Chiral diphosphinites derived from 2,2-biphosphole as a new class of stereodynamic ligands for enantioselective hydrogenation†

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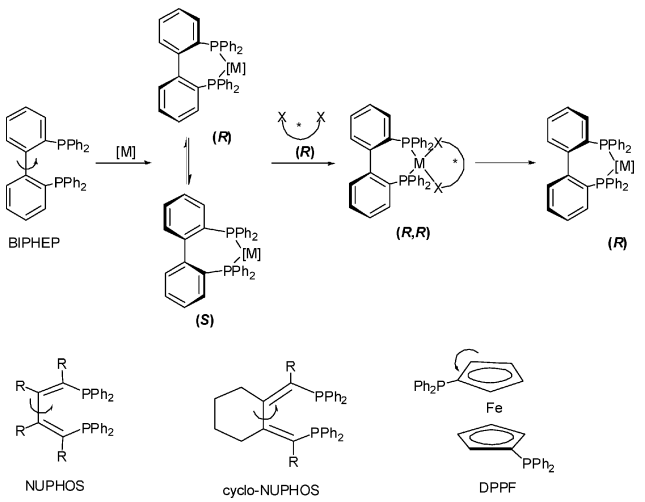
New stereodynamic diphosphinites derived from 2,2′-biphosphole, were synthesised by introduction of a linker obtained from chiral diols between the two phosphorus atoms and used for catalytic hydrogenation through a dual chirality control induced by Rh-coordination. The application of these ligands in hydrogenation of dimethyl itaconate shows that the enantioselectivity strongly depends on steric and electronic properties of the chiral linker whereas the sense of enantioselection is determined by the configuration of these stereocentres. These stereodynamic diphosphinites induce higher enantioselectivities than the analogous stereodynamic diphosphanes derived from 2,2-biphosphole.

Introduction

The design and synthesis of new ligands is key for the development of new transition metal catalysed asymmetric processes. Advances in this area have been traditionally guided by the concept that stereochemically rigid enantiopure ligands are required to achieve high enantioselectivities.[1] Chiral diphosphanes have proved to be one of the most successful and widely used ligands for this purpose in particular the highly versatile BINAP which belongs to the atropos[2] class of diphosphane ligands since its axial chiral conformation can be resolved.[1c] A conceptually new approach has emerged where achiral and *meso* ligands can be used to convey asymmetry in enantioselective catalysis.[3] Therefore, conformationally flexible tropos[2] diphosphane ligands are intentionally used to either magnify the stereochemical induction of a chiral ligand or act as the only source of asymmetry for enantioselective transformation. In the latter case, coordination of the ligand to the transition metal slows interconversion of its conformations and as a consequence a metastable enantiopure assembly can be resolved by a chiral controller and used for catalysis with or without it (Scheme 1). Enantiopure complexes with tropos diphosphanes such as BIPHEP,[4] NUPHOS,[5] cyclo-NUPHOS or DPPF[6] demonstrated good to excellent enantioselectivities and could efficiently replace complexes bearing classical enantiopure ligands.

The advantage of this approach to asymmetric catalysis over the traditional one is that catalysts can be optimised by the synthesis of achiral or *meso* ligands instead of the synthesis of enantiopure ones which requires elaborate and expensive methods (*e.g.* asymmetric synthesis or resolution). Consequently, the design of new catalysts, based on dynamic chirality control (*e.g.*, N-chirality control[7] or dual chirality control of axial and N-chirality[8]) by a chiral activator through complexation is an important field.



Scheme 1 BIPHEP, NUPHOS, cyclo-NUPHOS and DPPF.

In a related approach, we have examined the dual chirality control of axial and P-chirality of 2,2′-biphosphole ligands.[9] In 2001, we reported the first application of the chiral stereochemically dynamic 2,2′-biphosphole (BIPHOS) to asymmetric allylic substitution[10] involving crystallisation-induced spontaneous resolution and kinetic stabilisation by coordination to a Pd centre. In a more convenient procedure, we have discovered that a dual chirality control can be achieved by introducing a chiral carbon linker between the two phosphorus atoms that favours a single enantiomeric form upon coordination to a metal.[11] Enantiomeric Pd- and Pt-complexes have then been obtained and the use of these stereodynamic diphosphanes derived from 2,2′-biphosphole in Pd-catalysed asymmetric allylic substitution has been demonstrated.[12] The modular construction of these stereodynamic ligands by the combination of a 2,2′-biphosphole framework and a chiral linker offers immense scope for structural variations and catalysts tuning. In this paper, we report an efficient synthetic method for the preparation of new stereodynamic chiral diphosphinite ligands derived from 2,2-biphosphole. Since the use

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of these stereodynamic ligands in asymmetric catalysis relies on obtaining enantiopure complexes, we have examined the dynamic chirality control of the axial and P-central chiralities upon coordination. The first evaluation of these new diphosphinite ligands in rhodium-catalysed asymmetric hydrogenation is also reported and compared with those obtained with the analogous stereodynamic diphosphane derived from 2,2-biphosphole.

Results and discussion

Synthesis and structure of diphosphinites derived from 2,2′-biphosphole

The strategy to obtain these new chiral diphosphinite ligands derived from 2,2-biphosphole is based on the introduction of a chiral alkoxy linker between the two phosphorus atoms. The most convenient route to introduce such a group seems to be the procedure reported by Mathey *et al.*[13] which involves a nucleophilic substitution reaction on a 1-cyanophosphole. Thus, we have investigated this nucleophilic substitution reaction on 1,1′-dicyano-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole **2**[14] by using various enantiomerically pure diols **3a–g**. The synthetic pathway involved three steps starting from tetraphosphole **1**[15] as shown in Scheme 2. In the first step, cleavage of the two phosphorus–phosphorus bonds using sodium naphthalene leads to the 2,2′-biphospholyl anion which reacts in the next step with BrCN to give compound **2**. Treatment of compound **2** with the lithium derivative of diols **3a–g** in high dilution conditions affords in the last step the air-stable diphosphinite compounds **4a–g** in high yield (71–86%).

These compounds have been characterised by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy, mass spectroscopy, and in addition, the molecular structures of **4a** and **4b′** have been established by X-ray diffraction (Fig. 1 and 2).

Compound **4a**[16] crystallises in a non-centrosymmetric space group ($P2_12_12_1$). The refinement of the Flack's parameter[17] [0.06(14)] clearly indicates that **4a** is enantiomerically pure in the solid state and the absolute configuration is $R[S_p,S_p,S_c]$ (R axial chirality, S_p phosphorus chiralities, S_c carbon chirality).

