A New Route to Cationic Half-Sandwich Ruthenium(II) Complexes with Chiral Cyclopentadienylphosphane Ligands

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Optically active cyclopentadienyl-linked phosphane ligands L_n of general formula $C_5H_5CH_2CH(R)PR'_2$ (R = Ph, R′ = Ph, L_1; R = Ph, R′ = Cy, L_2; R = mesityl, R′ = Ph, L_3) and $C_5H_5CH(R)CH_2PPh_2$ (R = Cy, L_4; R = Bzl, L_5) are synthesised by ring-opening reactions of 1-R-spiro[2.4]hepta-4,6-dienes (R = Ph, Cy, mesityl, benzyl), with lithium phosphides $LiPR'_2$ (Ar = Ph, Cy). Reaction of the ligands L_n with $[RuH(\eta^5\text{-}C_7H_{11})_2][BF_4]$ in acetonitrile at reflux affords the bis(acetonitrile) ruthenium(II) complexes $[Ru(\eta^5\text{-}C_5H_4(C_2H_3R)PR'_2\text{-}\kappa P)(CH_3CN)_2][BF_4]$, in which the ligands are coordinated to the metal through the cyclopentadienyl and the phosphane moieties forming a chelate, in almost quantitative yields. The complexes are active catalysts in the redox isomerisation of geraniol affording chiral citronellal but with low enantioselectivity. They also catalyze an aldol-type C–C coupling reaction between 3-buten-2-ol and benzaldehyde affording almost racemic 4-hydroxy-3-methyl-4-phenyl-2-butanone with good diastereoselectivity (*syn*/*anti* ratio up to 77:23).

Introduction

Organometallic ruthenium complexes are becoming increasingly important in homogeneous catalyses such as reduction, oxidation, isomerisation, and carbon−carbon bond-formation.[1] The preparation of the necessary ruthenium catalysts most often starts from $RuCl_3{\cdot}nH_2O$, $[Ru(H_2O)_6]^{2+}$, $[RuCl_2(PPh_3)_3]$, $[RuCl_2(COD)]_n$, or $[RuCl_2(cymene)]_n$.[2] Analogously, the chemistry of cyclopentadienylruthenium complexes is based on few starting materials, mainly on the readily available precursors $[Ru(Cp)Cl(PPh_3)_2]$ and $[Ru(Cp)Cl(CO)_2]$.[2] However, the selective replacement of either PPh_3 or CO has proved difficult, limiting the synthetic utility. Coordinatively unsaturated complexes and complexes with labile ligands are the most promising candidates for catalytic applications, since the availability of a vacant coordination site is a prerequisite for both stoichiometric and catalytic organic transformations at the transition metal centre. Therefore, more labile systems, including $[Ru(Cp)(CH_3CN)_3]^+$,[3] and [Ru(Cp)Cl(COD)],[4] have been developed. In particular, the cationic complex $[Ru(Cp)(CH_3CN)_3]^+$ is a promising versatile intermediate since the acetonitrile ligands (AN) are substitutionally labile and can be replaced by other ligands.[5,6] This complex can be regarded as a source of the highly active coordinatively unsaturated fragment $[Ru(Cp)]^+$, which may well have interesting potential in catalysis. Indeed, several C−C bond-forming reactions catalysed by this compound have been reported by Trost.[7] Kirchner has shown that substitution of one acetonitrile ligand in $[Ru(Cp)(AN)_3]^+$ for tertiary phosphanes PR_3 $[Ru(Cp)(AN)_2(PR_3)]^+$ [8a] also gave a very active catalyst for the redox isomerisation of allylic alcohols,[8b] and C−C bond-formation.[8c−8l] Various attempts have been made to link the Cp and phosphorus moieties in such compounds through a spacer. In almost all cases, these complexes contain a PPh_3 ligand, as the synthesis, starting from $[RuCl_2(PPh_3)_3]$, gives no alternate choice.[9] Only in one case could bis(acetonitrile) complexes be isolated by Takahashi in which the linker connects through an ester group at the cyclopentadienyl ligand.[10] These complexes were tested in catalytic allylic amination and alkylation with excellent results.[11] Prompted by the results of Kirchner and Takahashi, we endeavoured to develop a synthetic route to $[Ru(Cp{-}P)(AN)_2]^+$-type chiral complexes containing a phosphane ligand tethered onto the cyclopentadienyl ring via a two-carbon linker (Cp−P). We have recently reported a route to such complexes,[12] and we have shown, in collaboration with Kirchner, that they react with alkynes displaying unusual reactivity.[13] Here we report on an improved method that affords the desired optically active ruthenium(II) complexes in almost quantitative yields, as well as a preliminary account of their application in catalytic organic transformations.

Results and Discussion

Synthesis of the Ligands

When we started our research, there was a dearth of general procedures to prepare chiral Cp−P ligands by a

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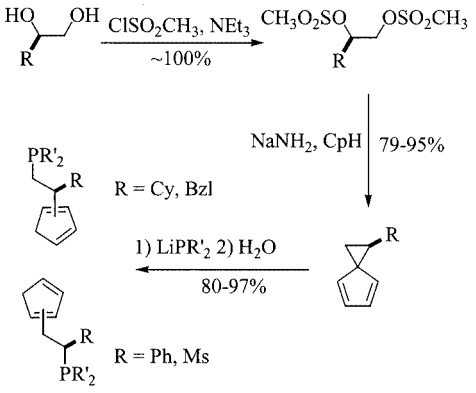
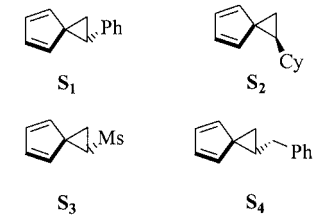
method that allows their modular construction by independent variation of the three components, namely the cyclopentadienyl, the linker, and the phosphane.[9] We have developed such a route by adapting the method first reported by Kauffmann,[14] which is based on the ring-opening reactions of spiro[2.4]hepta-4,6-dienes.[15] Traditionally, the spiro compounds have been synthesised by bis-alkylation of cyclopentadiene with the corresponding dibromoalkane in the presence of sodium amide or sodium hydride.[16] However, a more convenient approach to introduce chirality into these spiroannulated precursors is the use of the corresponding bis(mesylate)s or bis(tosylate)s as alkylating reagents. Rieger has used this route to synthesise ethyl-bridged bis(cyclopentadienyl) ligands starting from styrene epoxide.[17] The same approach was recently adopted by Whitby for the synthesis of chiral indenyl-linked phosphane ligands.[18] Our synthetic strategy is based on the use of chiral vicinal diols as starting materials, as depicted in Scheme 1. The chiral diols can be obtained in high enantiomeric purity by several methods, for example Sharpless asymmetric dihydroxylation,[19] Jacobsen hydrolytic kinetic resolution of epoxides,[20] and biological means. They are easily converted into the bis(methanesulfonate) esters in almost quantitative yield by reaction with methanesulfonyl chloride. Displacement of the methanesulfonate groups by excess cyclopentadiene/sodium amide affords the spiroannulated dienes in excellent yields (79−95%). The formation of the spiro compound involves first a nucleophilic substitution of one mesylate group by the cyclopentadienyl anion, followed by a fast deprotonation of the resulting substituted cyclopentadiene, and finally a second nucleophilic substitution of the other mesylate group and ring closure. The nucleophilic substitution at the chiral carbon is entirely stereoselective and proceeds with complete inversion of configuration at the stereogenic centre.[15] The chiral spiro compounds that have been synthesised by this methodology are shown in Scheme 2.

