = 7.8, 1H), 5.24 (d, J = 6.0, 1H), 3.70 (d, 3JHP = 11.7, 3H), 2.70 (sept, 3JHH = 7.2, 1H), 1.89 (s, 3H), 1.02 (d, 3JHH = 6.9, 3H), 1.00 (d, 3JHH = 6.9, 3H). 13C{1H} NMR (101 MHz): 140.0–121.4 (C, CH, Ar), 111.6 (d, 2JCP = 1.1, C), 96.9 (s, C), 91.7 (d, 2JCP = 4.1, CH), 91.4 (d, 2JCP = 4.6, CH), 87.5 (d, 2JCP = 6.6, CH), 87.2 (d, 2JCP = 5.9, CH), 54.6 (d, 2JCP = 3.6, CH3), 30.1 (s, CH), 21.7 (s, CH3), 21.5 (s, CH3), 17.5 (s, CH3). 31P{1H} NMR (121 MHz): +118.3 (s). Anal.: calcd for C29H29Cl2OPRuS, C 55.42%, H 4.65%, S 5.10%; found, C 55.97%, H 5.01%, S 4.89%.

Ru3, [RuCl2(η6-p-cymene)(L3)]. The procedure was the same as that followed to prepare Ru1. Starting from L3 (270 mg, 0.76 mmol) and Ru dimer D1 (186 mg, 0.30 mmol), the desired complex was obtained as a dark red solid. Yield: 217 mg (55%).

IR: 3052, 2959, 2869, 1470, 1448, 1435, 1378, 1109, 1029, 752, 694, 550. 1H NMR (400 MHz): 8.30 (dd, J = 11.6, 7.6, 1H), 7.84 (t, J = 9.2, 2H), 7.64 (d, J = 7.6, 1H), 7.46–7.34 (m, 5H), 7.21 (td, J = 7.2, 1.2, 1H), 7.11 (td, J = 7.6, 1.2, 1H), 7.00 (dd, J = 7.6, 1.2, 1H), 5.41 (d, J = 6.4, 1H), 5.31 (d, J = 6.0, 1H), 5.27 (d, J = 6.0, 1H), 5.18 (d, J = 5.6, 1H), 3.61 (d, 3JHP = 11.6, 3H), 2.63 (sept, 3JHH = 6.8, 1H), 1.93 (s, 3H), 0.92 (d, 3JHH = 7.2, 3H), 0.86 (d, 3JHH = 7.2, 3H). 31P{1H} NMR (162 MHz): +110.2 (s). HRMS: calcd for C29H29ClOPRuS2 ([M] − Cl), 625.0123; found, 625.0126.

Ru4, [RuCl2(η6-p-cymene)(L4)]. The procedure was the same as that followed to prepare Ru1. Starting from L4 (70 mg, 0.20 mmol) and Ru dimer D1 (48 mg, 0.08 mmol), the desired complex was obtained as a dark red solid. Yield: 70 mg (68%).

IR: 3060, 2959, 2869, 1446, 1436, 1387, 1308, 1154, 1095, 1045, 815, 764, 721, 701, 584, 568, 468. 1H NMR (400 MHz): 8.13 (tt, J = 8.4, 1.6, 2H), 7.98 (ddd, J = 13.2, 7.6, 0.8, 1H), 7.91 (d, J = 6.8, 1H), 7.86 (t, J = 7.6, 2H), 7.71 (td, J = 7.6, 1.2, 1H), 7.64 (td, J = 7.6, 0.8, 1H), 7.52 (td, J = 7.6, 2.0, 1H), 7.37–7.27 (m, 3H), 5.68 (d, J = 6.0, 1H), 5.62 (dd, J = 6.4, 1.2, 1H), 5.50 (d, J = 6.0, 1H), 5.31 (d, J = 6.0, 1H), 3.72 (d, 3JHP = 11.6, 3H), 2.72 (sept, 3JHH = 6.8, 1H), 1.87 (s, 3H), 1.17 (d, 3JHH = 6.8, 3H), 0.97 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 141.9–121.2 (C, CH, Ar), 112.1 (s, C), 97.4 (s, C), 93.8 (d, 2JCP = 5.4, CH), 90.9 (d, 2JCP = 3.8, CH), 87.6 (d, 2JCP = 6.3, CH), 86.7 (d, 2JCP = 5.9, CH), 54.2 (d, 2JCP = 4.0, CH3), 30.1 (s, CH), 22.3 (s, CH3), 21.1 (s, CH3), 17.5 (s, CH3). 31P{1H} NMR (162 MHz): +117.0 (s). Anal.: calcd for C29H29Cl2O3PRuS, C 52.73%, H 4.42%, S 4.85%; found, C 51.15%, H 4.51%, S 4.42%.

Ru5, [RuCl2(η6-p-cymene)(L5)]. The procedure was the same as that followed to prepare Ru1. Starting from L5 (185 mg, 0.64 mmol) and Ru dimer D1 (162 mg, 0.26 mmol), the desired complex was obtained as a dark red solid. Yield: 201 mg (65%).

IR: 3049, 2958, 2919, 2868, 1583, 1469, 1449, 1399, 1185, 1109, 1057, 898, 843, 802, 755, 725, 696, 556, 424. 1H NMR (300 MHz): 8.11 (dt, J = 7.8, 1.2, 1H), 8.04–8.00 (m, 1H), 7.96 (ddd, J = 7.8, 1.5, 0.9, 1H), 7.89 (ddd, J = 11.1, 7.8, 1.2, 1H), 7.78–7.71 (m, 2H), 7.59–7.56 (m, 1H), 7.52–7.31 (m, 5H), 5.59 (d, J = 6.3, 1H), 5.49 (d, J = 6.3, 1H), 5.47 (m, 1H), 4.76 (d, J = 5.7, 1H), 2.54 (sept, 3JHH = 6.9, 1H), 2.06 (s, 3H), 2.04 (d, 2JHP = 11.4, 3H), 0.90 (d, 3JHH = 6.9, 3H), 0.38 (d, 3JHH = 6.9, 3H). 13C{1H} NMR (101 MHz): 156.1–111.6 (C, CH, Ar), 107.8 (s, C), 94.2 (s, C), 93.8 (d, 2JCP = 6.7, CH), 89.6 (d, 2JCP = 8.8, CH), 86.4 (d, 2JCP = 2.6, CH), 81.4 (d, 2JCP = 3.2, CH), 29.8 (s, CH), 22.8 (s, CH3), 19.1 (s, CH3), 17.5 (s, CH3), 12.1 (d, 1JCP = 37.4, CH3). 31P{1H} NMR (121 MHz): +15.2 (s). Anal.: calcd for C29H29Cl2OPRu, C 58.39%, H 4.90%; found, C 60.59%, H 5.04%.

Ru6, [RuCl2(η6-p-cymene)(L6)]. The procedure was the same as that followed to prepare Ru1. Starting from L6 (166 mg, 0.52 mmol) and Ru dimer D1 (114 mg, 0.19 mmol), the desired complex was obtained as a dark red solid. Yield: 145 mg (62%).

IR: 3054, 2958, 2925, 2867, 1581, 1469, 1449, 1434, 1398, 1264, 1182, 1109, 1039, 844, 802, 759, 699, 533, 516. 1H NMR (400 MHz): 8.10 (dt, J = 7.6, 1.2, 1H), 8.04 (d, J = 8.0, 1H), 8.01–7.94 (m, 3H), 7.51–7.38 (m, 7H), 5.23 (d, J = 6.0, 2H), 5.11 (d, J = 6.0, 1H), 4.51 (d, J = 5.6, 1H), 3.71 (m, 1H), 2.66 (sept, 3JHH = 7.2, 1H), 1.89 (s, 3H), 1.10 (dd, J = 18.0, 7.2, 3H), 0.97 (dd, J = 14.0, 6.8, 3H), 0.92 (d, 3JHH = 6.8, 3H), 0.68 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 155.3–111.7 (C, CH, Ar), 109.2 (s, C), 93.9 (d, 2JCP = 4.5, C), 93.6 (s, CH), 88.9 (d, 2JCP = 2.4, CH), 86.1 (d, 2JCP = 7.4, CH), 83.4 (d, 2JCP = 4.6, CH), 29.9 (s, CH), 26.2 (d, 1JCP = 23.5, CH), 22.3 (s, CH3), 20.3 (s, CH3), 19.1 (d, 2JCP = 6.2, CH3), 18.7 (s, CH3), 17.5 (s, CH3). 31P{1H} NMR (121 MHz): +21.5 (s). Anal.: calcd for C31H33Cl2OPRu, C 59.62%, H 5.33%; found, C 59.08%, H 5.64%.

Ru8, [RuCl2(η6-p-cymene)(L8)]. The procedure was the same as that followed to prepare Ru1. Starting from L8 (180 mg, 0.39 mmol) and Ru dimer D1 (96 mg, 0.16 mmol), the desired complex was obtained as a dark red solid. Yield: 180 mg (75%).