On the other hand, **4b′**[18] is also enantiomerically pure in solid state [space group $P2_12_12_1$, Flack's parameter = –0.03(6)]. Its chirality is described as $S[R_p,R_p,R_c,R_c]$.

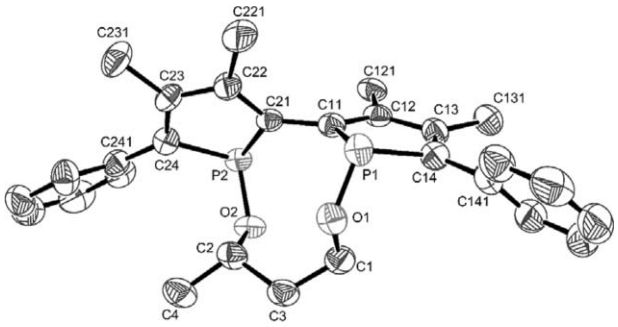


Fig. 1 Molecular view of $R[S_p,S_p,S_c]$-**4a** with atom labelling scheme. Ellipsoids drawn at the 50% probability level. P(1)–C(11)–C(21)–P(2) torsion angle: –121.0(3)°.

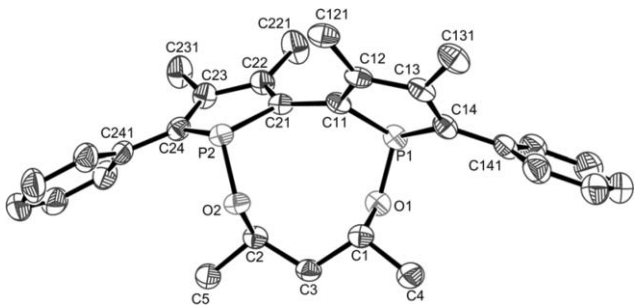
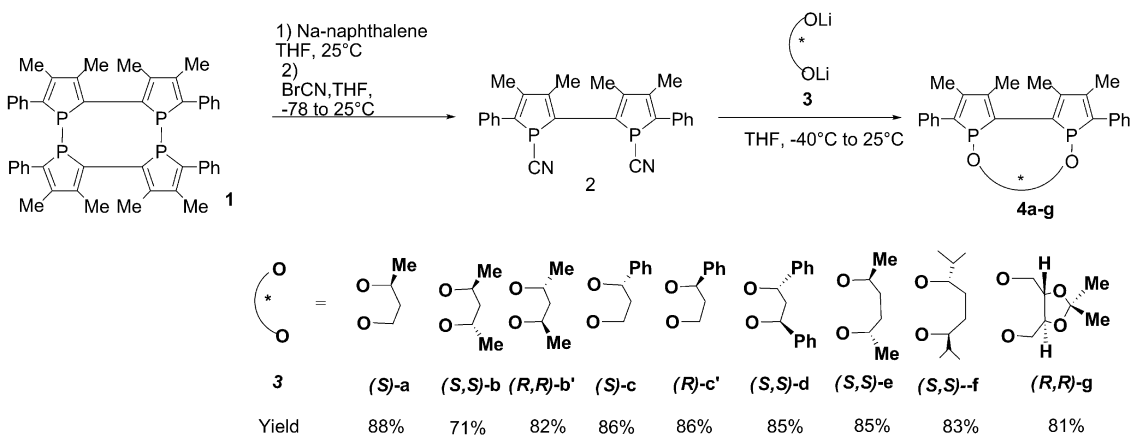


Fig. 2 Molecular view of $S[R_p,R_p,R_c,R_c]$-**4b′** with atom labelling scheme. Ellipsoids drawn at the 50% probability level. P(1)–C(11)–C(21)–P(2) torsion angle: 120.4(1)°.

It is worth mentioning the influence of the chirality of the starting diol on the axial and central configuration of the skeleton 2,2′-biphosphole in solid state as the (*S*) configuration of **2a** provides the $R[S_p,S_p]$ configuration of **4a** whereas the (*R*,*R*) configuration of **2b′** leads to the $S[R_p,R_p]$ configuration of **4b′**.

In solution, the diphosphinites **4a–g** have been observed by NMR as a single compound even within the temperature range –60 °C to +85 °C, corresponding probably to an equilibrium mixture of several diastereoisomers interconverting rapidly on the NMR time scale. The stereochemical analysis of the different possibilities of combining axial and central chiralities in 2,2′-biphosphole shows the occurrence of six really inequivalent diastereoisomers[19] for diphosphinites **4** (Fig. 3).



Scheme 2 Synthesis of diphosphinites **4a–g**.

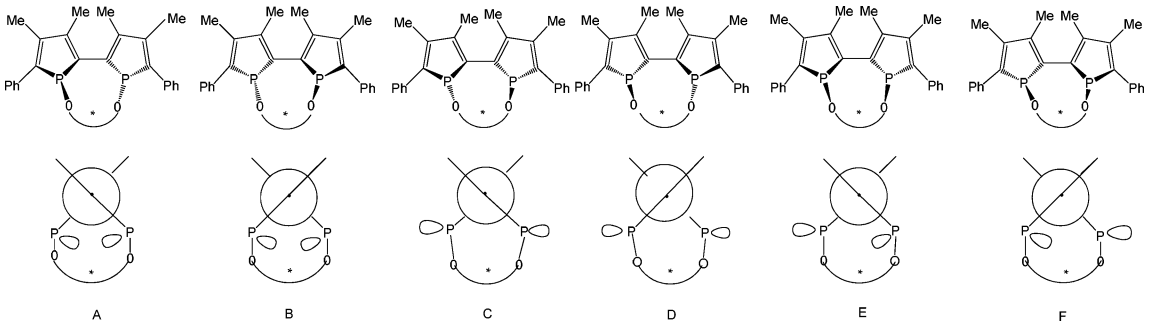


Fig. 3 The six diastereoisomers of diphosphinites **4** corresponding to the different possibilities of combining axial and central chiralities of a 2,2′-biphosphole framework. Each diastereoisomer is also represented in a Newman projection along the axis of the C–C linking the phosphole rings.

Among the six diastereoisomers, the formation of two diastereoisomers (A and B forms) is prevented by the length of the alkoxy linker between the two phosphorus atoms. In the case of the diphosphanes derived from the 2,2′-biphosphole, three diastereoisomers (C, D and E (or F) forms)[13] were observed as an equilibrium mixture at room temperature. The isomerisation process involves a phosphorus-inversion inducing atropoinversion,[20] the driving force being the pyramidal inversion barrier of the phosphorus atom.[21] As this reduced inversion barrier is not affected by π-donor substituents on the phosphorus,[22] we assume for diphosphinites derived from 2,2′-biphosphole a similar isomerisation process (Fig. 4) between the four most favoured diastereoisomers occurring rapidly in solution.

