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Asymmetric Hydrovinylation and Hydrogenation with Metal Complexes of C_3-Symmetric Tris-Binaphthyl Monophosphites

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Neutral allyl–palladium complexes stabilised by bulky tris-binaphthyl monophosphite ligands have been prepared and fully characterised in solution by NMR spectroscopy, which evidenced a dynamic equilibrium between two diastereomeric species. The new allyl–palladium phosphite complexes have been evaluated as catalytic precursors in the asymmetric hydrovinylation of styrene; they show moderate activity and good to excellent chemo- and enantioselectivity depending on the substituent at the ligand 2′-binaphthyl position. Remarkably, the palladium complex bearing the ligand with an adamantyl ester substituent led to 92 % *ee* toward (*R*)-3-phenyl-1-butene, which suggests that the ester functionality might provide a secondary hemilabile interaction with the metal, thus favouring the enantioselectivity control. Rhodium(I) complexes formed in situ with the same ligands were further applied in the hydrogenation of dimethyl itaconate, but gave limited activity. The best enantioselectivity (62 %) was achieved with the same ligand that contained the adamantyl ester substituent.

1. Introduction

Ligands that contain significantly different chemical functions such as hard and soft donors (often called hemilabile) have found increasing use in catalysis[1] owing to the possibility of generating accessible coordination vacancies or protecting active catalytic sites through a dynamic "on/off" chelating effect with the metal centre (Figure 1). In addition, they can also play important roles in the stabilisation of highly unsaturated intermediates, in the interactions with reactive polar species or even in the activation of substrates. Chiral hemilabile ligands that have this bifunctional character have been demonstrated to advantageously influence the catalytic activity and selectivity in several asymmetric reactions, such as hydrovinylation[2–4] and hydrogenation of alkenes[5–11] among others.[12–15]

Catalytic hydrovinylation has emerged as an important heterodimerisation reaction between ethylene and an activated olefin, often with the generation of a new stereogenic carbon atom.[16–19] This reaction, when applied to vinylarenes, is of great interest for enantioselective synthesis, because it provides a short route to enantiopure 2-arylpropionic acids.[20,21] Furthermore, it has recently been employed in the stereoselective construction of benzylic all-carbon quaternary stereocentres,[22–24] a structural motif that is present in several pharmacologically relevant compounds. The major drawbacks that concern hydrovinylation of vinylarene substrates are the subsequent isomerisation of 3-aryl-1-butenes to more stable 2-aryl-2-butenes, and the formation of homodimers as side products (Figure 2). Therefore, the control of the chemo- and enantioselectivity are both crucial aspects and the main challenges to this catalytic process.[16–19]

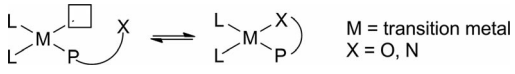

Figure 1. Dynamic "on/off" chelating effect between metal and P-heterodonor ligand.

Although some work on catalytic hydrovinylation has been carried out with cobalt[25,26] and ruthenium[27] complexes, nickel(II)[28–33] and palladium(II)[34–38] organometallic precursors modified with P-donor ligands are the most representative systems and they have been extensively studied. Hydrovinylation constitutes a paradigmatic example of a catalytic reaction in which the use of chiral monophosphorus ligands (and those that contain substituents capable of secondary interactions) has been demonstrated to be crucial,[2–4,31] whereas chelating diphosphines and

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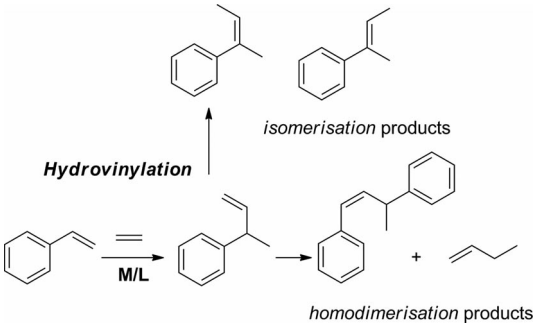


Figure 2. Possible products in the asymmetric hydrovinylation of styrene.

other bidentate ligands have been shown to inhibit the reaction by using nickel and palladium catalysts.[17,39–41] Early studies on asymmetric hydrovinylation were performed using Hayashi's monodentate phosphine (MOP)[42] in the nickel-catalysed hydrovinylation of several vinylarenes[3,28,29,40] and norbornene[43] (with *ee* values up to 80%). Carbohydrate-derived phosphinites also produced active and selective Ni catalysts for the hydrovinylation of vinylarene substrates (up to 81% *ee*).[43] However, the best results, in terms of enantioselectivity, have been obtained with binaphthyl-type phosphoramidite ligands, the nickel complexes of which afforded chemoselectivities to 3-aryl-1-butenes in the range of 99%, and enantiomeric excesses higher than 90%.[20,21,23,30,33,44–49] Recently, allyl–palladium complexes that contain several types of monodentate *P*-chiral phosphines,[36,50–52] phosphinite[34] and binaphthyl-based diamidophosphite[53] have also achieved high chemoslectivities and remarkable enantioselectivities in the hydrovinylation of styrene (Figure 3).

