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Tuning of the Structures of Chiral Phosphane-Phosphites: Application to the Highly Enantioselective Synthesis of α-Acyloxy Phosphonates by Catalytic Hydrogenation

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Abstract: A family of new chiral phosphane-phosphites **5** has been prepared and employed in the synthesis of rhodium complexes of formulation [Rh(cod)(**5**)]BF_4 (**7**). The use of bulky phosphane or phosphite groups in the preparation of **7** avoids the formation of undesired disubstituted complexes, one of which (**9a**) has been isolated and characterized. Ligands **5** display important differences from the bulkier phosphane-phosphites **1**: complexes **7**—unlike their rigid [Rh(cod)(**1**)]BF_4 counterparts—show fluxional behaviour in solution, consistent with backbone oscillation around the coordination plane. A detailed screening of ligands **1** and **5** in catalytic asymmetric hydrogenations of enol phosphonates **12** demonstrated a critical influence of the steric characteristics of the phosphane-phosphite in the course of the reaction, and optimization of the two phosphorus functionalities resulted in the production of versatile and efficient catalysts for this class of hydrogenations: enantioselectivities of up to 98% *ee* were thus obtained with substrates bearing an alkyl substituent in the β-position, while for their challenging aryl counterparts values of up to 92% *ee* were achieved. The coordination mode of phosphonate **12a** towards a Rh phosphane-phosphite fragment has also been investigated and a preference of the olefin fragment to occupy the position *cis* to the phosphite group has been observed. From this observation an interpretation of the configurations of the hydrogenated phosphonates has also been made.

Keywords: asymmetric catalysis · enantioselectivity · hydrogenation · P ligands · rhodium

Introduction

The use of chiral bifunctional ligands (L–L′) has become a powerful strategy in catalyst design for enantioselective processes. In recent years a wide variety of chelating ligands combining P, S, N, C or O donor groups[1] have been described, and the optimization of their structures has produced impressive results in a broad range of enantioselective catalytic transformations.[2]

Electronic dissimilarity in coordinating functions of L–L′ is a highly useful feature. L–L′ may allow better adjustment than symmetric L–L to the specific electronic requirements of a reaction,[3] or may even reduce the number of participant reaction intermediates, facilitating stereochemical control of the process.[4] In this regard, phosphane-phosphites are appealing compounds, due to the differences in the donor abilities of their phosphorus functions, arising from the strong π-acceptor character of the phosphite group.[5] The first applications of chiral phosphane-phosphites in asymmetric catalysis, studied by Takaya and Nozaki, provided very high enantioselectivities in the hydroformylation of olefins,[6] while more recently the scope of this class of ligands has been considerably expanded and they have provided efficient catalysts for several enantioselective transformations such as hydrogenation, hydroboration or allylic substitution, among others.[7] Moreover, the production of new chiral catalysts containing phosphane and phosphite functionalities by the use of mixtures of monodentate[8] or self-assembled ligands[9] has also been studied.

We have recently synthesized a family of modularly designed phosphane-phosphites **1** and have employed them in the highly enantioselective hydrogenation of dimethyl itaconate and methyl (*Z*)-α-acetamidocinnamate (MAC).[5,10] Alternatively, ligands of type **2** have provided enantioselectivi-

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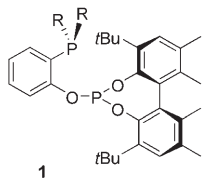
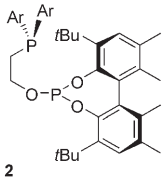
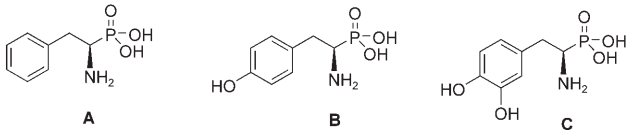




R = alkyl, aryl

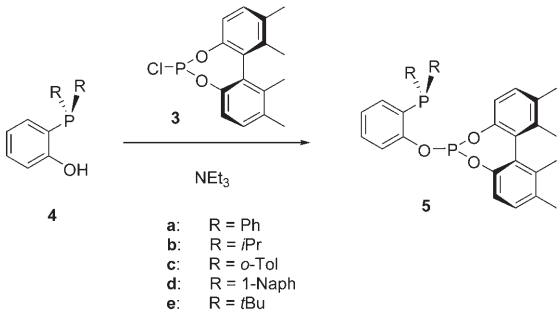
ties around the 80% *ee* level in the asymmetric hydrogenation of *N*-aryl imines.[11] The easily tuneable structures of compounds **1** and **2** make them appropriate tools with which to examine the hydrogenation of challenging substrates: the reduction of enol ester phosphonates for the synthesis of biologically[12] and synthetically[13] important chiral α-hydroxy phosphonates, for instance, is of great interest. Studies covering the scope of this transformation have used important rhodium catalysts bearing DuPHOS,[14a] BisP* or Miniphos ligands,[14b] and these investigations have provided excellent enantioselectivities in hydrogenations of β-alkyl-substituted phosphonates, although catalyst performance is significantly reduced with β-aryl substrates. Notably, the latter can provide convenient access[15] to important phosphorus analogues of phenylalanine (**A**), tyrosine (**B**) or DOPA



(**C**).[16] In this full account we report a detailed study of the application of phosphane-phosphite (P-OP) ligands to the enantioselective hydrogenation of enol-ester phosphonates in studies including the synthesis of new ligands and catalyst precursors, supplemented with X-ray and NMR structural data for pertinent rhodium complexes. Part of this work has been published in a preliminary form.[17]

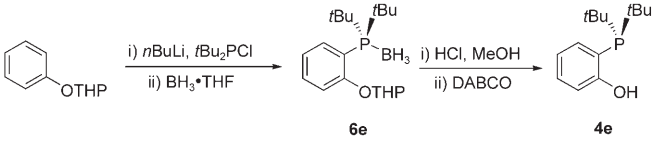
Results and Discussion

Ligand synthesis: After the observation of low reaction rates in hydrogenations of α,β-unsaturated phosphonates with catalysts based on ligands **1**, we next examined structurally related ligands bearing less sterically demanding phosphite groups. Accordingly, chlorophosphite **3** (Scheme 1) was prepared from the corresponding bisphenol,[18] while to provide the other component a set of phenol-phosphanes **4** was used. In addition to the previously reported **4a**–**c**,[5,11] additional examples were prepared in order to widen the tuneability of this ligand family. The 1-naphthyl derivative **4d** was thus synthesized by demethylation of the corresponding *o*-anisyl phosphane,[5] while the *tert*-butyl phosphane **4e** was



Scheme 1. Synthesis of phosphane-phosphites **5**.

prepared by a modification of the procedure described by Schmalz (Scheme 2).[19] Finally, condensation of **3** with phenol-phosphanes **4** readily provided the series of phosphane-phosphites **5**.



Scheme 2. Preparation of phosphane **4e**.

Synthesis and structures of catalyst precursors: With the intent to apply ligands **5** in catalytic hydrogenations, we first studied the synthesis of catalyst precursors of formulation [Rh(cod)(**5**)]BF_4 (complexes **7**). As previously reported in the case of ligands **1**,[5] reactions between [Rh(cod)$_2$]BF_4 and stoichiometric amounts of chiral phosphane-phosphites **5b**, **5e** and **2a** (Ar = Ph) provided the corresponding complexes **7b**, **7e** and [Rh(cod)(**2a**)]BF_4 (**8a**) in good yields, but when the reaction was attempted with ligand **5a** a mixture composed of the desired compound **7a** and a second species **9a**, in a ratio of 1:4, was observed. Characterization of the latter complex only showed signals for coordinated **5a** in the ^{1}H NMR spectrum, while the ^{31}P{^{1}H} data consisted of two complex multiplets in the regions characteristic of phosphanes and phosphites, respectively. These signals match a simulated spectrum of a split (by coupling with the ^{103}Rh nucleus) AA′XX′ spin system (Figure 1).[20] Remarkable among the calculated ^{31}P–^{31}P coupling constants is one of high magnitude (400 Hz), diagnostic of a *trans* arrangement of a phosphane and a phosphite group[21] and indicative of the existence of two **5a** molecules bonded to a Rh atom. Dinuclear-type structures for this compound were ruled out by an X-ray analysis, which finally identified **9a** as [Rh(**5a**)$_2$]BF_4 (Figure 2). This compound displays a distorted square-planar geometry with P-Rh-P angles between *trans* disposed functionalities around 165°. The two ligands are coordinated with phosphane and phosphite groups occupying mutually *trans* positions, as might be expected from their

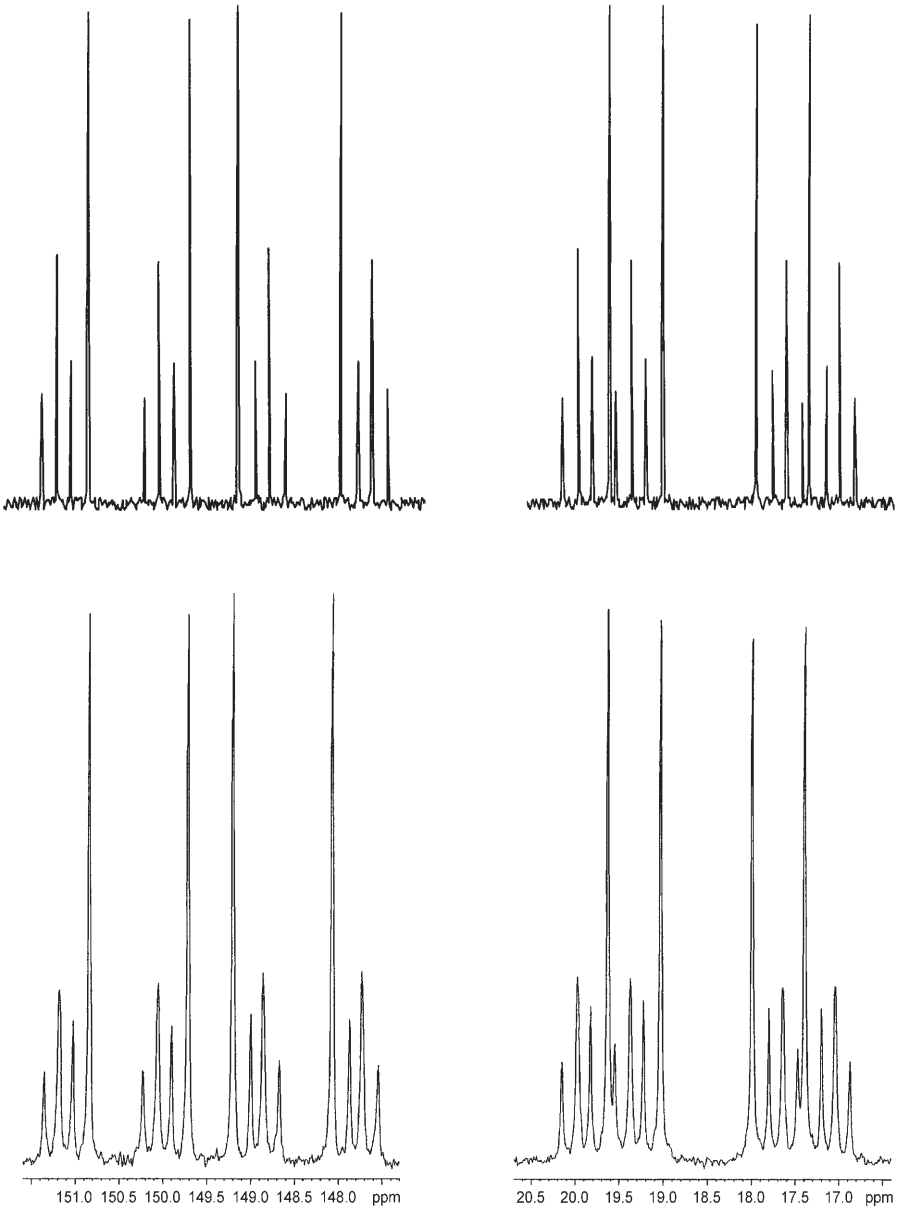
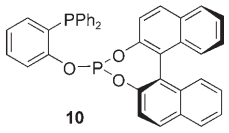


Figure 1. Calculated (top) and experimentally measured (bottom) $^{31}P\{^{1}H\}$ NMR spectra for complex **9a**. Coupling constants used for the simulated spectrum: $J_{PC,Rh} = 121$ Hz, $J_{PO,Rh} = 228$ Hz, $J_{PC,PC} = J_{PO,PO} = -70$ Hz, $J_{PC,PO\,(cis)} = 33$ Hz, $J_{PC,PO\,(trans)} = 400$ Hz.

matched electronic properties. Notably, the closeness of the phosphane functionalities allows an offset π-stacked arrangement between two phenyl rings,[22] with a distance of 3.77 Å between their centroids, so the arrangement of the two **5a** ligands gives rise to a rather congested structure that should not be attainable with a *t*Bu-substituted phosphite or with phosphane-phosphites containing bulky phosphane groups, explaining experimental observations.

While the dissimilar bonding abilities of phosphane and phosphite functionalities are useful for stereocontrol in asymmetric catalysis, they inherently favour the formation of undesired disubstituted complexes. The simultaneous formation of 1:1 and 1:2 rhodium/ligand compounds should be a consequence of competition between $[Rh(cod)_2]BF_4$ and $[Rh(cod)(\mathbf{5})]BF_4$ for free **5**, so in order to destabilize this situation we instead started from the more labile $[Rh(cod)(thf)_2]BF_4$, prepared by chloride abstraction from $[Rh(Cl)(cod)]_2$ by $AgBF_4$ in THF.[23] In good accord with our expectations, addition of an equivalent of ligand **5a** to the THF solvate yielded the monosubstituted compound $[Rh(cod)(\mathbf{5a})]BF_4$ (complex **7a**) in good yield. This methodology was also applied to the synthesis of the *o*-tolyl (**7c**) and 1-naphthyl (**7d**) derivatives.