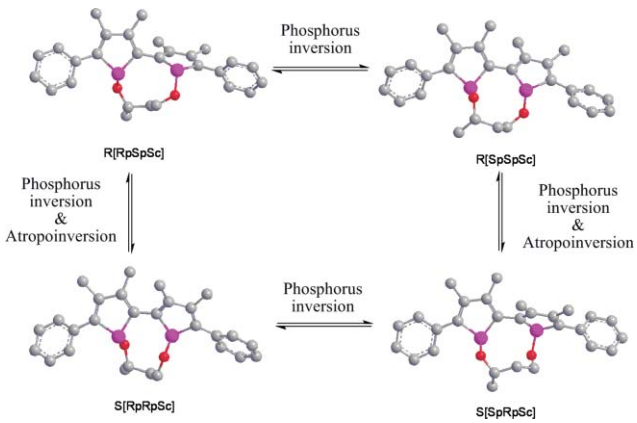


Fig. 4 Isomerisation process for compound **4**.

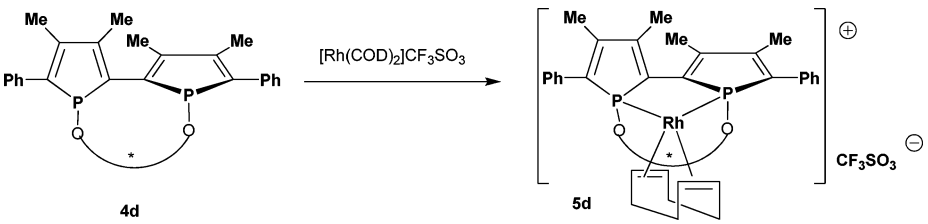
In order to evaluate these new chiral stereodynamic diphosphinite ligands in Rh-catalysed hydrogenation, we first of all examined the dynamic chirality control of the axial and P-central chiralities upon coordination to rhodium(I).

Complexing of diphosphinites derived from 2,2′-biphosphole

Initial complexing experiments, performed with platinum(II) precursors[23] had enabled us to show that diastereo- and enantiopure platinum complexes can be obtained with stereodynamic diphosphinite ligands **4**. The coordination of platinum locked up both axial and central chiralities of the 2,2′-biphosphole framework as a result of the hindered inversion of the phosphorus configurations as well as atropo-inversion of 2,2′-biphosphole on the metal centre.

Dynamic chirality control of ligands **4** could be also obtained by coordination to the rhodium centre. For example, reaction of $[Rh(COD)_2]CF_3SO_3$ in dichloromethane with one equivalent of **4d** quantitatively led to the cationic complex **5d**, $[Rh(COD)\mathbf{4d}]CF_3SO_3$, according to ^{31}P NMR spectroscopy (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **5d** indicates the formation of a diastereomerically pure complex with two diastereotopic phosphorus atoms as evident by the appearance of two doublets ($\delta p = 130.87$ (d, $J_{PRh} = 161.5$ Hz), 133.49 (d, $J_{PRh} = 171.5$ Hz), $J_{PP} < 1$ Hz). These two diastereotopic phosphorus atoms are consistent with the opposite configuration of the two phosphorus atoms in the rhodium complex **5d**.

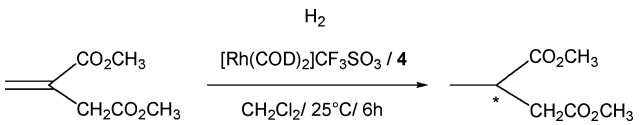
The mononuclear structure of complex **5d** was confirmed by FAB mass spectrum which shows the molecular ion corresponding to $[Rh(COD)L]^+$. As complexing to a metal centre locks both the central phosphorus configuration and the axial configurations of 2,2′-biphosphole, the rhodium complex **5d** is obtained as a diastereo- and enantiopure complex. Unfortunately, **5d** gave red hygroscopic and water sensitive powder after evaporating the solvent. All attempts to purify this complex failed and no single crystals could be obtained.



Scheme 3 Synthesis of the rhodium complex **5d**.

Hydrogenation of dimethyl itaconate

Although chiral diphosphanes have played a dominant role in the success of asymmetric hydrogenation, many chiral diphosphinites have proved to be effective ligands for rhodium-catalysed asymmetric hydrogenation of C=C double bonds.[24] The catalytic performance of the new diphosphinites **4a–g** were explored in the asymmetric hydrogenation of dimethyl itaconate (Scheme 4). In the first set of experiments, the effect of the solvent and hydrogen pressure in the yield and selectivity of the reaction were investigated for the catalytic system containing ligand **4b′**.



Scheme 4 Asymmetric hydrogenation of dimethyl itaconate.

We used the catalyst prepared *in situ*[25] by adding the diphosphinite **4b′** to $[Rh(COD)_2]CF_3SO_3$.[26] The results, summarised in Table 1, show the efficiency of the hydrogenation depended on the nature of the solvent (entries 1–3). When the experiment was carried out using MeOH, the hydrogenation gives the (*S*)-methyl succinate as a product in 53% conversion with only 33% enantioselectivity (entry 1) probably due to the decomposition of the diphosphinite **4b′** in this protic solvent. Ligand **4b′** is stable in other solvents. However in an aprotic and coordinating solvent such as THF, the catalyst was less effective affording both lower conversion and enantioselectivity (entry 2). Thus, the catalyst performance (in terms of activity and enantioselectivity) was best when a weakly coordinating solvent such as dichloromethane was used (entry 3).

Interestingly, both enantioselectivity and activity were enhanced when hydrogen pressure was raised from 10 to 40 bar (entry 4 *vs.* entry 6). At 10 bar, 87% conversion was achieved in 12 h with low enantioselectivity (21%). Further increase of hydrogen pressure to 20 bar resulted in a complete conversion of the dimethyl itaconate in 6 h as well as an appreciable increase of enantioselectivity from 21% to 55%. Finally, at 40 bar of hydrogen pressure a slight increase in enantioselectivity was observed (60%). The positive effect of the pressure on the enantioselectivity contrasts with the usual decrease in enantioselectivity with diphosphane ligands when the hydrogen pressure is raised.[1c,27]

For comparison, the rest of the ligands were tested in dichloromethane as a solvent, at hydrogen pressure of 40 bar and a ligand-to-rhodium ratio of 1.4. The results are compiled in Table 2.