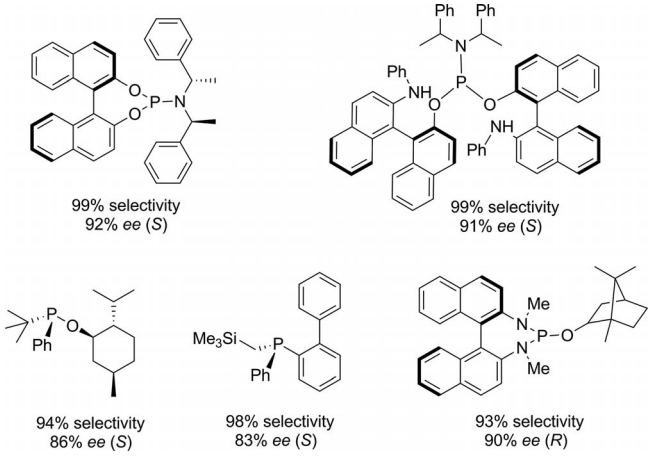


Figure 3. Examples of chiral phosphorus ligands used in hydrovinylation of styrene.

The chiral binaphthyl fragment is one of the most ubiquitous moieties in successful ligands for asymmetric catalysis.[54] Recently, Reetz et al.[55] and Pereira et al.[56,57] have independently reported the synthesis of tris-binaphthyl monophosphites with helical triskelion structures (Figure 4), as well as their first applications as ligands in asymmetric catalysis. The C_3-symmetric chiral monophosphites **1**–**4** have been used in Rh-catalysed hydroformylation of substituted aryl olefins,[57] thus leading to active and regioselective systems, although they present low enantioselectivity. In parallel, the monophosphite ligands **5** and **6** have been applied in the Rh-catalysed hydrogenation of homoallylic alcohols, a special class of olefins for which the sterically hindered adamantanoyl-derived **5** led to remarkable enantioselectivities (up to 98% *ee*).[55] However, the performance of this type of ligand in the hydrogenation of benchmark olefins has not been reported. Additionally, by taking into account the precedents of successful ligands for asymmetric hydrovinylation, phosphite **1**–**5** arise a promising candidates for this reaction. Therefore, herein we describe the preparation of new allyl–palladium complexes that contain this group of C_3-symmetric tris-binaphthyl monophosphite ligands, as well as their application in the asymmetric hydrovinylation of styrene. Furthermore, we also report the asymmetric hydrogenation of dimethyl itaconate catalysed by rhodium(I) complexes prepared in situ from the same ligands.

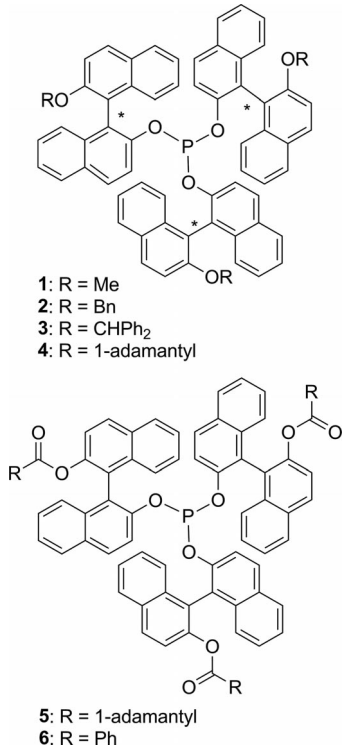


Figure 4. C_3-symmetric tris-binaphthyl monophosphite ligands.

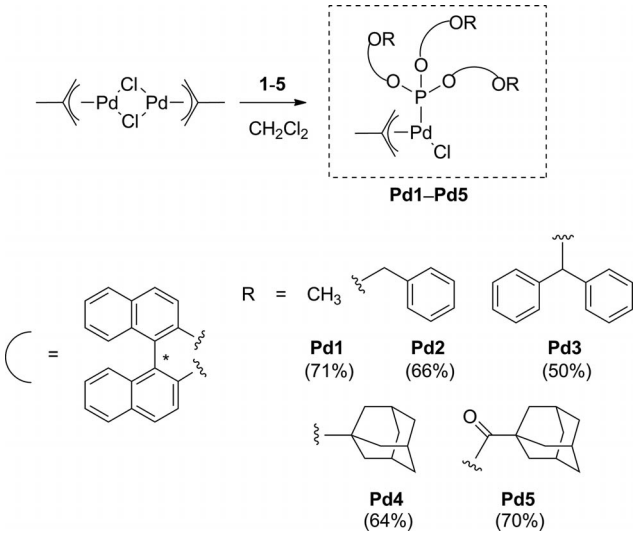
2. Results and Discussion

2.1 Synthesis of Allyl–Palladium/Monophosphite Complexes

The monophosphite ligands **1**–**5** were synthesised from the corresponding mono-protected 1,1′-bi-2-naphthol (BINOL) derivatives and PCl_3 in basic medium following the previously described methods.[55–57] The neutral allylic complexes were prepared according to a standard procedure[52] by treatment of the 2-methylallyl-chloropalladium