From a practical point of view it was pertinent to examine whether a phosphane-phosphite derived from the commercially available BINOL would behave similarly to ligands of type **5**, as the bisphenol used in the preparation of the latter requires several synthetic steps in the laboratory. For this purpose we chose the phosphane-phosphite **10**, previously described



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by Pringle,[24] and prepared the corresponding complex $[Rh(cod)(\mathbf{10})]BF_4$ (**11**) by the procedure described for **7a**.

With the goal of gaining information relating to the structure of coordinated **5** in a catalyst precursor, we performed an X-ray diffraction study of compound **7a**: an ORTEP view is depicted in Figure 3 along with selected bond lengths and angles. Compound **7a** displays a square-planar coordination geometry, with a P-Rh-P bite angle of 86°, somewhat smaller than that determined in Rh(Cl)(CO)(**1a**) (89°; R = Ph).[5] On the other hand, the dihedral angle between the aryl rings of the biphenyl is 54°, a value very similar to those found in BINOL moieties in BINAPHOS derivatives (52–54°)[25] and appreciably smaller than that observed in coordinated **1a** (63°). The removal of the *t*Bu groups has thus produced a narrowing of the angle between the aromatic halves of the biphenyl fragment,[26] an

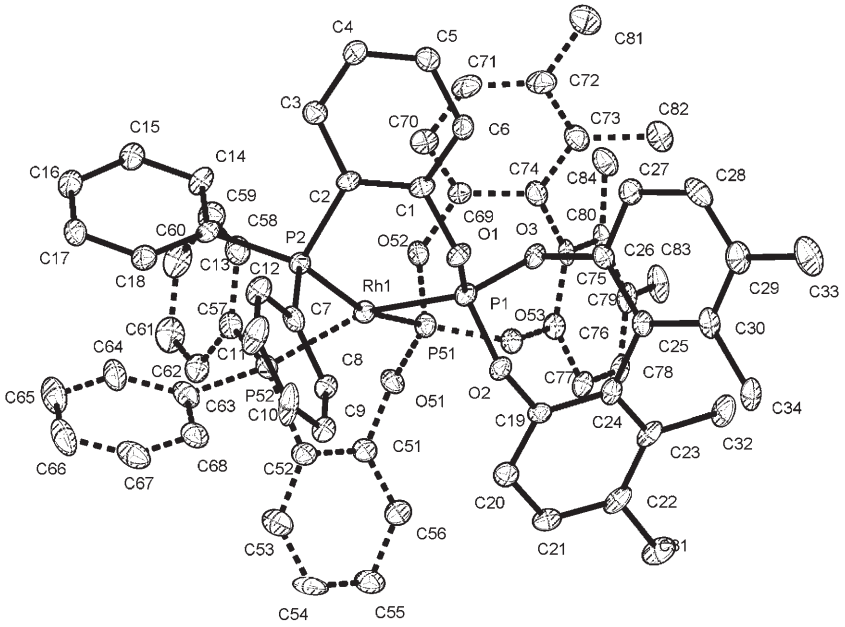


Figure 2. ORTEP view of the cation of **9a**. H atoms have been omitted and bonds in the back ligand are drawn dashed for clarity. Selected bond lengths [Å] and angles [°]: Rh1−P1 2.2198(16), Rh1−P2 2.3191(15), P1-Rh1-P2 87.12(6), P1-Rh1-P51 93.94(6), P1-Rh1-P52 163.03(6), P2-Rh1-P52 98.65(6).

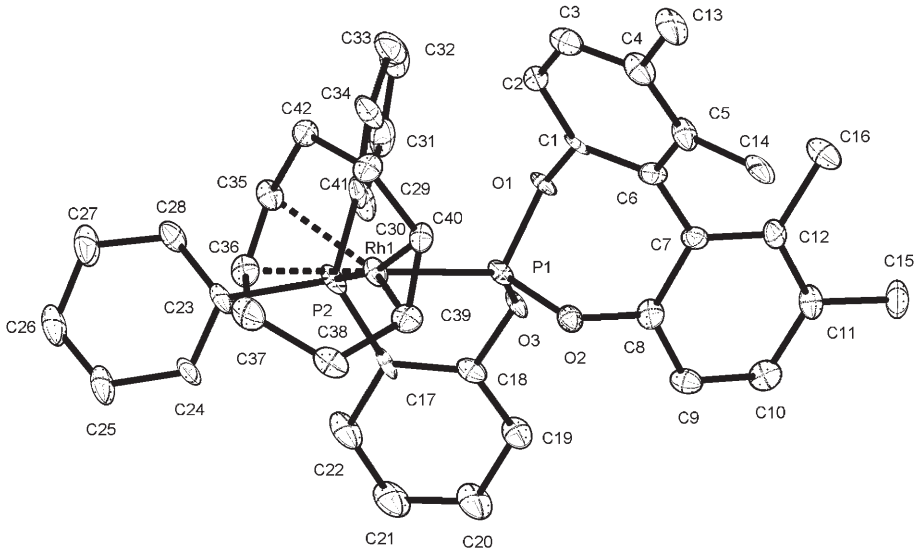


Figure 3. ORTEP view of the cation of **7a**. H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]. Rh1−P1 2.1913(11), Rh1−P2 2.2835(12), Rh1−C35 2.265(5), Rh1−C36 2.314(4), Rh1−C39 2.237(5), Rh1−C40 2.252(4), C35−C36 1.366(8), C39−C40 1.353(7), P1-Rh1-P(2) 85.69(4).

effect also observed in the calculated structures of a series of iridium complexes bearing P-OP ligands.[11] An interesting feature of this structure is the *syn* orientation of the bridged phenylene with respect to the *exo* aryl part (constituted by carbons C7–C12) of the biphenyl fragment. This arrangement, also observed in disubstituted **9a**, is the opposite of the *anti* orientation observed in complexes derived from **1**, which has been attributed to an interaction between the phenylene backbone and a *t*Bu group of the phosphite, additionally causing the rigidity of coordinated **1**.[5] From these considerations it might be expected that **7** should display fluxional behaviour resulting from backbone flipping, and to investigate this possibility we examined compounds [Rh(cod)(**1b**)]BF_4 (R = *i*Pr) and [Rh(cod)(**5b**)]BF_4 by 2D NOESY spectroscopy (Figure 4). As a diagnostic measure of the mobility of the coordinated P-OP system we examined the NOE signals between the methyne protons of the isopropyl groups (H^b, H^c) and the aromatic proton adjacent to the phosphine group (H^a). As expected, the complex derived from **1b** only showed a NOE with one of the isopropyl moieties. Conversely, compound **7b** exhibited signals for the two methynes, in good accord with a dynamic process involving backbone oscillation around the coordination plane. We further tried to observe both conformers separately, but only one set of signals was observed down to 180 K in the $^{31}P\{^1H\}$ experiment. Thus, the removal of *t*Bu substituents in the phosphite has a dual effect, both reducing the hindrance exerted by this group and increasing the flexibility of the complex. This dynamic behaviour may be of importance, since it causes a less defined position of the phosphane substituents and, in addition, should permit better accommodation of sterically congested substrates such as phosphonates **12** (see below).[27]

Hydrogenation of unsaturated phosphonates: Catalyst screening for the hydrogenation of phosphonates **12** was started with complexes [Rh(cod)(**1**)]BF_4 and the unsubstituted substrate **12a** (Scheme 3). Interestingly, the catalyst derived from ligand **1a** produced a high enantioselectivity (entry 1, Table 1), but the reaction was rather slow, and stronger conditions (20 atm, 40 °C) were needed to complete the reaction at a lower catalyst loading (entry 2). The reaction was further slowed by any increase in the size of the β substituent of the

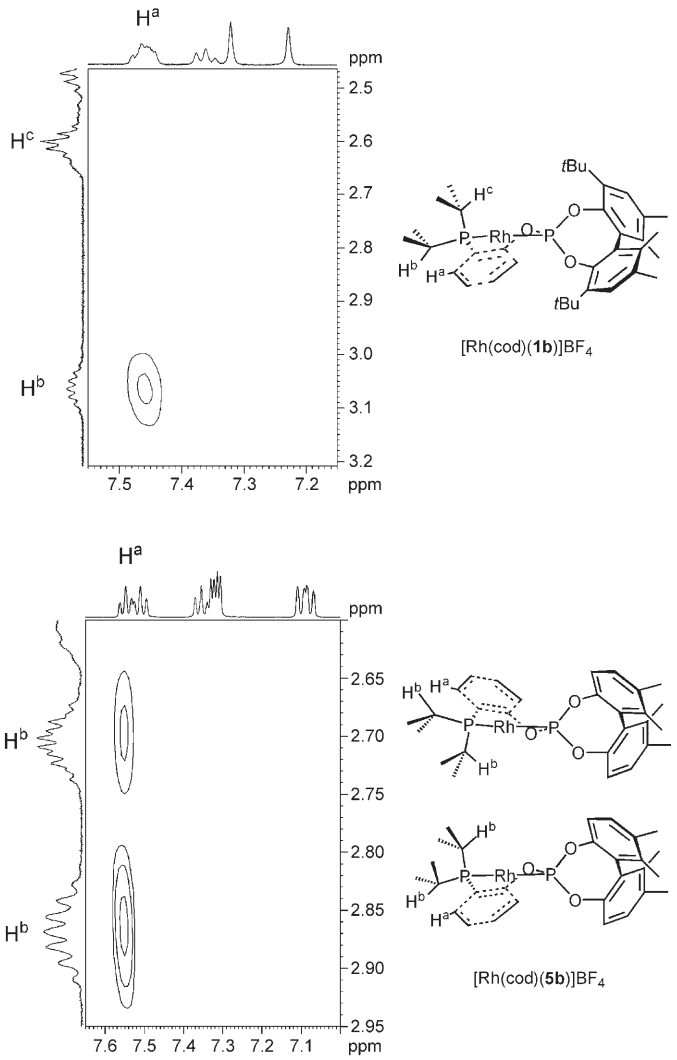
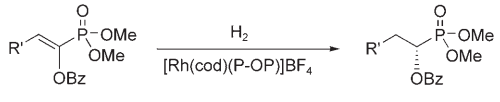


Figure 4. Sections of the 2D NOESY experiments for compounds [Rh(cod)(**1b**)]BF_4 and [Rh(cod)(**5b**)]BF_4.



12 **13**

a: R' = H
b: R' = Et
c: R' = *i*Pr
d: R' = *n*Bu
e: R' = Ph
f: R' = 4-Me-C_6H_4
g: R' = 4-MeO-C_6H_4
h: R' = 3,4-$(MeO)_2$-C_6H_3

Scheme 3. Hydrogenation of phosphonates **12**.

substrate, with uncompleted reactions being observed in the hydrogenation of **12b** in the presence of catalysts derived from **1a** or **1b** (entries 7, 8).

Two strategies to improve catalyst activity were devised: firstly, the use of ligands **2**, with more flexible ethane backbones, and secondly, use of phosphane-phosphite systems containing smaller phosphite groups. Accordingly, the catalyst precursor **8a** produced a significant improvement in catalyst activity, with a moderate enantioselectivity value (entry 9). Likewise, precatalyst **7a** exhibited good activity and gave a slightly increased optical purity of **13b** (entry 10). Most notably, though, use of the isopropyl complex **7b** gave a completed reaction with an excellent enantioselectivity of 95% *ee* (entry 11). Interestingly, use of this catalyst at a lower catalyst loading (S/C = 500) also produced a completed reaction without loss of enantiomeric excess (entry 12).

Table 1. Hydrogenation of **12a–12d** in the presence of [Rh(cod)(P–OP)]BF_4.[a]

Entry	Substrate	P-OP	Conversion	% *ee* (Conf.)
1[b]	**12a**	**1a**	20	95 (*S*)
2[b,c]	**12a**	**1a**	100	94 (*S*)
3	**12a**	**1a**	100	93 (*S*)
4	**12a**	**2a**	100	88 (*S*)
5	**12a**	**5a**	100	85 (*R*)
6	**12a**	**5b**	100	91 (*R*)
7	**12b**	**1a**	25	85 (*S*)
8	**12b**	**1b**	18	78 (*S*)
9	**12b**	**2a**	93	82 (*S*)
10	**12b**	**5a**	100	89 (*R*)
11	**12b**	**5b**	100	95 (*R*)
12[b]	**12b**	**5b**	100	96 (*R*)
13	**12b**	**5c**	70	87 (*R*)
14	**12b**	**5d**	100	98 (*R*)
15	**12b**	**5e**	10	n.a.
16	**12b**	**10**	100	86 (*R*)
17	**12c**	**5a**	100	91 (*R*)
18	**12c**	**5b**	100	98 (*R*)
19	**12d**	**5a**	100	91 (*R*)
20	**12d**	**5b**	100	96 (*R*)

[a] Conditions: 4 atm H_2, 25 °C, CH_2Cl_2, S/C = 100, 24 h, unless otherwise stated. Degree of conversion was determined by ^1H NMR and enantiomeric excess by HPLC, while absolute configuration was assigned by comparison of optical rotation with literature values. n.a. = not analysed. [b] S/C = 500. [c] 20 atm H_2, 40 °C.

