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A Comparison of Phosphaferrocene and Phospharuthenocene Ligands in Rh^+-Catalysed Enamide Hydrogenation Reactions: Superior Performance of the Phospharuthenocene

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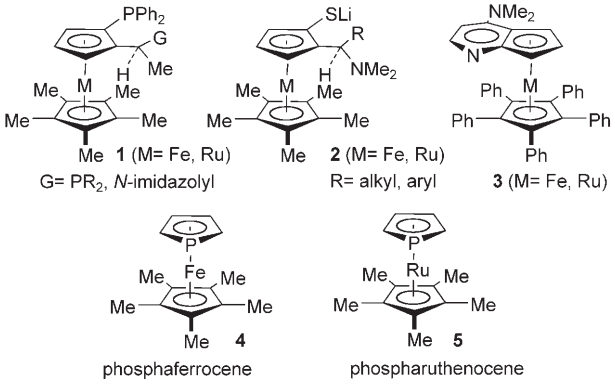
Abstract: Enantiopure Cp*-substituted 3,4-dimethyl-5-phenylphosphametallocene-2-methanols (M = Fe, Ru) have been prepared from the corresponding 2-carboxy-(−)-menthylphospholide anion and elaborated into 2-CH_2PPh_2 phosphametallocenes (**13**: M = Fe; **14**: M = Ru) and 2-CH_2PtBuR substituted phospharuthenocenes (R = *t*Bu, Me). The crystal structures of complexes $[Rh(1,5\text{-cod})(\eta^2\text{-L})]^+BF_4^-$ (L = **13**, **14**) reveal significantly different aryl group configurations. Comparative studies of the hydrogenation of *para*-substituted *N*-acetylcinnamate esters with these pre-catalysts show a superior performance for the phospharuthenocene derivative in terms of both rate and enantioselectivity.

Keywords: enamides · enantioselectivity · hydrogenation · metallocenes · phosphorus heterocycles

Introduction

Ferrocene-based planar-chiral ligands are widely used in metal-catalysed enantioselective catalysis,[1–7] but their replacement by the correponding ruthenocenes is rarely attempted. A probable explanation[8,9] lies in the observation that substituting Fe by Ru causes little electronic change if both coordinating functions are anchored to the same cyclopentadienyl ring, so that the dominant perturbations should reflect the longer Ru-centroid distance; because this relaxes the chiral architecture to confer better substrate access but diluted spatial organisation, the likely outcome (increased rate but lowered *ee*) is usually undesirable.[10] Experimental studies of Josiphos-type ligands **1** in Pd-catalysed allylic substitution reactions and Rh-catalysed hydroboration reactions,[8] as well as substituted aminomethylmetallocenethiolates **2** in copper-catalysed allylic acetate substitution reactions,[11] support this reasoning strongly. Equally, Fu's pioneering study of the effects of substituting Ru for Fe in chiral azaindenyl complexes **3** produced results broadly in agreement with this analysis, with only a single case showing slightly enhanced enantioselectivity with ruthenium.[9]



This simple logic might be expected to fail in cases in which there is strong communication between the metal and the donor set[12] and, here, we present data which confirm that the substitution of iron by ruthenium can show significant catalytic benefit when heterolyl-functionalised metallo-

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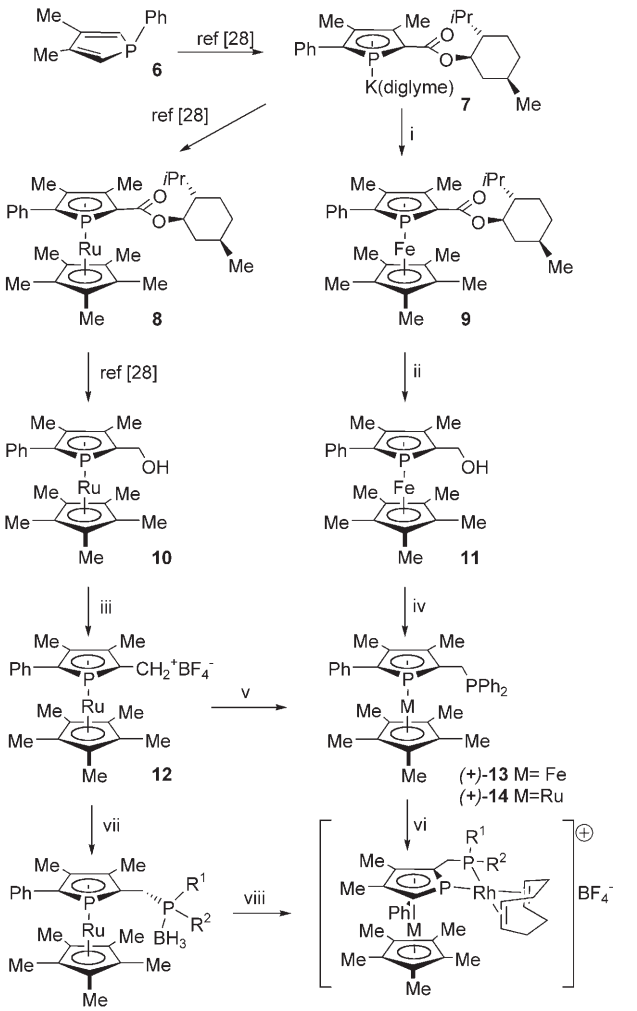
cenes are used as ligands. The results were obtained as part of a program that aims to extend the chemistry of the phosphaferrocene ligand class (which has been shown inter alia[13–17] to give benchmark performance in enantioselective allylic alcohol isomerisation,[18,19] Kinugasa[20] and azomethineimine[3+2] cycloaddition chemistry[21,22] by Fu as well as in allylic substitutions[23] and hydrosilylations[24] by Hayashi/Ogasawara) to include other ligands derived from the wider family of phosphametallocenes. Specifically, our objective was to ascertain whether the phospharuthenocenes developed in this laboratory[25–28] and also elegantly studied by the Hayashi/Ogasawara group[24,29,30] might provide a more conveniently handled ligand platform than the corresponding phosphaferrocenes. The proposition is clearly conditional upon turnover numbers and rates, enantioselection, and so forth, remaining competitive. Since no systematic comparison of the phosphaferrocene and phospharuthenocene families was available,[31] new mixed phosphametallocene–methylphosphane ligands incorporating ruthenium and iron centres have been prepared, compared crystallographically and, to allow comparison with the widest range of more classical ligands, evaluated in side-by-side studies using standard *N*-acetylcinnamate ester substrates. These confirm that using Ru centres in place of Fe can be advantageous in terms of ease of functionalisation, catalytic rates and *ee's* simultaneously.

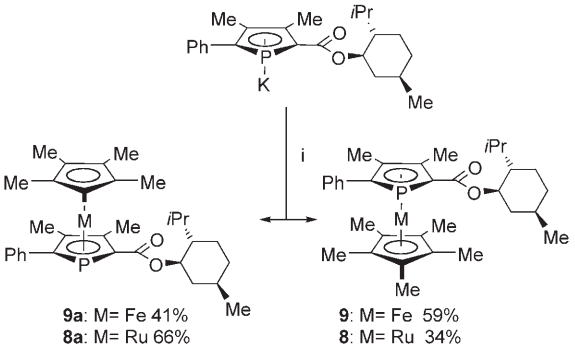
Results and Discussion

Synthesis: Ganter has developed an elegant route to an enantiopure planar-chiral Cp-containing phosphaferrocene,[32] but the better-performing Cp*-containing phosphaferrocenemethylphosphanes used in Fu's groundbreaking studies[17–19] have only been accessible previously by methods involving preparative chiral HPLC,[17,33,34] a technique that is not yet widely available in academic laboratories. For the studies here, the ligands were obtained by a more universal route, using our recently described menthylester technology to resolve the planar chirality of the phosphametallocene[28] (Scheme 1). The preparation of the phospharuthenocene-menthyl esters **8** and **8a** has already been described[28] and a similar chemistry was employed to obtain the previously unknown phosphaferrocene analogues **9** and **9a** (Scheme 2). These can be separated by crystallisation to give pure diastereomers, which are isomorphous with their ruthenium-containing homologues and can easily be distinguished visually. Their configurations were confirmed through X-ray diffrac-



Scheme 1. Reagents and conditions: i) $FeCl_2$ (1 equiv), Cp*Li (1 equiv), THF, 0 °C→RT, 30 min, then **7**, (1 equiv), 0 °C, 2 h; crystallisation from MeOH/Et_2O; ii) $LiAlH_4$, (2 equiv) THF, RT, 4 h; iii) $HBF_4.Et_2O$ (1.2 equiv), CH_2Cl_2, 0 °C→RT, 20 min; iv) $HBF_4.Et_2O$ (1.2 equiv), CH_2Cl_2, −30 °C, 30 s, then Ac_2O (0.9 equiv), $HPPh_2$ (2 equiv), RT, 10 min, then NaOH (2 M aq, excess); v) $HPPh_2$ (2 equiv), CH_2Cl_2, 0 °C→RT, 20 min, then NaOH (2 M aq, excess); vi) [Rh(acac)(1,5-cod)] (1.0 equiv), $HBF_4{\cdot}Et_2O$ (1.0 equiv), THF, 0 °C→RT, 30 min, then ligand (**13** or **14**), (1 equiv), 25 °C, 10 min; vii) RR′PH(BH_3) (1 equiv), *n*BuLi (1 equiv), THF, −78 °C, 30 min, then **12** (1 equiv), THF, −78 °C→RT, 5 min; viii) $HBF_4{\cdot}Et_2O$ (4.0 equiv), CH_2Cl_2, 25 °C, 4 h, then use as "ligand" in protocol vi.