IR: 3051, 2957, 2924, 2868, 1624, 1579, 1469, 1449, 1435, 1398, 1306, 1263, 1183, 1158, 1108, 1058, 1028, 1002, 844, 821, 801, 755, 699, 560, 458. 1H NMR (400 MHz): 8.03–8.00 (m, 2H), 7.96 (d, J = 8.0, 1H), 7.93 (d, J = 7.2, 1H), 7.74 (dd, J = 10.8, 7.6, 1H), 7.53–7.47 (m, 1H), 7.46–7.41 (m, 3H), 7.40–7.29 (m, 3H), 5.56 (d, J = 6.4, 1H), 5.38 (d, J = 6.8, 1H), 5.37–5.35 (m, 1H), 4.97 (m, 1H), 4.61 (d, J = 5.6, 1H), 4.38 (m, 1H), 4.34 (m, 1H), 4.26 (m, 1H), 3.66 (s, 5H), 2.55 (sept, 3JHH = 6.8, 1H), 2.03 (s, 3H), 0.89 (d, 3JHH = 7.2, 3H), 0.33 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 155.0–111.4 (C, CH, Ar), 109.1 (s, C), 94.6 (d, 2JCP = 4.4, C), 93.8 (s, CH), 88.9 (d, 2JCP = 9.1, CH), 87.8 (s, CH), 81.5 (s, CH), 78.0 (d, JCP = 12.1, CH), 75.0 (d, 1JCP = 54.0, C), 74.3 (d, 2JCP = 8.2, CH), 70.0 (s, ov, 6CH), 69.6 (d, JCP = 8.1, CH), 29.6 (s, CH), 22.6 (s, CH3), 19.0 (s, CH3), 17.1 (s, CH3). 31P {1H} NMR (162 MHz): +15.8 (s). Anal.: calcd for C38H35Cl2FeOPRu, C 59.55%, H 4.60%; found, C 59.59%, H 5.00%.

Ru9, [RuCl2(η6-p-cymene)(L9)]. The procedure was the same as that followed to prepare Ru1. Starting from L9 (140 mg, 0.31 mmol) and Ru dimer D1 (74 mg, 0.12 mmol), the desired complex was obtained as a dark red solid. Yield: 101 mg (55%).

1H NMR (400 MHz): 8.43 (dd, J = 13.2, 7.6 1H), 8.30–8.22 (m, 3H), 8.16–8.07 (m, 3H), 7.94 (d, J = 6.8, 1H), 7.59 (d, J = 6.4, 1H), 7.55 (d, J = 7.6, 1H), 7.43–7.20 (m, 9H), 5.27 (d, J = 6.0, 2H), 5.20 (d, J = 6.0, 1H), 5.04 (d, J = 6.0, 1H), 2.80 (sept, 3JHH = 6.8, 1H), 1.90 (s, 3H), 0.94 (d, 3JHH = 6.8, 3H), 0.86 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 155.9–120.7 (C, CH, Ar), 111.5 (s, C), 95.7 (s, C), 91.1 (d, 2JCP = 2.4, CH), 89.7 (d, 2JCP = 3.4, CH), 86.2 (d, 2JCP = 6.5, CH), 85.8 (d, 2JCP = 5.7, CH), 30.0 (s, CH), 21.6 (s, CH3), 21.3 (s, CH3), 17.6 (s, CH3). 31P{1H} NMR (162 MHz): +19.8 (s). HRMS: calcd for C40H33ClOPRuS ([M] − Cl), 729.0716; found, 729.0745.

Ru10, [RuCl2(η6-p-cymene)(L10)]. The procedure was the same as that followed to prepare Ru1. Starting from L10 (190 mg, 0.62 mmol) and Ru dimer D1 (140 mg, 0.23 mmol), the desired complex was obtained as a dark red solid. Yield: 251 mg (89%).

IR: 3051, 2958, 2868, 2838, 1438, 1374, 1103, 1027, 817, 755, 694, 554. 1H NMR (400 MHz): 8.28 (dt, J = 7.6, 1.6, 1H), 8.19 (m, 1H), 8.15 (ddd, J = 12.4, 7.6, 1.2, 1H), 7.79–7.74 (m, 2H), 7.70 (dd, J = 7.2, 2.0, 1H), 7.61 (td, J = 7.6, 1.6, 1H), 7.54–7.42 (m, 5H), 5.64 (d, J = 5.6, 1H), 5.57 (d, J = 6.0, 1H), 5.34 (d, J = 6.0, 1H), 5.17 (d, J = 5.6, 1H), 2.55 (sept, 3JHH = 7.2, 1H), 2.08 (d, 2JHP = 9.6, 3H), 2.07 (s, 3H), 0.83 (d, 3JHH = 7.2, 3H), 0.57 (d, 3JHH = 7.2, 3H). 13C{1H} NMR (101 MHz): 140.7–121.7 (C, CH, Ar), 107.2 (s, C), 94.5 (s, C), 91.7 (d, 2JCP = 5.8, CH), 88.7 (d, 2JCP = 6.9, CH), 88.1 (d, 2JCP = 3.7, CH), 83.1 (d, 2JCP = 4.6, CH), 29.8 (s, CH), 22.0 (s, CH3), 20.0 (s, CH3), 17.5 (s, CH3), 11.2 (d, 1JCP = 37.1, CH3). 31P{1H} NMR (162 MHz): +22.6 (s). Anal.: calcd for C29H29Cl2PRuS, C 56.86%, H 4.77%, S 5.24%; found, C 56.69%, H 5.07%, S 5.26%.

Ru11, [RuCl2(η6-p-cymene)(L11)]. The procedure was the same as that followed to prepare Ru1. Starting from L11 (400 mg, 1.20 mmol) and Ru dimer D1 (244 mg, 0.40 mmol), the desired complex was obtained as a dark red solid. Yield: 405 mg (79%).

IR: 3044, 2959, 2923, 2866, 1467, 1435, 1371, 1102, 1034, 801, 752, 704, 546, 528. 1H NMR (400 MHz): 8.28 (d, J = 8.0, 1H), 8.21 (d, J = 9.2, 1H), 7.99 (m, br, 2H), 7.78 (m, 1H), 7.62–7.57 (m, 3H), 7.53–7.47 (m, 4H), 5.42 (d, J = 6.0, 2H), 4.94 (d, J = 6.0, 1H), 4.67 (d, J = 5.6, 1H), 3.76 (m, 1H), 2.71 (sept, 3JHH = 7.2, 1H), 1.86 (s, 3H), 1.07–1.02 (m, 6H), 1.01 (dd, 3JHP = 15.6, 3JHH = 6.8, 3H), 0.78 (d, 3JHH = 7.2, 3H). 13C{1H} NMR (101 MHz): 141.0–121.6 (C, CH, Ar), 108.4 (s, C), 94.4 (s, br, C), 93.2 (s, br, CH), 88.3 (d, 2JCP = 3.9, CH), 88.3 (d, 2JCP = 3.6, CH), 85.5 (s, br, CH), 85.0 (s, br, CH), 29.8 (s, CH), 25.1 (d, 1JCP = 22.7, CH), 22.2 (s, CH3), 21.0 (s, CH3), 19.9 (s, CH3), 19.0 (s, CH3), 17.6 (s, CH3). 31P{1H} NMR (162 MHz): +25.4 (s, br). Anal.: calcd for C31H33Cl2PRuS, C 58.12%, H 5.19%, S 5.00%; found, C 57.92%, H 5.47%, S 4.64%.

Ru12, [RuCl2(η6-p-cymene)(L12)]. The procedure was the same as that followed to prepare Ru1. Starting from L12 (80 mg, 0.17 mmol) and Ru dimer D1 (42 mg, 0.07 mmol), the desired complex was obtained as a dark red solid. Yield: 78 mg (73%).

IR: 2960, 1636, 1436, 1401, 1372, 1158, 1106, 1030, 754, 694, 549, 492. 1H NMR (400 MHz): 8.21–8.16 (m, 2H), 8.09 (s, br, 1H), 7.80–7.72 (m, 2H), 7.55 (m, 1H), 7.49–7.45 (m, 6H), 5.47 (d, J = 6.4, 1H), 5.33 (d, J = 6.0, 1H), 5.21 (d, J = 6.4, 1H), 5.06 (d, J = 6.0, 1H), 5.01 (s, 1H), 4.46 (s, 1H), 4.42 (s, 1H), 4.35 (s, 1H), 3.69 (s, 5H), 2.53 (sept, 3JHH = 7.2, 1H), 1.95 (s, 3H), 0.86 (d, 3JHH = 7.2, 3H), 0.55 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 140.5–121.5 (C, CH, Ar), 108.9 (s, C), 95.0 (s, C), 92.8 (s, br, CH), 88.7 (s, br, CH), 88.3 (s, br, CH), 82.6 (s, br, CH), 79.1 (d, JCP = 15.9, CH), 74.1 (s, br, CH), 70.6 (s, br, CH), 70.3 (s, 5CH), 69.7 (m, br, CH), 29.7 (s, CH), 22.4 (s, CH3), 19.9 (s, br, CH3), 17.2 (s, CH3). 31P{1H} NMR (162 MHz): +20.6 (s). Anal.: calcd for C38H35Cl2FePRuS, C 58.32%, H 4.51%, S 4.10%; found, C 56.75%, H 4.75%, S 3.76%.