To complete the study, the behaviour of ligands bearing other phosphane substituents was also investigated. In the hydrogenation of **12b** the isopropyl catalyst was only slightly outperformed by the 1-naphthyl derivative, which gave a 98% *ee* (entry 14), while **7c** and **7e** gave lower conversions (entries 13, 15). Hydrogenation of substrates **12c** and **12d** with precatalyst **7b** also gave excellent enantioselectivities, with 98 and 96% *ee* values, respectively (entries 18, 20). As previously noted,[14b] the enantioselectivity increases with the size of the β substituent of the phosphonate, as is demonstrated in the results obtained with **7b**: 91 (H), 95 (Et), 96 (*n*Bu) and 98% *ee* (*i*Pr).

Previous reports have demonstrated that compounds **12** with aryl substituents at the R′ position are particularly difficult to hydrogenate with high enantioselectivity, and in the next step in our study we investigated the performance of **7** in the reduction of these aromatic derivatives. Studies were initiated with a screening of the hydrogenation of **12h** (a convenient precursor for **C**), with the best conversion being obtained with catalyst precursor **7a**, which afforded a good enantioselectivity of 82% *ee* (entry 7, Table 2), while use of

Table 2. Hydrogenation of β-aryl **12e–12h** in the presence of [Rh(cod)(P–OP)]BF_4.[a]

Entry	Substrate	P-OP	Conversion	% *ee* (Conf)[b]
1	**12e**	**5a**	100	82 (*R*)
2	**12e**	**5b**	100	92 (*R*)
3	**12f**	**5a**	100	87 (*R*)
4	**12f**	**5b**	80	83 (*R*)
5	**12g**	**5a**	100	82 (*R*)
6	**12g**	**5b**	43	91 (*R*)
7	**12h**	**5a**	100	82 (*R*)
8	**12h**	**5b**	60	86 (*R*)
9	**12h**	**5c**	2	n.a.
10	**12h**	**5d**	5	n.a.
11	**12h**	**5e**	5	n.a.
12	**12h**	**10**	100	81 (*R*)

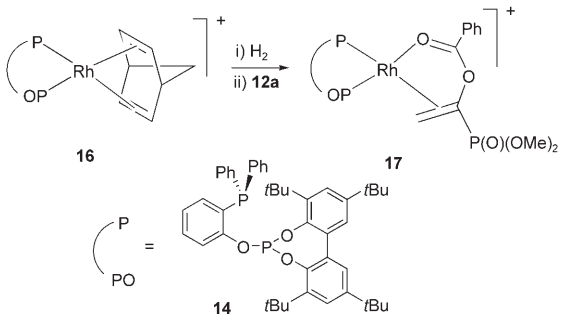
[a] See footnote in Table 1 for conditions and determinations. [b] The configurations of **13f** and **13h** were both tentatively assigned as *R* by analogy with the signs of optical rotation and HPLC elution order of **13e** and **13g**.

precatalyst **7b** increased the enantioselectivity to 86% *ee* (entry 8), although it was less reactive. Moreover, bulkier catalysts derived from **5c–e** gave negligible conversions (entries 9–11). Notably, the isopropyl catalyst **7b** gave outstanding enantioselectivities with phenyl and anisyl substrates—92 and 91% *ee*, respectively—although in the latter case an incomplete reaction (43% conversion) was observed (entries 2, 6). Attempts to increase the levels of conversion through the use of higher pressures were unsuccessful. Catalyst precursor **7b** was more enantioselective than the phenyl derivative **7a** both in the aliphatic and in the aromatic series, the sole exception to this being represented by the *p*-tolyl substrate **12f**, for which the best value (87% *ee*) was obtained with the phenyl catalyst (entries 3, 4).

Finally, the catalyst precursor **11** behaved very similarly to **7a**. The BINOL catalyst hydrogenated substrates **12a** (entry 16, Table 1) and **12g** (entry 12, Table 2) with complete conversion and with only slightly lower enantioselectivities than **7a**.

Coordination mode of 12 and mechanistic considerations: Two elements for asymmetric induction can be considered in the structures of phosphane-phosphites: the atropisomerism of the phosphite group and the asymmetric distribution of phosphane substituents (e.g., propeller-like structures in ligands bearing PAr_2 groups).[5] Although the second element operates in rigid ligands **1**, it should be minimized in flexible **2a**.[11] The relatively similar enantioselectivities provided by ligands **1a** and **2a** in the hydrogenation of **12a** (93 and 82% *ee*, respectively) and **12b** (85 and 82% *ee*, respectively) point to the phosphite as the principal source of stereoinduction.

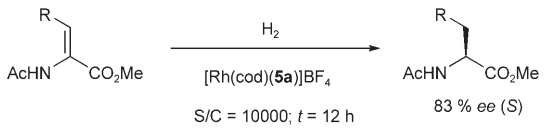
Because of the heterobifunctional nature of P-OP ligands, investigation of the coordination mode of olefins **12** towards the $[Rh(P\text{-}OP)]^+$ fragment may provide valuable information about the course of the reaction. Several attempts were made to generate a species of formulation $[Rh(P\text{-}OP)(\mathbf{12a})]^+$ by hydrogenation of complexes [Rh(diolefin)(P-OP)]BF_4, followed by the addition of an excess of **12a**. These reactions afforded samples not clean enough for NMR analysis, with the exception of that starting with [Rh(nbd)(**14**)]BF_4 (**16**, Scheme 4), which generated the



Scheme 4. Synthesis of **17**.

adduct [Rh(**14**)(**12a**)]BF_4 (**17**). Compound **17** shows three signals in its $^{31}P\{^1H\}$ NMR spectrum recorded at 240 K: a doublet of doublets at $\delta = 137.4$ ppm ($J_{P,Rh} = 259$ Hz, $J_{P,P} = 68$ Hz) due to the phosphite group, together with a doublet of doublets of doublets at $\delta = 6.1$ ppm ($J_{P,Rh} = 149$ Hz, $J_{P,P} = 68$, 12 Hz) for the phosphane function, while the coordinated phosphonate appears as a doublet centred at 10.6 ppm due to the coupling with the ^{31}P nucleus of the phosphane. The $^1J_{Rh,P}$ coupling constants are very similar to those found in [Rh(**1a**)(mac)]BF_4,[28] in which the olefin bond occupies the position *cis* to the phosphite.[5] As reported before for a diphosphine derivative,[14c] there is an exchange between free and coordinated **12a**, and this process allows ready identification of the proton positioned *cis* to the phosphonate group of the coordinated olefin in the phase-sensitive 2D NOESY. Interestingly, a NOE cross-peak was observed between this proton and those of a *t*Bu substituent, these observations being indicative of a *cis* relationship between the olefin and the phosphite, which is in good accord with the dominant importance of the latter group in the stereochemical course of the reaction.

An examination of the results collected in Tables 1 and 2 indicates that *S* products were in all cases obtained from catalysts with ligands with *S* configurations (and conversely *R* products from *R* ligands). The stereochemical sense of the hydrogenation is also coincident with the hydrogenation of MAC (Scheme 5).[14a] Interestingly, precatalyst **7a** is much more reactive towards hydrogenation of MAC than it is towards **12**, and can give completed reactions under similar conditions at significantly lower catalyst loadings.



Scheme 5. MAC hydrogenation.

Investigations into Rh-catalysed asymmetric hydrogenations of olefins tend to contemplate two alternatives for the mechanism, known as the unsaturated and the dihydride routes.[29] In the specific case of the reduction of substrates **12** with catalysts bearing electron-rich phosphanes, Gridnev and Imamoto have proposed a mixed mechanism combining both routes.[14b] The coincidence in stereochemistry of hydrogenations of MAC and **12** with our ligands allow the application of models for enamide hydrogenation following either mechanism to explain the configuration observed in the hydrogenation of **12**. With the aid of a quadrant diagram[30] it can be visualized that an *R* phosphite should offer greater encumbrance in the upper right quadrant (Figure 5).

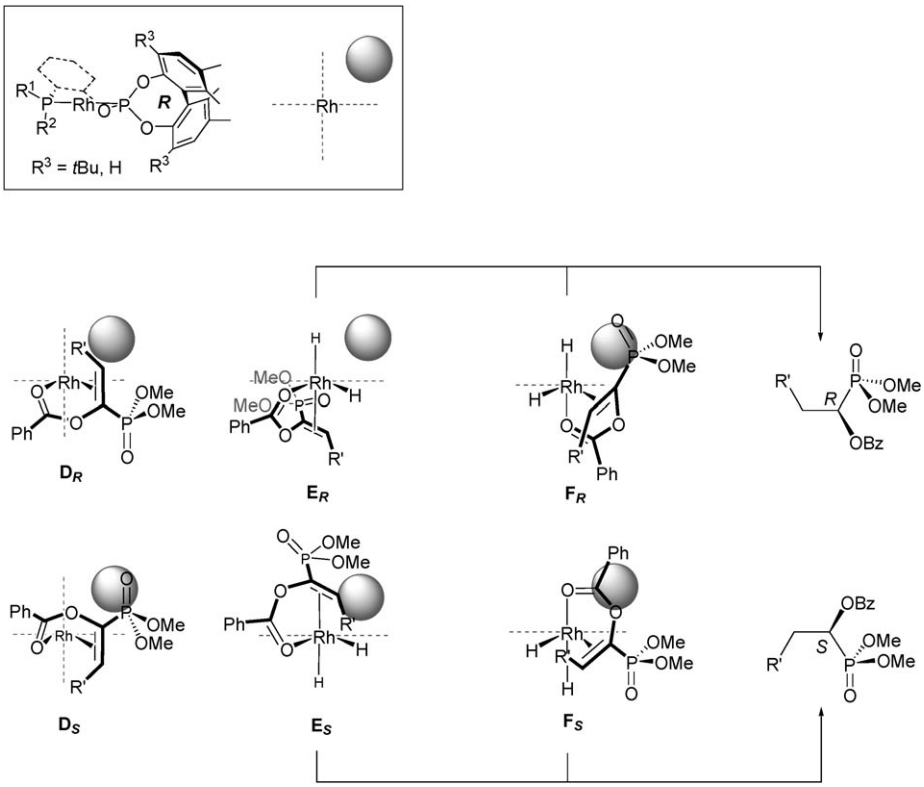


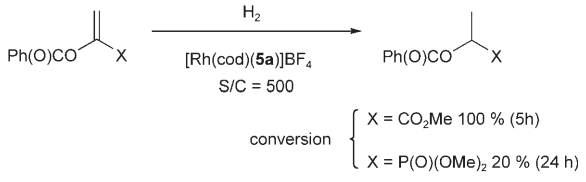
Figure 5. An interpretation of the stereochemical sense of the hydrogenation.

If a dihydride route were involved in these reactions, dihydrides with the olefin in the equatorial plane and the carbonyl oxygen in the axial position would be expected.[14b,31] Now, if the preferential olefin coordination *cis* to the phosphite is kept, dihydrides **F** should be formed. Investigations into the relative stabilities of these complexes suggest that the chelated substrate produces the major steric impediment and that preferred formation of $\mathbf{F}_R$ (over $\mathbf{F}_S$) should therefore be expected. In an unsaturated mechanism, on the other hand, the reaction should proceed through complexes of composition [Rh(P-OP)(**12**)]$^+$ (**D**). Detailed theoretical calculations by Feldgus and Landis explained the different reactivity of Rh^I adducts in terms of the influence of the dissimilar interaction between the olefin fragment and the chiral ligand on the course of the hydrogen addition.[32] Application of this model to our system points to a preferred addition of hydrogen to $\mathbf{D}_R$ from the axial top position, giving rise to dihydride $\mathbf{E}_R$.

In view, firstly, of the observation that intermediate complexes $[Rh(P{-}P)(H)_2(S)_2]^+$[33] (P–P = diphosphine, S = solvent) in the dihydride route are stabilized by strongly basic ligands and, secondly, of the appreciably lower donor ability of phosphane-phosphites in relation to diphosphanes, it is plausible to expect a preference for the unsaturated route in hydrogenations with P-OP ligands. On this assumption, though without the intention to set out a mechanistic proposal, it is, however, possible to make some additional comments concerning the influence of the phosphane-phosphite in the process.

Because of the size of the $P(O)(OMe)_2$ group, phosphonates **12** are sterically more encumbered than most of the olefins so far subjected to study in asymmetric hydrogenations (e.g., enamides, itaconates or enol esters) possessing a planar group bonded to the α-olefinic carbon. The detrimental effect of the $P(O)(OMe)_2$ group on the reaction rate was confirmed by comparison of the hydrogenation of methyl α-benzoyloxyacrylate with that of **12a** (Scheme 6). Under the conditions of entry 1 in Table 1 the enol ester was completely hydrogenated in less than 5 h, while, as stated, **12a** produced a 20% conversion after 24 h.

An important influence of the size of the phosphite component on the rate of the reaction was observed during the catalyst screening. On inspection of species **D** derived from ligands **1** it would be expected that the $P(O)(OMe)_2$ group should encounter steric encumbrance mainly with the upper *t*Bu group (for the *R* configuration in the phosphite) but also to a significant extent with the lower *t*Bu substituent.



Scheme 6.

Logically, the phosphonate-phosphite interaction should be significantly reduced with ligands **5**. The phosphonate group should also give rise to steric interaction with the phosphane substituents in the dihydrides **E**, in good accord with the lower levels of conversion obtained with catalysts containing bulky phosphane groups. In this picture, the flexibility of the Rh-(P-OP) fragment may play an important role in the reactivity through diminution of its steric interaction with coordinated **12**.[34] This is shown by the faster reaction provided by **8a** in relation to [Rh(cod)(**1a**)]BF_4. Similarly, this dynamic effect should favour the higher activity of precatalysts **7** in relation to those derived from ligands **1**.