Abstract in French: *Les pentaméthylcyclopentadiényl-(2-hydroxyméthyl-3,4-diméthyl-5-phénylphospholyl)métallocènes énantiopurs (M = Fe, Ru) ont été préparés à partir de l'anion 2-carboxy-(−)-menthylphospholure correspondant. Ils ont été élaborés en phosphamétallocènes 2-CH_2PPh_2 (**13**; M = Fe, **14**; M = Ru) et phospharuthénocènes 2-CH_2PtBuR (R = tBu, Me). Les structures cristallographiques des complexes [Rh-(1,5-cod)(η^2-L)]$^+BF_4^-$ (L=**13**, **14**) présentent des configurations significativement différentes des groupements aryles. L'étude comparée de l'activité de ces précatalyseurs dans la réaction d'hydrogénation des esters N-acétylcinnamates para-substitués démontre une meilleure performance du ligand phospharuthénocène à la fois en termes de cinétique et d'énantiosélection.*



Scheme 2. Effect of the metal centre upon diastereoselectivity for the syntheses of phosphametallocenes **8**, **8a** and **9**, **9a** as deduced by NMR analysis of the crude reaction mixtures. Conditions: $[RuCl(Cp^*)]_4$ (0.25 equiv), THF, 25 °C, 15 min, or "$[FeCl(Cp^*)]$", (1.0 equiv), THF, 0 °C, 30 min.

tion studies (Figure 1). Superimposing the structures of the phospharuthenocene- and phosphaferrocenementhyl esters **8** and **9** reveals very similar geometries (Figure 2), but the difference in metal radius is sufficient to cause an inversion of reaction diastereoselectivity, so that the crude reaction products are present in a ratio of 59:41 in favour of the (S_{Fc}) and 66:34 in favour of (R_{Rc}), respectively.[35] Consequently, when reaction mixtures are purified solely by crystallisation, the first crop of crystals shows an (*R*)-**8** configuration at the phosphametallocene for Ru, but (*S*)-**9a** for Fe. Essentially classical literature methods[26,36] were adapted to elaborate **8** and **9** into the phosphametallocenemethylphosphanes **13** and **14**, typically on scales of about 250 mg (Scheme 1).

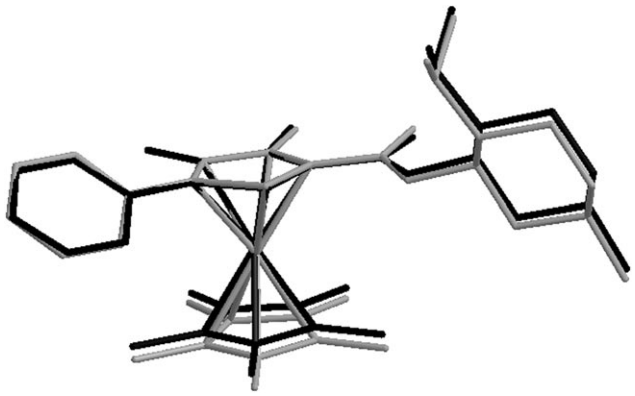
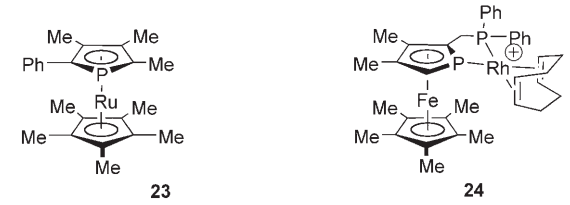


Figure 2. Superimposed molecular structures of diastereomeric phospharuthenocene **8** (grey)[28] and phosphaferrocene **9** (black). Intercentroid distances for **8**: 3.607, for **9**: 3.320 Å.

The compounds in the phospharuthenocene series were more easily handled and transformed than the phosphaferrocenes, because of a generally higher resistance to oxidation in solution and on silica, and more specifically as a result of the stability of the phospharuthenocenemethylium cation **12**. Classical ruthenocenemethylium complexes are extremely robust[37,38] and, unlike the corresponding phosphaferrocene derivative,[36] compound **12** could be isolated, purified by crystallisation, and stored on the bench over a period of several months. Its stability permitted further new phospharuthenocene methylphosphane borane complexes **15**, **16** and **17**, to be synthesised conveniently through deprotonation of $H_3BPHtBu_2$ or (±)-$H_3BPHtBuMe$ at −78 °C and subsequent treatment of the product anions with a finely powdered suspension of **12** in diethyl ether, the protocol being designed to allow the coupling reaction to proceed rapidly whilst minimising a facile competing reduction of phospharuthenocenemethylium ion **12** into the 2-methyl phospharuthenocene derivative **23**. This side reaction could not be fully prevented in the case of **17**. Complexes **15** and



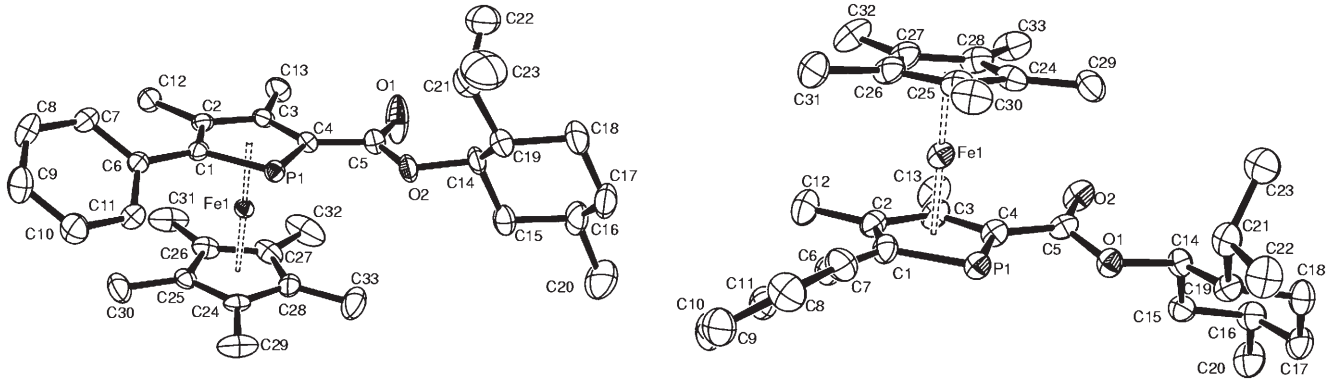


Figure 1. Left: Structure of the (R_{Fc}) diastereomeric phosphaferrocene precursor **9** (orange-red hexagons) employed in this study. Selected bond lengths: Fe1−C3 2.067(2), Fe1−C2 2.083(2), Fe1−C1 2.102(2), Fe1−P1 2.289(1), P1−C4 1.785(2), P1−C1 1.785(2), C1−C2 1.434(2), C2−C3 1.423(2), C2−C12 1.510(2), C3−C4 1.433(2), C3−C13 1.501(2), C4−C5 1.479(2) Å. Right: Structure of diastereomeric phosphaferrocene (S_{Fc})-**9a** (orange-red rhomboids). Selected bonds lengths from one of two very similar molecules in the unit cell: Fe1−C3 2.056(3), Fe1−C4 2.068(3), Fe1−C2 2.080(3), Fe1−C1 2.094(4), Fe1−P1 2.291(1), P1−C4 1.783(3), P1−C1 1.784(3), C1−C2 1.418(5), C2−C3 1.435(5), C3−C4 1.434(5), C4−C5 1.473(5) Å.

16 were separated by chromatography (40–65 μm SiO_2; EtOAc/C_5H_{12} 1:10; R_f **15** = 0.27, R_f **16** = 0.18)[39] and assigned through an X-ray analysis of the slower running diastereomer, which was shown to be the ($R_{Rc}S_p$)-combination **16** on the basis of its distinctly different P–CH_3 and P–BH_3 bond lengths (Figure 3).

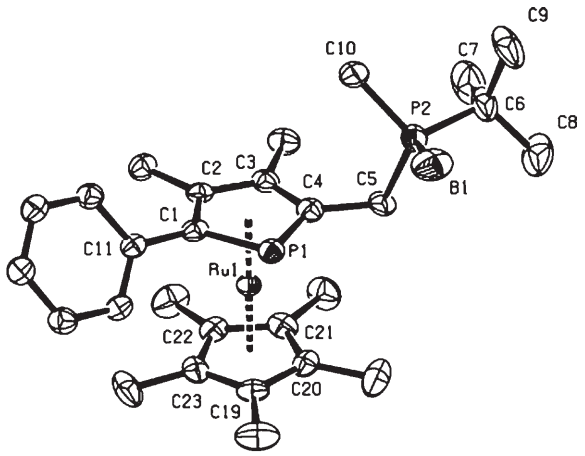


Figure 3. Configurational assignment of **16**. Bond lengths (expressed as an average of the two molecules in the unit cell): Ru1–P1 2.398(1), Ru1–C1 2.228(5), Ru1–C2 2.1954, Ru1–C3 2.186(5), Ru1–C4 2.2056, P1–C1 1.787(5), P1–C4 1.777(6), P2–C10 1.820(5), C1–C2 1.442(8), C2–C3 1.429(7), C3–C4 1.439(8), P2–C5 1.843(5), P2–B1 1.927(9) Å.

Coordination: Coordination of bidentate phosphanes to rhodium centres to give $[Rh(cod)(L_2)]^+$ ions does not always occur cleanly[41] and, to minimise the possibility of multiple catalytically active species in solution, the new ligands **13** and **14** were converted into relatively air-stable [Rh(cod)(phosphametallocenemethylphosphane)]$^+BF_4$ complexes **18** and **19** by using a $[Rh(acac)(cod)]$[42,43]/H^+ system[44] and crystallised prior to use. The proligands **15**–**17** were deboronated by using fluoboric acid etherate[45] to give the corresponding phosphonium salts, which were directly[46,47] coordinated to rhodium by the same method to furnish **20**–**22**. These essentially quantitative reactions gave complexes that were stable enough to be stored for periods of months under nitrogen without decomposition.