Ru13, [RuCl2(η6-p-cymene)(L13)]. The procedure was the same as that followed to prepare Ru1. Starting from L13 (180 mg, 0.53 mmol) and Ru dimer D1 (125 mg, 0.20 mmol), the desired complex was obtained as a dark red solid. Yield: 250 mg (97%).

1H NMR (400 MHz): 7.97 (dd, J = 12.0, 8.4, 2H), 7.71–7.66 (m, 2H), 7.52–7.44 (m, 4H), 7.37 (tt, J = 8.0, 1.6, 1H), 7.28 (d, J = 7.6, 1H), 7.18 (t, J = 7.6, 1H), 7.12 (d, J = 8.0, 1H), 5.63 (d, J = 6.0, 2H), 5.45 (d, J = 6.4, 1H), 5.19 (d, J = 5.2, 1H), 2.47 (sept, 3JHH = 7.2, 1H), 2.15 (s, 3H), 2.01 (d, 2JHP = 10.8, 3H), 0.81 (d, 3JHH = 7.2, 3H), 0.29 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 138.9–126.2 (C, CH, Ar), 106.5 (s, C), 95.1 (s, C), 93.7 (s, br, CH), 91.0 (s, br, CH), 85.6 (s, CH), 81.3 (s, CH), 29.6 (s, CH), 22.7 (s, CH3), 19.1 (s, CH3), 17.7 (s, CH3), 13.5 (d, 1JCP = 37.2, CH3). 31P{1H} NMR (162 MHz): +24.6 (s). Anal.: calcd for C29H29Cl2PRuS2, C 54.03%, H 4.54%, S 9.95%; found, C 53.28%, H 4.96%, S 9.50%.

Ru6*, [RuCl2(η6-methyl benzoate)(L6)]. Phosphine L6 (60 mg, 0.19 mmol) was dissolved in 20 mL of dichloromethane, Ru dimer D2 (48 mg, 0.077 mmol) was added and the dark suspension was stirred for 1 h and filtered. The solvent was removed under vacuum and the residue was recrystallized in dichloromethane/hexane to furnish the title product as a brown solid. Yield: 87 mg (87%).

IR: 3039, 2959, 2869, 1728 ν(CvO), 1625, 1583, 1470, 1450, 1435, 1400, 1294, 1277, 1185, 1110, 845, 803, 759, 698. 1H NMR (400 MHz): 8.14 (dt, J = 7.6, 1.6, 1H), 8.04 (d, J = 7.2, 2H), 7.96 (d, J = 7.2 1H), 7.93 (d, J = 8.8 1H), 7.52–7.39 (m, 7H), 6.43 (d, J = 6.4, 1H), 6.31 (d, J = 5.6, 1H), 5.52 (m, 1H), 4.96 (t, J = 6.0, 1H), 4.72 (t, J = 6.0, 1H), 3.87 (s, 3H), 3.81 (m, 1H), 1.13 (dd, J = 18.0, 7.2, 3H), 1.03 (dd, J = 15.6, 7.2, 3H). 13C{1H} NMR (101 MHz): 167.1 (s, CvO), 164.5 (s, CvO), 155.3–111.8 (C, CH, Ar), 96.6 (s, CH), 94.4 (s, CH), 90.7 (s, CH), 85.5 (s, CH), 83.8 (s, CH), 53.2 (s, CH3), 52.1 (s, CH3), 27.0 (d, 1JCP = 24.6, CH), 19.5 (d, 2JCP = 4.9, CH3), 19.0 (s, CH3). 31P{1H} NMR (162 MHz): +25.8 (s). Anal.: calcd for C29H27Cl2O3PRu, C 55.60%, H 4.34%; found, C 54.91%, H 4.34%.

Ru9*, [RuCl2(η6-methyl benzoate)(L9)]. The procedure was the same as that followed to prepare Ru6*. Starting from L9 (200 mg, 0.44 mmol) and Ru dimer D2 (90 mg, 0.15 mmol), the desired complex was obtained as a brownish solid. Yield: 140 mg (63%).

IR: 3083, 3073, 2951, 1728 ν(CvO), 1618, 1581, 1469, 1449, 1435, 1400, 1374, 1281, 1187, 1110, 846, 802, 755. 1H NMR (400 MHz): 8.36 (d, J = 8.0, 1H), 8.19 (d, J = 6.8, 1H), 8.13 (d, J = 8.0, 1H), 8.07 (dd, J = 13.0, 7.6, 1H), 8.04–7.95 (m, 3H), 7.78 (dd, J = 13.2, 8.0, 1H), 7.63 (d, J = 7.6, 1H), 7.58 (dd, J = 8.0, 2.0, 1H), 7.47–7.31 (m, 7H), 7.28–7.21 (m, 2H), 6.53 (d, J = 6.4, 1H), 6.48 (d, J = 6.0, 1H), 5.49 (tt, J = 9.6, 4.8, 1H), 5.20 (t, J = 6.0, 1H), 5.03 (t, J = 5.6, 1H), 3.95 (s, 3H). 13C{1H} NMR (101 MHz): 167.1 (s, CvO), 156.2–111.4 (C, CH, Ar), 95.89 (s, CH), 95.85 (s, CH), 89.2 (s, CH), 85.3 (s, CH), 84.4 (s, CH), 53.3 (s, CH3), 52.1 (s, CH3). 31P{1H} NMR (162 MHz): +22.4 (s). HRMS: calcd for C38H27ClO3PRuS ([M] − Cl), 731.0151; found, 731.0144.

Ru11*, [RuCl2(η6-methyl benzoate)(L11)]. The procedure was the same as that followed to prepare Ru6*. Starting from L11 (214 mg, 0.64 mmol) and Ru dimer D2 (150 mg, 0.24 mmol), the desired complex was obtained as a brown solid. Yield: 246 mg (80%).

IR: 3036, 2952, 2866, 1730 ν(CvO), 1433, 1372, 1293, 1277, 1106, 760, 695, 545, 516. 1H NMR (400 MHz): 8.31 (d, J = 9.2, 1H), 8.22 (m, 1H), 8.03 (d, J = 9.2, 1H), 8.01 (d, J = 8.8, 1H), 7.93 (dd, J = 10.8, 8.0 1H), 7.80 (m, 1H), 7.63–7.56 (m, 2H), 7.52–7.46 (m, 4H), 6.45 (d, J = 6.0, 1H), 6.26 (d, J = 6.0, 1H), 5.33 (m, 1H), 5.20 (t, J = 6.0, 2H), 3.91 (s, 3H), 3.82 (m, 1H), 1.15 (dd, J = 14.4, 6.8, 3H), 1.07 (dd, J = 18.0, 6.8, 3H). 13C{1H} NMR (101 MHz): 167.1 (CvO), 164.4 (CvO), 139.4–121.6 (C, CH, Ar), 95.1 (d, 2JCP = 3.5, CH), 94.5 (d, 2JCP = 3.8, CH), 89.5 (s, CH), 85.2 (d, 2JCP = 3.6, CH), 84.9 (d, 2JCP = 2.0, CH), 53.3 (s, CH3), 52.1 (s, CH3), 25.7 (d, 1JCP = 24.2, CH), 19.3 (d, 2JCP = 6.2, CH3), 18.7 (s, CH3). 31P{1H} NMR (162 MHz): +31.3 (s). Anal.: calcd for C29H27Cl2O2PRuS, C 54.21%, H 4.23%, S 4.99%; found, C 54.17%, H 4.39%, S 4.98%.

Ru13*, [RuCl2(η6-methyl benzoate)(L13)]. The procedure was the same as that followed to prepare Ru6*. Starting from L13 (200 mg, 0.59 mmol) and Ru dimer D2 (134 mg, 0.22 mmol), the desired complex was obtained as a dark red solid. Yield: 213 mg (76%).

IR: 3053, 2950, 1728 ν(CvO), 1434, 1377, 1110, 896, 749, 503. 1H NMR (400 MHz): 8.00 (ddd, J = 12.4, 7.6, 1.2, 1H), 7.74 (d, J = 7.6, 1H), 7.69–7.64 (m, 2H), 7.52–7.41 (m, 5H), 7.27 (m, 1H), 7.21–7.13 (m, 2H), 6.41 (d, J = 6.0, 1H), 6.35 (d, J = 5.6, 1H), 5.54 (m, 1H), 5.42 (d, J = 5.6, 1H), 5.39 (d, J = 5.6,

1H), 3.83 (s, 3H), 2.14 (d, 2JHP = 11.6, 3H). 31P{1H} NMR (162 MHz): +25.4 (s). HRMS: calcd for C27H23ClO2PRuS2 ([M] − Cl), 610.9603; found, 610.9595.