Conclusion

A series of novel chiral phosphane-phosphites **5** has been synthesized and used in the preparation of a series of complexes [Rh(cod)(**5**)]BF_4. These show important structural differences from the analogues based on ligands **1** in terms of steric encumbrance, dihedral angle of the biphenyl phosphite and dynamic properties. Extensive screening in hydrogenations of unsaturated phosphonates **12** has shown this reaction to be very sensitive to steric effects. Optimization of the sizes of the two phosphorus functionalities in the chiral ligands has resulted in enantioselectivities of up to 98% *ee* with aliphatic substrates, while values of up to 92% *ee* have been achieved for β-aryl olefins. The latter reagents significantly outperform other catalysts examined for this reaction. A coordination study of the complex [Rh(**14**)(**12a**)]BF_4, representative of the Rh^I intermediate adduct of the hydrogenation unsaturated route, has shown that the olefin group prefers the position *cis* to the phosphite. This arrangement is in good accord with the configuration observed in the hydrogenated products.

Experimental Section

General: All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or by use of standard Schlenk-type techniques. All solvents were distilled under nitrogen in the presence of the following desiccants: sodium-benzophenone-ketyl for diethyl ether (Et_2O) and tetrahydrofuran (THF), sodium for *n*-hexane and toluene, CaH_2 for dichloromethane (CH_2Cl_2), and NaOMe for methanol (MeOH). NMR spectra were obtained on Bruker DPX 300, DRX 400 or DRX 500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. HPLC analyses were performed with a Waters 2690 instrument, HRMS data were obtained with a Jeol JMS-SX 102 A mass spectrometer, and optical rotations were measured on a Perkin–Elmer Model 341 polarimeter.

(*R*)-5,5′,6,6′-Tetramethyl-2,2′-bisphenoxyphosphorous chloride (3): (*R*)-5,5′,6,6′-Tetramethyl-2,2′-bisphenol[18] (1.20 g, 4.95 mmol) was azeotropically dried with toluene (2×30 mL), dissolved in THF and added dropwise to a mixture of PCl_3 (0.50 mL, 5.7 mmol) and pyridine (0.90 mL, 11.1 mmol) in THF. The suspension was stirred for 4 h and filtered, and the solvent was evaporated under vacuum to yield **6** as a white, foamy solid (1.29 g, 85%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.03 (s, 6H; 2×Me), 2.30 (s, 6H; 2×Me), 6.93 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 7.02 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 7.18 ppm (d, $J_{H,H}$ = 8.0 Hz, 2H; 2× H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 17.8 (2×Ar-*Me*), 20.6 (Ar-*Me*), 20.7 (Ar-*Me*), 119.0 (d, $J_{C,P}$ = 2 Hz; CH arom), 119.2 (d, $J_{C,P}$ = 2 Hz; CH arom), 129.0 (C_q arom), 129.9 (CH arom), 130.5 (CH arom), 130.5 (C_q arom), 134.7 (C_q arom), 135.7 (C_q arom), 137.4 (C_q arom), 138.3 (C_q arom), 146.1 (d, $J_{C,P}$ = 4 Hz; OC_q arom), 147.5 ppm (d, $J_{C,P}$ = 1 Hz; OC_q arom); $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ = 169.0 ppm; HRMS (CI): *m*/*z*: calcd for $C_{16}H_{16}O_2PCl$: 306.0576; found: 306.0574 $[M]^+$.

(2-Hydroxyphenyl)-bis-(1-naphthyl)phosphane (4d): BBr_3 (7.22 mL, 6.8 mmol) was added at −78°C to a solution of (2-hydroxyphenyl)-bis-(1-naphthyl)phosphine[35] (1.23 g, 3.1 mmol) in CH_2Cl_2 (40 mL). The resulting solution was stirred overnight at room temperature, the solvent was evaporated, toluene (25 mL) was added to the obtained residue, and the system was once more evaporated to dryness. The resulting solid was treated with MeOH (20 mL) at 0°C and stirred for two days, after which solvent removal yielded the phosphonium bromide as a white solid, which was suspended in Et_2O (30 mL) and treated with NEt_3. The mixture was stirred for 2 h and filtered, and solvent removal yielded the phosphine **4d** as a white, foamy solid (0.54 g, 45%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.29 (brs, 1H; OH), 6.82 (m, 2H; 2×H arom), 6.97 (t, $J_{H,H}$ = 6.0 Hz, 1H; H arom), 7.08 (t, $J_{H,H}$ = 6.0 Hz, 2H; 2×H arom), 7.31 (m, 3H; 3×H arom), 7.47 (m, 4H; 4×H arom), 7.86 (m, 4H; 4× H arom), 8.34 ppm (dd, $J_{H,H}$ = 8.0, 4.0 Hz, 2H; 2×H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 115.9 (CH arom), 119.1 (C_q arom), 121.6 (CH arom), 126.0 (2×CH arom), 126.2 (CH arom), 126.4 (2×CH arom), 126.6 (CH arom), 126.8 (2×CH arom), 129.0 (2×CH arom), 130.3 (2× CH arom), 131.2 (d, $J_{C,P}$ = 5 Hz; 2×C_q arom), 132.1 (CH arom), 133.0 (2×CH arom), 133.9 (d, $J_{C,P}$ = 5 Hz; 2×C_q arom), 135.4 (C_q arom), 135.5 (C_q arom), 135.8 (d, $J_{C,P}$ = 4 Hz; CH arom), 159.6 ppm (d, $J_{C,P}$ = 19 Hz; C_q arom); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = −47.0 ppm; HRMS (CI): *m*/*z*: calcd for $C_{26}H_{19}OP$: 378.1174; found: 378.1172 $[M]^+$.

Di-*tert*-butyl-(2-tetrahydropyranoxyphenyl)phosphaneborane (6e): *n*BuLi (6.9 mL, 1.6 M in hexanes, 11.0 mmol) was slowly added at −78°C to a solution of 2-phenoxytetrahydropyran[7c] (1.64 g, 9.2 mmol) in THF (20 mL). The mixture was stirred for 0.5 h, allowed to warm to room temperature and further stirred for 16 h, and the reaction mixture was cooled to −78°C and di(*tert*-butyl)chlorophosphine (2.1 mL, 11.0 mmol) was added dropwise. The mixture was stirred for 1 h, $BH_3{\cdot}SMe_2$ (1.0 mL, 10 mmol) was added, and the resulting mixture was stirred overnight, after which water (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3×25 mL), and the organic fractions were collected, dried over Na_2SO_4 and filtered. Evaporation of the resulting solution and purification by column chromatography (*n*-hexanes/AcOEt 9:1), followed by recrystallization from Et_2O/hexanes 1:1, yielded the corresponding phosphane-borane as a white solid (1.53 g, 49%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (brm, 3H; BH_3), 1.30 (d, $J_{H,P}$ = 12.9 Hz, 9H; CMe_3), 1.34 (d, $J_{H,P}$ = 13.2 Hz, 9H; CMe_3), 1.63 (m, 3H; CH_2 and C*H*H), 1.95 (m, 3H; CH_2 and C*H*H), 3.64 (m, 1H; OC*H*H), 3.95 (m, 1H; OC*H*H), 5.33 (m, 1H; OC*H*(CH_2)O), 7.00 (dd, $J_{H,H}$ = 8.5, 7.5 Hz, 1H; H arom), 7.19 (dd, $J_{H,H}$ = 8.4, $J_{H,H}$ = 2.1 Hz, 1H; H arom), 7.04 (dd, $J_{H,H}$ = 8.1, 7.5 Hz, 1H; H arom), 8.34 ppm (dd, $J_{H,P}$ = 14.1, $J_{H,H}$ = 7.8 Hz, 1H; H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 21.1 (CH_2), 25.0 (CH_2), 29.5 (2×C*Me*$_3$), 30.8 (CH_2), 33.7 (d, $J_{C,P}$ = 24 Hz; *C*Me$_3$), 34.0 (d, $J_{C,P}$ = 26 Hz; *C*Me$_3$), 64.8 (OCH_2), 98.9 (O*C*H(CH_2)O), 114.1 (d, $J_{C,P}$ = 4 Hz; CH arom), 115.1 (d, $J_{C,P}$ = 39 Hz; C_q arom), 121.6 (d, $J_{C,P}$ = 12 Hz; CH arom), 133.1 (CH arom), 140.4 (d, $J_{C,P}$ = 14 Hz; CH arom), 159.0 ppm (OC_q arom); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96 MHz): δ = 2.5 ppm (d, $^1J_{BP}$ = 61 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 55.6 ppm (brm); HRMS (CI): *m*/*z*: calcd for $C_{19}H_{33}BO_2P$: 335.2311; found: 335.2319 $[M-H]^+$.

Di-*tert*-butyl-(2-hydroxyphenyl)phosphane (4e): $HBF_4{\cdot}OEt_2$ (1.8 mL, 54% wt in Et_2O, 12.9 mmol) was added at 0°C to a solution of **6e** (1.45 g, 4.3 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred overnight at room temperature and treated with deoxygenated water (20 mL), the resulting mixture was stirred for 12 h, and a saturated solution of $NaHCO_3$ (40 mL) was added. The organic layer was separated, the aqueous one was extracted with CH_2Cl_2 (3×25 mL), the organic fractions

were collected, dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The resulting residue was extracted with *n*-hexanes (3×25 mL) and filtered, and solvent evaporation yielded **3e** as a white solid (0.80 g, 74%). Spectroscopic data obtained for this compound are in accord with those reported in the literature.[36]

(*R*)-[2-(Diphenylphosphino)phenyl]-1,1′-(5,5′,6,6′-tetramethyl)biphenyl-2,2′-diyl phosphite (5a): A solution of (2-hydroxyphenyl)diphenylphosphine (0.39 g, 1.6 mmol) in toluene (30 mL) was added dropwise to (*R*)-5,5′,6,6′-tetramethyl-2,2′-bisphenoxyphosphorous chloride (0.48 g, 1.6 mmol) and NEt_3 (0.33 mL, 2.4 mmol) dissolved in toluene (30 mL). The resulting suspension was stirred for 24 h, the mixture was filtered, volatiles were removed, and the obtained solid was dissolved in Et_2O and passed through a short pad of neutral alumina. The solution was evaporated to yield a white solid (0.24 g, 28%). $[\alpha]_D^{20} = -17.5$ (c = 1.0, THF); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.96 (s, 3H; Me), 1.98 (s, 3H; Me), 2.23 (s, 3H; Me), 2.26 (s, 3H; Me), 6.72 (m, 2H; 2×H arom), 6.86 (d, $J_{H,H}$ = 8.4 Hz, 1H; H arom), 6.95 (d, $J_{H,H}$ = 8.4 Hz, 1H; H arom), 7.02 (t, $J_{H,H}$ = 7.6 Hz, 1H; H arom), 7.11 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 7.19 (dd, $J_{H,H}$ = 8.4, 4.4 Hz, 1H; H arom), 7.33 ppm (m, 11H; 11 H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 17.7 (Me), 17.8 (Me), 29.2 (2×Me), 119.1 (CH arom), 120.4 (d, $J_{C,P}$ = 10 Hz; CH arom), 124.9 (CH arom), 128.7 (CH arom), 128.8 (CH arom), 128.8 (CH arom), 128.9 (CH arom), 129.0 (CH arom), 129.2 (CH arom), 129.8 (CH arom), 130.0 (CH arom), 130.3 (C_q arom), 130.4 (CH arom), 130.9 (d, $J_{C,P}$ = 5 Hz; C_q arom), 133.5 (2×C_q arom), 134.2 (2×CH arom), 134.4 (2×CH arom), 134.7 (CH arom), 136.3 (dd, $J_{C,P}$ = 11, 3 Hz; Cq arom), 136.7 (2×C_q arom), 137.8 (2×C_q arom), 146.5 (m; 2×C_q arom), 154.2 ppm (m; C_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = −17.1 (d, P−C), 134.5 ppm (d, $J_{P,P}$ = 14 Hz; P−O); HRMS (EI): m/z: calcd for $C_{34}H_{30}O_3P_2$: 548.1670; found: 548.1673 $[M]^+$.

(*R*)-[2-(Diisopropylphosphino)phenyl]-1,1′-(5,5′,6,6′-tetramethyl)biphenyl-2,2′-diyl phosphite (5b): This compound was prepared as described for **5a**. White, foamy solid (0.20 g, 45%); $[\alpha]_D^{20} = -18.3$ (c = 1.0, THF); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (m, 6H; CH*Me*$_2$), 1.08 (m, 6H; CH*Me*$_2$), 2.02 (s, 3H; Me), 2.03 (s, 3H; Me), 2.16 (m, 2H; 2×C*H*Me$_2$), 2.28 (s, 3H; Me), 2.30 (s, 3H; Me), 7.11 (m, 6H; 6×H arom), 7.30 (m, 1H; H arom), 7.43 ppm (m, 1H; H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 17.5 (2×Ar-*Me*), 19.7 (d, $J_{C,P}$ = 9 Hz; CH*Me*$_2$), 20.2 (d, $J_{C,P}$ = 17 Hz; CH*Me*$_2$), 20.3 (2×Ar-*Me*), 23.1 (d, $J_{C,P}$ = 13 Hz; C*H*Me$_2$), 23.4 (d, $J_{C,P}$ = 13 Hz; C*H*Me$_2$), 118.8 (CH arom), 119.0 (CH arom), 120.0 (d, $J_{C,P}$ = 11 Hz; CH arom), 123.6 (CH arom), 128.6 (m; C_q arom), 129.1 (C_q arom), 129.4 (CH arom), 129.8 (CH arom), 130.1 (CH arom), 130.6 (C_q arom), 133.3 (C_q arom), 134.1 (C_q arom), 135.2 (d, $J_{C,P}$ = 10 Hz; CH arom), 136.7 (C_q arom), 137.5 (C_q arom), 146.6 (2×C_q arom), 155.8 ppm (m; C_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = −1.8 (br, P−C), 135.3 ppm (d, $J_{P,P}$ = 25 Hz; P−O); HRMS (CI): m/z: calcd for $C_{28}H_{35}O_3P_2$: 481.2061; found: 481.2073 $[M+H]^+$.