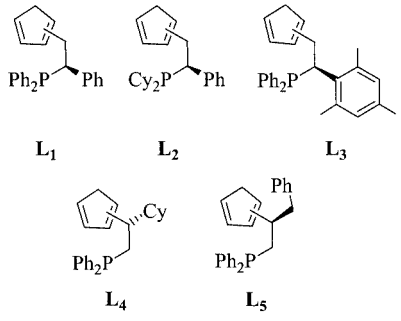


Scheme 1

The ring-opening reaction of (*S*)-1-R-spiro[2.4]hepta-4,6-dienes (R = phenyl, mesityl) with lithium diphenylphosphide or lithium dicyclohexylphosphide proceeds with complete regiospecificity by attack of the nucleophile at the activated benzylic position of the cyclopropane ring affording the ligands L_{1-3}. Interestingly, this regioselectivity is the opposite to that found for the nucleophilic opening of phenyl epoxide and phenyl episulfide with lithium phosphides; in that context, the attack of the nucleophile proceeds regioselectively at the less-hindered site.[21] The ring-opening reaction proceeds with complete inversion of the configuration at the stereogenic centre, as is demonstrated by X-ray crystal structure determinations of some derived metal complexes.[12,15] The opposite regioselectivity is observed in the ring-opening reaction of (*R*)-1-benzylspiro[2.4]hepta-4,6-diene and (*S*)-1-cyclohexylspiro[2.4]hepta-4,6-diene, which lack the activated benzylic position in the cyclopropane ring. In this case, the nucleophilic attack with lithium diphenylphosphide occurs on the unsubstituted carbon atom of the cyclopropane ring, affording the ligands L_4 and L_5.[22] The same regioselectivity has been observed in the ring-opening of 2-cyclohexylspiro(cyclopropane-1,1′-indene).[18] For convenience of storage, the lithium salts of the ligands can be reacted with H_2O to afford the cyclopentadienyl(alkyl)phosphanes as a mixture of two positional isomers depending on to which olefinic carbon atom of the Cp the linker is attached. The ligands are shown in Scheme 3. The overall yields for three steps (starting from the diols) are excellent (63 to 88%).



Scheme 2

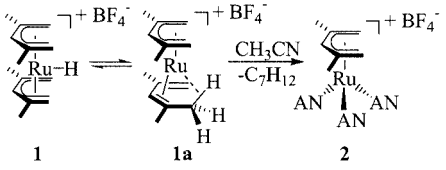


Scheme 3

Synthesis of the Ruthenium Complexes

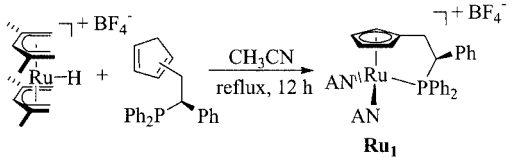
We have recently reported that reaction of $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$ with the Cp-linked phosphane ligand L_1 in a 1:2 ratio in a mixture of acetonitrile and ethanol at room temperature, in the presence of Li_2CO_3 and KPF_6, affords the cationic complex $[Ru(\eta^5\text{-}C_5H_4CH_2CH(Ph)PPh_2\text{-}\kappa P)(AN)_2][PF_6]$ in 70−75% yield.[12] However, apart from the desired compound, side products were also formed that have not been identified yet. The purification of the desired

complex was accomplished by a cumbersome crystallisation step. Therefore, we sought for a better synthetic route. A paper from Cox and Roulet provided inspiration for a new method.[23] The paper reports: "Dissolution of complex **1** in deoxygenated acetonitrile leads to rapid displacement of one molar equiv. of 2,4-dimethylpenta-1,3-diene and formation of the cation $[Ru(\eta^5\text{-}C_7H_{11})(AN)_3]^+$". [Bis($\eta^5$-2,4-dimethylpentadienyl)hydridoruthenium] tetrafluoroborate (**1**) is known to show a fluxional behaviour, as the hydrido ligand is involved in three-centre Ru−H−C agostic interactions with all terminal methylene groups of the dimethylpentadienyl ligands (Scheme 4).[24]



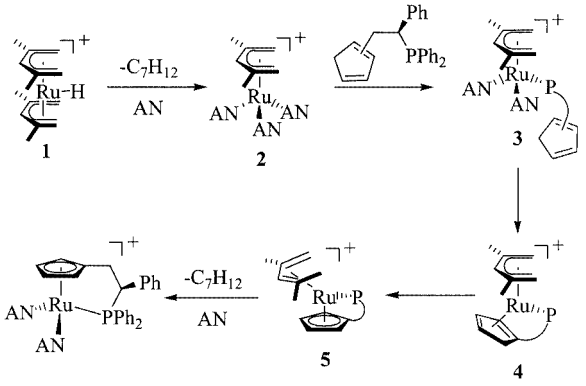
Scheme 4

The species **1a**, which is in equilibrium with **1**, is highly reactive towards two-electron ligands, and the η^4-C_7H_{12} ligand is substitutionally labile, as it is easily replaced by acetonitrile. We performed the reaction between L_1 and $[Ru(\eta^5\text{-}C_7H_{11})_2H][BF_4]$, and we were delighted to obtain the pure bis(acetonitrile) complex **Ru$_1$** in almost quantitative yield (Scheme 5).



Scheme 5

A possible reaction mechanism that accounts for the formation of **Ru$_1$** is presented in Scheme 6. At first, **2** may be formed, with subsequent coordination of phosphorus to afford **3**. The reaction has been followed by means of a ^{31}P NMR experiment, revealing the formation of intermediate species with ^{31}P resonances at about $\delta = 30$ ppm. The coordination of the phosphorus atom seems to be very fast, as no signals of the free ligands could be observed ($\delta = 0.4$ and 0.9 ppm). No other intermediates could be detected, and the species convert into the final complex, which shows a singlet at $\delta = 88.7$ ppm. The evolution of **3** to **4** involves the intramolecular coordination of the cyclopentadiene group, which is favoured on thermodynamic grounds by the formation of a chelate species. At this stage, an intramolecular H-transfer between the cyclopentadiene and the dimethylpentadienyl group may be postulated. It may occur with participation of the metal through a hydrido species. The species **5** thus formed contains the labile η^4-dimethylpentadiene ligand that is replaced by acetonitrile affording the desired compound in a straightforward way. When the reaction is carried out on a gram scale, the evolution of the mixture can easily be followed by the colour changes of the solution. Initially, the mixture is brown-yellow and becomes immediately yellow upon addition of the ligand. Upon refluxing, a red-orange colour appears and lasts for a few minutes, eventually converting to an orange-yellow colour.