dimer (1 equiv.) with ligands **1**–**5** (2 equiv.) at 25 °C under a N_2 atmosphere (Scheme 1). After observing the complete disappearance of the ^{31}P NMR spectroscopic free ligand signal in the range of δ = 130–136 ppm, the solvent was removed under vacuum and the resulting pale brown foam was suspended in *n*-pentane. Finally, the solids were filtered, washed with *n*-pentane and properly dried under vacuum. Complexes **Pd1**, **Pd2**, **Pd3**, **Pd4** and **Pd5** were obtained in moderate to good yields (50–71%) as air-stable white solids and were characterised by NMR spectroscopy techniques.

For each complex, the ^{31}P NMR spectra showed a pair of major and minor sharp signals with close chemical shifts, around δ = 120 ppm, clearly indicating the presence of an unequal mixture of two interchanging isomers in solution, (R_{Pd}) and (S_{Pd}),[36,58] the ratio of which ranges from 1:1.5 (**Pd3**) to 1:4 (**Pd1**). Selected spectroscopic data is presented in Table 1, whereas full details on NMR spectroscopic characterisation and isomeric ratios can be found in the Experimental Section.



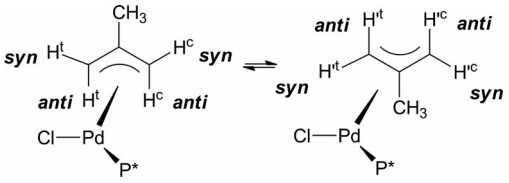
Scheme 1. Preparation of complexes **Pd1**–**Pd5**.

Table 1. Selected NMR spectroscopic data of **Pd1**–**Pd5**, in $CDCl_3$, at 25 °C.[a]

Complex %	^{31}P NMR δ [ppm]	^{1}H NMR δ [ppm] (multiplicity, *J* [Hz], integral)					
		H^c *anti*	allyl–CH_3	H^c *syn*	H^t *anti**	H^t *syn**	OR**
Pd1							
Major 80	121.0	0.61 (s, 1H)	1.01 (s, 3H)	2.09 (s, 1H)	2.54 (d, 17.0, 1H)	3.89 (d, 9.5, 1H)	3.44 (s, 3H)
Minor 20	121.0	1.45 (s, 1H)	1.04 (s, 3H)	2.51 (s, 1H)	3.02 (d, 16.5, 1H)	4.12 (d, 9.0, 1H)	3.58 (s, 3H)
Pd2							
Major 78	121.9	0.48 (s, 1H)	0.65 (s, 3H)	2.13 (s, 1 H)	2.51 (d, 17.0, 1H)	3.85 (d, 10.0, 1H)	4.68 (d, 12.4, 1H) 4.72 (d, 12.4, 1H)
Minor 22	121.6	1.19 (s, 1H)	0.94 (s, 3H)	2.31 (s, 1H)	2.82 (d, 16.4, 1H)	4.04 (d, 11.0, 1H)	4.70 (d, 12.4, 1H) 4.76 (d, 12.4, 1H)
Pd3							
Major 60	120.2	0.51 (s, 1H)	0.99 (s, 3H)	1.87 (s, 1H)	2.45 (d, 17.0, 1H)	3.87 (d, 9.5, 1H)	6.11 (s, 1H)
Minor 40	119.4	1.16 (s, 1H)	1.05 (s, 3H)	2.28 (s, 1H)	2.72 (d, 17.0, 1H)	4.05 (d, 10.0, 1H)	6.03 (s, 1H)
Pd4							
Major 68	118.2	0.50 (s, 1H)	0.81–1.88 ov. (s, 3H)	0.81–1.88 ov. (s, 1H)	2.42 (d, 17.2, 1H)	3.82 (d, 12.0, 1H)	0.81–1.88 ov. (m, 45H)
Minor 32	118.9	0.81–1.88 ov. (s, 1H)		2.13 (s, 1H)	3.00 (d, 16.4, 1H)	4.03 (d, 10.4, 1H)	
Pd5							
Major 71	118.0	0.85 (s, 1H)	1.14 (s, 3H)	1.23–1.78 ov. (s, 1H)	1.87 (d, 16.0, 1H)	3.86 (d, 12.0, 1H)	1.23–1.78 ov. (m, 45H)
Minor 29	118.9	1.23–1.78 ov. (s, 1H)	1.23–1.78 ov. (s, 3H)		3.13 (d, 16.0, 1H)	4.29 (d, 12.0, 1H)	

[a] Multiplicity: s singlet, d doublet; m multiplet, br. s broad signal, ov. overlapped signal. *$J_{P,H}$ coupling constants [Hz] are shown in parentheses after the multiplicity. **$J_{H,H}$ coupling constants [Hz] are shown in parentheses after the multiplicity.