(*R*)-{2-[Di(*o*-tolyl)phosphino]phenyl}-1,1′-(5,5′,6,6′-tetramethyl)biphenyl-2,2′-diyl phosphite (5c): The preparation of this phosphane-phosphite was analogous to that described for **5a**. White, foamy solid (0.19 g, 50%); $[\alpha]_D^{20} = -11.0$ (c = 1.0, THF); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.00 (s, 3H; Me), 2.03 (s, 3H; Me), 2.27 (s, 3H; Me), 2.31 (s, 3H; Me), 2.47 (s, 6H; 2×Me), 6.62 (d, $J_{H,H}$ = 8.1 Hz, 1H; H arom), 6.72 (m, 1H; H arom), 6.81 (dd, $J_{H,H}$ = 12, 4 Hz, 2H; 2×H arom), 6.92 (d, $J_{H,H}$ = 8 Hz, 1H; H arom), 6.99 (d, $J_{H,H}$ = 8 Hz, 1H; H arom), 7.11 (m, 4H; 4×H arom), 7.32 ppm (m, 6H; 6×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 17.8 (2×Ar-*Me*), 20.6 (2×Ar-*Me*), 21.4 (d, $J_{C,P}$ = 22 Hz, Ar-*Me*), 21.6 (d, $J_{C,P}$ = 22 Hz, Ar-*Me*), 119.0 (CH arom), 121.0 (d, $J_{C,P}$ = 9 Hz; CH arom), 125.2 (CH arom), 126.5 (CH arom), 128.5 (C_q arom), 128.8 (C_q arom), 129.1 (CH arom), 129.2 (CH arom), 129.8 (CH arom), 130.0 (CH arom), 130.3 (CH arom), 130.3 (CH arom), 130.4 (CH arom), 130.4 (CH arom), 130.5 (CH arom), 130.9 (m; C_q arom), 133.4 (C_q arom), 133.5 (CH arom), 133.7 (CH arom), 134.0 (C_q arom), 134.2 (C_q arom), 134.4 (C_q arom), 134.5 (CH arom), 136.8 (C_q arom), 137.8 (C_q arom), 143.0 (C_q arom), 143.3 (C_q arom), 146.7 (m; 2×C_q arom), 154.8 ppm (m; C_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = −32.7 (d, P−C), 134.9 ppm (d, $J_{P,P}$ = 30 Hz; P−O); HRMS (CI): m/z: calcd for $C_{36}H_{34}O_3P_2$: 576.1983; found: 576.1984 $[M]^+$.

(*R*)-{2-[Di(1-naphthyl)phosphino]phenyl}-1,1′-(5,5′,6,6′-tetramethyl)biphenyl-2,2′-diyl phosphite (5d): This compound was prepared as described for **5a**. White, foamy solid (0.18 g, 53%); $[\alpha]_D^{20} = -15.9$ (c = 1.0, THF); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.89 (s, 3H; Me), 1.92 (s, 3H; Me), 2.13 (s, 3H; Me), 2.23 (s, 3H; Me), 6.39 (d, $J_{H,H}$ = 8 Hz, 1H; H arom), 6.51 (m, 1H; H arom), 6.62 (m, 2H; 2×H arom), 6.91 (t, $J_{H,H}$ = 7.2 Hz, 1H; H arom), 7.03 (m, 3H; 3×H arom), 7.29 (m, 4H; 4×H arom), 7.46 (m, 4H; 4×H arom), 7.87 (m, 4H; 4×H arom), 8.53 ppm (m, 2H; 2×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 17.3 (s; Ar-*Me*), 17.4 (s; Ar-*Me*), 20.1 (s; Ar-*Me*), 20.2 (s; Ar-*Me*), 118.8 (d, $J_{C,P}$ = 8 Hz; CH arom), 120.3 (d, $J_{C,P}$ = 10 Hz; CH arom), 124.8 (s; CH arom), 125.8 (s; CH arom), 125.9 (s; CH arom), 126.3 (s, 2×CH arom), 126.4 (m; 2×CH arom), 126.5 (s; CH arom), 126.6 (s; CH arom), 126.7 (s; CH arom), 126.8 (s; C_q arom), 126.9 (s; C_q arom), 127.0 (s; C_q arom), 128.3 (s; C_q arom), 128.5 (s; CH arom), 128.6 (s; CH arom), 129.3 (s; CH arom), 129.6 (s; 2×CH arom), 129.7 (s; CH arom), 130.4 (s; CH arom), 130.5 (s; C_q arom), 132.5 (s; C_q arom), 132.6 (s; C_q arom), 133.1 (s; CH arom), 133.3 (s; CH arom), 133.9 (d, $J_{C,P}$ = 14 Hz; C_q arom), 134.0 (s; C_q arom), 135.2 (s; CH arom), 135.3 (s; C_q arom), 135.8 (d, $J_{C,P}$ = 17 Hz; C_q arom), 136.3 (s; C_q arom), 137.4 (s; C_q arom), 146.1 (s; C_q arom), 146.3 (s; C_q arom), 154.4 ppm (m; C_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = −34.9 (d; P−C), 134.5 ppm (d, $J_{P,P}$ = 18 Hz; P−O); HRMS (CI): m/z: calcd for $C_{42}H_{34}O_3P_2$: 648.1983; found: 648.1976 $[M]^+$.

(*R*)-[2-(Di-*tert*-butylphosphino)phenyl]-1,1′-(5,5′,6,6′-tetramethyl)biphenyl-2,2′-diyl phosphite (5e): Application of the procedure described for **5a** yielded slightly impure compound **5e**. Further purification attempts were unsuccessful due to product decomposition, but these impurities do not interfere in the preparation of [Rh(cod)(**5e**)]BF_4. White, foamy solid (0.20 g, ca. 50%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (d, $J_{H,P}$ = 10.8 Hz, 9H; CMe_3), 1.23 (d, $J_{H,P}$ = 10.5 Hz, 9H; CMe_3), 2.02 (s, 3H; Me), 2.04 (s, 3H; Me), 2.29 (s, 3H; Me), 2.30 (s, 3H; Me), 7.13 (m, 7H; 7×H arom), 7.74 ppm (d, $J_{H,H}$ = 6.3 Hz, 1H; H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 17.8 (2×Ar-*Me*), 20.5 (Ar-*Me*), 20.6 (Ar-*Me*), 30.8 (d, $J_{C,P}$ = 8 Hz; C*Me*$_3$), 31.0 (d, $J_{C,P}$ = 8 Hz; C*Me*$_3$), 33.0 (d, $J_{C,P}$ = 24 Hz, *C*Me$_3$), 33.1 (d, $J_{C,P}$ = 22 Hz, *C*Me$_3$), 119.2 (d, $J_{C,P}$ = 2 Hz; CH arom), 119.4 (d, $J_{C,P}$ = 3 Hz; CH arom), 122.0 (dd, $J_{C,P}$ = 7, 3 Hz; CH arom), 123.4 (CH arom), 129.4 (C_q arom), 129.7 (CH arom), 129.8 (Cq arom), 129.9 (CH arom), 130.5 (CH arom), 131.0 (d, $J_{C,P}$ = 4 Hz; C_q arom), 133.3 (C_q arom), 134.2 (C_q arom), 136.2 (d, $J_{C,P}$ = 3 Hz; CH arom), 136.8 (C_q arom), 137.7 (C_q arom), 147.2 (m, 2×OC_q arom), 157.1 ppm (dd, $J_{C,P}$ = 23, 5 Hz; OC_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 9.7 (d, P−C), 133.7 ppm (d, $J_{P,P}$ = 65 Hz; P−O); HRMS (CI): m/z: calcd for $C_{30}H_{39}O_3P_2$: 509.2374; found: 509.2372 $[M+H]^+$.

[Rh(cod)(5a)]BF_4 (7a): A suspension of $[Rh(cod)Cl]_2$ (0.040 g, 0.082 mmol) and $AgBF_4$ (0.032 g, 0.16 mmol) in THF (5 mL) was vigorously stirred for 45 minutes protected from light. The resulting mixture was filtered over a short pad of celite, ligand **5a** (0.090 g, 0.16 mmol) in THF (5 mL) was added dropwise, the reaction mixture was stirred for 1 h and filtered, and the solvent was evaporated. The product was precipitated as an orange solid from CH_2Cl_2/Et_2O 1:2 (0.090 g, 66%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.90 (m, 1H; C*H*H), 1.97 (s, 3H; Me), 2.05 (s, 3H; Me), 2.20 (m, 3H; 3×C*H*H), 2.33 (s, 3H; Me), 2.37 (s, 3H; Me), 2.60 (m, 4H; 4×C*H*H), 4.10 (brs, 1H; =CH), 4.76 (brs, 1H; =CH), 5.73 (brs, 2H; 2×=CH), 7.02 (d, $J_{H,H}$ = 8 Hz, 1H; H arom), 7.08 (m, 2H; 2×H arom), 7.31 (m, 6H; 6×H arom), 7.62 ppm (m, 9H; 9×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 17.6 (Me), 17.8 (Me), 20.6 (2×Me), 27.2 (CH_2), 28.4 (CH_2), 32.4 (CH_2), 32.9 (CH_2), 100.7 (t, $J_{C,P}$ = 6 Hz, $J_{C,Rh}$ = 6 Hz; =CH), 106.6 (t, $J_{C,P}$ = 7 Hz, $J_{C,Rh}$ = 7 Hz; =CH), 112.4 (dd, $J_{C,P}$ = 10 Hz, $J_{C,Rh}$ = 6 Hz; =CH), 113.5 (dd, $J_{C,P}$ = 13 Hz, $J_{C,Rh}$ = 5 Hz; =CH), 116.5 (d, $J_{C,P}$ = 12 Hz; C_q arom), 117.2 (d, $J_{C,P}$ = 12 Hz; C_q arom), 118.4 (CH arom), 119.0 (CH arom), 122.2 (CH arom), 126.0 (d, $J_{C,P}$ = 8 Hz; CH arom), 126.7 (C_q arom), 127.7 (d, $J_{C,P}$ = 10 Hz; C_q arom), 128.3 (C_q arom), 129.7 (CH arom), 129.9 (CH arom), 130.1 (CH arom), 130.2 (CH arom), 130.6 (CH arom), 131.1 (CH arom), 132.4 (CH arom), 133.1 (CH arom), 133.4 (2×CH arom), 133.5 (CH arom), 134.5 (CH arom), 134.7 (CH arom), 134.8 (CH arom), 135.7 (C_q arom), 136.2 (C_q arom), 138.2 (C_q arom), 138.6 (C_q arom), 145.8 (d, $J_{C,P}$ = 5 Hz; C_q arom), 146.2 (d, $J_{C,P}$ = 13 Hz; C_q arom), 155.1 ppm (d, $J_{C,P}$ = 10 Hz;

C_q arom); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ = 16.4 (dd, $J_{P,Rh}$ = 136 Hz; P–C), 132.3 ppm (dd, $J_{P,Rh}$ = 267 Hz, $J_{P,P}$ = 61 Hz; P–O); elemental analysis (%) calcd for $C_{42}H_{42}BF_4O_3P_2Rh$: C 55.4, H 4.8; found: C 55.4, H 4.9.