Ru2′, [RuCl(η6-p-cymene)(κ2P,S-L2)]PF6. Complex Ru2 (56 mg, 0.089 mmol) was dissolved in 20 mL of dichloromethane, thallium hexafluorophosphate (34 mg, 0.094 mmol) was added and the reddish suspension was stirred for 2 h. Water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with water, dried with anhydrous sodium sulfate, filtered and the solvent was removed under vacuum. The crude yellow product was recrystallised in dichloromethane/hexane. Yield: 53 mg (81%).

IR: 3089, 2968, 2876, 1618, 1471, 1438, 1391, 1108, 1020, 839 ν(PF6 −), 762, 558. 1H NMR (400 MHz): 8.21 (dd, J = 6.0, 3.2, 1H), 8.11 (dd, J = 7.6, 1.6, 1H), 8.06 (dd, J = 6.4, 3.2, 1H), 7.75–7.71 (m, 2H), 7.66–7.54 (m, 6H), 7.48 (t, J = 8.0, 1H), 6.34 (d, J = 6.4, 1H), 6.14 (d, J = 6.4, 1H), 6.09 (d, J = 6.0, 1H), 6.04 (d, J = 6.0, 1H), 3.89 (d, 3JHP = 12.4, 3H), 2.56 (sept, 3JHH = 6.8, 1H), 2.06 (s, 3H), 1.13 (d, 3JHH = 6.8, 3H), 0.83 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 152.9–123.9 (C, CH, Ar), 114.2 (s, C), 103.1 (s, C), 92.8 (d, 2JCP = 6.0, CH), 92.2 (d, 2JCP = 3.4, CH), 91.8 (d, 2JCP = 4.1, CH), 88.4 (d, 2JCP = 2.7, CH), 56.6 (d, 2JCP = 12.1, CH3), 31.4 (s, CH), 22.1 (s, CH3), 20.7 (s, CH3), 18.7 (s, CH3). 31P{1H} NMR (162 MHz): +138.7 (s). HRMS: calcd for C29H29ClOPRuS ([M] − PF6), 593.0403; found, 593.0406.

Ru3′, [RuCl(η6-p-cymene)(κ2P,S-L3)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru3 (100 mg, 0.15 mmol) and TlPF6 (56 mg, 0.16 mmol), the desired complex was obtained as a pale red solid. Yield: 95 mg (82%).

IR: 3085, 2967, 1471, 1437, 1389, 1146, 1108, 1018, 840 ν(PF6−), 756, 705, 558. 1H NMR (400 MHz): 7.97 (dd, J = 8.0, 1.2, 1H), 7.86–7.78 (m, 3H), 7.67 (dd, J = 7.6, 1.2, 1H), 7.62–7.51 (m, 6H), 7.46 (td, J = 7.6, 1.2, 1H), 6.54 (d, J = 6.4, 1H), 6.43 (d, J = 6.0, 1H), 6.30 (dd, J = 6.4, 1.2, 1H), 6.19 (d, J = 6.0, 1H), 3.62 (d, 3JHP = 11.6, 3H), 2.57 (sept, 3JHH = 6.8, 1H), 2.01 (s, 3H), 1.14 (d, 3JHH = 6.8, 3H), 0.84 (d, 3JHH = 6.8, 3H). 13C{1H} NMR (101 MHz): 140.5–127.4 (C, CH, Ar), 114.2 (s, C), 103.2 (s, C), 95.2 (d, 2JCP = 4.9, CH), 94.5 (d, 2JCP = 3.7, CH), 94.4 (d, 2JCP = 5.6, CH), 90.8 (d, 2JCP = 3.3, CH), 56.2 (d, 2JCP = 12.5, CH3), 31.2 (s, CH), 22.1 (s, CH3), 20.8 (s, CH3), 18.3 (s, CH3). 31P{1H} NMR (162 MHz): +145.5 (s). Anal.: calcd for C29H29ClF6OP2RuS2, C 45.23%, H 3.80%, S 8.33%; found, C 44.35%, H 4.05%, S 7.79%.

Ru9′, [RuCl(η6-p-cymene)(κ2P,S-L9)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru9 (30 mg, 0.039 mmol) and TlPF6 (14 mg, 0.040 mmol), the desired complex was obtained as a red solid. Yield: 30 mg (88%).

1H NMR (400 MHz): 8.33–8.21 (m, M + m), 8.10–7.85 (m, M + m), 7.73–7.60 (m, M + m), 7.57–7.42 (m, M + m), 7.42–7.27 (m, M + m), 7.18 (t, J = 7.7, 1H, M), 6.71 (d, J = 6.4, 1H, M), 6.44 (d, J = 6.4, 1H, m), 6.38 (d, J = 5.6, 1H, m), 6.36 (d, J = 5.6, 1H, M), 5.87 (d, J = 6.4, 1H, m), 5.83(d, J = 6.8, 1H, M), 5.66 (d, J = 6.4, 1H, m), 5.10 (d, J = 6.0, 1H, M), 2.44 (sept, 3JHH = 6.8, 1H, M), 2.34 (sept, 3JHH = 6.0, 1H, m), 2.06 (s, 3H, M), 1.99 (s, 3H, m), 1.28 (d, 3JHH = 6.8, 3H, m), 1.07 (d, 3JHH = 7.2, 3H,

M), 0.85 (d, 3JHH = 6.8, 3H, m), 0.44 (d, 3JHH = 6.8, 3H, M). 13C{1H} NMR (101 MHz, major isomer): 155.6–121.5 (C, CH, Ar), 112.0 (s, C), 105.3 (s, C), 96.9 (d, 2JCP = 7.6, CH), 89.0 (d, 2JCP = 5.2, CH), 86.9 (s, CH), 86.6 (s, CH), 31.3 (s, CH), 23.2 (s, CH3), 18.8 (s, br, CH3), 18.3 (s, CH3). 31P{1H} NMR (162 MHz): +50.1 (s, m), +44.4 (s, M). HRMS: calcd for C40H33ClOPRuS ([M] − PF6), 729.0716; found, 729.0742.

Ru10′, [RuCl(η6-p-cymene)(κ2P,S-L10)]BF4. The procedure was the same as that followed to prepare Ru2′. Starting from Ru10 (60 mg, 0.098 mmol) and TlBF4 (29 mg, 0.10 mmol), the desired complex was obtained as a pale red solid. Yield: 50 mg (71%).

IR: 3063, 2961, 2862, 1437, 1392, 1103, 1084, 1046 ν(BF4−), 898, 759, 696, 522. 1H NMR (400 MHz): 8.18 (d, J = 7.2, 1H), 8.09–8.00 (m, 2H), 7.85–7.77 (m, 2H), 7.69–7.53 (m, 7H), 6.45 (d, J = 6.0, 1H, M), 6.41 (d, J = 6.4, 1H, m), 6.35 (d, J = 6.4, 1H, M), 6.27 (d, J = 6.4, 1H, m), 6.04 (d, J = 6.0, 1H, m), 6.00 (d, J = 6.4, 1H, m), 5.74 (d, J = 6.4, 1H, M), 5.64 (d, J = 6.8, 1H, M), 2.70 (d, 2JHP = 10.4, 3H, m), 2.51 (sept, 3JHH = 6.8, 1H, m), 2.45 (d, 2JHP = 11.6, 3H, M), 2.30 (sept, 3JHH = 7.2, 1H, M), 1.97 (s, 3H, m), 1.88 (s, 3H, M), 1.18 (d, 3JHH = 6.8, 3H, M), 1.16 (d, 3JHH = 6.4, 3H, m), 0.95 (d, 3JHH = 6.8, 3H, M), 0.90 (d, 3JHH = 6.8, 3H, m). 13C{1H} NMR (101 MHz, only the major isomer peaks are listed): 152.0–124.0 (C, CH, Ar), 112.9 (s, C), 104.3 (s, C), 94.5 (d, 2JCP = 5.8, CH), 89.8 (d, 2JCP = 4.5, CH), 88.0 (d, 2JCP = 2.0, CH), 86.2 (d, 2JCP = 3.4, CH), 31.1 (s, CH), 22.0 (s, CH3), 21.4 (s, CH3), 17.9 (s, CH3), 12.2 (d, 1JCP = 36.9, CH3). 31P{1H} NMR (162 MHz): +47.4 (s, M), +39.8 (s, m). HRMS: calcd for C29H29ClPRuS ([M] − BF4), 577.0454; found, 577.0449.

Ru11′, [RuCl(η6-p-cymene)(κ2P,S-L11)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru11 (50 mg, 0.078 mmol) and TlPF6 (31 mg, 0.090 mmol), the desired complex was obtained as a dark red solid. Yield: 49 mg (84%).