Phase-sensitive $^1H,^1H$ NOESY experiments showed that, in analogy to related complexes,[36,37,50] both isomers interchange by the apparent allyl pseudorotation and the η^3–η^1–η^3 allylic shift mechanisms; and in the latter case, the allyl group opens at the carbon atom located in a *trans* position relative to the phosphite ligand (Scheme 2).



Scheme 2. Pseudorotation on the 2-methylallyl group.

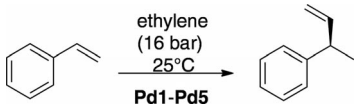
The ^1H NMR spectra showed that terminal allyl protons in a *trans* position relative to the phosphorus atom, H^t_{syn} and H^t_{anti}, appear as doublets and occur at higher chemical-shift values than those in the *cis*-relative position, H^c_{syn} and H^c_{anti}. With respect to the nonaromatic protons, it is worth highlighting the significantly lower chemical-shift values of the methyl group (δ = 0.65–1.14 ppm) and the *anti*-*cis*-protons (δ = 0.48–1.45 ppm) of the allyl moieties (Table 1) when compared with similar allyl complexes.[36,37,50] This fact might be due to the effect of the close aromatic rings of the phosphite ligand in a crowded environment. Furthermore, the benzylic protons in **Pd2** are diastereotopic, as evidenced by two different signals coupled to each other with typical second-order effects for each major and minor species.[52]

2.2 Asymmetric Hydrovinylation of Styrene with Allyl–Palladium/Monophosphite Catalysts

The neutral allylic palladium complexes **Pd1**–**Pd5** described above were evaluated as catalytic precursors in styrene hydrovinylation. The activation of the precatalysts was carried out by chloride abstraction with $AgBF_4$ in dichloromethane in the presence of styrene to stabilise the cationic Pd species.[36,50] After filtration of the AgCl formed, the solution was introduced into an autoclave, which was immediately pressurised with 16 bar of ethylene for 6 or 24 h. The reaction was analysed by GC, and the results are listed in Table 2.

The results presented in Table 2 clearly show that catalytic activity is significantly dependent on the ligand OR substituent, with **Pd5** being the most active catalytic system (TOF = 117 h^{-1}) (Table 2, entry 8) and **Pd4** the less active (TOF = 6 h^{-1}) (Table 2, entries 6 and 7). It is worth mentioning that all catalytic systems showed high chemoselectivity (>90%) towards 3-phenyl-1-butene. However, when higher conversions were achieved, the isomerisation to 3-phenyl-2-butenes increased (Table 2, entries 2, 3 and 6, 7). A remarkable fact about these new palladium catalysts is the lack of styrene dimerisation, possibly due to the bulkiness of the ligand, which might preclude the coordination of a second styrene molecule to the Pd(η^3-styryl) intermediate.[36]

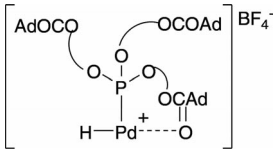
Table 2. Catalytic results with **Pd1**–**Pd5** in hydrovinylation of styrene.[a]



Entry	Precursor[b]	Conv. [%][c]	3-Ph-1-butene [%][d]	TOF [h^{-1}][e]	*ee* [%]
1[f]	(*S*,*S*,*S*)-**Pd1**	7.5	97.6	25	39 (*R*)
2	(*S*,*S*,*S*)-**Pd1**	14.8	95.6	25	39 (*R*)
3[g]	(*S*,*S*,*S*)-**Pd1**	57.2	73.0	24	40 (*R*)
4	(*S*,*S*,*S*)-**Pd2**	30.5	92.6	51	71 (*R*)
5[f]	(*R*,*R*,*R*)-**Pd3**	7.2	98.6	24	26 (*S*)
6	(*S*,*S*,*S*)-**Pd4**	3.5	97.8	6	–
7[g]	(*S*,*S*,*S*)-**Pd4**	13.9	91.1	6	62 (*R*)
8	(*S*,*S*,*S*)-**Pd5**	70.0	85.4	117	92 (*R*)

[a] Reaction conditions (unless otherwise stated): CH_2Cl_2 (15 mL), Pd/styrene ratio: 1:1000; T = 25 °C, $P_{ethylene}$ = 16 bar, t = 6 h. [b] (*R*) and (*S*) refer to the binaphthyl configuration. [c] Styrene converted. [d] Percentage of 3-phenyl-1-butene in the total amount of codimers (see Figure 2). [e] Average turnover frequency (TOF) after 6 h reaction. [f] Pd/styrene ratio: 1:2000. [g] After 24 h reaction. The quantitative distribution of products and their enantiomeric excesses were determined by GC analysis with 30 m Agilent HP5 and 30 m Chiraldex DM columns.