[Rh(cod)(5b)]BF_4 (7b): Ligand **5b** (0.072 g, 0.15 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise to a solution of $[Rh(cod)_2]BF_4$ (0.061 g, 0.15 mmol) in CH_2Cl_2 (5 mL). The resulting orange solution was stirred for 3 h, concentrated, filtered and finally treated with Et_2O (30 mL), and the resulting solid was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O 1:2, yielding **7b** as yellow crystals (0.075 g, 65%). ^1H NMR (CD_2Cl_2, 500 MHz): δ = 1.20 (dd, $J_{H,H}$ = 7.0 Hz, $J_{H,P}$ = 14.0 Hz, 3H; CHMe*Me*), 1.35 (dd, $J_{H,H}$ = 7.0 Hz, $J_{H,P}$ = 15.5 Hz, 3H; CHMe*Me*), 1.42 (dd, $J_{H,H}$ = 7 Hz, $J_{H,P}$ = 4.5 Hz, 3H; CHMe*Me*), 1.45 (dd, $J_{H,H}$ = 7.0 Hz, $J_{H,P}$ = 4.5 Hz, 3H; CHMe*Me*), 2.01 (s, 3H; Me), 2.08 (s, 3H; Me), 2.37 (s, 3H; Me), 2.38 (s, 3H; Me), 2.26 (m, 8H; 8×C*H*H), 2.71 (m, 1H; C*H*Me$_2$), 2.88 (m, 1H; C*H*Me$_2$), 3.88 (m, 1H; =CH), 5.55 (m, 1H; =CH), 5.89 (m, 1H; =CH), 6.49 (m, 1H; =CH), 6.83 (dd, $J_{H,H}$ = 8.0, 4.5 Hz, 1H; H arom), 7.08 (d, $J_{H,H}$ = 8.5 Hz, 1H; H arom), 7.11 (d, $J_{H,H}$ = 8.5 Hz, 1H; H arom), 7.32 (d, $J_{H,H}$ = 8.5 Hz, 1H; H arom), 7.33 (d, $J_{H,H}$ = 8.5 Hz, 1H; H arom), 7.36 (t, $J_{H,H}$ = 7.5 Hz, 1H; H arom), 7.52 (t, $J_{H,H}$ = 7.5 Hz, 1H; H arom), 7.56 ppm (t, $J_{H,H}$ = 7.5 Hz, 1H; H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 17.7 (Ar-*Me*), 17.7 (d, $J_{C,P}$ = 5 Hz; CHMe*Me*), 17.9 (Ar-*Me*), 18.2 (d, $J_{C,P}$ = 4 Hz; CHMe*Me*), 20.3 (d, $J_{C,P}$ = 5 Hz; CHMe*Me*), 20.5 (Ar-*Me*), 20.6 (d, $J_{C,P}$ = 4 Hz; CHMe*Me*), 20.7 (Ar-*Me*), 26.6 (d, $J_{C,P}$ = 24 Hz, *C*HMe$_2$), 27.4 (d, $J_{C,P}$ = 22 Hz, *C*HMe$_2$), 29.1 (CH_2), 30.0 (CH_2), 30.9 (CH_2), 31.2 (CH_2), 95.3 (t, $J_{C,P}$ = $J_{C,Rh}$ = 8 Hz; =CH), 100.7 (t, $J_{C,P}$ = $J_{C,Rh}$ = 7 Hz; =CH), 108.9 (dd, $J_{C,P}$ = 13 Hz, $J_{C,Rh}$ = 4 Hz; =CH), 113.3 (m; =CH), 118.6 (CH arom), 118.9 (d, $J_{C,P}$ = 3 Hz; CH arom), 122.5 (CH arom), 125.8 (d, $J_{C,P}$ = 5 Hz; CH arom), 127.6 (C_q arom), 128.0 (C_q arom), 128.8 (C_q arom), 130.5 (CH arom), 130.7 (CH arom), 132.3 (CH arom), 133.7 (CH arom), 135.6 (C_q arom), 136.3 (C_q arom), 138.0 (C_q arom), 138.8 (C_q arom), 145.7 (d, $J_{C,P}$ = 6 Hz; C_q arom), 146.6 (d, $J_{C,P}$ = 13 Hz; C_q arom), 155.9 ppm (dd, $J_{C,P}$ = 8, 3 Hz; C_q arom); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ = 21.6 (dd, $J_{P,Rh}$ = 137 Hz; P–C), 132.2 ppm (dd, $J_{P,Rh}$ = 267 Hz, $J_{P,P}$ = 57 Hz; P–O); elemental analysis (%) calcd for $C_{36}H_{46}BF_4O_3P_2Rh$: C 55.5, H 6.0; found: C 55.1, H 6.0.

[Rh(cod)(5c)]BF_4 (7c): This compound was prepared as described for **7a**. Orange crystals (0.075 g, 60%); ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.67 (s, 3H; Me), 1.83 (m, 2H; 2×C*H*H), 1.89 (s, 3H; Me), 2.00 (s, 3H; Me), 2.16 (m, 2H; 2×C*H*H), 2.24 (s, 3H; Me), 2.33 (s, 3H; Me), 2.53 (m, 2H; 2×C*H*H), 2.67 (s, 3H; Me), 2.79 (m, 2H; 2×C*H*H), 3.89 (m, 2H; 2×=CH), 5.74 (m, 1H; =CH), 5.90 (m, 1H; =CH), 7.00 (m, 3H; 3×H arom), 7.15 (s, 1H; H arom), 7.24 (m, 4H; 4×H arom), 7.56 (m, 7H; 7×H arom), 8.77 ppm (d, $J_{H,H}$ = 17 Hz, 1H; H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 17.2 (Ar-*Me*), 17.6 (Ar-*Me*), 20.2 (Ar-*Me*), 20.3 (Ar-*Me*), 22.7 (Ar-*Me*), 25.3 (Ar-*Me*), 26.9 (2×CH_2), 34.0 (CH_2), 34.4 (CH_2), 97.9 (m; =CH), 105.6 (m; =CH), 111.9 (m; =CH), 113.1 (m; =CH), 118.2 (CH arom), 118.3 (CH arom), 122.6 (CH arom), 125.1 (2×C_q arom), 125.2 (CH arom), 125.5 (C_q arom), 125.9 (C_q arom), 126.9 (CH arom), 127.0 (CH arom), 127.3 (d, $J_{C,P}$ = 10 Hz; C_q arom), 127.5 (C_q arom), 128.0 (C_q arom), 130.4 (2×CH arom), 130.8 (CH arom), 132.7 (CH arom), 132.8 (CH arom), 132.9 (CH arom), 134.1 (CH arom), 135.5 (CH arom), 136.0 (CH arom), 138.0 (2×C_q arom), 138.7 (CH arom), 141.4 (C_q arom), 142.6 (C_q arom), 145.9 (C_q arom), 146.0 (C_q arom), 153.8 ppm (d, $J_{C,P}$ = 10 Hz; C_q arom); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 17.3 (dd, $J_{P,Rh}$ = 136 Hz; P–C), 136.9 ppm (dd, $J_{P,Rh}$ = 277 Hz, $J_{P,P}$ = 54 Hz; P–O); elemental analysis (%) calcd for $C_{44}H_{46}BF_4O_3P_2Rh{\cdot}0.5\,CH_2Cl_2$: C 58.3, H 5.2; found: C 58.6, H, 5.3.

[Rh(cod)(5d)]BF_4 (7d): This complex was prepared by the procedure described for **7a**. Yellow solid (0.090 g, 70%); ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.93 (s, 3H; Me), 2.04 (s, 3H; Me), 2.26 (s, 3H; Me), 2.37 (s, 3H; Me), 2.10 (m, 8H; 8×C*H*H), 3.60 (m, 1H; =CH), 3.92 (m, 1H; =CH), 5.82 (m, 1H; =CH), 6.04 (m, 1H; =CH), 7.04 (m, 6H; 6×H arom), 7.32 (m, 3H; 3×H arom), 7.61 (m, 6H; 6×H arom), 7.84 (d, $J_{H,H}$ = 8 Hz, 1H; H arom), 8.06 (m, 4H; 4×H arom), 8.41 (d, $J_{H,H}$ = 7 Hz, 1H; H arom), 9.32 ppm (dd, $J_{H,H}$ = 21, 7 Hz, 1H; H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 17.6 (Ar-*Me*), 17.9 (Ar-*Me*), 20.6 (Ar-*Me*), 20.6 (Ar-*Me*), 25.5 (CH_2), 27.1 (CH_2), 34.3 (CH_2), 34.6 (CH_2), 98.3 (m; =CH), 105.9 (m; =CH), 111.8 (d, $J_{C,P}$ = 11 Hz; =CH), 114.4 (m; =CH), 118.3 (CH arom), 118.5 (C_q arom), 118.8 (CH arom), 120.3 (C_q arom), 120.9 (C_q arom), 123.1 (CH arom), 123.8 (C_q arom), 125.5 (m; C_q arom), 125.8 (C_q arom), 126.0 (2×CH arom), 126.2 (CH arom), 126.7 (CH arom), 127.5 (2×CH arom), 127.7 (CH arom), 127.9 (CH arom), 128.0 (CH arom), 128.2 (C_q arom), 130.2 (CH arom), 130.6 (2×CH arom), 131.5 (CH arom), 132.8 (d, $J_{C,P}$ = 10 Hz; C_q arom), 132.8 (C_q arom), 134.2 (CH arom), 134.2 (CH arom), 134.6 (CH arom), 134.7 (C_q arom), 135.5 (d, $J_{C,P}$ = 7 Hz; C_q arom), 135.8 (CH arom), 136.0 (CH arom), 136.3 (CH arom), 138.4 (C_q arom), 138.9 (C_q arom), 144.4 (d, $J_{C,P}$ = 33 Hz; C_q arom), 146.2 (d, $J_{C,P}$ = 12 Hz; C_q arom), 154.0 ppm (d, $J_{C,P}$ = 10 Hz; C_q arom); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 17.7 (dd, $J_{P,Rh}$ = 139 Hz; P–C), 139.0 ppm (dd, $J_{P,Rh}$ = 274 Hz, $J_{P,P}$ = 51 Hz; P–O); elemental analysis (%) calcd for $C_{50}H_{46}BF_4O_3P_2Rh{\cdot}0.5\,CH_2Cl_2$: C 61.3, H 4.8; found: C 60.9, H 4.5.

[Rh(cod)(5e)]BF_4 (7e): This complex was prepared as described for **7b**. Orange solid (0.072 g, 60%); ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.33 (d, $J_{H,P}$ = 14.7 Hz, 9H; CMe$_3$), 1.68 (d, $J_{H,P}$ = 15.0 Hz, 9H; CMe$_3$), 1.94 (s, 3H; Me), 2.01 (s, 3H; Me), 2.28 (m, 6H; 6×C*H*H), 2.31 (s, 6H; 2×Me), 2.68 (m, 2H; 2×C*H*H), 4.29 (m, 1H; =CH), 5.06 (m, 1H; =CH), 6.09 (m, 1H; =CH), 6.49 (dd, $J_{H,H}$ = 8.1 Hz, $J_{H,P}$ = 4.5 Hz, 1H; H arom), 6.67 (m, 1H; =CH), 7.10 (m, 5H; 5×H arom), 7.35 (t, $J_{H,H}$ = 8.1 Hz, 1H; H arom), 7.83 ppm (t, $J_{H,H}$ = 6.6 Hz, 1H; H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 17.4 (Ar-*Me*), 17.6 (Ar-*Me*), 20.3 (2×Ar-*Me*), 26.3 (CH_2), 28.1 (CH_2), 30.0 (d, $J_{C,P}$ = 6 Hz; C*Me$_3$*), 31.8 (CH_2), 32.8 (CH_2), 33.4 (d, $J_{C,P}$ = 6 Hz; C*Me$_3$*), 39.4 (d, $J_{C,P}$ = 11 Hz, *C*Me$_3$), 39.8 (d, $J_{C,P}$ = 12 Hz, *C*Me$_3$), 90.4 (dd, $J_{C,P}$ = 7, $J_{C,Rh}$ = 7 Hz; =CH), 94.6 (dd, $J_{C,P}$ = 9, $J_{C,Rh}$ = 9 Hz; =CH), 107.5 (d, $J_{C,P}$ = 7 Hz; C_q arom), 112.6 (d, $J_{C,P}$ = 11 Hz; =CH), 115.5 (dd, $J_{C,P}$ = 30, 10 Hz; C_q arom), 118.0 (CH arom), 118.8 (CH arom), 119.0 (d, $J_{C,P}$ = 6 Hz; =CH), 121.7 (CH arom), 123.9 (CH arom), 127.3 (C_q arom), 128.7 (C_q arom), 130.1 (CH arom), 130.3 (CH arom), 133.5 (CH arom), 135.3 (CH arom), 136.1 (C_q arom), 137.4 (C_q arom), 138.7 (C_q arom), 145.5 (d, $J_{C,P}$ = 6 Hz; OC_q arom), 146.5 (d, $J_{C,P}$ = 13 Hz; OC_q arom), 154.9 ppm (dd, $J_{C,P}$ = 8, 6 Hz; OCq arom); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 33.7 (dd, $J_{P,Rh}$ = 133 Hz; P–C), 127.5 ppm (dd, $J_{P,Rh}$ = 266, $J_{P,P}$ = 62 Hz; P–O); elemental analysis (%) calcd for $C_{38}H_{50}O_3BF_4P_2Rh$: C 56.6, H 6.2; found: C 56.4, H 6.3.