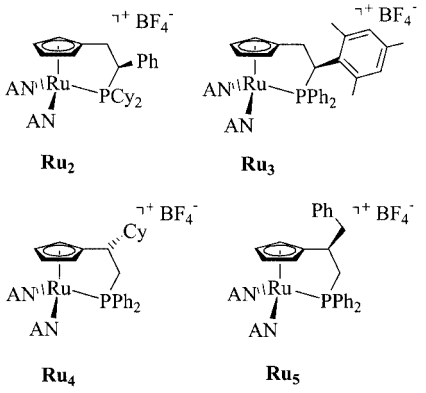


Scheme 6

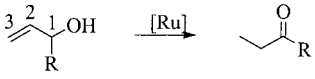
According to this synthetic procedure, the ruthenium complexes depicted in Scheme 7 could be obtained in almost quantitative yields. They were characterised by analytical and spectroscopic methods. The phosphorus resonates at low field in **Ru$_{1-3}$** ($\delta \approx 88$ ppm); the same signal appears at higher field in **Ru$_4$** and **Ru$_5$** ($\delta \approx 52$ ppm). In the free ligands, the phosphorus shows two signals in the ^{31}P NMR spectrum due to the two regioisomers at about $\delta = 0.5$ (L_1), 18 (L_2), −6 (L_3), −18 (L_4), and −20 ppm (L_5). The large downfield shift upon coordination is characteristic of the formation of a five-membered chelate ring.[25] In the ^1H NMR spectra, the signals of the C−H hydrogen of the linker are low-field shifted in **Ru$_{1-3}$** ($\delta = 4.66$, 4.19, and 5.42 ppm respectively); for comparison, the hydrogen resonates at $\delta = 1.94$ and 2.55 ppm for **Ru$_4$** and **Ru$_5$** respectively. The coordinated acetonitrile ligands give rise to two doublets with a long range coupling (^5J) with phosphorus of about 1 Hz. Easy replacement of the acetonitrile ligands with CD_3CN was confirmed by means of ^1H NMR spectroscopy, suggesting that they are substitutionally labile.

Catalytic Applications

With several chiral complexes in hand, we began a preliminary screening of their catalytic activity in organic transformations. Kirchner has reported that $[Ru(Cp)(AN)_2(PPh_3)]^+$, in which the phosphane is not connected to the Cp, is a highly active catalyst at 57 °C for the redox isomerisation of allylic alcohols to give the corresponding carbonyl compounds.[8b] We tested **Ru$_1$** in this reaction and, in line with his report, we found that it catalyses the isomerisation of allylic alcohols (R = H, Me, Ph) at room temperature [Equation (1)]; details are given in the Exp. Sect.



Scheme 7



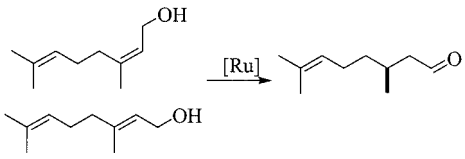
(1)

Kirchner also found that C^1-substituted allylic alcohols react much more quickly than those featuring substituents at the C^3 carbon; heating was required to effect the conversion of 2,3-disubstituted alcohols, while C^1- and C^3-disubstituted alcohols were not converted. To test the reactivity of our optically active complexes in the redox isomerisation of pro-chiral allylic alcohols, we chose geraniol and nerol as substrates. Isomerisation of diethylgeranylamine for the production of practically optically pure (+)-citronellal catalysed by a Rh^+/BINAP complex is a very important industrial process leading to key intermediates for the fragrance and flavour industry.[26] Comparable success has not been achieved for the corresponding isomerisation of readily available geraniol or nerol. To the best of our knowledge, the hitherto best catalyst system reported is based on a Rh^+/BINAP complex, and affords citronellal with 60% *ee*.[27] Initially, the reaction was performed in CH_2Cl_2 at room temperature and at reflux but only modest or no conversion into citronellal was obtained, corroborating the finding of Kirchner that C^3-disubstituted alcohols are not prone to undergo the redox isomerisation. However, when we performed the reaction in THF at reflux, we were pleased to observe conversion of the alcohol to citronellal [Equation (2)]. The results are summarised in Table 1.

Table 1. Redox isomerisation of geraniol and nerol[a]

Catalyst	Substrate	Product	Conversion	ee
Ru_1	geraniol	(+)-citronellal	73%	19%
Ru_1	nerol	citronellal	18%	*nd*
Ru_2	geraniol	−	0%	−
Ru_3	geraniol	(−)-citronellal	71%	8%
Ru_4	geraniol	(+)-citronellal	97%	17%
Ru_4	nerol	(−)-citronellal	35%	*nd*
Ru_5	geraniol	(+)-citronellal	32%	13%

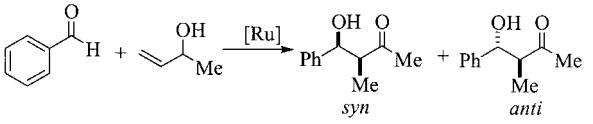
[a] The values given in the table are the average of at least two runs. See the Exp. Sect. for more details.



(2)

The conversion depends strongly on the complex used, the best results being found for **Ru_1** and **Ru_4** for the conversion of geraniol. The poor conversion of nerol has already been observed in other catalytic systems.[27] **Ru_2** is not active under these conditions; this fact may be ascribed to the steric bulkiness or the high Lewis basicity of the PCy_2 fragment. Unfortunately, the complexes are not able to induce high enantioselectivity. Further studies are necessary to determine if this catalytic system could be improved. Nevertheless, the results obtained with our complexes, although moderate, represent the first application of a ruthenium catalyst in the isomerisation of geraniol to optically enriched citronellal.[28]

The mechanistic rationale for the ruthenium-catalysed redox isomerisation of allylic alcohols postulates the formation of a ruthenium-enolate complex.[29] We envisioned that the formed enolate could be trapped by an electrophile, and indeed we found that an aldol-type product was formed via a ruthenium-catalysed cross-coupling of 3-buten-2-ol and benzaldehyde [Equation (3)].



(3)

It has recently been reported that $[RuCl_2(PPh_3)_3]$ catalyses this reaction.[30] The results obtained with our complexes are detailed in Table 2. The yields are not satisfactory due to the concurrent isomerisation of the allylic alcohol to

Table 2. Aldol reaction between benzaldehyde and 3-buten-2-ol[a]

Catalyst	Loading (mol %)	Solvent	Yield (%)	*syn*/*anti*
Ru_1	5	CH_2Cl_2	31	69:31
	1		25	74:26
	0.1		26	67:33
	5	THF	57	76:24
	1		80	77:23
	0.1		51	77:23
Ru_2	1	THF	49	71:29
Ru_3	1	THF	47	62:38
Ru_4	1	THF	49	60:40
Ru_5	1	THF	53	63:37

[a] Reactions carried out at room temperature until complete consumption of the allylic alcohol. Isolated yields based on benzaldehyde are reported. The diastereoselectivity was based on ^1H NMR analysis of the crude product. The values given in the table are the average of at least two runs.

butan-2-one; this may also explain the non-linear dependence of product yield on catalyst loading. The enantioselectivity is also disappointing, and a maximum of 5% *ee* has been obtained. However, the diastereoselectivity is appreciable, favouring the *syn* diastereomer. A substantial improvement in both yield and diastereoselectivity could be obtained upon switching from CH_2Cl_2 to THF, and it is noteworthy that the catalysts are quite active even at low loading. Further studies to improve the catalyst performance are intended.