The influence of the phosphametallocene metal centre upon the precatalyst architecture was investigated by X-ray determinations of the phosphaferrocene (±)-**18**/phospharuthenocene (+)-**19** couple[48] used in the catalytic comparison below (Figure 4). Simple inspection of Figure 4 indicates that the differences between **18** and **19** are far greater than

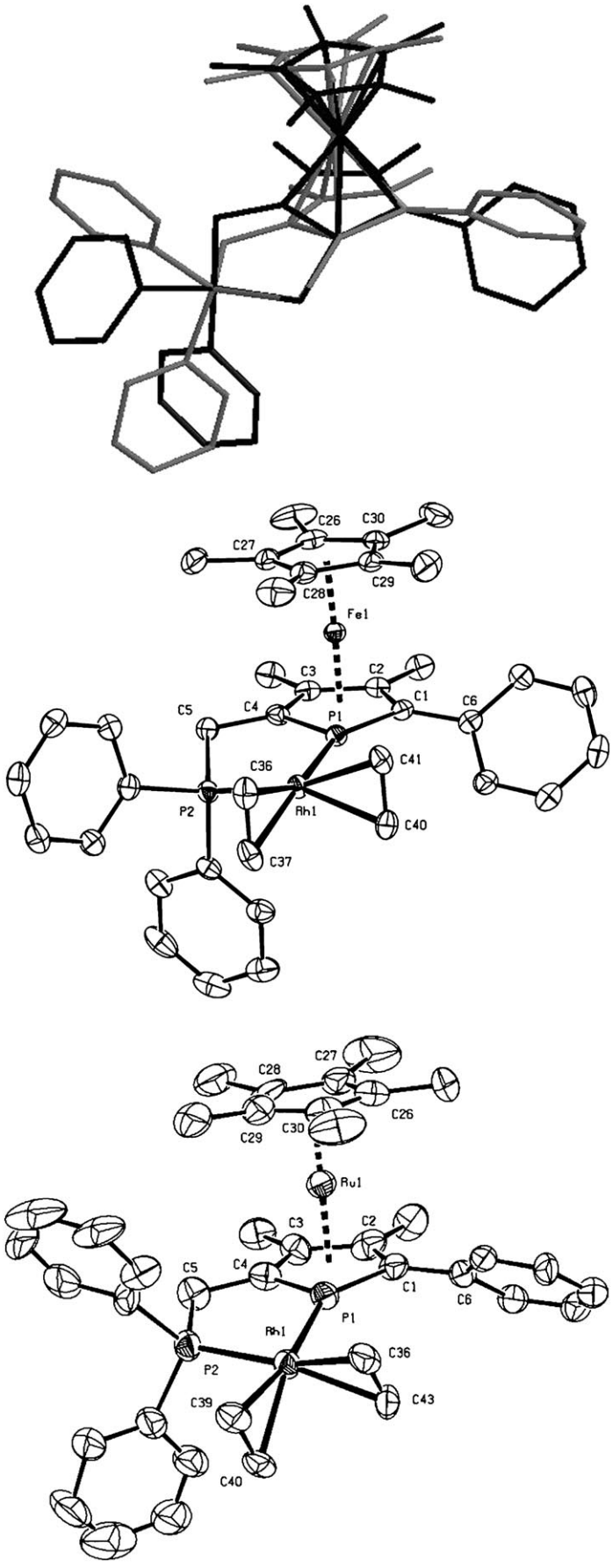


Figure 4. Top: superimposition of the heavy atom skeletons of the precatalysts $[Rh(1,5\text{-cod})\{M\text{-}\eta^5Cp^*\text{-}\eta^5\text{-}(PC_4PhMe_2CH_2PPh_2)\}]^+[BF_4]^-$ M = Fe (black, and middle **18**) and M = Ru (grey and bottom **19**) obtained by overlapping as closely as possible the P(sp^3), Rh and P(sp^2) centres. The BF_4^- and CH_2 atoms of the cod ligand (which shows a clockwise twist of 11.0° for **18**, 7.9° anticlockwise for **19**)[40] are omitted for clarity below, cod is omitted entirely in the top part of the figure.

those between **8** and **9**, and an analysis quantifying these differences in Brunner's terms[49] is given in Table 1. The phosphaferrocene complex (±)-**18** strongly resembles the homologue (+)-**24**, previously described by Tanaka et al.[19] and shows a classical[50] $-PPh_2$ aryl group disposition having a pseudo λ-configuration at the methylene bridge and an edge-on axial phenyl. The second "*endo*" phenyl lies equatorially, face-on to the diene and intercalates nicely between two methyl groups of the Cp* ligand. The sp^3 phosphorus lies significantly (0.69 Å) above (*exo* to) the best phospholyl plane as, to a lesser degree (0.23 Å), does the rhodium atom.

The phospharuthenocene (+)-**19** complex is more unusual, with the aryl groups showing rare face (*P*) and edge (*M*) orientations.[49] The increased intercentroid distance of 3.59 Å for **19** (compare 3.34 Å for **18**) appears to relax the structure so that the "*endo*" aryl is free to move clear of the Cp* moiety. The $C_{(ipso)}$ atoms of the PPh groups swing downwards towards the phospharuthenocene core to the point at which they are almost equidistant from the plane defined by Rh, P2 and C5 (1.51 above for C20; 1.50 Å below for C14) and the sp^3 phosphorus therefore lies *exo*- to the phospholyl by only 0.47 Å. The rhodium rises out of the phospholyl plane significantly (0.60 Å) to compensate. The more axial phenyl group *exo* to the phosphametallocene twists to become face on, leaving the *"endo"* aryl edge-oriented. The overall outcome upon changing the central metal from Fe to Ru is therefore a formal inversion of chirality at the PPh_2 functionality, which suggests that **18** and **19** might show contrasting properties when employed as catalysts.[49] Their well-differentiated chiralities are clear from Figure 5.[51]

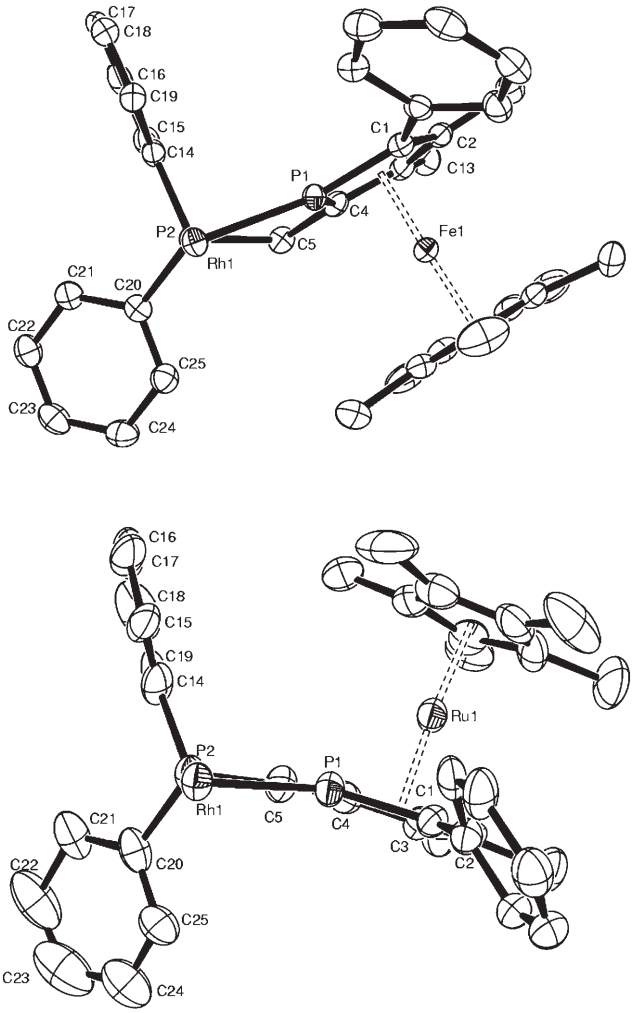


Figure 5. Complexes (±)-**18** (top) and (+)-**19** (bottom) as viewed down the Rh–$P(sp^3)$ bond, showing how retention of a given chirality at the PPh_2 function upon passing from M = Fe to M = Ru requires inversion at the phosphametallocene component. The BF_4^- counterion and cod are omitted. Note that the (−)-phosphaferrocene enantiomer is shown, rather than the (+)-hand employed in the catalysis.

Catalysis: A competitive evaluation of the performance of the homologous phosphaferrocene **13** and phospharuthenocene **14** ligands was made for the Rh^+-catalysed homogenous hydrogenation of methyl *N*-acetylcinnamate (MAC) and several *para*-substituted derivatives (1 mol% catalyst, EtOH, 20 °C, 1 bar H_2). For related work on phosphaferrocenemethylphosphanes only, see.[17,52] The study was undertaken as a comparison rather than an attempt to achieve the highest possible excesses (for example, the convenient BF_4^- counterion was preferred over PF_6^-, which has been previously found to give better enantioselectivity when **24** was used as the catalyst[17]), but even the non-optimised conditions delivered good results (Table 2). The key conclusion is that the nature of the phosphametallocene metal centre influences the *ee* strongly, with the phospharuthenocene precatalyst **19** giving significantly better performance than its phosphaferrocene homologue **18** across the entire range of substituents tested (excesses being 13 to 22 percentage

Table 1. A parameterisation of the PPh_2 groups found in complexes **18**, **19** and **24**, expressed according to Brunner's conventions, with all angles given in degrees.[49] (For a database of related structures and a detailed explanation of definitions, see reference [49].)

						Ph group *exo* to phosphametallocene			Ph group *endo* to phosphametallocene			
	R/*S*	bridge twist	$P(sp^2)$ α[a]	$P(sp^3)$ α[b]	β[c]	ax/eq	γ[d]	orientation (chirality type)[49]	β[c]	ax/eq	γ[d]	orientation (chirality type)[49]
24	*R*	λ	14.6	−21.3	94.6	ax	−1.9	edge-(*P*)	−145.9	eq	89.7	face-(*M*)
18[e]	*R*	λ	11.4	−21.9	93.0	ax	−1.2	edge-(*P*)	−146.6	eq	76.5	face-(*M*)
19	*R*	[f]	−7.6	3.8	120.3	eq	−59.7	face-(*P*)	−113.2	ax	4.2	edge-(*M*)

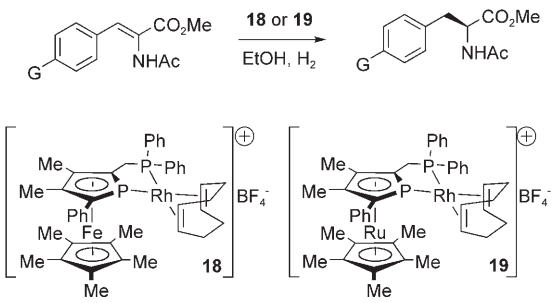
[a] Torsion angle: $P(sp^2)\alpha = CH_2$-$P(sp^3)$-Rh-$P(sp^2)$. [b] Torsion angle: $P(sp^3)\alpha = C(CH_2P)$-$P(sp^2)$-Rh-$P(sp^3)$. [c] Torsion angle: $\beta = P(sp^2)$-Rh-$P(sp^3)$-C(ipso). [d] Torsion angle: γ = Rh-$P(sp^3)$-C(ipso)-C(*ortho*). [e] The data for the *rac*-complex **18** are given for the (*R*)-hand. [f] The dihedral defining the bridge configuration in the phospharuthenocene, being very close to flat, makes a description as λ or δ inappropriate.

Table 2. Data for the products obtained through hydrogenation of *p*-substituted methyl *N*-acetylcinnamates. Conditions: 1 mol% preformed [Rh(1,5-cod){M-η^5-(Cp*)-η^5-($PC_4PhMe_2CH_2PPh_2$)}][BF_4] (M = Fe, Ru), 1 bar H_2, 25 °C, 12 h, EtOH.