Table 1 Asymmetric hydrogenation of dimethyl itaconate using Rh complex modified by diphosphinite **4b′**

Entry	Solvent	P_{H_2}/bar	Conversion (%)[a] (*t*/h)	ee (%) (conf.)[b]
1	MeOH	20	53 (12)	33 (*S*)
2	THF	20	38 (12)	11 (*S*)
3	CH_2Cl_2	20	100 (12)	55 (*S*)
4	CH_2Cl_2	10	87 (12)	21 (*S*)
5	CH_2Cl_2	20	100 (6)	55 (*S*)
6	CH_2Cl_2	40	100 (6)	60 (*S*)

Reaction conditions: ligand : [Rh]= 1.4 : 1, S/C= 150, T = 20 °C. [a] Determined by ^{1}H NMR. [b] Determined by chiral GC.

Table 2 Asymmetric hydrogenation of dimethyl itaconate catalysed by Rh complexes modified by diphosphinites **4**

Entry	Ligand	Conversion (%)[a]	ee (%)[b] (conf.)
1	**4a**	100	40(*R*)
2	**4b**	100	58(*R*)
3	**4b′**	100	60(*S*)
4	**4c**	75	85(*R*)
5	**4c′**	71	83(*S*)
6	**4d**	100	82(*R*)
7	**4e**	100	60(*R*)
8	**4f**	100	31(*R*)
9	**4g**	100	49(*S*)

Reaction conditions: CH_2Cl_2, ligand : [Rh] = 1.4 : 1, S/C = 150, T = 20 °C, P = 40 bar, t = 6 h. [a] Determined by ^{1}H NMR. [b] Determined by chiral GC.

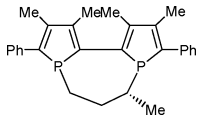
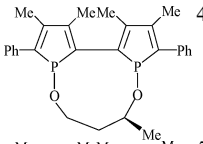
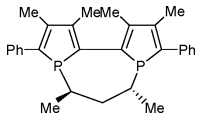
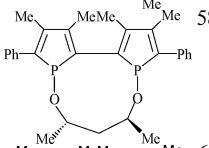
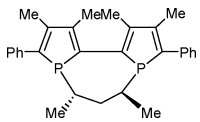
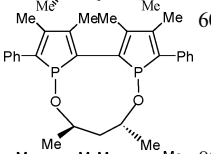
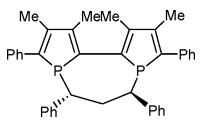
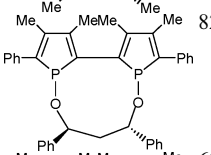
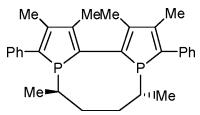
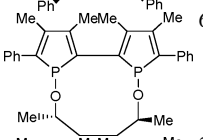
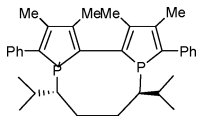
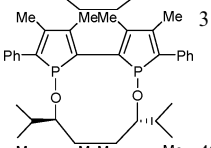
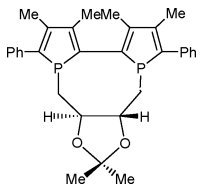
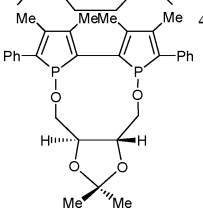
All of the ligands gave catalytic systems which are active in hydrogenation of dimethyl itaconate producing enantiomeric excess in the range of 31 to 85%. The best enantiomeric excesses are obtained with the ligands **4c**, **4c′** and **4d** (Table 2, entries 4–6). A comparison of the results shows that the enantioselectivity is strongly influenced by the substituent at the stereocentre(s) of the backbone. Ligands **4a**, **4b**, **4b′** and **4e** which have methyl substituent(s) led to ee values in the range of 40 to 60% (entries 1, 2, 3, and 7). With phenyl substituent(s) at the stereocentre(s) of the chiral backbone (entries 4, 5 and 6), the ee values reach 82–85%.

It is interesting to note that the ligands **4b** and **4b′** (compare entries 2 and 3) and the ligands **4c** and **4c′** (compare entries 4 and 5) totally control the chiralities of the 2,2′-biphosphole framework in the rhodium catalyst as already observed in the case of palladium complexes of diphosphanes derived from 2,2′-biphosphole.[28]

In addition, the sense of enantiodiscrimination is predominantly controlled by the configuration of the stereocentres of the chiral backbone. Ligand **4c**, which has the (*S*) alkoxyl backbone configuration, resulted in an ee of 85% (*R*) whereas ligands **4c′** which has the (*R*) backbone configuration led to an ee of 83% (*S*). Further evidence is provided by using related diphosphinite ligands, the (*R*) enantiomer of the methylsuccinate is obtained with ligands **4a**, **4b**, **4c**, **4d**, **4e** and **4f** derived from the (*S*) or (*S,S*) diols **3** whereas the (*S*) enantiomer is obtained with the ligand **4b′**, **4c′** and **4g** derived from the (*R*) or (*R,R*) diols **3**.

Finally, the catalytic performance of these diphosphinites rhodium complexes were compared with those obtained with the analogous diphosphanes rhodium complex (Table 3). All of the diphosphanes gave catalytic systems that are more active in hydrogenation of dimethyl itaconate as complete conversions were achieved in 3 h at room temperature under an hydrogen pressure of 20 bar. However, the enantioselectivities were significantly lower with all the ligands (around 30% except in two cases, entries 1 and 7). Contrary to the diphosphinites, the enantioselectivity is less affected by the modification of the substituent at the stereocentre of the backbone. In addition, the enantioselectivity is not very sensitive to hydrogen pressure. These results suggest a different mechanism of stereoselection for the diphosphanes and the diphosphinites. A comparison of the results of Table 3 shows an improvement of ee values by changing the chiral backbone.

Table 3 Asymmetric hydrogenation of dimethyl itaconate with rhodium complexes modified by diphosphane and diphosphinite ligands derived from 2,2′-biphosphole

Entry	Diphosphane[a] ee (%) (conf.)	Diphosphinite[b] ee (%) (conf.)
1	 15 (*R*)	 40 (*R*)
2	 29 (*R*)	 58 (*R*)
3	 30 (*S*)	 60 (*S*)
4	 32 (*R*)	 82 (*R*)
5	 30 (*R*)	 60 (*R*)
6	 28 (*R*)	 31 (*R*)
7	 3	 49 (*S*)

Reaction conditions:[a] MeOH, ligand : [Rh] = 1.4 : 1, S/C = 150, T = 20 °C, P = 20 bar, t = 3 h. [b] CH_2Cl_2, ligand : [Rh] = 1.4 : 1, S/C = 150, T = 20 °C, P = 40 bar, t = 6 h.