IR: 3062, 2965, 1470, 1436, 1390, 842 ν(PF6−), 760, 695, 558, 505. 1H NMR (400 MHz): 8.07 (t, J = 8.0, 2H), 8.00 (d, J = 7.6, 1H), 7.71–7.59 (m, 5H), 7.51–7.43 (m, 4H), 6.58 (d, J = 6.8, 1H), 6.08 (d, J = 6.0, 1H), 6.03 (d, J = 6.0, 1H), 5.87 (d, J = 6.4, 1H), 3.75 (m, br, 1H), 2.36 (sept, 3JHH = 6.8, 1H), 2.07 (s, 3H), 1.43 (dd, 3JHH + 3JHP = 14.4, 6.4, 3H), 1.35 (dd, 3JHH + 3JHP = 20.4, 7.2, 3H), 1.11 (d, 3JHH = 7.2, 3H), 0.56 (d, 3JHH = 6.8, 3H). 13C {1H} NMR (101 MHz): 153.0–123.2 (C, CH, Ar), 113.3 (s, C), 97.9 (s, br, C), 93.7 (d, 2JCP = 6.3, CH), 91.6 (d, 2JCP = 5.7, CH), 91.3 (s, CH), 85.7 (s, CH), 31.4 (s, CH), 29.3 (d, 1JCP = 27.0, CH), 23.1 (s, CH3), 19.4 (s, CH3), 18.4 (s, CH3), 18.2 (d, 2JCP = 4.5, CH3), 17.8 (d, 2JCP = 7.2, CH3). 31P{1H} NMR (162 MHz): +68.1 (s). Anal.: calcd for C31H33ClF6P2RuS, C 49.64%, H 4.43%, S 4.27%; found, C 49.68%, H 4.89%, S 4.09%.

Ru12′, [RuCl(η6-p-cymene)(κ2P,S-L12)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru12 (50 mg, 0.064 mmol) and TlPF6 (24 mg, 0.069 mmol), the desired complex was obtained as a red solid. Yield: 35 mg (61%).

1H NMR (400 MHz): 8.20–8.00 (m, 4H), 7.76–7.47 (m, 8H), 6.27–6.22 (m, 3H, 1M + 2 m), 6.07 (d, J = 6.4, 1H, M), 5.74 (d, J = 6.0, 1H, m), 5.63 (d, J = 7.2, 1H, m), 5.53 (d, J = 5.2, 2H, M), 5.18 (s, 1H, M), 4.94 (s, 1H, M), 4.71 (s, 1H, m), 4.66 (s, 2H, M + m), 4.58 (s, 1H, M), 4.36 (s, 1H, m), 4.17 (s, 5H, M),

4.01 (s, 5H, m), 3.99 (s, 1H, m), 2.43 (sept, 3JHH = 7.6, 1H, M), 2.30 (sept, 3JHH = 8.4, 1H, m), 1.77 (s, 3H, m), 1.71 (s, 3H, M), 1.17 (d, 3JHH = 7.2, 3H, m), 0.97 (d, 3JHH = 6.8, 3H, M), 0.93 (d, 3JHH = 7.2, 3H, M), 0.88 (d, 3JHH = 6.4, 3H, m). 13C{1H} NMR (101 MHz): 151.7–123.9 (C, CH, Ar), 113.1 (s, C, m), 111.8 (s, C, M), 104.4 (s, C, m), 100.2 (s, C, M), 95.3 (d, 2JCP = 3.1, CH, M), 94.9 (d, 2JCP = 5.6, CH, m), 90.5 (d, 2JCP = 3.8, CH, M), 90.1 (d, 2JCP = 3.4, CH, M), 89.2 (d, 2JCP = 3.9, CH, m), 88.4 (s, CH, m), 86.8 (d, 2JCP = 3.8, CH, M), 86.7 (d, 2JCP = 3.5, CH, m), 76.5 (d, JCP = 10.4, CH, m), 74.6 (d, JCP = 8.1, CH, M), 73.0 (d, JCP = 8.5, CH, m), 72.6 (d, JCP = 10.6, CH, m), 72.2 (d, JCP = 14.4, CH, M), 71.5 (d, JCP = 9.4, CH, M), 71.3 (d, JCP = 11.8, CH, m), 70.9 (s, 5CH, m), 70.8 (d, JCP = 6.2, CH, M), 70.3 (s, 5CH, M), 31.6 (s, CH, M), 31.2 (s, CH, M), 22.4 (s, CH3, m), 21.7 (s, CH3, M), 21.2 (s, CH3, M), 20.9 (s, CH3, m), 18.1 (s, CH3, M), 17.6 (s, CH3, m). 31P{1H} NMR (162 MHz): +53.0 (s, m), +48.8 (s, M). HRMS: calcd for C38H35ClFePRuS ([M] − PF6), 747.0279; found, 747.0293.

Ru13′, [RuCl(η6-p-cymene)(κ2P,S-L13)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru13 (136 mg, 0.21 mmol) and TlPF6 (81 mg, 0.23 mmol), the desired complex was obtained as a pale red solid. Yield: 100 mg (63%).

IR: 3057, 2964, 2925, 1437, 1391, 1147, 1103, 841 ν(PF6−), 749, 694, 558. 1H NMR (400 MHz): 7.90 (dt, J = 8.0, 1.6, 2H), 7.80–7.65 (m, 6H), 7.65–7.42 (m, 14H), 7.36 (dd, J = 12.0, 7.6, 2H), 6.62 (d, J = 6.0, 1H, M), 6.57 (d, J = 6.4, 1H, M), 6.44 (d, J = 6.4, 1H, m), 6.39 (d, J = 6.4, 1H, m), 6.13 (d, J = 6.4, 1H, M), 6.08 (d, J = 6.0, 1H, M), 5.53 (d, J = 6.4, 1H, m), 5.35 (d, J = 6.0, 1H, m), 2.53 (m, 1H, M), 2.41 (m, 1H, m), 2.50 (d, 2JHP = 18.4, 3H, m), 2.46 (d, 2JHP = 10.0, 3H, M), 2.01 (s, 3H, m), 1.95 (s, 3H, M), 1.19 (d, 3JHH = 6.8, 3H, m), 1.15 (d, 3JHH = 6.8, 3H, M), 1.00 (d, 3JHH = 6.8, 3H, m), 0.88 (d, 3JHH = 6.8, 3H, M). 13C{1H} NMR (101 MHz): 146.2–127.7 (C, CH, Ar), 113.5 (s, C, m), 113.1 (s, C, M), 104.0 (s, C, m), 101.4 (s, C, M), 97.4 (d, 2JCP = 5.8, CH, m), 94.8 (s, br, CH, M), 93.8 (d, 2JCP = 4.5, CH, M), 92.5 (s, br, CH, M), 91.9 (d, 2JCP = 3.8, 2CH, 2 m), 89.9 (d, 2JCP = 3.8, CH, M), 89.3 (d, 2JCP = 4.2, CH, m), 31.2 (s, CH, M), 30.9 (s, CH, m), 21.9 (s, CH3, M), 21.8 (s, CH3, m), 21.6 (s, CH3, m), 21.5 (d, 1JCP = 34.6, CH3, M), 21.0 (s, CH3, M), 18.1 (s, CH3, M), 18.0 (s, CH3, m), 11.8 (d, 1JCP = 40.2, CH3, m). 31P{1H} NMR (162 MHz): +54.9 (s, m), +50.0 (s, M). Anal.: calcd for C27H23ClF6O2P2RuS2, C 42.89%, H 3.07%, S 8.48%; found, C 42.95%, H 2.85%, S 7.75%.

Ru11*′, [RuCl(η6-methyl benzoate)(κ2P,S-L11)]PF6. The procedure was the same as that followed to prepare Ru2′. Starting from Ru11* (130 mg, 0.20 mmol) and TlPF6 (78 mg, 0.22 mmol), the desired complex was obtained as a brown solid. Yield: 120 mg (73%).

IR: 3092, 2959, 2872, 1734 ν(CvO), 1436, 1390, 1298, 1280, 1114, 840 ν(PF6−), 761, 695, 558. 1H NMR (400 MHz): 8.19 (d, J = 6.8, 1H), 8.04 (d, J = 8.0, 2H), 7.69–7.56 (m, 5H), 7.55–7.44 (m, 4H), 7.21 (d, br, J = 5.2, 1H), 6.75 (d, J = 6.0, 1H), 6.49 (s, br, 2H), 5.84 (t, br, J = 5.2, 1H), 3.75 (m, 1H), 3.73 (s, 3H), 1.43–1.33 (m, 6H). 13C{1H} NMR (101 MHz): 163.3 (CvO), 152.8–122.3 (C, CH, Ar), 96.6 (d, 2JCP = 1.8, CH), 94.6 (d, 2JCP = 3.8, CH), 90.5 (s, CH), 89.3 (d, 2JCP = 5.4, C), 88.7 (d, 2JCP = 1.0, CH), 87.9 (d, 2JCP = 2.6, CH), 53.7 (s, CH3), 30.2 (d, 1JCP = 27.2, CH), 18.3 (d, 2JCP = 4.4,

CH3), 17.8 (d, 2JCP = 7.1, CH3). 31P{1H} NMR (162 MHz): +67.8 (s). HRMS: calcd for C29H27ClO2PRuS ([M] − PF6), 607.0201; found, 607.0205.