G[a]	*R*/*S*	*ee* [%] (yield [%]) precatalyst **18** (M = Fe)	*R*/*S*	*ee* [%] (yield [%]) precatalyst **19** (M = Ru)
H (MAC)	*S*	79 (>99)	*S*	96 (>99)
F	*S*	76 (>99)	*S*	94 (>99)
Cl	*S*	80 (>99)	*S*	93 (>99)
MeO	*S*	72 (>99)	*S*	93 (>99)
Me	*S*	79 (>99)	*S*	92 (>99)
NO_2	*S*	62 (>99)	*S*	84 (>99)

[a] See Scheme 3.

points higher) and clearing the 90% *ee* barrier in all cases except those in which G = NO_2 (Scheme 3). Furthermore, all reactions catalysed by **18** and **19** were completed quantitatively. This compares favourably with previous work using **24**,[17] despite a fivefold reduction in catalyst loading.[53]



Scheme 3. Comparison of hydrogenation reactions of enamides using phosphametallocene-containing precatalysts **18** and **19**.

To complement the data for the enantiomeric excess, the influence of the metal centre upon reaction rate was also examined, through experiments in which falling hydrogen pressure in parallel computer-monitored microreactors was plotted against time for cells containing M = Fe (**18**) and M = Ru (**19**) based precatalysts. Optimal turnovers with MAC were obtained shortly before the substrate was consumed,[54,55] after an induction time of approximately 1 h for both systems. The electron-withdrawing characteristics of the phosphametallocene functionality[56] are consistent with the moderate rates observed (TOF = 83 for Ru, 63 for Fe; compare, for example, 1100 for Phanephos[57] and 5000 h^{-1} for DuanPhos[58] under broadly similar conditions), but, again, the Ru-based ligand reproducibly showed better performance than the phosphaferrocene.

Further results were obtained from purely phospharuthenocene-based systems. An examination of the *ee* profile as a function of temperature, conducted with precursor **19** and 4-MeOMAC as the substrate, showed an inverse relationship (−20°, 97%; 0°, 97%; 20°, 93%; 40 °C, 91% *ee*).[59,60] With the alkyl-substituted phosphane containing precatalysts **20**–**22**, a high *ee* in favour of the (*S*)-amino acid was observed in all cases (Table 3); thus the inverted chirality of the *t*Bu and Me groups in complexes **20** and **21** affects neither the *ee* nor the handedness of the product.[61] This dominance of the

Table 3. Data for the hydrogenation of methyl *N*-acetylcinnamate (MAC). Conditions: 2 mol% preformed [Rh(1,5-cod){Ru-η^5-(Cp*)-η^5-($PC_4PhMe_2CH_2PR_2$)}][BF_4], 1 bar H_2, 25 °C, 12 h, MeOH.

Ligand	Precatalyst	Product	Yield [%]	*ee* [%]
15	**20**	*S*	>99	94
16	**21**	*S*	>99	94
17	**22**	*S*	~50	91

phosphametallocene over the highly efficient PMe*t*Bu moiety[62–64] shows that the phospharuthenocene expresses its chirality strongly, thereby underlining its potential in ligand design.[65]

Conclusion

Overall, this study has shown that the easily available menthylester-substituted phospholide anion **7** provides a useful macroscopic-scale access to enantiopure phosphametallocene-based planar-chiral ligands, without recourse to preparative chiral HPLC. In the phospharuthenocene case, elaboration is particularly straightforward because of high general stability, complemented by very easy FGI at the stable phospharuthenocenemethylium ion **12**, and this has allowed the preparation of the first examples of enantiopure planar-chiral phospharuthenocenephosphane ligands **14**–**17**. When employed in a side-by-side comparison, the new phospharuthenocene-based ligand **14** significantly outperformed the corresponding phosphaferrocene **13** across a range of substrates in a classical Rh^+-catalysed enantioselective process and allowed improvements in both catalytic rate and enantioselectivity to be made simultaneously.

In general terms, this work shows that the consequences of substituting a first-row metal in a metallocene-based ligand by a heavier congener can go beyond the simple geometrical relaxation of the catalytic coordination sphere that was discussed in the introduction; replacing ferrocene-based ligands by their ruthenium-containing homologues might, therefore, be far more beneficial than is generally assumed if the ligand coordination sphere is tightly packed. For the heterometallocene systems, the results confirm that a judicious variation of the included metal centre offers potential for improving performance as a ligand significantly, with this prospect being particularly likely if the heteroatom is "soft" enough to interact strongly with the heterometallocene metal centre. One clear conclusion is that the already excellent performance of phosphametallocene ligands in enantioselection, as obtained using the phosphaferrocene class,[13–24] should be amenable to significant further optimisation.

Experimental Section

General: All operations were performed either by using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under dry purified argon. Column chroma-

tography was performed under nitrogen on 63–200 μm silica or 50–160 μm neutral alumina as appropriate. (*1R*)-(−)-Menthylchloroformate was purchased from Fluka and used as received [{RuCp*Cl}$_4$],[66] "[FeCp*Cl]",[13,67,68] 1-phenyl-3,4-dimethylphosphole,[69] [K(diglyme)(PC$_4$-2-CO$_2$-(−)-menthyl-3,4-Me$_2$-5-Ph] (**7**)[28,70] and [Rh(acac)(cod)][42,43] were obtained as described previously. Enamide substrates were prepared by standard methods;[71,72] *rac*-Me*t*BuPHBH$_3$ was prepared from MePCl$_2$ and *t*BuMgCl in diethyl ether by Kuchen and Hägele's protocol,[73] followed by reduction with LiAlH$_4$ and treatment with BH$_3$·SMe$_2$ according to Imamoto's general method;[74] *t*Bu$_2$PH·BH$_3$ was prepared similarly from *t*Bu$_2$PCl. Solvents distilled under dry nitrogen included ethanol and methanol from the corresponding magnesium or sodium alkoxide, THF and diglyme from sodium–benzophenone ketyl, pentane from sodium–benzophenone ketyl–tetraglyme, diethyl ether from sodium hydride or calcium hydride and dichloromethane from P$_4$O$_{10}$. The last was stored for short periods over 4 Å molecular sieves. Deuterobenzene, deuteroacetone and deuterotetrahydrofuran were used as received from Eurisotop (Saclay), and deuterochloroform was deacidified through neutral alumina prior to use. NMR measurements were made on a Bruker Avance 300 spectrometer and are referenced to internal C$_6$D$_5$H or CHCl$_3$ and external H$_3$PO$_4$ as appropriate. Mass spectra were obtained under 70 eV electron impact or chemical ionisation using ammonia on a Hewlett Packard 5989B spectrometer. Enantiomeric excesses were determined on a Waters 510 HPLC apparatus fitted with a Daicel chiralcel OD-H column and a photodiode detector operating at 254 nm. Optical rotations were obtained on a Perkin Elmer PE 241 polarimeter operating at 589 nm. Combustion analyses were performed by Marie-Françoise Bricot at the "Service de microanalyse du CNRS", Gif sur Yvette, France.

Synthesis of compounds 8 and 8a: A solution of [{RuCp*Cl}$_4$] (4.02 g, 3.70 mmol) in THF (60 mL) was treated with a solution of **7** (8.15 g 15.0 mmol) in THF (60 mL) and the mixture was stirred for 15 min. The THF was removed under reduced pressure and the solids were extracted with pentane (400 mL). The extracts were then filtered and evaporated to dryness. Flash chromatography (neutral alumina, dichloromethane/pentane 1:9) gave a yellow band, the initial fractions of which were enriched in the (R_{Ru})-**8** diastereomer. The products eluted were combined so as to create two fractions, one having greater than 35% *de* in favour of the (S_{Ru})-**8a** diastereomer and the other less. Both fractions were crystallised from a minimum quantity of refluxing Et$_2$O/MeOH (3:4). In the first instance, yellow hexagonal crystals (750 mg, 8.4%) of the (S_{Ru})-**8a** diastereomer with a *de* >99.5% were obtained from the (S_{Ru})-rich fraction, with further recrystallisation raising the yield to 20%. Likewise (*R*)-**8** (*de* > 99.5%; 1.8 g, 20%) was obtained through a single crystallisation of the (S_{Ru})-depleted fraction, with the overall yield being raised to 55% by repetition.

*Data for (R_{Ru})-**8***: $[\alpha]_D^{25}=+76.4°$ ($c=1.0$ in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25°C): $\delta=-25.4$ ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta=$ 7.33–7.16 (m, 5H; Ar), 4.69 (ddd, $J=4.2$, 10.7, 10.7 Hz, 1H; OC*H*), 2.28 (s, 3H; Me), 2.16–2.00 (m, 2H; menthyl), 2.02 (s, 3H; Me), 1.79 (s, 15H; Cp*), 1.85–1.68 (m, 2H; menthyl), 1.63–1.41 (m, 2H; C*H*+C*H*, menthyl), 1.16–0.89 (m, 3H; menthyl), 0.97 (d, $J=6.5$ Hz, 3H; CH_3, menthyl), 0.92 (d, $J=7.1$ Hz, 3H; CH_3, menthyl), 0.79 ppm (d, $J=7.1$ Hz, 3H; CH_3, menthyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=171.3$ (d, J(P,C)= 17.6 Hz, C=O), 138.5 (d, J(P,C)=17.5 Hz, ipso-Ph), 129.7 (d, J(P,C)= 7.0 Hz), 127.7 (s), 125.9 (s), 104.8 (d, J(P,C)=56.9 Hz, P*C*Ph), 94.9 (d, J(P,C)=4.9 Hz, PC*C*Me), 94.7 (d, J(P,C)=5.1 Hz, PC*C*Me), 88.7 (S, Cp*), 82.4 (d, J(P,C)=61 Hz, PCC=O), 73.8 (s, *C*H), 47.3 (s, *C*H), 41.8 (s, *C*H$_2$), 34.4 (s, *C*H$_2$), 31.6 (s, *C*H), 26.2 (s, *C*H), 23.4 (s, *C*H$_2$), 22.2 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 16.4 (s, *C*H$_3$), 12.9 (s, PCC*Me*), 12.6 (s, PCC*Me*), 10.4 ppm (s, Cp*).