Conclusions

A series of stereodynamic chiral diphosphinites derived from 2,2′-biphosphole have been synthesised by a versatile three-step methodology. By the introduction of a relatively simple diol backbone between the two phosphorus atoms, the axial and P-chiralities can be controlled and locked upon coordination to rhodium to afford diastereo- and enantiopure rhodium complexes efficient for asymmetric hydrogenation of dimethyl itaconate. Notable features are the direct use of these stereodynamic diphosphinites to convey enantioselectivity in Rh-catalysed hydrogenation through an *in situ* dual chirality control. The enantioselectivity observed in hydrogenation of dimethyl itaconate is likely to be governed by the electronic properties rather than the steric factors of the ligand. The enantiomeric excess values are strongly influenced by the nature of the alkoxy linker whereas the sense of the enantioselection is determined by the configuration of the stereocentres.

The systematic variation of the substituents at the stereocentres at the ligand backbone provides therefore a rational approach to catalyst optimization. Further studies including mechanistic studies and computer modelling to determine the origin of the enantioselectivity are currently in progress. The application of the stereodynamic chiral diphosphinites derived from 2,2′-biphosphole in a broad range of rhodium group metal-catalysed asymmetric transformations is also being explored.

Experimental section

General comments

All reactions were carried out under dry argon by using Schlenk glassware and vacuum line techniques. The experiments requiring H_2 pressure were carried out in a stainless sell high pressure reactor. 1D and 2D NMR experiments were carried out using the Bruker AC 200 and AV 500 instruments. ^{1}H-2D-COSY45{^{31}P} and ^{1}H–^{13}C{^{31}P} (HMQC, HMBC) methods using standard pulse sequences have been employed to establish atom connectivities and spatial relationships. Mass spectra were obtained on a TSQ 7000 Thermoquest instrument (DCI), Nermag R10-10 (FAD) and on a Q/TOF Waters (HR) instruments. Optical rotations were measured with a Perkin Elmer 241 polarimeter.

Typical procedure for the preparation of diphosphinites 4. In a Schlenk tube under argon, the diol (1.05 mmol) was stirred in dry THF (4 mL). The solution was cooled to −40 °C and nBuLi (1.6 M in hexane, 2.10 mmol) was added. The reaction mixture was allowed to warm to room temperature for 30 min. This solution and a THF solution (4 mL) of **3** (1.05 mmol) were transferred dropwise by a cannula at the same time into another Schlenk tube containing 200 mL of dry THF cooled at −40 °C. The reaction mixture was then allowed warm to room temperature for 16 h. After evaporation to dryness, the resulting residue was dissolved in pentane and filtered through Celite. Pentane was then removed under reduced pressure.

***R*[*S*$_p$,*S*$_p$,*S*$_c$]-(−)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(butane-1,3-dioxy)-2,2′-biphosphole 4a.** Obtained from (*S*)-(+)-1,3-butanediol. Yellow solid. Yield: 88% (0.425 mg, 0.924 mmol). mp = 212 °C. $[\alpha]^{25}_D$ = −628.5 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.67 (d, $J_{H,H}$ = 10.00 Hz, 3H, CH_3), 1.19 (m, 1H, CH_2), 1.46 (m, 1H, CH_2), 2.17 (d, $J_{H,P1}$ = 5.00 Hz, 3H, CH_3–C–C), 2.19 (d, $J_{H,P1}$ = 5.00 Hz, 3H, CH_3–C–C), 2.20 (d, $J_{H,P}$ = 5.00 Hz, 3H, CH_3–C–CPh), 2.22 (d, $J_{H,P}$ = 5.00 Hz, 3H, CH_3–C–CPh), 3.44 (m, 2H, CH_2–O), 3.54 (m, 1H, C*H*–O), 7.29 (m, 2H, Ph), 7.46 (m, 6H, Ph), 7.53 (m, 2H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.81 (s, *C*H$_3$–C–C), 14.83 (s, *C*H$_3$–C–C), 15.84 (d, $J_{C,P}$ = 7.55 Hz, *C*H$_3$–C–CPh), 15.91 (d, $J_{C,P}$ = 8.81 Hz, *C*H$_3$–C–CPh), 22.72 (s, CH$_3$), 38.90 (s, CH$_2$), 64.60 (d, $J_{C,P1}$ = 13.84 Hz, CH$_2$–O), 73.08 (d, $J_{C,P2}$ = 13.84 Hz, CH–O), 125.98 (s, Ph), 126.22 (s, Ph), 128.50 (s, Ph), 128.66 (d, $J_{C,P1}$ = 7,55 Hz, C$_{ortho}$), 128.92 (d, $J_{C,P2}$ = 7.55 Hz, C$_{ortho}$), 137.22 (d, $J_{C,P1}$ = 17.61 Hz, Ph–*C*–P), 137.46 (s, *C*–P), 137.71 (d, $J_{C,P1}$ = 17.61 Hz, Ph–*C*–P), 138.11 (s, *C*–P), 143.15 (d, $J_{C,P2}$ = 15.09 Hz, CH$_3$–*C*–C), 143.86 (d, $J_{C,P2}$ = 16.36 Hz, CH$_3$–*C*–C–Ph), 144.06 (d, $J_{C,P1}$ = 18.87 Hz, CH$_3$–*C*–C), 144.30 (d, $J_{C,P1}$ = 16.36 Hz, CH$_3$–*C*–C–Ph). ^{31}P{^{1}H}

NMR (202 MHz, $CDCl_3$): δ 113.52 (d, P1, $J_{P1,P2}$ = 2.03 Hz), 121.17 (d, P2, $J_{P1,P2}$ = 2.03 Hz). MS (DCI, *m/z*) 461 (M + H^+, 100). HRMS (ES^+, *m/z*) calcd. for $C_{28}H_{31}O_2P_2$ (M + H^+) 461.1799, found 461.1831. Single crystals were obtained by slow evaporation of dichloromethane.