The enantioselectivity increased in the order **Pd3** < **Pd1** < **Pd4** < **Pd2** < **Pd5**, which does not match with the increasing bulkiness of the OR substituent at the phosphite ligand. Whereas the enantioselectivities obtained with **Pd4** (62% *ee*) and **Pd2** (71% *ee*) can be considered moderate, the result obtained with **Pd5** (92% *ee*) can be regarded as one of the best reported so far with palladium complexes in the hydrovinylation of styrene.[16–18] These results suggest that the adamantyl ester group at the ligand is the key feature that increases the stability of C_3-symmetric helical structures[55] and/or might favour secondary interactions with palladium, thereby increasing the enantiodiscrimination (Scheme 3). However, no experimental evidence of this interaction could be obtained since ^{31}P and ^1H NMR spectra of solutions of the precursors in $CDCl_3$ after the chloride abstraction showed only broad signals slightly shifted from those of the neutral precursors. The limited stability of these solutions precluded us from carrying out the ^{13}C NMR spectra.

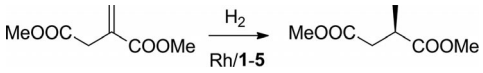


Scheme 3. A proposal for Pd–carbonyl secondary interactions.

2.3 Asymmetric Hydrogenation of Dimethyl Itaconate with Rhodium(I)/Monophosphite Catalysts

The screening of monophosphite ligands was further performed in the rhodium-catalysed hydrogenation of dimethyl

Table 3. Catalytic asymmetric hydrogenation of dimethyl itaconate.[a]



Entry	Precursor	Ligand[b]	P(H_2) [bar]	*t* [h]	Conversion [%]	TOF [h^{-1}]	*ee* [%]
1	[Rh(cod)$_2$]BF_4	(*S*,*S*,*S*)-**1**	10	48	98	2.0	40 (*S*)
2	[Rh(cod)$_2$]BF_4	(*S*,*S*,*S*)-**2**	10	48	99	2.1	50 (*S*)
3	[Rh(cod)$_2$]BF_4	(*R*,*R*,*R*)-**3**	10	48	17	0.4	n.d.[c]
4[d]	[Rh(cod)$_2$]OTf	(*S*,*S*,*S*)-**4**	10	48	20	0.2	10 (*S*)
5[d]	[Rh(cod)$_2$]OTf	(*S*,*S*,*S*)-**4**	2	48	5	0.1	31 (*S*)
6[d]	[Rh(cod)$_2$]OTf	(*S*,*S*,*S*)-**5**	10	24	99	2.1	20 (*R*)
7[d]	[Rh(cod)$_2$]OTf	(*S*,*S*,*S*)-**5**	2	48	87	0.9	62 (*R*)

[a] Reaction conditions (unless otherwise stated): CH_2Cl_2 (4 mL), Rh/dimethyl itaconate ratio: 1:100, ligand/Rh ratio: 2:1, *T* = 25 °C. [b] (*R*) and (*S*) refer to the binaphthyl configuration. [c] n.d.: not determined. [d] Rh/dimethyl itaconate ratio: 1:50.

itaconate. In a standard procedure, the catalysts, generated in situ by reaction of [Rh(cod)$_2$]BF_4 (cod = cyclooctadiene) or [Rh(cod)$_2$]OTf and ligands **1**–**5**, in dry CH_2Cl_2, were placed in a stainless-steel autoclave. Then, a solution of dimethyl itaconate was added and the autoclave was filled with the desired hydrogen pressure. The catalytic reactions were monitored by GC analysis, and results are presented in Table 3.