*Data for (S_{Ru})-**8a***: $[\alpha]_D^{25}=-125.0°$ (c=1.0 in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25°C): $\delta=-28.6$ ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta=$7.33–7.18 (m, 5H; Ar), 4.67 (ddd, $J=4.2$, 10.7, 10.7 Hz, 1H; OC*H*), 2.27 (s, 3H; Me), 2.24–2.1 (m, 2H; menthyl), 2.02 (s, 3H; Me), 1.77 (s, 15H; Cp*), 1.88–1.64 (m, 2H; menthyl), 1.60, 1.43 (m, 2H; C*H*+C*H*, menthyl), 1.24–0.90 (m, 3H; menthyl), 1.00 (d, $J=7.0$ Hz, 3H; CH_3, menthyl), 0.96 (d, $J=6.5$ Hz, 3H; CH_3, menthyl), 0.85 ppm (d, $J=7.0$ Hz, 3H; CH_3, menthyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=171.0$ (d,-J(P,C)=18.1 Hz, C=O), 138.4 (d, J(P,C)=17.6 Hz, ipso-Ph), 129.8 (d, J(P,C)=6.8 Hz), 127.8 (s), 125.9 (s), 103.3 (d, J(P,C)=56.7 Hz, P*C*Ph), 95.1 (d, J(P,C)=4.8 Hz, PC*C*Me), 94.3 (d, J(P,C)=5.1 Hz, PC*C*Me), 88.7 (Cp*), 83.7 (d, J(P,C)=58.9 Hz, P*C*C=O), 74.2 (*C*H), 47.0 (*C*H), 41.2 (*C*H$_2$), 34.4 (*C*H$_2$), 31.5 (*C*H), 25.7 (*C*H), 23.2 (*C*H$_2$), 22.2 (*C*H$_3$), 21.2 (*C*H$_3$), 16.5 (*C*H$_3$), 12.9 (PCC*Me*), 12.6 (PCC*Me*), 10.3 ppm (Cp*); elemental analysis calcd (%) for C$_{33}$H$_{45}$O$_2$PRu: C 65.43, H 7.49; found: C 65.47, H 7.47.

Synthesis of compounds 9 and 9a: A suspension of finely powdered electrical grade FeCl$_2$ (3.00 g, 23.0 mmol) in THF (50 mL) was refluxed for three hours. After cooling, LiCp* (3.30 g, 25.8 mmol) in THF (135 mL) was added as a suspension by canula at 0°C over a period of 30 min and the resulting deep green solution was stirred for a further 15 min. A solution of phospholide **7** (13.8 g 26.1 mmol) in THF (50 mL) was then added over a period of 30 min and the resulting orange solution was stirred overnight. Solvents were removed under reduced pressure at room temperature and the residue was extracted into pentane (250 mL), which was filtered through celite and evaporated to dryness. Extraction of impurities with methanol (20 mL) gave an orange solid containing crude **9** and its complementary diastereomer **9a** in a ratio of about 3:2. The crude residue was twice extracted with MeOH (10 mL) and recrystallised from the minimum boiling hexane/methanol (6:4) at 0°C to give orange-red rhomboids of the (S_{Fe})-**9a** diastereomer (1.60 g, 25%). $[\alpha]_D^{25}=-45.1°$ ($c=1.0$ in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25°C): $\delta=-40.9$ ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta=7.33$–7.16 (m, 5H; Ar), 4.66 (ddd, $J=4.4$, 10.9, 10.9 Hz, 1H; OC*H*), 2.31 (s, 3H; Me), 2.12, (m, 1H; menthyl), 2.08 (m, 1H; menthyl), 2.16 (s, 3H; Me), 1.63 (s, 15H; Cp*), 1.71, (m, 1H; menthyl), 1.67 (m, 1H; menthyl), 1.50, (m, 1H; menthyl), 1.47 (m, 1H; menthyl), 1.09, 1.02, 0.90 (m, 3H; menthyl), 0.93 (d, $J=6.5$ Hz, 3H; CH_3, menthyl), 0.90 (d, $J=7.0$ Hz, 3H; CH_3, menthyl), 0.76 ppm (d, $J=7.0$ Hz, 3H; CH_3, menthyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=172.8$ (d, J(P,C)=19.2 Hz, C=O), 139.8 (d, J(P,C)=17.8 Hz, ipso-Ph), 130 (d, J(P,C)=9.2 Hz), 128.2 (s), 126.1 (s), 102.6 (d, J(P,C)=53.4 Hz, P*C*Ph), 95.8 (d, J(P,C)=4.8 Hz, PC*C*Me), 93.5 (d, J(P,C)=5.5 Hz, PC*C*Me), 84.0 (Cp*), 82.3 (d, J(P,C)=54.0 Hz, P*C*C=O), 74.8 (*C*H), 47.8 (*C*H), 41.3 (*C*H$_2$), 34.9 (*C*H$_2$), 32.0 (*C*H), 26.3 (*C*H), 23.6 (*C*H$_2$), 22.4 (*C*H$_3$), 21.4 (*C*H$_3$), 16.5 (*C*H$_3$), 14.1 (PCC*Me*), 13.4 (PCC*Me*), 10.1 ppm (Cp*).

Further addition of diethyl ether to the mother liquor and crystallisation at −35°C generates orange-red hexagonal plates of diastereopure **9** (980 mg, 16%). $[\alpha]_D^{25}=+6.7°$ ($c=1.0$ in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25°C): $\delta=-39.3$ ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta=$ 7.33–7.16 (m, 5H; Ar), 4.66 (ddd, $J=4.4$, 10.9, 10.9 Hz, 1H; OC*H*), 2.34 (s, 3H; Me), 2.12, (m, 1H; menthyl), 1.98 (m, 1H; menthyl), 2.16 (s, 3H; Me), 1.79 (s, 15H; Cp*), 1.71(m, 1H; menthyl), 1.68 (m, 1H; menthyl), 1.49 (m, 1H; menthyl), 1.44 (m, 1H; menthyl), 1.11 (m, 1H; menthyl), 1.06 (m, 1H; menthyl), 0.94 (m, 1H; menthyl), 0.93 (d, $J=6.5$ Hz, 3H; CH_3, menthyl), 0.87 (d, $J=7.0$ Hz, 3H; CH_3, menthyl), 0.69 ppm (d, $J=$ 7.0 Hz, 3H; CH_3, menthyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=172.6$ (d, J(P,C)=15.7 Hz, C=O), 138.9 (d, J(P,C)=17.7 Hz, ipso-Ph), 129.2 (d, J(P,C)=9.1 Hz), 127.5 (s), 125.4 (s), 102.2 (d, J(P,C)=54.1 Hz, P*C*Ph), 95.6 (d, J(P,C)=5.1 Hz, PC*C*Me), 93.0 (d, J(P,C)=5.5 Hz, PC*C*Me), 83.2 (Cp*), 79.5 (d, J(P,C)=57.4 Hz, P*C*C=O), 73.9 (*C*H), 47.1 (*C*H), 41.3 (*C*H$_2$), 34.1 (*C*H$_2$), 31.3 (*C*H), 25.8 (*C*H), 23.0 (*C*H$_2$), 22.0 (*C*H$_3$), 20.7 (*C*H$_3$), 15.9 (*C*H$_3$), 13.3 (PCC*Me*), 12.6 (PCC*Me*), 9.6 ppm (Cp*); MS (EI-70 eV): *m/z* (%): 561 (87) [M^+], 423 (100) [M^+−menthene]; elemental analysis calcd (%) for C$_{33}$H$_{45}$FeO$_2$P: C 70.71, H, 8.09; found: C 70.66, H 8.16.

Synthesis of compound 10: Diastereopure phospharuthenocene ester **8**[28] (1.00 g, 1.65 mmol) was added to a suspension of LiAlH$_4$ (200 mg, 5.3 mmol) in of THF (50 mL) and the mixture was stirred at reflux for 3.5 h. Successive addition at 0°C of water (200 μL), aqueous 3.75 M NaOH (200 μL) and further water (600 μL) was followed by filtration under nitrogen and evaporation on a vacuum line. The pale cream solid product was transferred to a Schlenk tube equipped with a water-cooled cold finger. After elimination of menthol under reduced pressure (50°C, 0.1 mmHg), the odourless white solid **10** (697 mg 93%) was collected. The product is sufficiently pure for further use but may be purified to analytical quality by chromatography upon neutral alumina (acetone).

$[\alpha]_D^{25} = +212°$ ($c = 1.0$ in CH_2Cl_2); ^{31}P ($CDCl_3$): $\delta = -37.1$ ppm; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ7.25–7.11 (m, 5H), 3.99 (dd, J(P,H) = 13.0 Hz, J(H,H) = 11.8 Hz, 1H), 3.92 (dd, J(P,H) = 8.0 Hz, J(H,H) = 11.8 Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.75 ppm (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 139.2$ (d, J(P,C) = 17.2 Hz, ipso-Ph), 129.9 (d, J(P,C) = 6.7 Hz), 128.0 (s), 125.9 (s), 101.6 (d, J(P,C) = 56.8 Hz), 96.6 (d, J(P,C) = 58 Hz), 94.2 (d, J(P,C) = 4.6 Hz), 92.7, (d, J(P,C) = 4.0 Hz), 88.3 (Cp*), 60.8 (d, J(P,C) = 22.5 Hz, CH_2OH), 13.4 (PCC*Me*), 11.5 (PCC*Me*), 11.1 (Cp*); elemental analysis calcd (%) for $C_{23}H_{29}OPRu$: C 60.91, H 6.45; found: C 60.25, H 6.42.

Synthesis of compound 11: Diastereomer **9** (410 mg, 0.73 mmol) was added at 0 °C to a freshly distilled solution of $LiAlH_4$ (250 mg, 6.8 mmol) in diethyl ether (50 mL) and the mixture was stirred at room temperature for two hours. After a further hour at reflux, the solution was quenched with methanol, (1 mL), then water (0.5 mL), and dried over anhydrous sodium sulfate. After filtration under nitrogen, the solution was evaporated to dryness in a Schlenk tube equipped with a cold finger and menthol was sublimed out of the product under reduced pressure (0.1 mmHg, 45 °C) for 3 h. The odourless orange solid **11** was recrystallised from minimum boiling methanol (240 mg, 81 %). $[\alpha]_D^{25} = -165°$ ($c = 0.5$ in CH_2Cl_2; very poor transmission was observed); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): $\delta = -64.7$ ppm ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$ (dt, J(P,H) = 7.3, 1.1 Hz, 2H), 7.24 (tt, J(P,H) = 7.3, 1.1, Hz, 2H), 7.13 (dψt, J(P,H) = 7.2, J(H,H) = 7.2, 1.6, Hz, 1H), 4.22 (ddd, J(P,H) = 15.7, 11.4, 5.8 Hz, 1H), 4.08 (ddd, J(P,H) = 11.4, J(H,H) = 6.8, 4.3 Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 1.66 ppm (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 139.7$ (d, J(P,C) = 17.4 Hz, ipso-Ph), 128.8 (d, J(P,C) = 9.1 Hz), 127.2 (s), 124.6 (s), 97.5 (d, J(P,C) = 53.8 Hz), 94.6 (d, J(P,C) = 54.3 Hz), 93.2(d, J(P,C) = 4.7 Hz), 89.4 (d, J(P,C) = 4.4 Hz), 82.1 (Cp*), 59.9 (d, J(P,C) = 22.8 Hz, CH_2OH), 13.4 (PCC*Me*), 10.7 (PCC*Me*), 9.6 ppm (Cp*); MS (EI-70 eV): m/z (%): 407 (100) [$M^+ - 1$], 389 (48) [$M^+ - H_3O$]; elemental analysis calcd (%) for $C_{23}H_{29}FeOP$: C 67.66, H 7.16; found: C 66.93, H 7.25. The compound reacts extremely rapidly with acids; adequate spectra in deuterochloroform could only be obtained with freshly deacidifed $CDCl_3$ (Al_2O_3).