Conclusion

A novel synthetic method has been developed that allows the one-pot synthesis of optically active cationic bis(acetonitrile)ruthenium(II) complexes of chiral cyclopentadienyl-linked phosphane ligands in very high yields. The method is general and allows the use of ligands bearing phosphanes with variable steric and electronic features. Moreover, the linker, which connects the cyclopentadienyl unit to the phosphane, can be straightforwardly modified. Considering the labile nature of the acetonitrile ligands, these complexes are potential candidates for catalytic implementation. Indeed, a preliminary study on their reactivity revealed that the complexes catalyse the isomerisation of geraniol to citronellal, as well as an aldol-type cross-coupling reaction between 3-buten-2-ol and benzaldehyde. Although the *ee* values obtained are rather low, the method is of interest for preparing other complexes that may find various applications in asymmetric catalysis.

Experimental Section

General Remarks: All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard methods. NMR spectra were recorded on a Varian Unity 500 spectrometer (500 MHz, ^{1}H; 125 MHz, ^{13}C; 202 MHz, ^{31}P) at room temperature. Chemical shifts are given in ppm relative to the solvent signal (^{1}H and ^{13}C) or to external H_3PO_4 (^{31}P). ^{1}H and ^{13}C{^{1}H} signal assignments were confirmed by ^{1}H,^{1}H-COSY, APT, ^{1}H,^{13}C-HETCOR, and NOE-difference experiments. (*R*)-1-Phenylethane-1,2-diol was obtained by reduction of (*R*)-mandelic acid with LAH.[31] (*S*)-1-Cyclohexylethane-1,2-diol was obtained by initial reduction of the arene ring of (*S*)-mandelic acid with hydrogen using 5% Rh on alumina as catalyst, followed by reduction of the carboxylic group with LAH.[32] (*R*)-3-Phenylpropane-1,2-diol was obtained by reduction of the corresponding acid with LAH. (*R*)-1-(2,4,6-Trimethylphenyl)ethane-1,2-diol was obtained by Sharpless asymmetric dihydroxylation of the corresponding olefin.[33] $[Ru(\eta^5\text{-}C_7H_{11})_2H][BF_4]$[34] was prepared according to a published procedure. All other chemicals were purchased and used without further purification.

Preparation of the Bis(methanesulfonate) Esters: NEt_3 (2.4 equiv.) was added to a solution of the diol in CH_2Cl_2 (ca. 10 mL/g). The solution was cooled in an ice-water bath and methanesulfonyl chloride (2.2 equiv.) in CH_2Cl_2 (5 mL/mL) was added dropwise over 1 h. The mixture was stirred for 1 h at 0 °C and then for 2 h at room temp. The mixture was poured into 1 M HCl. The layers were separated and the aqueous phase was washed with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed successively with 1 M HCl, saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. The solution was then filtered, and the solvent was removed under reduced pressure. The bis(methanesulfonate) esters were obtained in almost quantitative yield and they were used without further purification for the preparation of the spiro compounds.

Preparation of the Spiro Compounds: Freshly cracked cyclopentadiene (2 equiv.) was added dropwise to a suspension of $NaNH_2$ (2.5 equiv.) in THF (ca. 25 mL/g). The addition of CpH was adjusted so as to maintain a gentle reflux. Upon complete addition, the mixture was stirred for 1/2 h and subsequently, a solution of the bis(methanesulfonate) in THF (ca. 15 mL/g) was added dropwise. The addition was accompanied by considerable heat evolution. The reaction mixture was stirred at room temperature overnight. MeOH and H_2O were carefully added, the mixture was diluted with Et_2O and the layers separated. The aqueous phase was washed with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and treated with decolourising charcoal. The solution was finally filtered, and the solvent removed under reduced pressure. The oil obtained was purified by filtration through a short column of basic alumina (activity I) with hexane as eluent. Reproducible elemental analyses could not be obtained, as the solvent could not be removed completely from the oily compounds.

Preparation of the Ligands by Ring Opening of the Spiro Compounds with Lithium Phosphides: The lithium phosphide was prepared by treating a solution of the secondary phosphane in THF (ca. 10 mL/g) with *n*BuLi (1.1 equiv.) at −78 °C. The deep-orange solution formed was stirred for 15 minutes at room temperature and then cooled again to −78 °C. At this temperature, the spiro compound (1.1 equiv.) dissolved in THF (1 mL/g) was added to the solution and the reaction mixture was allowed to reach room temperature overnight. The solvent was removed under reduced pressure and the oil left was washed several times with hexane until precipitation of the lithium salt of the ligand. This was dissolved in THF and degassed H_2O was added. After several extractions with CH_2Cl_2, the combined organic phases were dried over $MgSO_4$ and treated with decolourising charcoal. The solution was filtered through a short column of basic alumina (activity I), and the solvent removed under reduced pressure affording the pure ligand as an air-sensitive oil or solid as a one to one mixture of two regioisomers. The signals in the ^{1}H NMR spectra are highly overlapped and could not be attributed. Accordingly, only selected ^{13}C NMR data and the ^{31}P resonances are given. The ligands were characterised as their derived ruthenium complexes.

Synthesis of the Ruthenium Complexes: A flask was charged with the ligand and **1** in equimolar amounts. CH_3CN (ca. 20 mL/g) was added and the solution refluxed overnight. Then, the solution was filtered through a short pad of deactivated alumina (activity V) and the solvents evaporated to dryness. The solid obtained was washed several times with Et_2O and dried under high vacuum.

(*S*)-1-Phenylspiro[2.4]hepta-4,6-diene (S_1): The title compound was prepared, according to the representative procedure, from 10.0 g of (*R*)-phenyl-1,2-bis(methanesulfonyloxy)ethane as a colourless or pale-yellow oil. Yield: 4.64 g (81%). $[\alpha]_D^{20} = +229$ (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 2.06 (dd, $^2J_{H,H}$ = 4.58, $^3J_{H,H}$ = 8.85 Hz, 1 H, CH_2), 2.32 (dd, $^2J_{H,H}$ = 4.58, $^3J_{H,H}$ = 7.93 Hz, 1 H, CH_2), 3.32 (t, $^3J_{H,H}$ = 8.24 Hz, 1 H, C*H*Ph), 5.92 (m, 1 H, C*H*), 6.21 (m, 1 H, C*H*), 6.45 (m, 1 H, C*H*), 6.50 (m, 1 H, C*H*), 7.18−7.30 (m,

5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.05 (*C*H$_2$), 30.85 (*C*HPh), 45.55 (*C*$_{spiro}$), 126.37 (*C*H, Ph), 127.93 (*C*H, Ph), 128.05 (*C*H, Ph), 128.57 (*C*H), 130.21 (*C*H), 135.73 (*C*H), 138.77 (*C*H), 139.28 (*C*, Ph) ppm. HRMS [M$^+$]: calcd. 168.09390; found 168.09335.