(–)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(pentane-2,4-dioxy)-2,2′-biphosphole, 4b. Obtained from (2*S*,4*S*)-(+)-pentanediol. Yellow solid. Yield: 71% (0.353 mg, 0.745 mmol). mp = 228 °C. $[\alpha]^{25}_D$ = – 317.0 (*c* 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.68 (d, $J_{H,H}$ = 6.16 Hz, 6H, C*H*$_3$), 1.20 (m, 2H, C*H*$_2$), 2.16 (d, $J_{H,P}$ = 6.16 Hz, 6H, C*H*$_3$–C–C), 2.20 (d, $J_{H,P}$ = 4.90 Hz, 6H, C*H*$_3$–C–CPh), 3.56 (m, 2H, C*H*–O), 7.25 (m, 2H, Ph), 7.41 (m, 4H, Ph), 7.52 (m, 4H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.82 (s, *C*H$_3$–C–CPh), 15.70 (d, $J_{C,P}$ = 7.09 Hz, *C*H$_3$–C–C), 22.74 (s, CH$_3$), 46.87 (s, CH$_2$), 73.71 (d, $J_{C,P}$ = 13.81 Hz, CH–O), 125.95 (s, Ph), 128.46 (s, Ph), 128.89 (d, $J_{C,P}$ = 10.39 Hz, C$_{ortho}$), 137.37 (dd, $J_{C,P}$ = 16.05 Hz, $J_{C,P}$ = 14.07 Hz, C–P), 137.63 (d, $J_{C,P}$ = 18.19 Hz, C$_{ipso}$), 143.06 (d, $J_{C,P}$ = 13.42 Hz, Ph–*C*–P), 144.07 (d, $J_{C,P}$ = 18.79 Hz, CH$_3$–*C*–C), 144.40 (dd, $J_{C,P}$ = 16.15 Hz, $J_{C,P}$ = 1.58 Hz CH$_3$–*C*–C–Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 113.67 (s). MS (DCI, *m/z*) 475 (M + H^+, 100%). HRMS (ES^+, *m/z*) calcd. for $C_{29}H_{33}O_2P_2$ (M + H^+) 475.1956, found 475.1956.

***S*[*R*$_p$,*R*$_p$,*R*$_c$,*R*$_c$]-(+)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(pentane-2,4-dioxy)-2,2′-biphosphole, 4b′.** Obtained from (2*R*,4*R*)-(–)-pentanediol. Yellow solid. Yield: 82% (0.468 mg, 0.861 mmol). mp = 223 °C. $[\alpha]^{25}_D$ = + 338.5 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.67 (d, $J_{H,H}$ = 6.20 Hz, 6H, C*H*$_3$), 1.21 (m, 2H, C*H*$_2$), 2.15 (d, $J_{H,P}$ = 6.20 Hz, 6H, C*H*$_3$–C–C), 2.20 (d, $J_{H,P}$ = 5.02 Hz, 6H, C*H*$_3$–C–CPh), 3.54 (m, 2H, C*H*–O), 7.25 (m, 2H, Ph), 7.41 (m, 4H, Ph), 7.51 (m, 4H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.86 (s, *C*H$_3$–C–CPh), 15.74 (d, $J_{C,P}$ = 7.15 Hz, *C*H$_3$–C–C), 22.75 (s, CH$_3$), 46.82 (m, CH$_2$), 73.72 (d, $J_{C,P}$ = 13.80 Hz, CH–O), 125.95 (s, Ph), 128.48 (s, Ph), 128.89 (d, $J_{C,P}$ = 10.38 Hz, C$_{ortho}$), 137.36 (d, $J_{C,P}$ = 15.92 Hz, *C*–P), 137.61 (d, $J_{C,P}$ = 18.28 Hz, C$_{ipso}$), 143.12 (d, $J_{C,P}$ = 13.23 Hz, Ph–*C*–P), 144.01 (d, $J_{C,P}$ = 18.80 Hz, CH$_3$–*C*–C), 144.45 (d, $J_{C,P}$ = 15.93 Hz, CH$_3$–*C*–C–Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 113.51 (s). MS (DCI, *m/z*) 475 (M + H^+, 100%). HRMS (ES^+, *m/z*) calcd. for $C_{29}H_{33}O_2P_2$ (M + H^+) 475.1956, found 475.1946. Single crystals were obtained by slow evaporation of dichloromethane.

(–)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(3-phenylpropane-1,3-dioxy)-2,2′-biphosphole, 4c. Obtained from (*S*)-(+)-1-phenyl-1,3-propanediol. Yellow solid. Yield: 86% (0.471 mg, 0.903 mmol). mp = 232 °C. $[\alpha]^{25}_D$ = –524.2 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (m, 1H, C*H*$_2$), 1.61 (m, 1H, C*H*$_2$), 2.04 (d, $J_{H,P2}$ = 4.95 Hz, 3H, C*H*$_3$–C–C), 2.20 (d, $J_{H,P1}$ = 4.91 Hz, 3H, C*H*$_3$–C–C), 2.23 (d, $J_{H,P2}$ = 5.55 Hz, 3H, C*H*$_3$–C–CPh), 2.25 (d, $J_{H,P1}$ = 5.15 Hz, 3H, C*H*$_3$–C–CPh), 3.50 (m, 2H, CH$_2$–O–P2), 4.45 (m, 1H, C*H*–O–P1), 6.95 (m, 7H, Ph), 7.02 (m, 3H, Ph), 7.30 (m, 1H, Ph), 7.50 (m, 4H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.56 (s, *C*H$_3$–C–C, P2), 14.85 (s, *C*H$_3$–C–C, P1), 15.94 (s, *C*H$_3$–C–CPh, P1), 16.00 (s, *C*H$_3$–C–CPh, P2), 41.08 (s, *C*H$_2$), 64.88 (d, $J_{C,P2}$ = 13.75 Hz, *C*H2–O), 77.30 (m, *C*H–O), 124.70 (s, Ph), 125.12 (s, Ph), 126.29 (s, Ph), 126.36 (s, Ph), 127.54 (s, Ph), 127.68 (s, Ph), 128.30 (s, Ph), 128.37 (s, Ph), 128.55 (s, Ph), 128.61 (s, Ph), 128.67 (s, Ph), 136.80 (d, $J_{C,P}$ = 17.61 Hz, C$_{ortho}$), 137.16 (d, $J_{C,P2}$ = 17.61 Hz, C–P2), 138.19 (d, $J_{C,P1}$ = 15.09 Hz, C–P1), 142.97 (s, C$_{ipso}$), 142.97 (s, Ph), 143.61 (d, $J_{C,P1}$ = 12.58 Hz, Ph–*C*–P1), 144.13 (d, $J_{C,P2}$ = 12.58 Hz, Ph–*C*–P2), 144.47 (d, $J_{C,P1}$ = 17.61 Hz, CH$_3$–*C*–C), 144.85 (d, $J_{C,P2}$ = 17.61 Hz, CH$_3$–*C*–C), 145.22 (d, $J_{C,P1}$ = 12.58 Hz, CH$_3$–*C*–C–Ph), 145.58 (d, $J_{C,P2}$ = 16.36 Hz, CH$_3$–*C*–C–Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 117.48 (d, P1, $J_{P1,P2}$ = 2.03 Hz), 121.10 (d, P2, $J_{P1,P2}$ = 2.03 Hz). MS (DCI, *m/z*) 523 (M + H^+, 100). HRMS (ES^+, *m/z*) calcd. for $C_{33}H_{33}O_2P_2$ (M + H^+) 523.1956, found 523.1931.