Synthesis of compound 12: Fluoroboric acid diethyl etherate (55 % HBF_4 in Et_2O, 177 μL, 1.30 mmol) was added as rapidly as possible to a solution of **10** (500 mg, 1.10 mmol) in dichloromethane (25 mL) at −78 °C. The slightly darkened solution was stirred for 10 min, warmed briefly to room temperature, and then evaporated to dryness. The residue was dissolved in a minimum of toluene and recrystallised by addition of pentane. The pale yellow product **12** was washed three times with pentane and dried (575 mg, 100 %). ^{31}P NMR (120 MHz, CD_2Cl_2, 25 °C): $\delta = -7.5$ ppm; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.47$–7.40 (m, 3H; Ar), 7.30–7.25 (m, 2H; Ar), 4.32 (d, J(P,H) = 21.1 Hz, 1H; C*H*H), 4.23 (d, J(P,H) = 8.2 Hz, 1H; CH*H*), 2.18 (s, 3H; CH_3), 1.78 (s, 15H; Cp*), 1.69 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): $\delta = 133.6$ (d, 16.2 Hz, ipso-Ph), 131.5 (s), 131.0 (s), 130.8 (d, J(P,C) = 8.9 Hz), 129.8 (d, J(P,C) = 63.8 Hz), 116.0 (d, J(P,C) = 6.7 Hz), 115.0 (d, J(P,C) = 69.7 Hz), 107.1 (d, J(P,C) = 5.2 Hz), 102.9 (Cp*), 78.1 (d, J(P,C) = 21.3 Hz, CH_2), 14.8 (PCC*Me*), 11.8 (Me of Cp*), 11.5 ppm (PCC*Me*).

Synthesis of compound 13: Compound **11** (400 mg, 0.98 mmol), was dissolved in dichloromethane (15 mL) and cooled to −30 °C, prior to being treated with fluoroboric acid diethyl etherate (55 % HBF_4 in Et_2O, 140 μL, 1.03 mmol) over a period of 30 s. The deep red solution was then treated with acetic anhydride (85 μL, 0.90 mmol) and diphenylphosphane (360 μL, 2.07 mmol) and the mixture was stirred for 10 min. After warming to room temperature, the mixture was treated with aqueous sodium hydroxide solution, (2 M, 10 mL) and stirred for 2 min. The organic fraction was separated, washed with water (2 × 15 mL) and dried over anhydrous $MgSO_4$. The product was purified by flash chromatography on neutral alumina (7 × 1.5 cm) with pentane (50 mL) to remove excess $HPPh_2$; further elution with ether furnished the product **13** as a deep orange solid (290 mg, 52 %). $[\alpha]_D^{25} = +174°$ ($c = 1.0$ in CH_2Cl_2; very poor transmission was observed); ^{31}P NMR (120 MHz, [D_8] THF, 25 °C): $\delta = -12.4$ (d, J(P,P) = 24.4 Hz), −50.7 ppm (d, J(P,P) = 24.4 Hz); ^1H NMR (300 MHz, [D_8] THF, 25 °C): $\delta = 7.47$–7.40 (m, 2H), 7.40–7.30 (m, 4H), 7.30–7.22 (m, 6H), 7.15 (ψt, J(P,H) = 7.5 Hz, 2H), 7.04 (ψt, J(P,H) = 7.5 Hz, 1H), 2.91 (dd, J(P,H) = 7.0 Hz, J(H,H) = 13.7 Hz, 1H), 2.88 (ddd, J(P,H) = 2.3 Hz, J-(P,H) = 15.3 Hz, J(H,H) = 13.7 Hz, 1H), 2.16 (s, 3H), 1.88 (s, 3H), 1.65 ppm (s, 15H; Cp*); ^{13}C NMR (75 MHz, [D_8] THF, 25 °C): $\delta = 141.2$ (d, J(P,C) = 17.4 Hz), 140.3 (d, J(P,C) = 17.8 Hz), 138.5 (d, J(P,C) = 17.2 Hz), 134.0 (dd, J(P,C) = 19.3, 2.0 Hz), 132.9 (d, J(P,C) = 18.0 Hz), 128.6 (s), 128.5 (s), 125.2 (s), 97.6 (d, J(P,C) = 54.3 Hz, P*C*Ph), 93.8 (dd, J(P,C) = 55.0 Hz, J(P,C) = 18.4 Hz, P*C*CH_2), 93.8 (dd, J(P,C) = 5.1 Hz, J(P,C) = 2.2 Hz, PC*C*Me), 89.0 (d, J(P,C) = 4.1 Hz, PC*C*Me), 82.3 (Cp*), 29.5 (dd, J(P,C) = 19.4 Hz, J(P,C) = 15.6 Hz, CH_2P), 14.2 (Me), 12.0 (d, J(P,C) = 3.6 Hz, Me), 10.0 ppm (Cp*); MS (EI-70 eV): m/z (%): 576 (24) [M^+], 390 (100) [$M^+ - PPh_2$], 375 (42) [$M^+ - PPh_2 - Me$]; elemental analysis calcd (%) for $C_{35}H_{38}FeP_2$: C 72.92, H 6.64; found: C 72.71, H 6.78.

Synthesis of compound 14: Diphenylphosphane (152 μL, 0.87 mmol) was added to a solution of phospharuthenocenemethylium cation **12** (233 mg, 0.44 mmol) in dichloromethane (20 mL) at 0 °C and the reaction mixture was allowed to come slowly to room temperature, during which time the orange colour lightened to pale yellow. The solution, containing the phosphonium salt **14**·HBF_4, was treated with aqueous NaOH (10 mL), washed with water (10 mL), and dried over sodium sulfate. Chromatography on alumina (using hexane to eliminate excess $HPPh_2$ followed by hexane/diethyl ether 1:1) gave, after removal of solvent, the white crystalline phospharuthenocenemethylphosphane **14** (213 mg, 77 %). $[\alpha]_D^{25} = +142°$ ($c = 1.0$ in CH_2Cl_2); ^{31}P NMR (120 MHz, C_6D_6, 25 °C): $\delta = -14.0$ (d, J(P,P) = 27.6 Hz), −32.4 ppm (d, J(P,P) = 27.6 Hz); ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.62$–7.52 (m, 4H), 7.28–7.25 (m, 2H), 7.13–6.98 (m, 9H), 2.92 (ddd, J(P,H) = 1.1 Hz, J(P,H) = 7.3 Hz , J(H,H) = 13.9 Hz, 1H), 2.82 (ddd, J(P,H) = 2.3 Hz, J(P,H) = 13.5 Hz , J(H,H) = 13.9 Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.75 ppm (s, 15H; Cp*); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 140.3$ (d, J(P,C) = 16.9 Hz), 140.0 (d, J(P,C) = 17.5 Hz), 138.8 (d, J(P,C) = 1.1 Hz), 138.5 (d, J(P,C) = 1.1 Hz), 134.2 (d, J(P,C) = 2.0 Hz), 134.1 (d, J(P,C) = 1.9 Hz), 133.0 (d, J(P,C) = 17.9 Hz), 130.1 (d, J(P,C) = 7.0 Hz), 129.2 (s), 128.3 (m), 127.9 (s), 101.2 (dd, J(P,C) = 58.2 Hz, J(P,C) = 1.6 Hz, P*C*Ph), 94.3 (dd, J(P,C) = 5.0 Hz, J(P,C) = 2.8 Hz, PC*C*Me), 93.5 (dd, J(P,C) = 58.9 Hz, J(P,C) = 19.1 Hz, P*C*CH_2), 91.2 (d, J(P,C) = 3.8 Hz, PC*C*Me), 87.3 (Cp*),30.2 (dd, J(P,C) = 19.5 Hz, J(P,C) = 13.8 Hz,CH_2P) 13.5 (Me), 12.1 (Me), 10.7 ppm (Cp*); NMR spectra are solvent-dependent and present a significantly different aryl signature in $CDCl_3$; elemental analysis calcd (%) for $C_{35}H_{38}P_2Ru$: C: 67.62, H 6.16; found: 67.96, H: 5.97.

Synthesis of compounds 15 and 16: Fluoroboric acid diethyl etherate (55 % HBF_4 in Et_2O, 177 μL, 1.30 mmol) was added as rapidly as possible with from a microsyringe to a solution of **10** (500 mg, 1.1 mmol) in dichloromethane (5 mL) at 0 °C. The solvents were evaporated under reduced pressure and the solid **12** was washed with diethyl ether (2 × 20 mL). A solution of *n*BuLi (0.91 mL of 1.6 M in hexane, 1.45 mmol) in THF (5 mL) was added dropwise to a solution of *rac*-*t*BuMePHBH_3 (177 mg, 1.5 mmol) in THF (5 mL) at −78 °C. The solid carbocation **12** prepared above was added as an diethyl ether suspension by canula and the mixture was stirred for 5 min. The orange mixture was allowed to warm to room temperature, yielding a pale yellow solution containing a 1:1 mixture of diastereomers **15** and **16**. These were separated on a 16 cm by 8 cm diameter column of neutral alumina in dichloromethane-pentane 1:5. R_f **15** = 0.11, R_f **16** = 0.054. Single crystals of **16** suitable for the X-ray diffraction study were obtained from dichloromethane/methanol. Attempts to separate these complexes by crystallisation repeatedly gave large crystals containing **15** and **16** in the starting ratio, even when quite highly enriched samples (ca. 90 %) were used. This presumably reflects twinning resulting from the similar spatial properties of the CH_3 and BH_3 groups and their small contribution to the overall molecular volume.