(*S*)-1-Cyclohexylspiro[2.4]hepta-4,6-diene (S$_2$): The title compound was prepared, according to the representative procedure, from 20.0 g of (*S*)-cyclohexyl-1,2-bis(methanesulfonyloxy)ethane as a colourless or pale-yellow oil. Yield: 9.15 g (79%). $[\alpha]_D^{20}$ = −36 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.90−2.0 (m, 11 H, Cy), 1.60 (dd, $^2J_{H,H}$ = 3.96, $^3J_{H,H}$ = 7.32 Hz, 1 H, C*H*$_2$), 1.79 (dd, $^2J_{H,H}$ = 3.96, $^3J_{H,H}$ = 8.55 Hz, 1 H, C*H*$_2$), 1.90 (m, 1 H, C*H*, Cy), 6.09 (m, 1 H, C*H*), 6.29 (m, 1 H, C*H*), 6.49 (m, 1 H, C*H*), 6.59 (m, 1 H, C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.18 (*C*H$_2$, Cy), 26.00 (*C*H$_2$, Cy), 26.22 (*C*H$_2$), 26.38 (*C*H$_2$, Cy), 32.91 (*C*H$_2$, Cy), 33.29 (*C*H$_2$, Cy), 35.23 (*C*HCy), 42.09 (*C*H, Cy), 42.77 (*C*$_{spiro}$), 127.50 (*C*H), 129.95 (*C*H), 135.67 (*C*H), 139.77 (*C*H) ppm. HRMS [M$^+$]: calcd. 174.14085; found 174.14067.

(*S*)-1-(2,4,6-Trimethylphenyl)spiro[2.4]hepta-4,6-diene (S$_3$): The title compound was prepared, according to the representative procedure, from 12.5 g of (*R*)-(2,4,6-trimethylphenyl)-1,2-bis(methanesulfonyloxy)ethane as a pale-yellow oil. Yield: 6.80 g (87%). $[\alpha]_D^{20}$ = +2 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 2.17 (dd, $^2J_{H,H}$ = 4.27, $^3J_{H,H}$ = 8.55 Hz, 1 H, C*H*$_2$), 2.23 (dd, $^2J_{H,H}$ = 4.27, $^3J_{H,H}$ = 9.16 Hz, 1 H, C*H*$_2$), 2.29 (s, 9 H, C*H*$_3$), 3.14 (t, $^3J_{H,H}$ = 8.85 Hz, 1 H, C*H*Ms), 5.85 (m, 1 H, C*H*), 6.34 (m, 1 H, C*H*), 6.50 (m, 1 H, C*H*), 6.58 (m, 1 H, C*H*), 6.83 (s, 2 H, Ms) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.23 (*C*H$_2$), 20.80 (*C*H$_3$), 28.61 (*C*HMs), 45.03 (*C*$_{spiro}$), 128.55 (*C*H, Ms), 129.11 (*C*H), 130.04 (*C*H), 133.19 (*C*, Ms), 135.94 (*C*, Ms), 137.52 (*C*H), 139.19 (*C*H) ppm. HRMS [M$^+$]: calcd. 210.14085; found 210.14114.

(*R*)-1-Benzylspiro[2.4]hepta-4,6-diene (S$_4$): The title compound was prepared, according to the representative procedure, from 25.4 g of (*S*)-benzyl-1,2-bis(methanesulfonyloxy)ethane as a pale-yellow oil. Yield: 14.3 g (95%). $[\alpha]_D^{20}$ = −11 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.71 (dd, $^2J_{H,H}$ = 4.27, $^3J_{H,H}$ = 7.32 Hz, 1 H, C*H*$_2$), 1.85 (dd, $^2J_{H,H}$ = 4.27, $^3J_{H,H}$ = 8.55 Hz, 1 H, C*H*$_2$), 2.30 (m, 1 H, C*H*Bzl), 2.94 (d, $^3J_{H,H}$ = 7.02 Hz, 2 H, C*H*$_2$Ph), 6.10 (m, 1 H, C*H*), 6.33 (m, 1 H, C*H*), 6.49 (m, 1 H, C*H*), 6.58 (m, 1 H, C*H*), 7.1−7.3 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.46 (*C*H$_2$), 28.29 (*C*HBzl), 38.32 (*C*H$_2$Ph), 43.20 (*C*$_{spiro}$), 126.10 (*C*H, Ph), 127.95 (*C*H, Ph), 128.29 (*C*H, Ph), 128.29 (*C*H), 130.68 (*C*H), 135.41 (*C*H), 139.64 (*C*H) 140.74 (*C*) ppm. HRMS [M$^+$]: calcd. 182.10955; found 182.10938.

(*S*)-[2-(Cyclopenta-1,4-dienyl)-1-phenylethyl]diphenylphosphane and (*S*)-[2-(Cyclopenta-1,3-dienyl)-1-phenylethyl]diphenylphosphane (L$_1$): The title compound was prepared as an equal mixture of two regioisomers according to the representative procedure from 5.0 g of S$_1$ and 5.0 g of $HPPh_2$ as a colourless solid. Yield: 9.2 g (97%). ^{13}C NMR ($CDCl_3$, selected data): δ = 33.67 (d, $^2J_{C,P}$ = 23.1 Hz, *C*H$_2$), 34.29 (d, $^2J_{C,P}$ = 23.0 Hz, *C*H$_2$), 41.07 (s, *C*H$_2$, Cp), 43.70 (s, *C*H$_2$, Cp), 45.28 (d, $^1J_{C,P}$ = 13.4 Hz, *C*HPh), 46.17 (d, $^1J_{C,P}$ = 14.4 Hz, *C*HPh), 140.83 (s, *C*, Cp), 140.90 (s, *C*, Cp), 144.69 (d, $^2J_{C,P}$ = 13.5 Hz, *C*, Ph), 147.20 (d, $^2J_{C,P}$ = 13.4 Hz, *C*, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 0.458 (s), 0.886 (s) ppm. HRMS [M$^+$]: calcd. 354.15374; found 354.15323.

(*S*)-Dicyclohexyl[2-(cyclopenta-1,4-dienyl)-1-phenylethyl]phosphane and (*S*)-Dicyclohexyl[2-(cyclopenta-1,3-dienyl)-1-phenylethyl]phosphane (L$_2$): The title compounds were prepared as an equimolar mixture of two regioisomers, according to the representative procedure, from 4.7 g of **S$_1$** and 5.0 g of $HPCy_2$ as a colourless solid. Yield: 8.6 g (93%). ^{13}C NMR ($CDCl_3$, selected data): δ = 32.83 (d, $^1J_{C,P}$ = 9.6 Hz, *C*H, Cy), 32.98 (d, $^1J_{C,P}$ = 8.6 Hz, *C*H, Cy), 33.24 (d, $^1J_{C,P}$ = 2.9 Hz, *C*H, Cy), 33.7 (d, $^1J_{C,P}$ = 2.9 Hz, *C*H, Cy), 34.79 (d, $^2J_{C,P}$ = 22.1 Hz, *C*H$_2$), 35.48 (d, $^2J_{C,P}$ = 23.0 Hz, *C*H$_2$), 39.37 (d, $^1J_{C,P}$ = 19.2 Hz, *C*HPh), 40.37 (d, $^1J_{C,P}$ = 20.1 Hz, *C*HPh), 40.93 (s, *C*H$_2$, Cp), 43.61 (s, *C*H$_2$, Cp), 142.50 (s, *C*, Cp), 142.53 (s, *C*, Cp), 145.03 (d, $^2J_{C,P}$ = 12.4 Hz, *C*, Ph), 147.60 (d, $^2J_{C,P}$ = 13.5 Hz, *C*, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 18.08 (s), 18.75 (s) ppm. HRMS [M$^+$]: calcd. 366.24764; found 366.24738.