The rhodium(I)/monophosphite complexes led, in general, to low activities (TOF ≤ 2 h^{-1}), thus achieving only moderate to low enantioselectivities depending on the OR substituent at the ligand. As in the case of the hydrovinylation reaction, the best enantioselectivity was achieved with ligand (*S*,*S*,*S*)-**5** [62% (*R*)], although the result is still far from that achieved with the same catalytic system in the hydrogenation of homoallylic alcohols (up to 98%)[55] or other monodentate ligands for the hydrogenation of a variety of olefins.[59–64]

To gain some insight in the active catalytic species, ^{31}P NMR spectroscopic studies were carried out. By using equimolar amounts of [Rh(cod)$_2$]OTf and monophosphites **1**–**5** in $CDCl_3$ at 25 °C, the spectra showed in all cases a doublet in the range δ = 101–108 ppm, with $J(^{103}Rh,^{31}P)$ = 260–268 Hz corresponding to a single phosphorus species. When a twofold excess amount of ligand was used, the ^{31}P NMR spectra revealed a 1:1 ratio between the same signal and a singlet in the range δ = 131–134 ppm, which is typical of the noncoordinated phosphite ligand, as illustrated in Figure 5 for monophosphite ligand **5**. These results indicate that only one bulky ligand can coordinate to the rhodium precursor as proposed by Reetz et al.[55] The ^{31}P NMR spectroscopic chemical shifts and coupling constants $J(^{103}Rh,^{31}P)$ are typical of [Rh(cod)(phosphite)]OTf-type complexes.[55] Furthermore, by using monophosphite ligand **2** in a Rh/ligand ratio 1:1, the ^{1}H and ^{13}C NMR spectra of the complex in solution showed one single signal at δ = 4.69 ppm and one single signal at δ = 70.2 ppm, which is characteristic of benzyloxy protons and carbon, respectively, thereby suggesting that the Rh/monophosphite complex has a monodentate nature with no significant hemilabile interaction, at least in the case of ligand **2**.

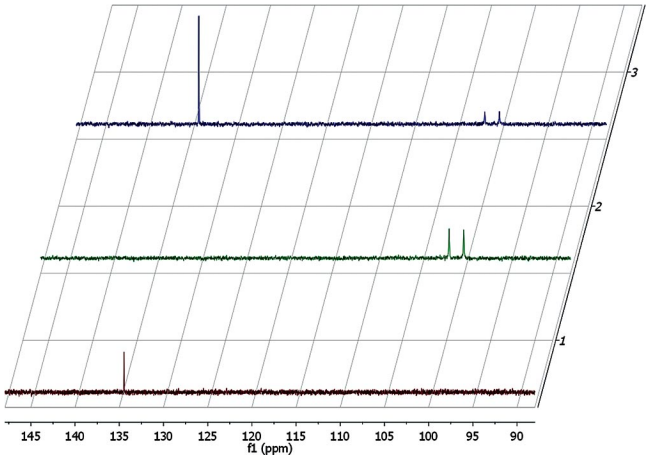


Figure 5. ^{31}P NMR spectra in $CDCl_3$ at 25 °C for (1) monophosphite **5**; (2) complex [Rh(cod)(**5**)]OTf (Rh/ligand ratio: 1:1); and (3) equimolar mixture of monophosphite **5** and the complex [Rh(cod)(**5**)]OTf (Rh/ligand ratio: 1:2).

3. Conclusion

We have developed a new family of five allyl–palladium complexes that contain tris-binaphthyl monophosphite ligands in good yields. Their NMR spectra evidenced the formation of an unequal mixture of two interchanging isomers that result from (*R*) and (*S*) stereochemistry at the palladium atom. With regard to their application as precatalysts in the asymmetric hydrovinylation of styrene, a significant dependence on the OR substituents at the ligand 2′-binaphthyl position was observed. All the systems presented chemoselectivities higher than 90% towards 3-phenyl-1-butene without the formation of styrene homodimerisation products and moderate formation of isomerisation products at moderate conversions. Whereas the palladium complexes bearing monophosphite ligands with methoxy, benzyloxy and 1-adamantyloxy substituents at the 2′-binaphthyl position led to moderate enantioselectivities (40–71% *ee*), the complex that contained an adamantyl ester derived monophosphite produced a remarkable enantiomeric excess of 92% toward (*R*)-3-phenyl-1-butene, which

is among the highest obtained with palladium complexes, and to the best of our knowledge, the highest *ee* achieved with a phosphite ligand in the asymmetric hydrovinylation of styrene.

Despite the excellent results reported with the C_3-monophosphite ligand that contained an adamantyl ester substituent in Rh-catalysed hydrogenation of homoallylic alcohols,[55] this family of ligands proved to be less effective for the hydrogenation of dimethyl itaconate as a model substrate, which suggests that the structure of the alkene is a crucial factor for enantiodiscrimination using this type of rhodium bulky monophosphite catalysts.