Ru-catalysed transfer hydrogenation

A 100 ml Schlenk flask was charged with the ruthenium precursor (0.02 mmol) and potassium tert-butoxide (11.2 mg, 0.1 mmol) and purged with three vacuum/nitrogen cycles. Under a gentle flow of nitrogen, 25 ml of 2-propanol were added and the flask heated to reflux (85 °C) for 15 minutes. After that time, acetophenone (0.47 mL, 4.0 mmol) was rapidly added to start the catalytic run. The reaction was monitored at the allotted times by taking aliquots of around 0.1 mL and analysing them by GC.

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Legends to figures

Scheme 1 Described preparation of rac-P(4-dibenzofuranyl)MePh.

Scheme 2 Heterocyclic P-stereogenic phosphines described in this paper**.**

Scheme 3 Lithiation of the heterocycles.

Scheme 4 Preparation of the heterocyclic P-stereogenic phosphine-boranes by the Jugé–Stephan method.

Fig. 1 ORTEP representation (thermal ellipsoids are drawn at the 50% probability level, H atoms are removed for clarity) of 4-DBF-Fc (left) and 4-DBT-Fc (right). Distances (Å) and angles (°) for 4-DBF-Fc: P(1)–B(1), 1.913(4); P(1)–C(4), 1.779(3); P(1)–C(17), 1.816(3); P(1)–C(5), 1.812(3); O(1)–C(15), 1.388(4); O(1)–C(16), 1.392(3); B(1)–P(1)–C(4), 114.32(16); B(1)–P(1)–C(17), 110.02(16); B(1)–P(1)–C(5), 113.67(17); C(15)–O(1)–C(16), 105.3(2). For 4-DBT-Fc: P(1)–B(1), 1.906(6); P(1)–C(10), 1.789(5); P(1)–C(11), 1.819(5); P(1)–C(17), 1.814(5); S(1)–C(27), 1.749(5); S(1)–C(28), 1.757(5); B(1)–P(1)–C(10), 117.8(3); B(1)–P(1)–C(11), 108.0(2); B(1)–P(1)–C(17), 114.0(3); C(27)–S(1)–C(28), 91.6(2).

Scheme 5 Unsuccessful synthesis of 4-DBTO2-Me.

Scheme 6 Preparation of 3-DBTO2.

Scheme 7 Free phosphinites and phosphines L1–13.

Scheme 8 Preparation of neutral ruthenium complexes.

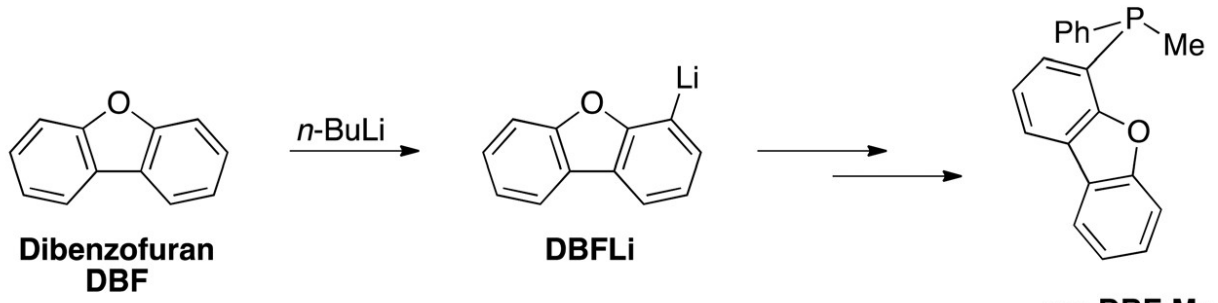
Scheme 9 Two possible isomers of the Ru complexes observed by 13C{1H} NMR spectroscopy.

Fig. 2 ORTEP representations (thermal ellipsoids are drawn at the 50% probability level, H atoms are removed for clarity) of Ru5, Ru6 and Ru10 (from left to right). The most relevant distances and angles are given in Table 1.

Scheme 10 Preparation of cationic ruthenium complexes.

Scheme 11 Ru-catalysed enantioselective transfer hydrogenation of acetophenone.

SCHEME 1

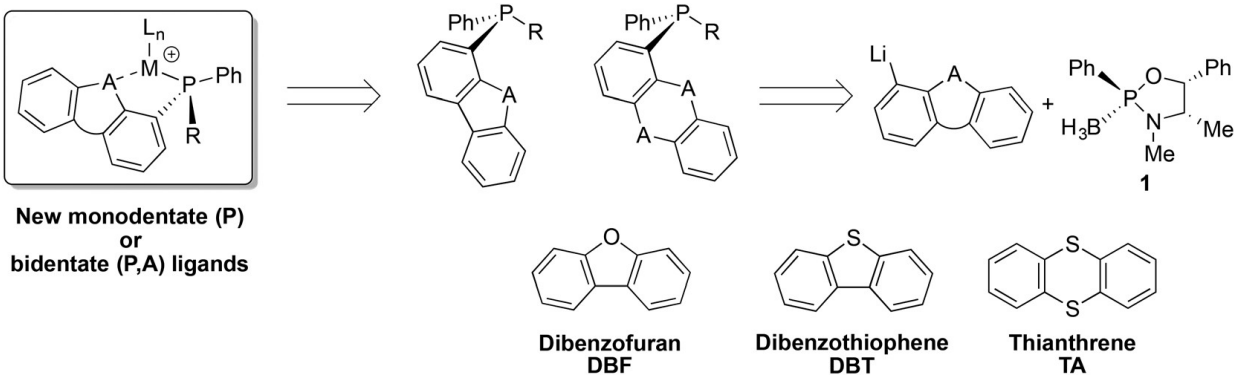


Dibenzofuran
DBF

DBFLi

***rac*-DBF-Me**

SCHEME 2



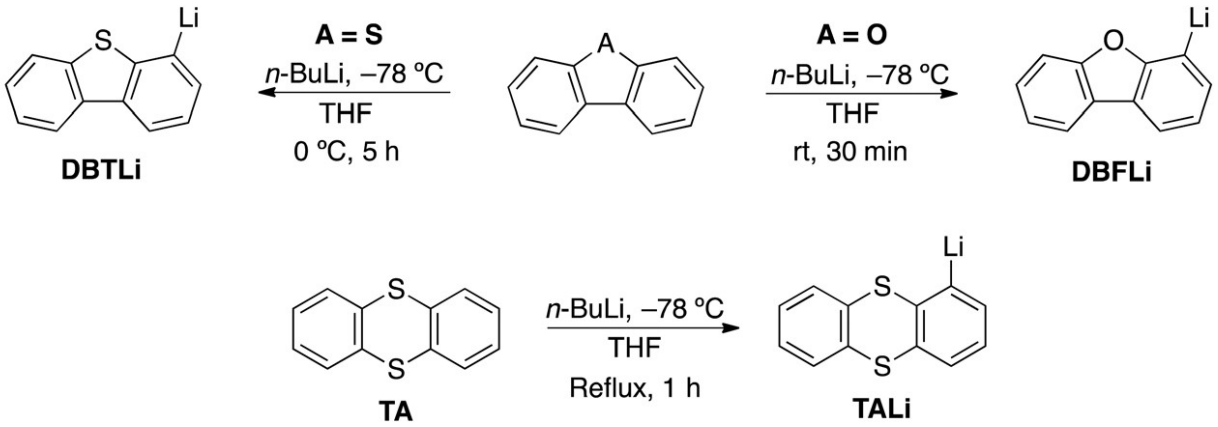
New monodentate (P) or bidentate (P,A) ligands