(*S*)-[2-(Cyclopenta-1,3-dienyl)-1-(2,4,6-trimethylphenyl)ethyl]diphenylphosphane and (*S*)-[2-(Cyclopenta-1,4-dienyl)-1-(2,4,6-trimethylphenyl)ethyl]diphenylphosphane (L$_3$): The title compounds were prepared as an equimolar mixture of two regioisomers, according to the representative procedure, from 3.1 g of **S$_3$** and 2.5 g of $HPPh_2$ as a colourless oil. Yield: 5.0 g (93%). ^{13}C NMR ($CDCl_3$, selected data): δ = 20.74 (*C*H$_3$), 21.36 (*C*H$_3$), 22.49 (*C*H$_3$), 22.65 (*C*H$_3$), 31.47 (d, $^2J_{C,P}$ = 20.1 Hz, *C*H$_2$), 32.12 (d, $^2J_{C,P}$ = 21.1 Hz, *C*H$_2$), 39.87 (d, $^1J_{C,P}$ = 17.2 Hz, *C*HMs), 40.85 (d, $^1J_{C,P}$ = 18.2 Hz, *C*HMs), 41.03 (s, *C*H$_2$, Cp), 43.56 (s, *C*H$_2$, Cp) ppm. ^{31}P NMR ($CDCl_3$): δ = −6.53 (s), −6.26 (s) ppm. HRMS [M$^+$]: calcd. 397.20852; found 397.20828.

(*R*)-[2-Cyclohexyl-2-(cyclopenta-1,3-dienyl)ethyl]diphenylphosphane and (*R*)-[2-Cyclohexyl-2-(cyclopenta-1,4-dienyl)ethyl]diphenylphosphane (L$_4$): The title compound was prepared as an equimolar mixture of two regioisomers, according to the representative procedure, from 2.1 g of **S$_2$** and 2.0 g of $HPPh_2$ as a colourless solid. Yield: 3.1 g (80%). ^{13}C NMR ($CDCl_3$, selected data): δ = 29.99 (d, $^1J_{C,P}$ = 15.3 Hz, *C*H$_2$), 31.37 (d, $^1J_{C,P}$ = 10.55 Hz, *C*H$_2$), 39.73 (s, *C*H$_2$, Cp), 40.81 (s, *C*H$_2$, Cp), 41.76 (d, $^3J_{C,P}$ = 8.54 Hz, *C*H, Cy), 42.16 (d, $^2J_{C,P}$ = 13.4 Hz, *C*HCy), 42.89 (d, $^2J_{C,P}$ = 13.4 Hz, *C*HCy), 43.03 (d, $^3J_{C,P}$ = 7.79 Hz, *C*H, Cy), 137.78 (d, $J_{C,P}$ = 14.4 Hz, *C*), 138.92 (d, $J_{C,P}$ = 13.4 Hz, *C*), 139.22 (d, $J_{C,P}$ = 14.4 Hz, *C*), 147.19 (d, $J_{C,P}$ = 3.8 Hz, *C*), 149.85 (d, $J_{C,P}$ = 4.8 Hz, *C*) ppm. ^{31}P NMR ($CDCl_3$): δ = −18.89 (s), −18.19 (s) ppm. HRMS [M$^+$]: calcd. 360.20069; found 360.20039.

(*S*)-[2-Benzyl-2-(cyclopenta-1,3-dienyl)ethyl]diphenylphosphane and (*S*)-[2-Benzyl-2-(cyclopenta-1,4-dienyl)ethyl]diphenylphosphane (L$_5$): The title compound was prepared as an equal mixture of two regioisomers according to the representative procedure from 6.5 g of **S$_4$** and 6.0 g of $HPPh_2$. Yield: colourless solid, 11.0 g (93%). ^{13}C NMR ($CDCl_3$, selected data): δ = 33.11 (d, $^1J_{C,P}$ = 12.4 Hz, *C*H$_2$), 34.41 (d, $^1J_{C,P}$ = 12.4 Hz, *C*H$_2$), 39.20 (d, $^2J_{C,P}$ = 15.45 Hz, *C*HBzl), 39.96 (d, $^1J_{C,P}$ = 15.3 Hz, *C*HBzl), 40.91 (s, *C*H$_2$, Cp), 41.32 (s, *C*H$_2$, Cp), 42.42 (d, $^3J_{C,P}$ = 8.54 Hz, *C*H$_2$Ph), 43.98 (d, $^3J_{C,P}$ = 9.55 Hz, *C*H$_2$Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = −20.56 (s), −20.47 (s) ppm. HRMS [M$^+$]: calcd. 368.16939; found 368.16937.

(*S*)-Bis(acetonitrile)[(η^5-2-cyclopentadienyl-1-phenylethyl)diphenylphosphane-κ*P*] ruthenium(II) Tetrafluoroborate (Ru$_1$). This compound was prepared, according to the representative procedure, from 2.8 g of **L$_1$** and 3.0 g of **1** as yellow crystals. The NMR spectroscopic data are identical to those already reported for [Ru{η^5-$C_5H_4CH_2CH(Ph)PPh_2$-κ*P*}$(CH_3CN)_2$][PF_6].[12] Yield: 4.73 g (96%). M.p.: 165−170 °C. $[\alpha]_D^{20}$ = +8.7 (*c* = 1, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2274 cm^{-1}, 1600, 1581, 1058, 704. MS (FAB): *m*/*z* = 536 [M$^+$], 495 [M$^+$ − CH_3CN], 454 [M$^+$ − 2CH_3CN]. $C_{29}H_{28}BF_4N_2PRu$ (623.38): calcd. C 55.87, H 4.53, N 4.49; found C 55.73, H 4.62, N 4.35.

(*S*)-Bis(acetonitrile)[dicyclohexyl(η^5-2-cyclopentadienyl-1-phenylethyl)phosphane-κ*P*]ruthenium(II) Tetrafluoroborate (Ru$_2$): This compound was prepared, according to the representative procedure, from 1.1 g of **L$_2$** and 1.13 g of **1** as a yellow solid. Yield: 1.9 g (100%). M.p.: 195−200 °C. $[\alpha]_D^{20}$= +97.5 (*c* = 1, CH_3CN).