Remarkably, both in the hydrovinylation and hydrogenation reactions, the catalytic species contain only one phosphite ligand coordinated to the metal. Furthermore, the best enantioselectivities were obtained with phosphite **5**, which bears an ester group, thus pointing towards a secondary interaction with the carbonyl group. This interaction apparently is not provided by the ether derivatives. Therefore, this family of C_3-symmetric P-O-tris-binaphthyl monophosphites is adaptable to the requirements of different metal intermediates, thereby widening the scope of transition-metal-catalysed asymmetric reactions in which they can be applied.[65–67]

Experimental Section

General: All compounds were manipulated under a nitrogen or argon atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using the following spectrometers: Varian XL-500, Mer-400 MHz, Varian Inova 300, Bruker DRX-250 and Bruker Avance 400, using $CDCl_3$ as solvent at 25 °C. To assign the allylic ^{13}C and ^{1}H NMR spectra, the terms *cis* and *trans* reflect the position with respect to the phosphite ligand in the square-planar complex. GC analysis for hydrovinylation of styrene was performed with an Agilent HP5 (30 m long, 0.32 mm) and Astec Chiraldex DM (25 m long, 0.25 mm) columns with helium as a carrier gas. GC analysis for hydrogenation of dimethyl itaconate was carried out with Agilent-7820-A and Agilent-6890 apparatuses equipped, respectively, with an HP-5 capillary column (30 m × 0.32 mm) and a β-cyclodextrin capillary column (Supelco β-Dex120, 30 m × 0.25 mm), with nitrogen and helium as a carrier gas, both with flame ionisation detectors.

Synthesis and Characterisation of Allyl–Palladium/Monophosphite Complexes

Chloro(η^3-2-Me-allyl){tris[(*R*)-2′-methoxy-1,1′-binaphthyl-2-yl]-phosphite}palladium(II) (Pd1): [{PdCl(η^3-2-Me-allyl)}$_2$] (39.3 mg, 0.1 mmol) and tris[(*R*)-2′-methoxy-1,1′-binaphthalene-2-yl]phosphite (**1**) (194.9 mg, 0.21 mmol) were dissolved in dichloromethane (10 mL), and the yellow solution was stirred for 1 h. The solvent was removed under vacuum and the pale brown foam was suspended in pentane. The fine solid obtained was filtered, washed with pentane and dried under vacuum, yield 160 mg (71%). Isomer ratio observed in solution 4:1. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 121.0 (major), 121.0 (minor) ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.61 major (s, 1 H, *anti-cis*-C*H*); 1.01 major, 1.04 minor (s, 3 H, allyl-CH_3); 1.45 minor (s, 1 H, *anti-cis*-C*H*); 2.09 major (s, 1 H, *syn-cis*-C*H*); 2.51 minor (s, 1 H, *syn-cis*-C*H*); 2.54 major (d, $J_{P,H}$ = 17 Hz, 1 H, *anti-trans*-C*H*); 3.02 minor (d, $J_{P,H}$ = 16.5 Hz, 1 H, *anti-trans*-C*H*); 3.44 major (s, 3 H, OCH_3), 3.58 minor (s, 3 H, OCH_3); 3.89 major (d, $J_{P,H}$ = 9.5 Hz, 1 H, *syn-trans*-C*H*); 4.12 minor (d, $J_{P,H}$ = 9 Hz, 1 H, *syn-trans*-C*H*); 6.82–7.97 (m, 36 H, Ar) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ = 122.0 major, 22.1 minor (s, allyl-CH_3); 56.0 major, 56.3 minor (s, OCH_3); 57.4 minor (s, *cis*-CH_2); 58.2 major (s, *cis*-CH_2); 78.3 major (d, $J_{P,C}$ = 52 Hz, *trans*-CH_2); 79.6 minor (d, $J_{P,C}$ = 51 Hz, *trans*-CH_2); 117.7 (s, *C* Binaph); 120–130 (m, *C*H, Binaph); 133.5, 133.7 (s, *C*, Binaph); 146.9 (s, *C*OP); 155.0 (s, *C*OMe) ppm. $C_{67}H_{52}ClO_6PPd$: calcd. C 71.47, H 4.65; found C 69.57, H 4.77.