[Rh(cod)(2a)]BF_4 (8a): This compound was prepared as described for **7b**. Yellow solid (62%). ^1H NMR (400 MHz; $CDCl_3$): δ = 1.59 (s, 9H; CMe$_3$), 1.65 (s, 9H; CMe$_3$), 1.73 (s, 3H; Me), 1.82 (s, 3H; Me), 2.03 (m, 3H; 3×C*H*H), 2.14 (m, 1H; C*H*H COD), 2.22 (s, 3H; Me), 2.24 (s, 3H; Me), 2.28 (m, 1H; C*H*H), 2.41 (m, 3H; 3×C*H*H), 2.59 (m, 1H; C*H*H), 3.07 (m, 1H; CH*H*), 4.00 (m, 1H; OC*H*H), 4.02 (brs, 1H; =CH), 4.38 (brs, 1H; =CH), 4.61 (m, 1H; OC*H*H), 5.17 (brs, 1H; =CH), 5.86 (brs, 1H; =CH), 7.14 (s, 1H; CH arom), 7.23 (s, 1H; CH arom), 7.34 (t, $J_{H,H}$ = 8.4 Hz, 2H; 2×CH arom), 7.51 (m, 3H; 3×CH arom), 7.63 (m, 3H; 3×CH arom), 8.02 ppm (t, $J_{H,H}$ = 9.2 Hz, 2H; 2×CH arom); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ = 16.4 (CH_3), 16.6 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 26.2 (dd, $J_{C,P}$ = 32, 12 Hz; CH_2), 28.8 (CH_2), 30.0 (2×CH_2), 31.5 (CH_2), 31.9 (C*Me$_3$*), 32.8 (C*Me$_3$*), 35.2 (2×*C*Me$_3$), 64.8 (OCH_2), 95.9 (brm; =CH), 107.3 (brm; =CH), 107.6 (brm; =CH), 110.5 (brm; =CH), 128.8 (CH arom), 128.9 (C_q arom), 129.1 (C_q arom), 129.5 (CH arom), 129.6 (C_q arom), 129.7 (C_q arom), 129.8 (CH arom), 130.0 (2×CH arom), 130.2 (CH arom), 131.0 (CH arom), 131.1 (CH arom), 131.9 (d, $J_{C,P}$ = 3 Hz; CH arom), 133.4 (CH arom), 134.4 (C_q arom), 134.6 (C_q arom), 135.4 (CH arom), 135.5 (CH arom), 135.8 (C_q arom), 136.6 (C_q arom), 137.3 (d, $J_{C,P}$ = 7 Hz; C_q arom), 137.5 (OC_q arom), 144.2 (d, $J_{C,P}$ = 14 Hz; OC_q arom), 144.8 ppm (d, $J_{C,P}$ = 10 Hz; OC_q arom); $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$): δ = 5.1 (dd, $J_{P,Rh}$ = 142 Hz; P–C), 130.9 ppm (dd, $J_{P,Rh}$ = 245 Hz, $J_{P,P}$ = 61 Hz; P–O); elemental analysis (%) calcd for $C_{46}H_{58}BF_4O_3P_2Rh{\cdot}0.5\,CH_2Cl_2$: C 58.6, H 6.2; found: C 58.8, H 6.4.

[Rh(5a)$_2$]BF_4 (9a): Compound **5a** (0.082 g, 0.15 mmol) in CH_2Cl_2 (10 mL) was slowly added to a solution of $[Rh(cod)_2]BF_4$ (0.061 g, 0.15 mmol) in CH_2Cl_2 (5 mL). The resulting orange solution was stirred for 1 h and treated with Et_2O (30 mL) and the obtained solid was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O 1:2 to give **9a** as a

yellow, crystalline solid (0.070 g, 80%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 1.51 (s, 6H; 2×Me), 1.88 (s, 6H; 2×Me), 2.23 (s, 6H; 2×Me), 2.32 (s, 6H; 2×Me), 6.28 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 6.73 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 6.97 (m, 12H; 12×H arom), 7.07 (t, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.19 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.27 (t, $J_{H,H}$ = 7.0 Hz, 2H; 2×H arom), 7.35 (t, $J_{H,H}$ = 7.0 Hz, 2H; 2×H arom), 7.44 (t, $J_{H,H}$ = 7.5 Hz, 4H; 4×H arom), 7.53 (t, $J_{H,H}$ = 7.5 Hz, 2H; 2×H arom), 7.63 (m, 4H; 4×H arom), 7.68 ppm (t, $J_{H,H}$ = 7.5 Hz, 2H; 2×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 17.1 (2×Ar-*Me*), 17.3 (2×Ar-*Me*), 20.2 (2×Ar-*Me*), 20.6 (2×Ar-*Me*), 118.0 (2×CH arom), 118.6 (2×CH arom), 122.5 (2×CH arom), 124.1 (dd, $J_{C,P}$ = 11, 6 Hz; 2×C_q arom), 124.5 (dd, $J_{C,P}$ = 13, 6 Hz; 2×C_q arom), 126.1 (2×CH arom), 127.3 (2×C_q arom), 127.8 (2×C_q arom), 128.2 (2×C_q arom), 128.8 (2×CH arom), 128.9 (4×CH arom), 129.0 (2×CH arom), 129.5 (2×CH arom), 129.7 (2×CH arom), 130.8 (2×CH arom), 131.5 (2×CH arom), 132.4 (2×CH arom), 132.4 (2×CH arom), 132.5 (2×CH arom), 133.2 (2×CH arom), 134.7 (2×C_q arom), 135.1 (2×C_q arom), 136.0 (2×CH arom), 136.1 (2×CH arom), 137.7 (2×C_q arom), 138.4 (2×C_q arom), 145.8 (brs, 4×C_q arom), 153.0 ppm (m; 2×C_q arom); ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz): δ = 18.5 (m, $J_{P,Rh}$ = 121 Hz, $J_{P,P}$ = 400, 70, 33 Hz; P–C), 149.4 ppm (m, $J_{P,Rh}$ = 228 Hz, $J_{P,P}$ = 400, 70, 33 Hz; P–O); elemental analysis (%) calcd for $C_{68}H_{60}BF_4O_6P_4Rh$: C 63.5, H 4.7; found: C 63.2, H, 4.6.

[Rh(cod)(10)]BF$_4$ (11): This compound was prepared from phosphane-phosphite **10** by the procedure described for **7a**. Yellow solid (0.065 g, 62%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.45 (m, 8H; 8×C*H*H), 4.14 (m, 1H; =CH), 4.82 (m, 1H; =CH), 5.66 (m, 1H; =CH), 5.82 (m, 1H; =CH), 7.05 (dd, $J_{H,H}$ = 7.5, 5.0 Hz, 1H; H arom), 7.27 (m, 9H; 9×H arom), 7.59 (m, 12H; 12×H arom), 7.94 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 8.03 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 8.07 (d, $J_{H,H}$ = 9.0 Hz, 1H; H arom), 8.33 ppm (d, $J_{H,H}$ = 9.0 Hz, 1H; H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 27.4 (CH_2), 28.6 (CH_2), 32.1 (CH_2), 32.6 (CH_2), 100.6 (t, $J_{C,P}$ = $J_{C,Rh}$ = 7 Hz; =CH), 106.1 (t, $J_{C,P}$ = $J_{C,Rh}$ = 7 Hz; =CH), 113.6 (m, 2×=CH), 116.7 (d, $J_{C,P}$ = 10 Hz; C_q arom), 117.3 (d, $J_{C,P}$ = 10 Hz; C_q arom), 120.6 (CH arom), 121.2 (CH arom), 122.2 (m; CH arom), 122.6 (m; CH arom), 126.0 (C_q arom), 126.1 (m; CH arom), 126.3 (CH arom), 126.5 (CH arom), 126.7 (C_q arom), 127.1 (2×CH arom), 127.3 (CH arom), 127.4 (CH arom), 128.1 (C_q arom), 128.8 (CH arom), 129.3 (CH arom), 129.8 (CH arom), 129.9 (CH arom), 130.3 (CH arom), 130.5 (CH arom), 131.4 (CH arom), 132.1 (C_q arom), 132.2 (C_q arom), 132.4 (CH arom), 132.5 (CH arom), 132.6 (C_q arom), 132.7 (C_q arom), 133.3 (CH arom), 133.5 (CH arom), 133.6 (CH arom), 134.6 (CH arom), 134.7 (CH arom), 134.9 (CH arom), 146.4 (d, $J_{C,P}$ = 5 Hz; C_q arom), 147.1 (d, $J_{C,P}$ = 13 Hz; C_q arom), 155.1 ppm (d, $J_{C,P}$ = 10 Hz; C_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 15.7 (dd, $J_{P,Rh}$ = 135 Hz; P–C), 137.8 ppm (dd, $J_{P,Rh}$ = 269 Hz, $J_{P,P}$ = 61 Hz; P–O); elemental analysis (%) calcd for $C_{46}H_{38}BF_4O_3P_2Rh{\cdot}H_2O$: C 60.8, H 4.4; found: C 60.8, H, 4.0.

[Rh(cod)(14)]BF$_4$ (15): Compound **14** (0.080 g, 0.11 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of $[(cod)_2Rh]BF_4$ (0.046 g, 0.11 mmol) in CH_2Cl_2 (10 mL), and the orange solution was stirred for 45 min, concentrated to a fourth of the initial volume, filtered and finally treated with Et_2O (40 mL). The resulting solid was washed with Et_2O (2×10 mL) and dissolved in CH_2Cl_2 (5 mL), and addition of Et_2O (40 mL) yielded **15** as a yellow solid (0.096 g, 84%); ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.31 (s, 18H; 2×CMe_3), 1.34 (s, 18H; 2×CMe_3), 2.24 (m, 8H; 4×CH_2), 4.81 (brm, 2H; 2×=CH), 4.89 (brm, 2H; 2×=CH), 6.95 (m, 1H; CH arom), 7.17 (s, 2H; 2×CH arom), 7.23 (s, 1H; CH arom), 7.29 (t, $J_{H,H}$ = 7.0 Hz, 1H; CH arom), 7.49 (m, 3H; 3×CH arom), 7.61 ppm (m, 10H; 10×CH arom); ^{13}C{^{1}H NMR (125 MHz; $CDCl_3$): δ = 29.6 (2×CH_2), 31.0 (2×CH_2), 31.3 (2×CMe_3), 31.7 (2×CMe_3), 35.2 (2×*C*Me_3), 35.7 (2×*C*Me_3), 101.7 (brm, 2×=CH), 111.1 (brm, 2×=CH), 121.2 (2×C_q arom), 123.4 (2×C_q arom), 125.7 (2×CH arom), 126.9 (2×C_q arom), 127.6 (2×CH arom), 129.9 (2×CH arom), 130.1 (2×CH arom), 130.7 (2×CH arom), 131.9 (2×CH arom), 132.8 (2×CH arom), 134.0 (2×C_q arom), 134.1 (2×CH arom), 134.3 (2×CH arom), 140.2 (2×C_q arom), 149.3 ppm (2×C_q arom); ^{31}P{^{1}H} NMR (162 MHz; $CDCl_3$): δ = 13.0 (dd, $J_{P,Rh}$ = 142 Hz; P–C), 130.9 ppm (dd, $J_{P,Rh}$ = 267 Hz, $J_{P,P}$ = 52 Hz; P–O); elemental analysis (%) calcd for $C_{54}H_{66}BF_4O_3P_2Rh$: C 63.9, H 6.6; found: C 63.4, H 6.3.

[Rh(nbd)(14)]BF$_4$ (16): 2,5-Norbornadiene (1.06 mL, 9.90 mmol) was slowly added to a solution of **15** (0.100 g, 0.10 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 48 h, the solvent was removed under reduced pressure, and the resulting solid was washed with Et_2O (2×10 mL) and dissolved in CH_2Cl_2 (10 mL). Addition of Et_2O (40 mL) produced precipitation of **15** as an orange solid (0.082 g, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.33 (s, 18H; 2×CMe_3), 1.34 (s, 18H; 2×CMe_3), 1.60 (m, 2H; 2×C*H*H), 4.08 (m, 2H; 2×=CH), 4.75 (m, 2H; 2×CH), 5.28 (m, 2H; 2×=CH NBD), 7.05 (m, 2H; 2×H arom), 7.17 (d, $J_{H,H}$ = 3 Hz, 2H; 2×H arom), 7.26 (m, 1H; H arom), 7.51 (m, 6H; 6×H arom), 7.62 ppm (m, 7H; 7×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 31.0 (2×C*Me*$_3$), 31.6 (2×C*Me*$_3$), 35.2 (2×*C*Me_3), 35.8 (2×*C*Me_3), 55.0 (CH_2), 71.9 (2×CH), 98.7 (m, 2×=CH); 120.6 (m, 2×=CH), 125.8 (2×CH arom), 126.4 (C_q arom), 126.6 (2×C_q arom), 126.8 (2×C_q arom), 127.1 (C_q arom), 127.6 (2×CH arom), 130.2 (2×CH arom), 130.4 (2×CH arom), 130.9 (2×C_q arom), 131.2 (2×CH arom), 132.6 (2×CH arom), 133.8 (2×CH arom), 133.9 (2×CH arom), 134.0 (CH arom), 140.4 (CH arom), 144.8 (C_q arom), 144.9 (C_q arom), 149.2 (C_q arom), 154.1 ppm (m, OC_q arom); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 15.2 (dd, $J_{P,Rh}$ = 147 Hz; P–C), 133.9 ppm (dd, $J_{P,Rh}$ = 279 Hz, $J_{P,P}$ = 67 Hz; P–O); elemental analysis (%) calcd for $C_{53}H_{62}BF_4O_3P_2Rh{\cdot}0.5\,CH_2Cl_2$: C 61.7, H 6.1; found: C 61.5, H 5.8.

[Rh(14)(12a)]BF$_4$ (17): Complex **16** (0.030 g, 0.03 mmol) was dissolved in DME (5 mL) in a Fischer–Porter vessel, and this was charged with H_2 (4 atm) at room temperature. The reaction mixture was stirred overnight and depressurized, and **12a** (0.030 g, 0.12 mmol) was then added under Ar. The mixture was stirred for 4 h, solvent was removed under vacuum, and the resulting residue was dissolved in $CDCl_3$ for NMR characterization. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.31 (s, 18H; 2×CMe_3), 1.36 (s, 18H; 2×CMe_3), 3.51 (brs, 6H; 2×OMe), 4.51 (brs, 1H; =CH), 5.19 (brs, 1H; =CH), 6.81 (brm, 1H; CH arom), 7.07 (brm, 1H; CH arom), 7.26 (brs, 2H; 2×CH arom), 7.32 (brm, 1H; CH arom), 7.54 ppm (brm, 18H; 18 CH arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 30.9 (C*Me*$_3$), 31.5 (C*Me*$_3$), 35.1 (*C*Me_3), 35.8 (*C*Me_3), 53.6 (2×OCH_3), 54.1 (=CHH), 122.0 (CH arom), 125.5 (2×CH arom), 127.0 (2×Cq arom), 127.9 (2×CH arom), 128.5 (CH arom), 129.0–130.6 (9×CH arom), 131.2 (2×Cq arom), 132.5 (2×CH arom), 133.2 (CH arom), 133.9 (2×CH arom), 134.0 (2×CH arom), 134.4 (Cq arom), 134.8 (CH arom), 139.8 (2×Cq arom), 145.7 (2×OCq arom), 148.8 (2×Cq arom), 154.0 (Cq arom), 154.8 (OCq arom), 164.3 ppm (COO); no =*C*,P(OBz) resonance was observed; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 250 K): δ = 6.0 (brdq, $J_{P,Rh}$ = 147 Hz, $J_{P,P}$ = 68, 12 Hz; P–OP), 10.6 (brd, $J_{P,P}$ = 12 Hz; P(O)$(OMe)_2$), 137.4 ppm (dd, $J_{P,Rh}$ = 255 Hz, $J_{P,P}$ = 68 Hz; P–O*P*).