^{1}H NMR (CD_2Cl_2): δ = 0.52 (m, 1 H, *Cy*), 1.0−2.21 (m, 21 H, *Cy*), 2.41 (d, $^5J_{H,P}$ = 0.91 Hz, 3 H, CH_3CN), 2.44 (d, $^5J_{H,P}$ = 0.92 Hz, 3 H, CH_3CN), 2.47−2.67 (m, 2 H, CH_2), 3.95 (m, 1 H, Cp), 4.19 (m, 1 H, C*H*Ph), 4.25 (m, 1 H, Cp), 5.05 (m, 1 H, Cp), 5.13 (m, 1 H, Cp), 7.26−7.41 (m, 5 H, Ph) ppm. ^{13}C NMR (CD_2Cl_2): δ = 4.45 (*C*H$_3$, *C*H$_3$CN), 4.67 (*C*H$_3$, *C*H$_3$CN), 26.83 (*C*H$_2$, *Cy*), 27.16 (*C*H$_2$, *Cy*), 27.40 (*C*H$_2$, *Cy*), 27.70 (d, $J_{C,P}$ = 13.4 Hz, *C*H$_2$, *Cy*), 28.48 (d, $^2J_{C,P}$ = 12.44 Hz, *C*H$_2$), 28.65 (*C*H$_2$, *Cy*), 30.92 (d, $J_{C,P}$ = 5.78 Hz, *C*H$_2$, *Cy*), 33.08 (d, $^1J_{C,P}$ = 17.34 Hz, *C*H, *Cy*), 36.06 (d, $^1J_{C,P}$ = 13.32 Hz, *C*H, *Cy*), 56.54 (d, $^1J_{C,P}$ = 18.22 Hz, *C*HPh), 57.62 (*C*H, Cp), 68.80 (*C*H, Cp), 77.86 (d, $J_{C,P}$ = 7.66 Hz, *C*H, Cp), 90.97 (d, $J_{C,P}$ = 3.89 Hz, *C*H, Cp), 102.88 (d, $J_{C,P}$ = 3.77 Hz, C_{ipso}, Cp), 127.44 (*C*, *C*N), 127.82 (*C*H), 128.21 (d, $J_{C,P}$ = 2.89 Hz, *C*H), 128.48 (*C*, *C*N), 129.21 (*C*H), 138.47 (d, $J_{C,P}$ = 8.67 Hz, *C*) ppm. ^{31}P NMR (CD_2Cl_2): δ = 88.78 (s, *P*Cy$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2274 cm^{-1}, 1600, 1058, 704. MS (FAB): *m*/*z* (%) = 549 (15) [M$^+$ + 1], 508 (85) [M$^+$ − CH$_3$CN], 466 (100) [M$^+$ − 2CH$_3$CN], 87 (100) [BF_4^-]. $C_{29}H_{40}BF_4N_2PRu$ (635.47): calcd. C 54.80, H 6.36, N 4.41; found C 55.18, H 6.60, N 3.91.

(*S*)-Bis(acetonitrile){[η^5-2-cyclopentadienyl-1-(2,4,6-trimethylphenyl)ethyl]diphenylphosphane-κ*P*}ruthenium(II) Tetrafluoroborate (Ru$_3$): This compound was prepared, according to the representative procedure, from 1.4 g of **L$_3$** and 1.33 g of **1** as a yellow solid. Yield: 2.3 g (99%). M.p.: 160−165 °C. $[\alpha]_D^{20}$= −12.4 (*c* = 1, CH_3CN). ^{1}H NMR (CD_2Cl_2): δ = 1.40 (s, 3 H, CH_3), 1.76 (d, $^5J_{H,P}$ = 1.22 Hz, 3 H, CH_3CN), 2.15 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.37 (d, $^5J_{H,P}$ = 0.92 Hz, 3 H, CH_3CN), 2.42−2.79 (m, 2 H, CH_2), 4.30 (m, 1 H, Cp), 4.45 (m, 1 H, Cp), 5.18 (m, 1 H, Cp), 5.31 (m, 1 H, Cp), 5.42 (m, 1 H, C*H*Ms), 6.48 (s, 1 H, *Ms*), 6.76 (s, 1 H, *Ms*), 7.20−7.50 (m, 10 H, Ph) ppm. ^{13}C NMR (CD_2Cl_2): δ = 3.29 (*C*H$_3$, *C*H$_3$CN), 4.48 (*C*H$_3$, *C*H$_3$CN), 20.80 (*C*H$_3$), 22.22 (*C*H$_3$), 22.63 (*C*H$_3$), 30.16 (d, $^2J_{C,P}$ = 10.55 Hz, *C*H$_2$), 60.71 (*C*H, Cp), 64.28 (d, $^1J_{C,P}$ = 23.12 Hz, *C*HMs), 65.37 (*C*H, Cp), 82.82 (d, $J_{C,P}$ = 7.66 Hz, *C*H, Cp), 87.19 (d, $J_{C,P}$ = 5.78 Hz, *C*H, Cp), 107.97 (d, $J_{C,P}$ = 4.77 Hz, C_{ipso}, Cp), 126.04 (*C*, *C*N), 127.63 (*C*, *C*N), 128.70 (d, $J_{C,P}$ = 9.55 Hz, *C*H), 128.48 (d, $J_{C,P}$ = 8.67 Hz, *C*H), 129.57 (*C*H), 129.82 (*C*H), 130.90 (*C*), 131.16 (*C*H), 131.43 (*C*H), 132.29 (d, $J_{C,P}$ = 8.67 Hz, *C*), 132.91 (d, $J_{C,P}$ = 9.67 Hz, *C*H), 135.50 (*C*), 136.14 (*C*), 136.57 (d, $J_{C,P}$ = 11.56 Hz, *C*H), 137.25 (*C*), 138.98 (*C*) ppm. ^{31}P NMR (CD_2Cl_2): δ = 86.78 (s, *P*Ph$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2274 cm^{-1}, 1629, 1600, 1581, 1058, 704. MS (FAB): *m*/*z* (%) = 579 (20) [M$^+$ + 1], 538 (60) [M$^+$ − CH$_3$CN + 1], 497 (100) [M$^+$ − 2CH$_3$CN + 1], 87 (100%) [BF_4^-]. $C_{32}H_{34}BF_4N_2PRu$ (665.45): calcd. C 57.75, H 5.15, N 4.21; found C 57.70, H 5.38, N 4.29.