Dibenzofuran DBF

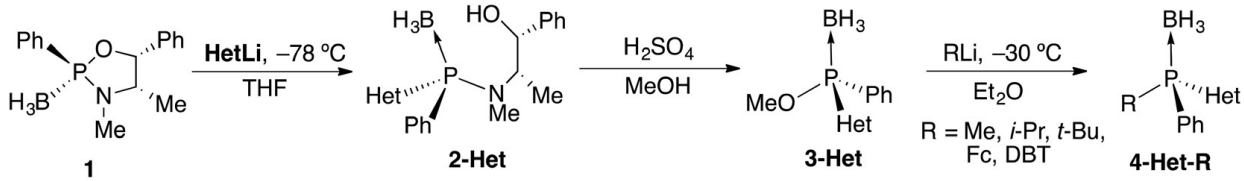
Dibenzothiophene DBT

Thianthrene TA

SCHEME 3

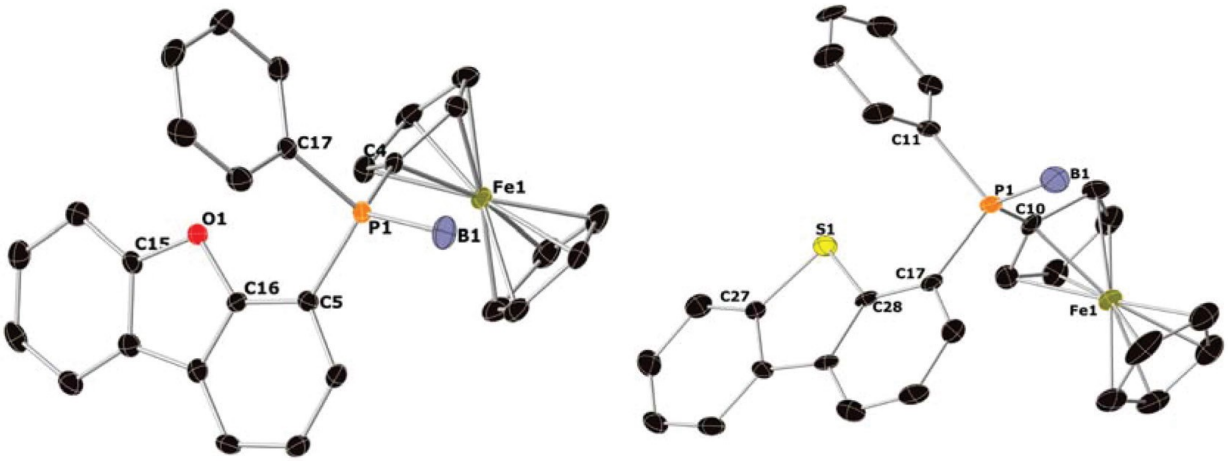

Li
S
DBTLi
A = S
n-BuLi, –78 °C
THF
0 °C, 5 h
A
A = O
n-BuLi, –78 °C
THF
rt, 30 min
Li
O
DBFLi
S
S
TA
n-BuLi, –78 °C
THF
Reflux, 1 h
Li
S
S
TALi

SCHEME 4

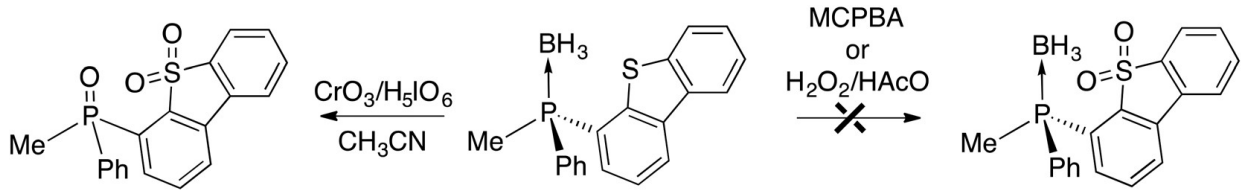


1 **2-Het** **3-Het** **4-Het-R**

FIGURE 1

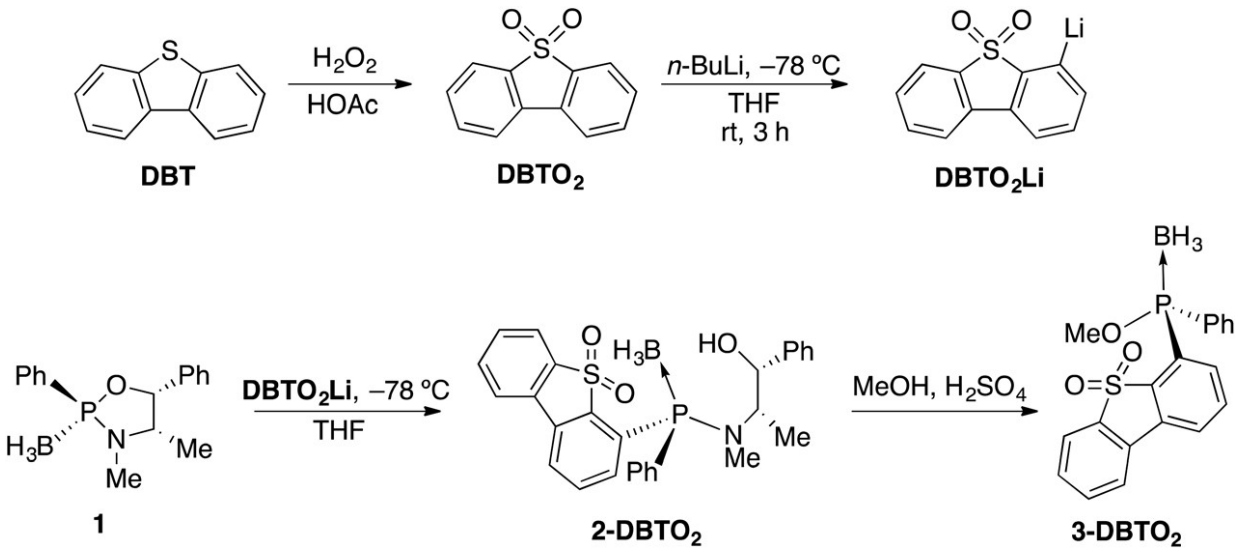


SCHEME 5

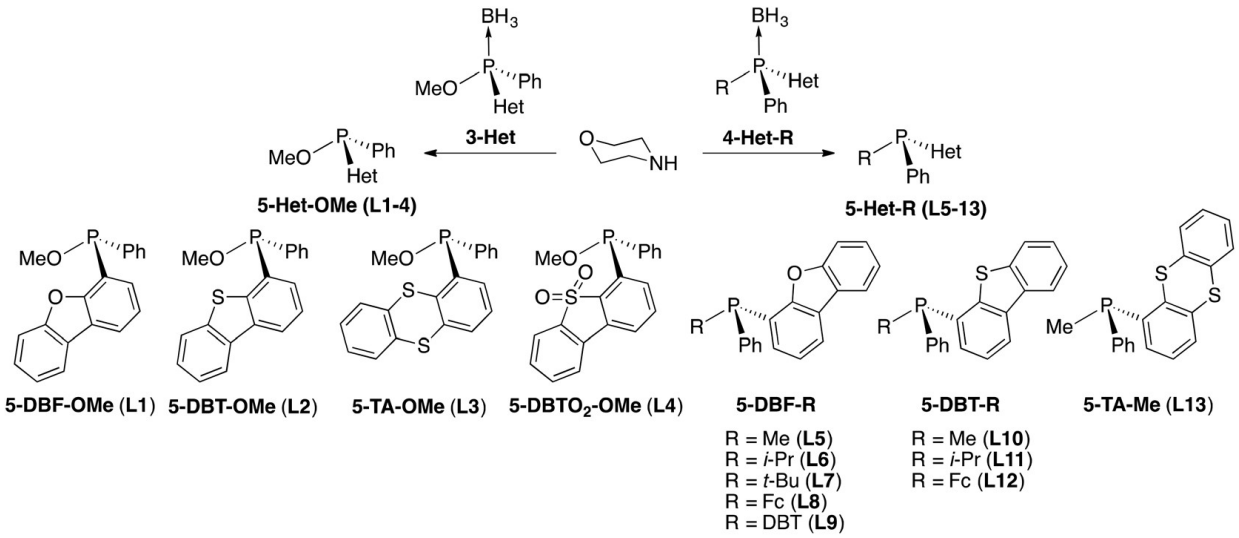


4-DBTO$_3$-Me **4-DBT-Me** **4-DBTO$_2$-Me**

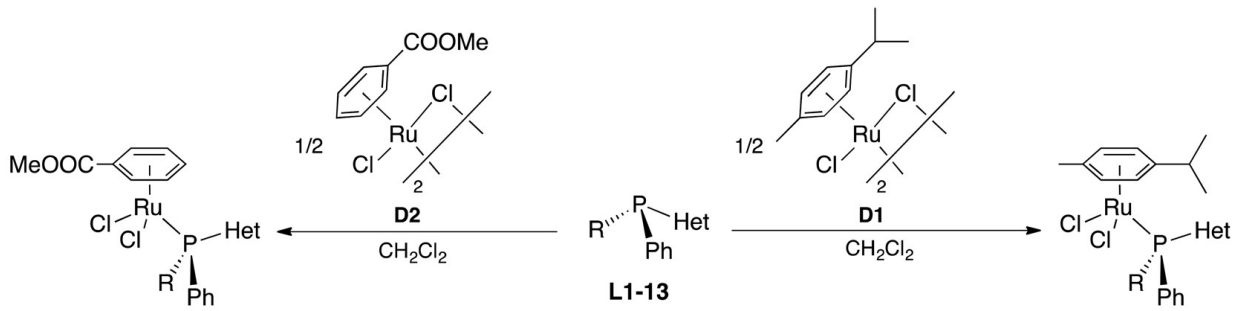
SCHEME 6


H2O2
HOAc
n-BuLi, –78 °C
THF
rt, 3 h
DBT
DBTO2
DBTO2Li
DBTO2Li, –78 °C
THF
MeOH, H2SO4
1
2-DBTO2
3-DBTO2

SCHEME 7


BH3
MeO
P
Ph
Het
3-Het
4-Het-R
R
5-Het-OMe (L1-4)
5-Het-R (L5-13)
5-DBF-OMe (L1)
5-DBT-OMe (L2)
5-TA-OMe (L3)
5-DBTO2-OMe (L4)
5-DBF-R
5-DBT-R
5-TA-Me (L13)
R = Me (L5)
R = i-Pr (L6)
R = t-Bu (L7)
R = Fc (L8)
R = DBT (L9)
R = Me (L10)
R = i-Pr (L11)
R = Fc (L12)