(+)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(3-phenylpropane-1,3-dioxy)-2,2′-biphosphole, 4c′. Obtained from (*R*)-(–)-1-phenyl-1,3-propanediol. Yellow solid. Yield: 86% (0.471 mg, 0.903 mmol). mp = 236 °C. $[\alpha]^{25}_D$ = + 526.8 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.37 (m, 1H, C*H*$_2$), 1.58 (m, 1H, C*H*$_2$), 2.00 (d, $J_{H,P2}$ = 5.00 Hz, 3H, C*H*$_3$–C–C), 2.16 (d, $J_{H,P2}$ = 5.00 Hz, 3H, C*H*$_3$–C–C), 2.21 (m, 6H, C*H*$_3$–C–CPh), 3.48 (m, 2H, C*H*$_2$–O–P2), 4.40 (m, 1H, C*H*–O–P1), 7.28 (m, 15H, Ph). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 117.56 (s, P1), 121.18 (s, P2).

(–)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(1,3-diphenylpropane-1,3-dioxy)-2,2′-biphosphole, 4d. Obtained from (1*S*,3*S*)-(–)-1,3-diphenylpropane-1,3-diol. Yellow solid. Yield: 85% (0.534 mg, 0.893 mmol). mp = 256 °C (decomposed). $[\alpha]^{25}_D$ = –278.5 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (m, 2H, C*H*$_2$), 2.06 (d, $J_{H,P}$ = 2.19 Hz, 6H, C*H*$_3$–C–C), 2.26 (d, $J_{H,P}$ = 2.19 Hz, 6H, C*H*$_3$–C–CPh), 4.54 (m, 2H, C*H*–O), 6.88 (m, 13H, Ph), 6.99 (m, 7H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.5 (s, *C*H$_3$–C–CPh), 15.99 (d, $J_{C,P}$ = 7.55 Hz, *C*H$_3$–C–C), 50.69 (s, *C*H$_2$), 78.2 (d, $J_{C,P}$ = 2.6 Hz, *C*H), 124.72 (s, Ph), 125.12 (s, Ph), 126.37 (s, Ph), 127.61 (s, Ph), 127.69 (s, Ph), 128.33 (d, $J_{C,P}$ = 11.32 Hz, C$_{ortho}$), 136.78 (m, C–P), 142.55 (s, C$_{ipso}$), 143.61 (d, $J_{C,P}$ = 12.58 Hz, Ph–*C*–P), 144.54 (d, $J_{C,P}$ = 17.61 Hz, CH$_3$–*C*–C), 145.69 (d, $J_{C,P}$ = 16.36 Hz, CH$_3$–*C*–C–Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 117.65 (s). MS (DCI, *m/z*) 599 (M + H^+, 100). HRMS (ES+, *m/z*) calcd. for $C_{39}H_{37}O_2P_2$ (M + H^+) 599.2269, found 599.2257.

(–)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(hexane-2,5-dioxy)-2,2′-biphosphole, 4e. Obtained from (2*S*,4*S*)-(+)-hexanediol. Yellow solid. Yield: 85% (0.436 mg, 0.893 mmol). mp = 229 °C. $[\alpha]^{25}_D$ = –357.8 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80 (d, $J_{H,H}$ = 10.00 Hz, 6H, C*H*$_3$), 1.02 (m, 2H, C*H*$_2$), 1.67 (m, 2H, C*H*$_2$), 2.20 (d, $J_{H,P}$ = 5.00 Hz, 6H, C*H*$_3$–C–C), 2.27 (d, $J_{H,P}$ = 5.00 Hz, 6H, C*H*$_3$–C–CPh), 3.72 (m, 2H, C*H*–O), 7.29 (m, 2H, Ph), 7.42 (m, 4H, Ph), 7.51 (m, 4H, Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.99 (s, *C*H$_3$–C–CPh), 15.99 (d, $J_{C,P}$ = 13.84 Hz, *C*H$_3$–C–C), 21.73 (d, $J_{C,P}$ = 2.51 Hz, *C*H$_3$), 27.46 (s, *C*H$_2$), 78.29 (d, $J_{C,P}$ = 13.84 Hz, *C*H–O), 125.91 (s, Ph), 128.53 (s, Ph), 128.73 (d, $J_{C,P}$ = 8.80 Hz, C$_{ortho}$), 137.57 (d, $J_{C,P}$ = 17.61 Hz, *C*–P), 140.38 (d, $J_{C,P}$ = 16.35 Hz, Ph–*C*–P), 142.23 (d, $J_{C,P}$ = 15.10 Hz, CH$_3$–*C*–C), 142.81 (d, $J_{C,P}$ = 16.35 Hz, CH$_3$–*C*–C–Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 104.25 (s). MS (DCI, *m/z*) 489 (M + H^+, 100).

(+)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(2,7-dimethyloctane-3,6-dioxy)-2,2′-biphosphole, 4f. Obtained from (3*S*,6*S*)-2,7-dimethyl-3,6-octanediol. Orange solid. Yield: 83% (0.474 mg, 0.872 mmol). mp = 203 °C. $[\alpha]^{25}_D$ = + 202.0 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.40 (d, $J_{H,H}$ = 5.00 Hz, 6H, C*H*$_3$), 0.46 (d, $J_{H,H}$ = 5.00 Hz, 6H, C*H*$_3$), 0.95 (d, $J_{H,H}$ = 5.00 Hz, 4H,

CH_2), 1.12 (m, 2H, C*H*), 2.21 (d, $J_{H,P}$ = 10.00 Hz, 6H, CH_3–C–C), 2.34 (d, $J_{H,P}$ = 10.00 Hz, 6H, CH_3–C–CPh), 3.05 (m, 2H, C*H*–O), 7.48 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.91 (s, CH_3–C–C), 16.09 (d, $J_{C,P}$ = 15.09 Hz, CH_3–C–CPh), 17.48 (s, CH_2), 18.62 (s, CH_3), 18.76 (s, CH_2), 19.57 (s, CH_3), 21.04 (s, $CH(CH_3)_2$), 89.98 (d, $J_{C,P}$ = 15.09 Hz, *C*H–O), 125.85 (s, Ph), 125.87 (s, Ph), 128.44 (s, Ph), 128.76 (d, $J_{C,P}$ = 8.80 Hz, C–P), 137.56 (d, $J_{C,P}$ = 17.61 Hz, Ph–*C*–P), 138.88 (d, $J_{C,P}$ = 16.36 Hz, CH_3–*C*–C), 142.66 (d, $J_{C,P}$ = 16.36 Hz, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 100.96 (s). MS (DCI, *m*/*z*) 545 (M + H^+, 100).