(*E*)-1-Benzoyloxy-1-dimethylphosphonyl-2-(3,4-dimethoxyphenyl)ethene (12g): $P(OMe)_3$ (2.4 mL, 20 mmol) was slowly added at 0°C to a solution of 2-(3,4-dimethoxyphenyl)acetyl chloride (4.3 g, 20 mmol) in THF (15 mL). After the addition the mixture was heated under reflux for 0.5 h. Solvent was evaporated under reduced pressure and the resulting residue was recrystallized in CH_2Cl_2/hexane 1:2 to give (*E*)-1-hydroxy-1-dimethylphosphonyl-2-(3,4-dimethoxyphenyl)ethene (4.05 g, 70%).

DBU (1.5 mL, 10.4 mmol) was slowly added at 0°C to a mixture of this olefin (2.5 g, 8.67 mmol) and benzoic anhydride (2.35 g, 10.4 mmol) in THF (50 mL). The reaction mixture was stirred for 20 min, allowed to warm to room temperature, diluted with AcOEt (100 mL) and washed with saturated aqueous solutions of $NaHCO_3$ (3×50 mL) and NaCl (3×50 mL), and the aqueous phases were reextracted with AcOEt (3×40 mL). Organic layers were collected and dried over $MgSO_4$ and filtered, and evaporation under reduced pressure yielded a residue that was purified by column chromatography (silica gel, AcOEt/hexane 6:1), yielding **7g** as a white solid (2.2 g, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.42 (s, 3H; Ar-O*Me*), 3.80 (s, 3H; Ar-O*Me*), 3.81 (d, $J_{H,P}$ = 11.0 Hz, 6H; 2×P–OMe), 6.75 (d, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 7.07 (m, 2H; 2×H arom), 7.22 (d, $J_{H,P}$ = 11.7 Hz, 1H; =C*H*), 7.47 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.62 (t, $J_{H,H}$ = 8.0 Hz, 1H; H arom), 8.14 ppm (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 53.5 (d, $J_{C,P}$ = 5 Hz, 2×P–OMe), 55.5 (Ar-O*Me*), 56.1 (Ar-O*Me*), 111.2

(CH arom), 111.7 (CH arom), 124.4 (CH arom), 125.1 (d, $J_{C,P}$ = 17 Hz; C_q arom), 129.0 (C_q arom), 129.1 (2×CH arom), 130.5 (2×CH arom), 134.4 (CH arom), 134.8 (d, $J_{C,P}$ = 230 Hz; =CO), 135.0 (d, $J_{C,P}$ = 28 Hz; =CH), 149.0 (C_q arom), 150.7 (C_q arom), 163.8 ppm (COO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 12.5 ppm; elemental analysis (%) calcd for $C_{19}H_{21}O_7P$: C 58.2, H 5.4; found: C 58.1, H 5.5.

(*E*)-1-Benzoyloxy-1-dimethylphosphonyl-2-(*p*-tolyl)ethene (12h): This compound was synthesized as described for **12g**. White solid (2.4 g, 70%); ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.27 (s, 3H; Me), 3.81 (d, $J_{H,P}$ = 11.2 Hz, 6H; 2×OMe), 7.07 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.27 (d, $J_{H,H}$ = 11.6 Hz, 1H; =CH), 7.40 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.49 (t, $J_{H,H}$ = 7.2 Hz, 2H; 2×H arom), 7.62 (t, $J_{H,H}$ = 7.2 Hz, 1H; H arom), 8.13 ppm (d, $J_{H,H}$ = 7.2 Hz, 2H; 2×H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 21.4 (Ar-*Me*), 53.3 (d, $J_{C,P}$ = 5 Hz; 2×OMe), 128.8 (2×CH arom), 129.2 (C_q arom), 129.3 (C_q arom), 129.6 (2×CH arom), 129.7 (2×CH arom), 130.3 (2×CH arom), 134.0 (CH arom), 134.9 (d, $J_{C,P}$ = 28 Hz; =CH), 135.8 (d, $J_{C,P}$ = 229 Hz; =CO), 140.3 (C_q arom), 163.6 ppm (COO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 12.4 ppm; elemental analysis (%) calcd for $C_{18}H_{19}O_5P$: C 62.4, H 5.5; found: C 62.5, H 5.5.

Representative procedure for enantioselective hydrogenation: Hydrogenations were performed as demonstrated below for **12b**. In a glove box, a Fischer–Porter reactor (80 mL) was charged with **12b** (0.073 g, 0.25 mmol) and catalyst precursor **8a** (0.002 g, 0.002 mmol) in CH_2Cl_2 (5 mL). The vessel was removed from the glove box, subjected to vacuum–hydrogen cycles and finally pressurized to 4 atm. The reaction mixture was kept stirring for 24 h, the reactor was then depressurized, and the obtained mixture was evaporated to dryness, treated with Et_2O and passed through a short pad of silica. The resulting residue was analysed by ^1H NMR to determine conversion and by chiral HPLC for enantiomeric excess as follows:

1-Benzoyloxy-1-dimethylphosphonylethane (13a): (Chiralcel OJ, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 98.5:1.5): t_1 = 40.8 min (*S*), t_2 = 47.8 min (*R*).

1-Benzoyloxy-1-dimethylphosphonylbutane (13b): (Chiralpak AD, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 95:5): t_1 = 11.2 min (*R*), t_2 = 13.4 min (*S*).

1-Benzoyloxy-1-dimethylphosphonyl-3-methylbutane (13c): (Chiralpak AD, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 95:5): t_1 = 10.1 min (*R*), t_2 = 12.5 min (*S*).

1-Benzoyloxy-1-dimethylphosphonylhexane (13d): (Chiralpak AD, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 95:5): t_1 = 11.6 min (*R*), t_2 = 13.0 min (*S*).

1-Benzoyloxy-1-dimethylphosphonyl-2-phenylethane (13e): (Chiralpak AD, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 95:5): t_1 = 18.9 min (*R*), t_2 = 21.0 min (*S*).

1-Benzoyloxy-1-dimethylphosphonyl-2-(4-methoxyphenyl)ethane (13g): (Chiralpak AD, 30°C, flow rate 1.0 mL min^{-1}, hexane/propan-2-ol 95:5): t_1 = 27.6 min (*R*), t_2 = 37.0 min (*S*).

1-Benzoyloxy-1-dimethylphosphonyl-2-(*p*-tolyl)ethane (13f): White solid; $[\alpha]_D^{20}$ = −108.0 (*c* = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.23 (s, 3H; Ar-*Me*), 3.17 (dt, $J_{H,P}$ = 10.5 Hz, $J_{H,H}$ = 14.5, 10.5 Hz, 1H; CHH), 3.29 (ddd, $J_{H,P}$ = 7.0 Hz, $J_{H,H}$ = 14.5, 4.0 Hz, 1H; CHH), 3.75 (d, $J_{H,P}$ = 11.0 Hz, 3H; OMe), 3.76 (d, $J_{H,P}$ = 11.0 Hz, 3H; OMe), 5.72 (ddd, $J_{H,P}$ = 8.5 Hz, $J_{H,H}$ = 10.5, 4.0 Hz, 1H; CHOBz), 7.00 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.11 (d, $J_{H,H}$ = 8.0 Hz, 2H; 2×H arom), 7.41 (t, $J_{H,H}$ = 7.0 Hz, 2H; 2×H arom), 7.54 (t, $J_{H,H}$ = 7.0 Hz, 1H; H arom), 7.98 ppm (d, $J_{H,H}$ = 7.0 Hz, 2H; 2×H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 21.0 (Ar-*Me*), 35.3 (CH_2), 53.2 (d, $J_{C,P}$ = 6 Hz, OMe), 53.5 (d, $J_{C,P}$ = 7 Hz, OMe), 68.6 (d, $J_{C,P}$ = 160 Hz, CHOBz), 128.5 (2×CH arom), 129.1 (2×CH arom), 129.2 (2×CH arom), 129.8 (2×CH arom), 133.0 (C_q arom), 133.1 (C_q arom), 133.3 (CH arom), 136.4 (C_q arom), 165.1 ppm (d, $J_{C,P}$ = 4 Hz; COO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 21.9 ppm; HRMS (CI): *m*/*z*: calcd for $C_{18}H_{22}O_5P$: 349.1205; found: 349.1199 $[M+H]^+$. Chiralpak AD, 30°C, hexane/propan-2-ol 90:10, flow rate 1.0 mL min^{-1}: t_1 = 9.4 min (*R*), t_2 = 11.9 min (*S*).

1-Benzoyloxy-1-dimethylphosphonyl-2-(3,4-dimethoxyphenyl)ethane (13h): White solid; $[\alpha]_D^{20}$ = −88.8 (*c* = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.14 (dt, $J_{H,P}$ = 10.2 Hz, $J_{H,H}$ = 14.7, 10.2 Hz, 1H; CHH), 3.26 (ddd, $J_{H,P}$ = 6.6 Hz, $J_{H,H}$ = 14.7, 4.0 Hz, 1H; CHH), 3.65 (s, 3H; Ar-O*Me*), 3.75 (d, $J_{H,P}$ = 10.5 Hz, 3H; OMe), 3.76 (s, 3H; Ar-O*Me*), 3.77 (d, $J_{H,P}$ = 10.5 Hz, 3H; OMe), 5.70 (ddd, $J_{H,P}$ = 8.2 Hz, $J_{H,H}$ = 10.2, 4.0 Hz, 1H; CHOBz), 6.74 (m, 3H; 3×H arom), 7.40 (t, $J_{H,H}$ = 7.0 Hz, 2H; 2×H arom), 7.53 (t, $J_{H,H}$ = 7.0 Hz, 1H; H arom), 7.97 ppm (d, $J_{H,H}$ = 7 Hz, 2H; 2×H arom); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 35.5 (CH_2), 53.6 (d, $J_{C,P}$ = 6 Hz, OMe), 53.8 (d, $J_{C,P}$ = 7 Hz, OMe), 55.9 (Ar-O*Me*), 56.0 (Ar-O*Me*), 68.9 (d, $J_{C,P}$ = 165 Hz, CHOBz), 111.4 (CH arom), 112.5 (CH arom), 121.6 (CH arom), 128.8 (2×CH arom), 128.9 (C_q arom), 129.4 (C_q arom), 130.0 (2×CH arom), 133.7 (CH arom), 148.2 (C_q arom), 149.0 (C_q arom), 165.2 ppm (d, $J_{C,P}$ = 5 Hz; COO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ = 21.8 ppm; HRMS (CI): *m*/*z*: calcd for $C_{19}H_{23}O_7P$: 394.1181; found: 394.1188 $[M]^+$. Chiralpak AD, 30°C, hexane/propan-2-ol 90:10, flow rate 1.0 mL min^{-1}: t_1 = 17.8 min (*R*), t_2 = 21.1 min (*S*).

Crystal data for 9a: $C_{139}H_{126}B_2Cl_6F_8O_{12}P_8Rh_2$, [2($C_{68}H_{60}O_6P_4Rh$), CH_2Cl_2, CH_2Cl_2, CH_2Cl_2, 2(BF_4)], M_w = 2828.30, yellow prism (0.27×0.26×0.25 mm^3) from CH_2Cl_2/hexane. Orthorhombic, space group $P2_12_12_1$ (no. 19); a = 17.6291(14), b = 19.4308(16), c = 20.5509(16) Å; $\alpha = \beta = \gamma$ = 90°; V = 7039.7(10) Å^3, Z = 2, ρ_{calcd} = 1.334 g cm^{-3}, $\lambda(Mo_{K\alpha1})$ = 0.71073 Å, $F(000)$ = 2900, μ = 0.506 mm^{-1}, T = 100(2) K. 61 149 reflections were collected with a Bruker–Nonius X8 Kappa Apex II CCD diffractometer in the range 6.08 < 2θ < 52.86° and 14 341 independent reflections [R(int) = 0.0680] were used in the structural analysis. Reflections were corrected for Lorentz polarisation effects and absorption was applied by (SADABS)[37]. The structure was solved by direct methods (SIR2002)[38] and refined against all F^2 data by full-matrix, least-squares techniques (SHELXTL-6.12)[39] to final $R1$ = 0.0683 [$I > 2\sigma(I)$], and to $wR2$ = 0.2022 for all data, with a goodness-of-fit on F^2 = 1.047 and 838 parameters. The absolute configuration of the structure has been undoubtedly established by anomalous dispersion effects in diffraction measurements on the crystal [Flack parameter x = −0.03(3)].[40]

CCDC-612 988 (**9a**) contains 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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