(*S*)-Bis(acetonitrile)[(2-cyclohexyl-η^5-2-cyclopentadienylethyl)diphenylphosphane-κ*P*]ruthenium(II) Tetrafluoroborate (Ru$_4$): The title compound was prepared, according to the representative procedure, from 1.1 g of **L$_4$** and 1.15 g of **1** as a yellow solid. Yield: 1.8 g (95%). M.p.: 142−145 °C. $[\alpha]_D^{20}$= +4 (*c* = 1, CH_3CN). ^{1}H NMR (CD_2Cl_2): δ = 0.80−1.86 (m, 11 H, *Cy*), 1.94 (m, 1 H, C*H*Cy), 1.97 (d, $^5J_{H,P}$ = 0.91 Hz, 3 H, CH_3CN), 2.21 (d, $^5J_{H,P}$ = 1.22 Hz, 3 H, CH_3CN), 2.92 (td, $J_{H,P}$ = 13.42, $J_{H,H}$ = 6.10 Hz, 1 H, CH_2), 3.18 (td, $J_{H,P}$ = 13.12, $J_{H,H}$ = 4.88 Hz, 1 H, CH_2), 4.02 (m, 1 H, Cp), 4.27 (m, 1 H, Cp), 5.12 (m, 1 H, Cp), 5.24 (m, 1 H, Cp), 7.39−7.56 (m, 10 H, Ph) ppm. ^{13}C NMR (CD_2Cl_2): δ = 3.69 (*C*H$_3$, *C*H$_3$CN), 4.12 (*C*H$_3$, *C*H$_3$CN), 26.37 (*C*H$_2$, *Cy*), 31.54 (*C*H$_2$, *Cy*), 33.44 (*C*H$_2$, *Cy*), 42.57 (d, $^2J_{C,P}$ = 20.10 Hz, *C*HCy), 42.72 (d, $^3J_{C,P}$ = 4.77 Hz, *C*H, *Cy*), 47.94 (d, $^1J_{C,P}$ = 33.54 Hz, *C*H$_2$), 57.48 (*C*H, Cp), 68.61 (*C*H, Cp), 79.98 (d, $J_{C,P}$ = 7.79 Hz, *C*H, Cp), 88.62 (d, $J_{C,P}$ = 5.65 Hz, *C*H, Cp), 112.82 (d, $J_{C,P}$ = 4.77 Hz, C_{ipso}, Cp), 126.56 (*C*, *C*N), 127.28 (*C*, *C*N), 129.05 (d, $J_{C,P}$ = 4.90 Hz, *C*H), 129.13 (d, $J_{C,P}$ = 4.77 Hz, *C*H), 130.38 (*C*H), 130.76 (*C*H), 132.05 (d, $J_{C,P}$ = 10.55 Hz, *C*H), 133.29 (d, $J_{C,P}$ = 11.56 Hz, *C*H), 133.53 (*C*), 133.82 (*C*) ppm. ^{31}P NMR (CD_2Cl_2): δ = 52.14 (s, *P*Ph$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2274 cm^{-1}, 1629, 1600, 1581, 1058, 704. MS (FAB): *m*/*z* (%) = 502 (60) [M$^+$ − CH$_3$CN + 1], 461 (100) [M$^+$ −2CH$_3$CN + 1], 87 (100) [BF_4^-]. $C_{29}H_{34}BF_4N_2PRu$ (629.42): calcd. C 55.33, H 5.44, N 4.45; found C 54.93, H 5.69, N 4.08.

(*S*)-Bis(acetonitrile)[(2-benzyl-η^5-2-cyclopentadienylethyl)diphenylphosphane-κ*P*]ruthenium(II) Tetrafluoroborate (Ru$_5$): The title compound was prepared, according to the representative procedure, from 2.69 g of **L$_5$** and 2.75 g of **1** as a yellow solid. Yield: 4.65 g (100%). $[\alpha]_D^{20}$= −10.7 (*c* = 1, CH_3CN). M.p.: 141−144 °C. ^{1}H NMR (CD_2Cl_2): δ = 1.99 (d, $^5J_{H,P}$ = 1.22 Hz, 3 H, CH_3CN), 2.18 (d, $^5J_{H,P}$ = 1.53 Hz, 3 H, CH_3CN), 2.55 (m, 1 H, C*H*Bzl), 2.82 (dd, $^2J_{H,H}$ = 13.43, $^3J_{H,H}$ = 8.24 Hz, 1 H, CH_2Ph), 2.95 (dd, $^2J_{H,H}$ = 13.43, $^3J_{H,H}$ = 6.72 Hz, 1 H, CH_2Ph), 3.02−3.18 (m, 2 H, CH_2), 4.12 (m, 1 H, Cp), 4.14 (m, 1 H, Cp), 5.06 (m, 1 H, Cp), 5.25 (m, 1 H, Cp), 7.01−7.74 (m, 15 H, Ph) ppm. ^{13}C NMR (CD_2Cl_2): δ = 3.78 (*C*H$_3$, *C*H$_3$CN), 4.16 (*C*H$_3$, *C*H$_3$CN), 38.60 (d, $^2J_{C,P}$ = 6.66 Hz, *C*HBzl), 41.12 (d, $^3J_{C,P}$ = 21.11 Hz, *C*H$_2$Ph), 50.36 (d, $^1J_{C,P}$ = 33.54 Hz, *C*H$_2$), 57.87 (*C*H, Cp), 67.78 (*C*H, Cp), 80.47 (d, $J_{C,P}$ = 8.67 Hz, *C*H, Cp), 88.39 (d, $J_{C,P}$ = 5.78 Hz, *C*H, Cp), 112.42 (d, $J_{C,P}$ = 4.77 Hz, C_{ipso}, Cp), 126.69 (*C*, *C*N), 126.86 (*C*H), 127.26 (*C*, *C*N), 128.76 *C*H), 129.13 (*C*H), 129.21 (*C*H), 129.33 (*C*H), 129.40 (*C*H), 130.56 (d, $J_{C,P}$ = 5.78 Hz, *C*H), 130.83 (d, $J_{C,P}$ = 1.88 Hz, *C*H), 132.18 (d, $J_{C,P}$ = 9.67 Hz, *C*H), 132.99 (*C*), 133.26 (d, $J_{C,P}$ = 11.43 Hz, *C*H), 133.62 (*C*), 139.77 (*C*) ppm. ^{31}P NMR (CD_2Cl_2): δ = 52.87 (s, *P*Ph$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2277 cm^{-1}, 1630, 1602, 1058, 744, 699. MS (FAB): *m*/*z* = 510 (30) [M$^+$ − CH$_3$CN + 1], 469 (100) [M$^+$ − 2CH$_3$CN + 1], 87 (100) [BF_4^-]. $C_{30}H_{30}BF_4N_2PRu$ (637.40): calcd. C 56.53, H 4.74, N 4.40; found C 56.65, H 4.67, N 4.31.

Procedure for the Isomerisation of Allylic Alcohols: In a representative experiment, an NMR tube was charged under nitrogen with the catalyst (1 mol %), CD_2Cl_2 was added (0.5 mL), followed by the allylic alcohol (prop-2-en-1-ol, but-3-en-2-ol, or 1-phenylprop-2-en-1-ol). The tube was capped and vigorously shaken. The reaction was monitored by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Typically, the reaction was completed (no olefinic protons were detected) after three hours at room temperature affording exclusively the carbonyl compounds with only traces of unidentified side-products.

Procedure for the Isomerisation of Geraniol and Nerol: A flask was charged with a catalytic amount of the ruthenium complex (5 mol %) and THF (10 mL) and the allylic alcohol (2 mL) were then added. The reaction mixture was refluxed for 24 hours. The solvent was then removed under reduced pressure and the residue was filtered through a short pad of silica gel eluting with Et_2O. The oil left after evaporation of the solvent was bulb-to-bulb distilled (100−110 °C/10 mbar) affording pure citronellal. The conversion was determined on the crude reaction product by ^{1}H NMR spectroscopy. The *ee* was determined by comparison of the optical rotation (neat) with that reported in the literature.[27]

Procedure for the Catalytic Aldol Reaction: A flask was charged with a catalytic amount of the ruthenium complex (5 to 0.1 mol %). The solvent was added (5 or 10 mL), followed by benzaldehyde (5 or 10 mmol) and then 3-buten-2-ol (10 or 20 mmol). The reaction mixture was stirred at room temperature until complete consumption of the allylic alcohol (checked by TLC). The solvent was then removed under reduced pressure and the residue was purified by

flash column chromatography (hexane/ethyl acetate, 7:3). The *syn*/*anti* ratio was determined by ^{1}H NMR spectroscopy. The enantioselectivities were determined by HPLC analysis with a Chiralpak AS column (eluent: hexane/2-propanol, 95:5; flow rate: 0.8 mL/min; column temperature: 30 °C; retention times for the *syn* diastereoisomer: 15 min and 22 min).

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