Data for (R_{Rc},R_P)-***15***: $[\alpha]_D^{25} = +181°$ ($c = 1.0$ in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): $\delta = 26.6$ (br), −33.4 ppm; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.26$–7.07 (m, 5H), 2.30 (ddd, J(H,H) = 14.4 Hz, J(P,H) = 29 Hz, J(P,H) = 4.4 Hz, 1H), 2.22 (ddd, J(H,H) = 14.4 Hz, J(P,H) = 27 Hz, J(P,H) = 6.8 Hz, 1H), 1.97 (s, 3H), 1.96 (s, 3H), 1.72 (s, 15H; Cp*), 1.23 (d, J(P,H) = 9.7 Hz, 3H; PCH_3), 1.18 (d, J(P,H) = 13 Hz, 9H; PC(CH_3)$_3$), 1.8–0.2 ppm (br m, 3H; BH_3); ^{13}C ($CDCl_3$): $\delta = 139.0$ (d, J(P,C) = 17.4 Hz, ipso-Ph), 129.6 (d, J(P,C) = 6.8 Hz, *o*-Ph), 127.8 (*m*-Ph), 125.6 (*p*-Ph), 100.3 (d, J(P,C) = 55.2 Hz), 95.1 (dd, J(P,C) = 4.6 Hz,

J(P,C) = 1.3 Hz), 91.6 (d, J(P,C) = 3.7 Hz), 88.4 (d, J(P,C) = 58.1 Hz), 87.7 (Cp*), 27.9 (d, J(P,C) = 31.6 Hz, P*C*Me$_3$), 25.4 (PC(*C*H$_3$)$_3$), 21.9 (dd, J(P,C) = 21 Hz, J(P,C) = 28 Hz, *C*H$_2$), 13.6 (PCC*Me*), 13.0 (PCC*Me*), 10.1 (Cp*), 5.0 ppm (dd, J(P,C) = 35 Hz, J(P,C) = 8.7 Hz, P*C*H$_3$).

Data for (R$_{Rc}$,S$_P$)-***16***: $[\alpha]_D^{25} = +140°$ (c = 1.0 in CH_2Cl_2); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): δ = 28.6 (br), −31.3 ppm; ^{1}H ($CDCl_3$): δ = 7.25–7.06 (m, 5H), 2.35 (ddd, J(H,H) = 14.7 Hz, J(P,H) = 31 Hz, J(P,H) = 11 Hz, 1H), 2.28 (ddd, J(H,H) = 14.7 Hz, J(P,H) = 23 Hz, J(P,H) = 6.4 Hz, 1H), 1.98 (s, 3H), 1.90 (s, 3H), 1.70 (s, 15H; Cp*), 1.19 (d, J(P,H) = 13 Hz, 9H; PC(C*H*$_3$)$_3$), 1.16 (d, J(P,H) = 9.5 Hz, 3H; PC*H*$_3$), 1.4–0.2 ppm (br m, 3H; BH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 138.9 (d, J(P,C) = 20 Hz, ipso-Ph), 129.7 (d, J(P,C) = 7.1 Hz, *o*-Ph), 127.7 (*m*-Ph), 125.6 (*p*-Ph), 101.3 (d, J(P,C) = 57 Hz), 93.5 (dd, J(P,C) = 5.3 Hz, J(P,C) = 1.4 Hz), 91.0 (d, J(P,C) = 4.3 Hz), 88.6 (d, J(P,C) = 61 Hz), 87.7 (Cp*), 28.1 (d, J(P,C) = 40 Hz, *C*Me$_3$), 25.6 (PC(*C*H$_3$)$_3$), 23.1 (dd, J(P,C) = 20 Hz, J(P,C) = 28 Hz, *C*H$_2$), 13.6 (PCC*Me*), 13.1 (PCC*Me*), 10.7 (Cp*), 5.2 ppm (dd, J(P,C) = 34.0 Hz, J(P,C) = 3.1 Hz, P*C*H$_3$); elemental analysis calcd (%) for $C_{28}H_{43}BP_2Ru$: C 60.76, H: 7.83; found: C 60.82, H 7.97. Mass (CI/NH$_3$): m/z: 554.

Synthesis of compound 17: Fluoroboric acid diethyl etherate (55% HBF_4 in Et_2O, 177 μL, 1.30 mmol) was added as rapidly as possible to a solution of **10** (500 mg, 1.10 mmol) in dichloromethane (25 mL) at 0 °C. The solvent was evaporated under reduced pressure and the product **12** was washed with ether (2 × 20 mL). A solution of *n*BuLi (0.90 mL of 1.6 M in hexane, 1.45 mmol) in hexane (5 mL) was added dropwise at −78 °C to a solution of P*t*Bu$_2$H·BH$_3$ (240 mg, 1.50 mmol) in THF (10 mL) and the mixture was allowed to stir for 15 min. A suspension of the carbocation prepared above in diethyl ether (15 mL) was then added by canula over a period of 2 min. After warming to room temperature, the pale yellow solution containing **17** (33%) and the reduction product **23** (62%) was evaporated to dryness and purified by chromatography.

Data for (R)-***17***: $[\alpha]_D^{25} = +174°$ (c = 1.0, DCM); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): δ = 45.8 (br), −28.3 ppm; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.24–7.16 (m, 4H), 7.15–7.07 (m, 1H; p-Ph), 2.58 (ddd, J(H,H) = 15.0 Hz, J(P,H) = 13.4 Hz, J(P,H) = 5.5 Hz, 1H; C*H*H), 2.41 (ddd, J(H,H) = 15.0 Hz, J(H,H) = 16.0 Hz, J(H,H) = 7.1 Hz, 1H; CH*H*), 2.03 (s, 3H), 1.99 (s, 3H), 1.72 (s, 15H), 1.36 (d, J(P,H) = 12.6 Hz, 9H), 1.31 ppm (d, J(P,H) = 11.9 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.2 (d, J(P,C) = 17.4 Hz, ipso-Ph), 129.6 (d, J(P,C) = 6.9 Hz, *o*-Ph), 127.7 (*m*-Ph), 125.5 (*p*-Ph), 100.2 (d, J(P,C) = 55.9 Hz, P*C*Ph), 95.7 (d, J(P,C) = 6.1 Hz, P*C*), 91.2 (d, J(P,C) = 3.8 Hz, P*C*), 90.4 (dd, J(P,C) = 59.7 Hz, J(P,C) = 2.6 Hz, PC*C*CH$_2$), 87.6 (Cp*), 33.0 (dd, J(P,C) = 24.0 Hz, J(P,C) = 8.0 Hz, P(*C*Me$_3$)$_2$), 29.2 (d, J(P,C) = 6.9 Hz, PC(*C*H$_3$)$_3$), 28.6 (PC-(*C*H$_3$)$_3$), 20.8 (dd, J(P,C) = 23.0 Hz, J(P,C) = 20.7 Hz, *C*H$_2$), 13.8 (PCC*Me*), 13.6 (PCC*Me*), 10.7 (Cp*); CI-MS: m/z (%): 595 (100), 437 (28).

Data for (S)-***23***: $[\alpha]_D^{25} = +217°$ (c = 1.0 in CH_2Cl_2); ^{31}P ($CDCl_3$): δ = 33.9 ppm; ^{1}H ($CDCl_3$): δ = 7.25–7.16 (m, 4H), 7.15–7.06 (m, 1H; *p*-Ph), 1.97 (s, 3H; *Me*CCPh), 1.87 (s, 3H; MeCCMe), 1.73 (s, 15H), 1.67 (d, J(P,H) = 9.9 Hz, 3H; PC*Me*); ^{13}C ($CDCl_3$): δ = 139.6 (d, J(P,C) = 16.9 Hz, ipso-Ph), 129.7 (d, J(P,C) = 6.6 Hz, *o*-Ph), 127.7 (*m*-Ph), 125.3 (*p*-Ph), 100.0 (d, J(P,C) = 56.6 Hz, P*C*Ph), 94.5 (d, J(P,C) = 4.9 Hz, PC*C*), 93.2 (d, J(P,C) = 56.5 Hz, P*C*Me), 90.8 (d, J(P,C) = 3.4 Hz, PC*C*), 87.3 (Cp*), 14.0 (d, J(P,C) = 23.0 Hz, PC*C*H$_3$), 13.5 ppm; elemental analysis calcd (%) for $C_{23}H_{29}PRu$: C 63.14, H 6.68; found: C 61.63, H 6.79; CI-MS: m/z (%): 438 (100).

Synthesis of compound 18: A solution of [Rh(cod)(acac)] (54 mg, 0.17 mmol) in THF (2 mL) was cooled to 0 °C and treated with fluoroboric acid diethyl etherate (55% HBF_4 in Et_2O, 23 μL, 0.17 mmol) to give a deep yellow-orange solution. After stirring for 30 s this mixture was treated over a period of 30 s with a solution of **13** (100 mg, 0.17 mmol) in THF (1 mL) and the mixture was stirred at room temperature for 10 min. The solvents were removed and the red solid was washed with hexane (2 × 0.5 mL) to give compound **18** (135 mg, 90%). ^{31}P NMR (120 MHz, [D$_8$] THF, 25 °C): δ = 62.3 (dd, J(P,Rh) = 137 Hz, J(P,P) = 25.7 Hz), 24.0 ppm (dd, J(P,Rh) = 170 Hz, J(P,P) = 25.7 Hz); ^{1}H NMR (300 MHz, [D$_6$] acetone, 25 °C): δ = 7.90–7.81 (m, 2H), 7.70–7.48 (m, 7H), 7.42–7.40 (m, 4H), 7.36–7.26 (m, 2H), 6.30 (br, 1H; C*H*), 5.83, (br, 1H; C*H*), 4.83 (br, 1H; C*H*), 4.52 (br, 1H; C*H*), 3.36 (t, J = 16.2 Hz, dd, J(P,H) = 23.0 Hz, J(P,H) = 1.1 Hz , 1H; PCCH*H*PPh$_2$), 2.96 (ddd, J(P,H) = 6.1 Hz, J(P,H) = 4.2 Hz , J(H,H) = 16.2 Hz, 1H; PCC*H*HPPh$_2$), 2.70–2.20 (m, 7H; C*H*$_2$, COD), 2.20 (s, 3H; Me), 2.19 (m, 1H; C*H*$_2$, COD), 2.00 (s, 3H; Me), 1.85 ppm (s, 15H; Cp*). Crystals suitable for the X-ray analysis were obtained by diffusion of ether into an acetone solution of the racemic compound, prepared similarly from a mixture of **9** and **9a**.