(+)-3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(2,3-*O*-isopropylidene-2,3-dihydroxybutane-1,4-dioxy)-2,2′-biphosphole, 4g. Obtained from (+)-(2*R*,3*R*)-2,3-*O*-isopropylidene-L-threitol. Yellow solid. Yield: 81% (0.453 mg, 0.851 mmol). mp = 236 °C. $[\alpha]^{25}_D$ = + 246.7 (*c* 0.3, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 6H, C*H*$_3$), 2.18 (d, $J_{H,P}$ = 5.00 Hz, 6H, C*H*$_3$–C–C), 2.22 (d, $J_{H,P}$ = 5.00 Hz, 6H, C*H*$_3$–C–CPh), 3.53 (m, 2H, C*H*$_2$), 3.62 (m, 2H, C*H*$_2$), 3.92 (m, 2H, C*H*–O), 7.30 (m, 2H, Ph), 7.43 (m, 4H, Ph), 7.52 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.93 (s, CH_3–C–CPh), 16.14 (d, $J_{C,P}$ = 12.50 Hz, CH_3–C–C), 26.59 (s, CH_3), 69.86 (d, $J_{C,P}$ = 15.09 Hz, CH_2), 75.89 (s, *C*H–O), 108.46 (s, $C(CH_3)_2$), 126.43 (s, Ph), 128.64 (s, Ph), 128.95 (d, $J_{C,P}$ = 8.80 Hz, C_{ortho}), 136.90 (d, $J_{C,P}$ = 17.61 Hz, Ph–*C*–P), 137.88 (dd, $J_{C,P}$ = 16.36 Hz, $J_{C,P}$ = 16.36 Hz, *C*–P), 142.33 (d, $J_{C,P}$ = 15.09 Hz, CH_3–*C*–C), 144.25 (d, $J_{C,P}$ = 15.09 Hz, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 117.12 (s). MS (DCI, *m*/*z*) 538 (M + NH_4^+, 100).

General procedure for the preparation of [Rh(COD)(Ligand)]TfMS

To a solution of 51 mg of $[Rh(COD)_2]$TfMS (0.11 mmol) in CH_2Cl_2 (5 mL) was added a solution of ligand **4** (0.11 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h and filtered through a pad of Celite. The solvent was removed under vacuum then the residue was washed with Et_2O (3 × 10 mL) and dried under vacuum.

3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(butane-1,3-dioxy)-2,2′-biphosphole-(1,5-cyclooctadiene) rhodium(I) trifluoromethansulfonate, 5a. Red solid (yield = 77%). ^1H NMR (200 MHz, $CDCl_3$): δ 1.21 (d, $J_{H,H}$ = 5.00 Hz, 3H, C*H*$_3$), 1.60 (m, 2H, C*H*$_2$), 2.06–2.38 (m, 14H, C*H*$_3$–C–C and CH_2, COD), 2.43–2.63 (m, 6H, CH_2, COD), 3.80 (m, 3H, C*H*$_2$–O and C*H*–O), 4.00 (br, 2H, CH, COD), 5.65 (br, 2H, CH, COD), 7.29–7.49 (m, 10H, Ph). ^{31}P NMR (81.015 MHz, $CDCl_3$): δ 154.44 (dd, $J_{Rh,P1}$ = 158.3 Hz, $J_{P1,P2}$ = 28.3 Hz, P1), 158.50 (dd, $J_{Rh,P2}$ = 158.9 Hz, $J_{P1,P2}$ = 27.7 Hz, P2). MS (FAB, MNBA matrix) *m*/*z* = 671 $[M–SO_3CF_3]^+$.

3,3′,4,4′-Tetramethyl-5,5′-diphenyl-1,1′-(1,3-diphenylpropane-1,3-dioxy)-2,2′-biphosphole-(1,5-cyclooctadiene) rhodium(I) trifluoromethansulfonate, 5d. Red solid (yield = 85%). ^{31}P NMR (81.015 MHz, $CDCl_3$): δ 130.87 (d, J_{PRh} = 161.5 Hz, P1), 133.49 (d, J_{PRh} = 171.5 Hz, P2). MS (FAB, MNBA matrix) *m*/*z* = 809 $[M–SO_3CF_3]^+$.

Typical hydrogenation procedure

$[Rh(COD)_2]$TfMS (10^{-2} mmol) and ligand **4** (1.4 × 10^{-2} mmol, 1,4 eq.) were introduced in a Schlenk tube under argon, with the solvent (CH_2Cl_2 or MeOH, 4 mL). The reaction mixture was stirred for 2 h to obtain the corresponding rhodium complex. The substrate (1.5 mmol, S/C = 150) was then added. After 10 min, this mixture was transferred through a cannula into the reactor. The Schlenk tube was washed with solvent (1 mL) and the solution was also transferred into the reactor. The clave was then pressurised with hydrogen, and magnetically stirred. When the reaction was over, the solvent was removed under reduced pressure. The ^1H NMR spectrum allowed us to determine the extent of the conversion. The residue was heated on an oil bath at 90 °C and the product was distilled under vacuum. 80 μL of product diluted into 1 mL of CH_2Cl_2 was passed over GC equipped with a chiral column β-DEX 225 to give the enantiomeric excess. Retention times of the two enantiomers are 32.3 min (*S*) and 33.5 min (*R*) in isotherm condition (90 °C).

^1H NMR (250 MHz, $CDCl_3$): δ 1.15 (d, 3H, CH_3), 2.33 (dd, 1H, CH_2), 2.67 (dd, 1H, CH_2), 2.85 (m, 1H, CH), 3.61 (s, 3H, $C(O)OCH_3$), 3.62 (s, 3H, $C(O)OCH_3$).

X-Ray crystallographic studies

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer (**4a**) or a Stoe IPDS diffractometer (**4b′**). Data were collected using monochromatic Mo Kα radiation (λ = 0.71073).

The structures were solved by direct methods (SIR97[29]) and refined by least-squares procedures on F^2 using SHELXL-97.[30] All H atoms were introduced in calculation in idealised positions and treated as riding on their parent C atoms. The drawing of the molecules was realised with the help of ORTEP32.[31]

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21 In phospholes, the inversion barrier for the pyramidal phosphorus is reduced, relative to that in phosphanes, as a result of the increase in aromatic character of the phosphole in the transition state. The activation barrier to phosphorus inversion in 2,2′-biphosphole is measured to be only 16.5 kcal mol^{-1} leading to phosphorus inversion at –60 °C, see ref. 9,13.
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