SCHEME 8



Ru6*, Ru9*, Ru11*, Ru13*

Ru1-6, Ru8-13

SCHEME 9

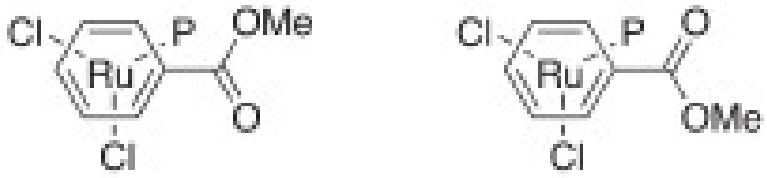
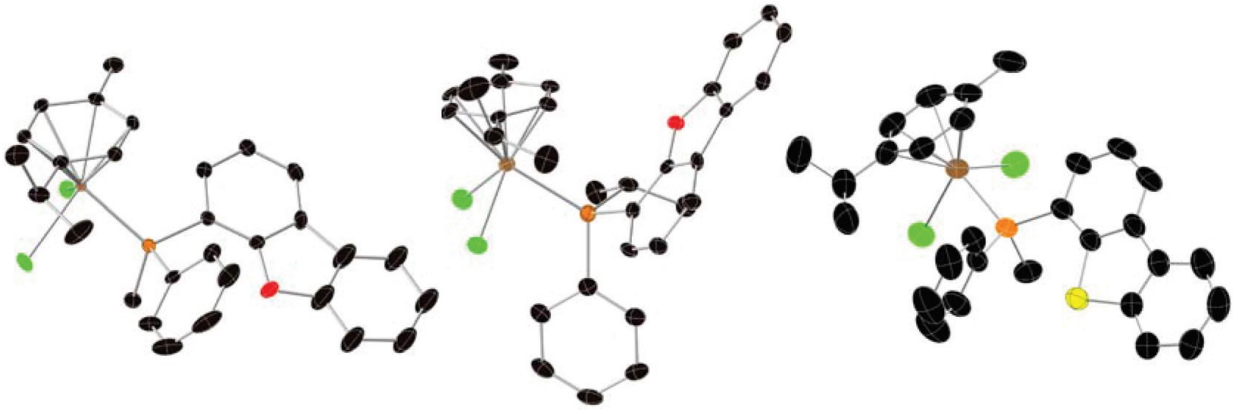


FIGURE 2



1184 **SCHEME 10**

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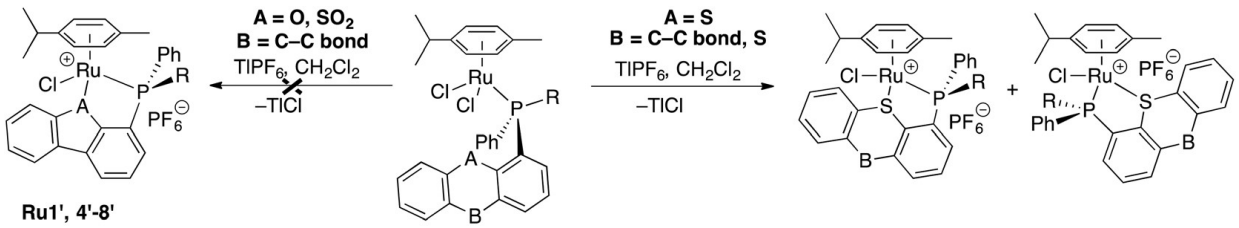

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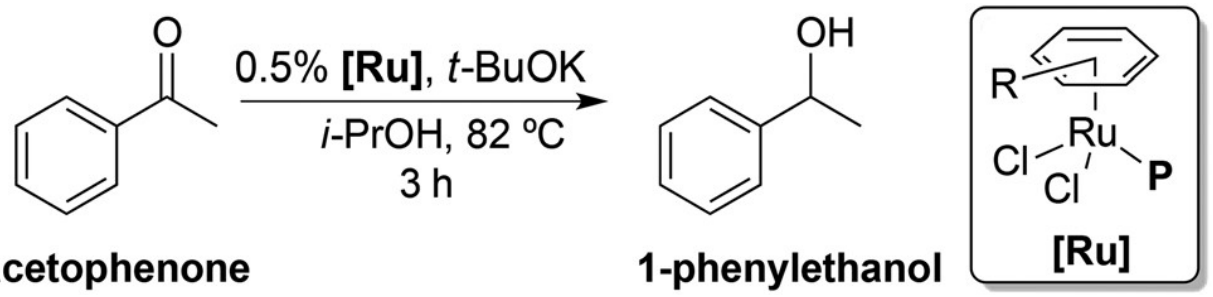
SCHEME 11



acetophenone **1-phenylethanol**

Table 1 Selected distances (Å) and angles (°) for complexes Ru5, Ru6 and Ru10

Parameter	Ru5 [a]	Ru6	Ru10
Ru–Cl	2.4093(10), 2.4188(11)	2.4065(12), 2.4069(13)	2.3983(11), 2.4242(11)
	2.4146(10), 2.4204(10)		
Ru–P	2.3362(11) 2.3378(11)	2.3737(13)	2.3432(11)
[b] $Ru–C_{arene}$	2.217 2.212	2.210	2.220
$P–C_{Ph}$	1.807(5) 1.824(4)	1.833(5)	1.818(4)
$P–C_{Het}$	1.822(4) 1.815(4)	1.825(5)	1.836(4)
$P–C_{R}$	1.820(5) 1.820(5)	1.865(5)	1.816(4)
P–Ru–Cl	84.32(4), 85.63(4) 86.65(4), 83.44(4)	91.17(5), 86.33(5)	85.08(4), 83.86(4)
Cl–Ru–Cl	88.53(4) 88.27(4)	87.69(5)	88.14(4)

[a] There are two crystallographically distinct molecules in the unit cell.
[b] Averaged value of the six η^6-Ph Ru–C distances.

Table 2 Results of the transfer hydrogenation of acetophenone catalysed by Ru complexes

Entry[a]	Precursor	Time/h	Conversion/%[b]	ee/%[c]
1	**Ru1**	1/3/5	31/79/>99	<5
2	**Ru2**	1/3/5	28/69/85	<5
3	**Ru2′**	1/3/5	40/73/82	<5
4	**Ru3**	1/3/5	11/28/39	<5
5	**Ru3′**	1/3/5	8/21/29	<5
6	**Ru4**	1/3/5	15/32/46	14(*R*)
7	**Ru5**	1/3/5	92/99/>99	<5
8	**Ru6**	1/3/5	35/78/>99	<5
9	**Ru6***	1/3/5	80/96/>99	<5
10	**Ru8**	1/3/5	25/68/83	6(*S*)
11	**Ru9**	1/3/5	32/75/92	13(*R*)
12	**Ru9***	1/3/5	54/91/>99	7(*R*)
13	**Ru9′**	1/3/5	10/29/36	<5
14	**Ru10**	1/3/5	16/32/41	<5
15	**Ru11**	1/3/5	19/49/75	56(*R*)
16	**Ru11***	1/3/5	52/96/>99	70(*R*)
17	**Ru11′**	1/3/5	4/9/17	10(*R*)
18	**Ru11*′**	1/3/5	19/48/63	70(*R*)
19	**Ru12**	1/3/5	21/58/83	30(*S*)
20	**Ru12′**	1/3/5	9/24/34	16(*S*)
21	**Ru13**	1/3/5	64/94/>99	<5
22	**Ru13***	1/3/5	50/83/95	<5
23	**Ru13′**	1/3/5	34/55/71	<5

[a] Catalytic conditions: Ru complex (0.02 mmol) and *t*-BuOK (0.1 mmol) dissolved in 25 mL of i-PrOH and activated at 85 °C for 15 minutes before adding acetophenone (4.0 mmol). [b] Conversion of acetophenone. [c] Enantiomeric excess at 24 h.