Synthesis of compound 19: A solution of [Rh(cod)(acac)] (35 mg, 0.10 mmol) in THF (2 mL) was cooled in an ice bath and treated with fluoroboric acid diethyl etherate (55% HBF_4 in Et_2O, 14 μL, 0.10 mmol). The darkened solution was stirred for 30 s and then further treated over a period of 30 s with a solution of **14** (70 mg, 0.11 mmol) in THF (1 mL), which caused a colour change to orange. The solvents were removed and the orange solid was washed with hexane (2 × 0.5 mL). Crystals suitable for the X-ray analysis were obtained by diffusion of diethyl ether into a solution of the compound in dichoromethane. ^{31}P NMR (120 MHz, [D$_8$] THF, 25 °C): δ = 61.3 (dd, J(P,Rh) = 138 Hz, J(P,P) = 27.2 Hz), 36.7 ppm (dd, J(P,Rh) = 170 Hz, J(P,P) = 27.2 Hz); ^{1}H NMR (300 MHz, [D$_6$] acetone, 25 °C): δ = 7.92–7.82 (m, 2H), 7.67–7.49 (m, 8H), 7.40–7.31 (m, 2H), 7.28–7.18 (m, 3H), 5.98 (br, 1H; C*H*), 5.53 (br, 1H; C*H*), 4.56 (br, 1H; C*H*), 4.48 (br, 1H; C*H*), 3.30 (ddd, J(P,H) = 31.1 Hz, J(P,H) = 5.1 Hz, J(H,H) = 15.5 Hz, 1H; PCCH*H*PPh$_2$), 2.74 (ddd, J(P,H) = 5.3 Hz, J(P,H) = 9.4 Hz , J(H,H) = 15.5 Hz, 1H; PCC*H*HPPh$_2$), 2.60–2.10 (m, 8H; C*H*$_2$, COD), 2.01 (s, 3H; Me), 1.95 (s, 3H; Me), 1.74 ppm (s, 15H; Cp*); ^{13}C NMR (75 MHz, [D$_6$] acetone, 25 °C): δ = 136.4 (d, J(P,C) = 13.8 Hz, ipso-Ph), 135.1 (d, J(P,C) = 11.6 Hz, *o*-PPh$_2$), 133.7 (d, J(P,C) = 10.8 Hz, *o*-PPh$_2$), 132.6 (d, J(P,C) = 2.5 Hz, *m*-PPh$_2$), 132.5 (d, J(P,C) = 2.3 Hz, *m*-PPh$_2$), 132.3 (d, J(P,C) = 43.7 Hz, ipso-PPh$_2$), 131.9 (d, J(P,C) = 41.4 Hz, ipso-PPh$_2$), 130.3 (d, J(P,C) = 3.7 Hz, *o*-Ph), 130.2 (s), 130.1 (s), 129.4 (s), 127.7 (s), 98.8 (dd, J = 9.2 Hz, J = 6.9 Hz, *C*H, COD), 97.8 (dd, J = 9.2 Hz, J = 6.9 Hz, *C*H, COD), 97.1 (dd, J = 12.6 Hz, J = 9.2 Hz, *C*H, COD), 96.7 (dd, J = 9.2 Hz, J = 9.2 Hz, *C*H, COD), 93.6 (dd, J = 17.2 Hz, J = 8.0 Hz), 92.7 (ddd, J = 32.2 Hz, J = 12.6 Hz, J = 4.6 Hz), 91.2 (Cp*), 90.9 (d, J = 6.9 Hz), 88.5 (dd, J = 9.2 Hz, J = 4.6 Hz), 31.7 (*C*H$_2$, COD), 31.1 (*C*H$_2$, COD), 30.7 (*C*H$_2$, COD), 30.3 (*C*H$_2$, COD), 26.7 (dd, J(P,C) = 25.3 Hz, J(P,C) = 26.4 Hz, *C*H$_2$PPh$_2$), 13.3 (d, 2.3 Hz, Me), 12.9 (d, 3.4 Hz, Me), 10.7 ppm (Cp*).

Synthesis of compound 20: The complex was prepared and isolated as for **21** below, but was characterised by ^{31}P NMR spectroscopy only. ^{31}P NMR (120 MHz, [D$_8$] THF, 25 °C): δ = 66.5 (dd, J(P,Rh) = 135 Hz, J(P,P) = 27 Hz), 33.6 ppm (dd, J(P,Rh) = 170 Hz, J(P,P) = 27 Hz).

Synthesis of compound 21: Compound **16**, (31.4 mg, 0.057 mol) in dichloromethane (3 mL) was treated with fluoroboric acid diethyl etherate (55% HBF_4 in Et_2O, 8 μL, 0.059 mmol) and the mixture was stirred for 4 h at room temperature. A solution of [Rh(cod)(acac)] (17.6 mg, 0.057 mmol) in THF (1 mL) was then cooled to 0 °C and treated with fluoroboric acid diethyl etherate (55% HBF_4 in Et_2O, 8 μL, 1 equiv) The darkened solution was stirred for 2 min and then treated dropwise at −78 °C with the solution of deboronated **16**·HBF_4 prepared above (0.057 mmol) over a period of 5 mins. The resulting deep yellow solution was allowed to warm to room temperature over 15 min and was then evaporated to dryness under reduced pressure. Successive washes with diethyl ether (3 × 2 mL) furnished the product as an orange-red solid. ^{31}P NMR (120 MHz, [D$_8$] THF, 25 °C): δ = 62.8 (dd, J(P,Rh) = 131 Hz, J(P,P) = 24 Hz), 35.8 ppm (dd, J(P,Rh) = 171 Hz, J(P,P) = 24 Hz); ^{31}P ((CD$_3$)$_2$CO): δ = 64.4 (dd, J(P,Rh) = 131 Hz, J(P,P) = 23.8 Hz), 37.0 ppm (dd, J(P,Rh) = 171 Hz, J(P,P) = 23.8 Hz); ^{1}H NMR (300 MHz, [D$_6$] acetone, 25 °C): δ = 7.42–7.24 (m, 5H; Ph), 5.89 (br, 1H; C*H*), 5.79 (br, 1H; C*H*), 5.71 (br, 1H; C*H*), 5.03 (br, 1H; C*H*), 2.63–2.31 (m, 6H; CH$_2$, COD), 2.22–2.10 (m, 2H; CH$_2$, COD), 2.13 (s, 3H; Me), 1.96 (s, 3H; Me), 1.88 (s, 15H; Cp*), 1.60 (d, J(P,H) = 8.0 Hz, PC*H*$_3$), 1.30 ppm (d, J(P,H) = 14.2 Hz, PC(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz, [D$_6$] acetone, 25 °C): δ = 136.5 (d, J(P,C) = 13.0 Hz, ipso-Ph), 130.8 (d, J(P,C) = 4.7 Hz, *o*-Ph), 129.2 (*m*-Ph), 127.9(*p*-Ph), 95.8 (dd, J(P,C) = 8.2 Hz, J(C,Rh) = 8.6 Hz, *C*H, COD), 95.1 (dd, J(P,C) = 13.2 Hz, , J(C,Rh) = 8.1 Hz, *C*H, COD), 93.7 (dd, J(C,Rh) = 1.1 Hz, J(P,C) = 12.6 Hz, PCC), 93.6 (dd, J(P,C) = 8.2 Hz, J(C,Rh) = 6.9 Hz, *C*H, COD), 92.3 (dd, J(P,C) = 8.6 Hz, J(C,Rh) = 7.8 Hz, *C*H, COD), 92.0 (dd, J(P,C) = 18 Hz, J(C,Rh) = 4.2 Hz, PCC), 91.5

(dd, J(C,Rh) = 1.1 Hz, J(P,C) = 9.0 Hz, PCC), 91.2 (Cp*), 88.9 (dd, J = 9.2 Hz, J(C,Rh) = 5.4 Hz, PCC), 34.2 (d, J(P,C) = 19.7 Hz , $C(CH_3)_3$), 32.6 (d, J(P,C) = 3.2 Hz, CH_2, COD), 31.5 (d, J(P,C) = 4.0 Hz, CH_2, COD), 30.9 (CH_2, COD), 29.4 (CH_2, COD), 26.9 (d, J(P,C) = 3.8 Hz, $PC(CH_3)_3$), 20.9 (dd, J(P,C) = 28.8 Hz, J(P,C) = 28.8 Hz, $PCCH_2P$), 13.2 (d, 2.9 Hz, Me),12.9 (d, 3.7 Hz, Me), 11.0 (Cp*), 10.1 ppm (d, J(P,C) = 21.7 Hz, PCH_3).

Synthesis of compound 22: The complex was prepared and isolated as for **21**, but was characterised by ^{31}P NMR spectroscopy only. ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): δ = 96.2 (dd, J(P,Rh) = 132 Hz, J(P,P) = 24.9 Hz), 46.6 ppm (dd, J(P,Rh) = 175 Hz, J(P,P) = 24.9 Hz); ^{31}P (THF): δ = 91.1 (dd, J(P,Rh) = 132 Hz, J(P,P) = 24.9 Hz), 41.4 ppm (dd, J(P,Rh) = 175 Hz, J(P,P) = 24.9 Hz).

Hydrogenation experiments: These were performed in (at least) duplicate in 80 mL Schlenk tubes. In a typical procedure, the substrate (4-GMAC, 50 mmol), the catalyst precursor (50 μmol) and a micro stirrer bar were placed in freshly distilled ethanol (6 mL) in the Schlenk tube, which was attached to an atmospheric pressure source of hydrogen. The mixture was carefully degassed by three freeze–pump–thaw cycles, refilled with hydrogen and then returned to room temperature. At this point the flask was sealed and the mixture was stirred for 12 h. Conversion was determined by drying the crude sample and analysis by ^{1}H NMR measurements. The product was then freed from organometallic impuritites by filtration through a 2 cm silica column in diethyl ether and analysed by (UV-detected) chiral HPLC on a chiraldex OD-H column using a hexane/isopropanol eluents under the following conditions: for G = H *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 9.7, (*S*) 12.4 min; for G = F *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 11.7, (*S*) 14.9 min; for G = Cl *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 12.2, (*S*) 16.6 min; for G = MeO *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 15.0, (*S*) 19.0 min; for G = Me *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 9.9, (*S*) 19.6 min; for G = NO_2 *i*PrOH/*n*-hexane 1:9, flow rate 1 mL min^{-1} elution time: (*R*) 28.6, (*S*) 34.6 min. Integration was checked using *rac*-substrates (prepared using an $[Rh(dppe)(cod)]^+BF_4^-$ catalyst) under the conditions given in Table 2.

CCDC-629059 (**9**), CCDC-629060 (**9a**), CCDC-629063 (**16**), CCDC-629061 (**18**) and CCDC-629062 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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