Chloro(η^3-2-Me-allyl){tris[(*R*)-2′-(benzyloxy)-1,1′-binaphthyl-2-yl]phosphite}palladium(II) (Pd2): The procedure was exactly the same as the one followed to prepare **Pd1** but by using monophosphite ligand **2**. From [{PdCl(η^3-2-Me-allyl)}$_2$] (37.8 mg, 0.096 mmol) and **2** (233 mg, 0.20 mmol), the title product was obtained as a white solid, yield 170 mg (66%). Isomer ratio observed in solution 3.5:1. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 1121.9 (major), 121.6 (minor) ppm. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 10.48 major (s, 1 H, *anti-cis*-C*H*); 0.65 major, 0.94 minor (s, 3 H, allyl-CH_3); 1.19 minor (s, 1 H, *anti-cis*-C*H*); 2.13 major (s, 1 H, *syn-cis*-C*H*); 2.31 minor (s, 1 H, *syn-cis*-C*H*); 2.51 major (d, $J_{P,H}$ = 17 Hz, 1 H, *anti-trans*-C*H*); 2.82 minor (d, $J_{P,H}$ = 16.4 Hz, 1 H, *anti-trans*-C*H*); 3.85 major (d, $J_{P,H}$ = 10 Hz, 1 H, *syn-trans*-C*H*); 4.04 minor (d, $J_{P,H}$ = 11 Hz, 1 H, *syn-trans*-C*H*); 4.68 major (d, $J_{H,H}$ = 12.4 Hz, 1 H, OCH_2Ph); 4.70 minor (d, $J_{H,H}$ = 12.4 Hz, 1 H, OCH_2Ph); 4.72 major, (d, $J_{H,H}$ = 12.4 Hz, 1 H, OCH_2Ph); 4.76 minor, (d, $J_{H,H}$ = 12.4 Hz, 1 H, OCH_2Ph); 6.76–7.90 (m, 51 H, Ar) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 121.6 major, 22.0 minor (s, allyl-CH_3); 57.9 major (s, *cis*-CH_2); 70.8 major, 71.0 minor (s, OCH_2Ph); 78.9 major (d, $J_{P,C}$ = 52 Hz, *trans*-CH_2); 118.7 (s, *C* Binaph); 119.7–130.6 (m, *C*H, Binaph); 133.7, 137.26 (s, 1 *C*, Binaph); 146.9 (s, *C*OP); 154.2 (s, *C*OCH$_2$Ph) ppm. $C_{85}H_{64}ClO_6PPd$: calcd. C 75.39, H 4.76; found C 75.19, H 4.61.

Chloro(η^3-2-Me-allyl){tris[(*S*)-2′-(diphenylmethoxy)-1,1′-binaphthyl-2-yl]phosphite}palladium(II) (Pd3): The procedure was the same as those previously described to prepare **Pd1** and **Pd2**, but by using monophosphite ligand **3**. From [{PdCl(η^3-2-Me-allyl)}$_2$] (11.5 mg, 0.029 mmol) and **3** (85 mg, 0.061 mmol), the title product was obtained as a white solid, yield 46 mg (50%). Isomer ratio observed in solution 1.5:1. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 1120.2 (major), 119.4 (minor) ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.51 major (s, 1 H, *anti-cis*-C*H*); 0.99 major, 1.05 minor (s, 3 H, allyl-CH_3); 1.16 minor (s, 1 H, *anti-cis*-C*H*); 1.87 major (s, 1 H, *syn-cis*-C*H*); 2.28 minor (s, 1 H, *syn-cis*-C*H*); 2.45 major (d, $J_{P,H}$ = 17 Hz, 1 H, *anti-trans*-C*H*); 2.72 minor (d, $J_{P,H}$ = 17 Hz, 1 H, *anti-trans*-C*H*); 3.87 major (d, $J_{P,H}$ = 9.5 Hz, 1 H, *syn-trans*-C*H*); 4.05 minor (d, $J_{P,H}$ = 10 Hz, 1 H, *syn-trans*-C*H*); 6.11 major, 6.03 minor (s, 1 H, OC*H*Ph$_2$); 6.3–8.0 (m, 66 H, Ar) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ = 122.3 minor, 22.3 major (s, allyl-CH_3); 58.1 major (s, *cis*-CH_2); 58.5 minor (s, *cis*-CH_2); 78.7 major (d, $J_{P,C}$ = 56 Hz, *trans*-CH_2); 79.2 minor (d, $J_{P,C}$ = 50 Hz, *trans*-CH_2); 82.4 (s, O*C*HPh$_2$); 116–133.8 (m, *C*H, Binaph); 141.4, 141.8 (s, 1 *C*, Binaph); 147.3 (s, *C*OP); 153.3 (s, *C*OCHPh$_2$) ppm. $C_{103}H_{76}ClO_6PPd$: calcd. C 78.17, H 4.84; found C 76.30, H 5.12.

Chloro(η^3-2-Me-allyl){tris[(*R*)-2′-(1-adamantyloxy)-1,1′-binaphthyl-2-yl]phosphite}palladium(II) (Pd4): The procedure was the same as described above. From [{PdCl(η^3-2-Me-allyl)}$_2$] (19.7 mg, 0.05 mmol) and **4** (135.4 mg, 0.11 mmol), the title product was obtained as a white solid, yield 95 mg (64%). Isomer ratio observed in solution 2.2:1. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 1118.2 (major), 118.9 (minor) ppm. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ =

10.50 major (s, 1 H, *anti-cis*-C*H*); 0.81–1.88 (m, 45 H, major and minor adamantyl protons; ov. 3 H, allyl-CH_3; ov. minor 1 H, *anti-cis*-C*H*; ov. major 1 H, *syn-cis*-C*H*); 2.13 minor (s, 1 H, *syn-cis*-C*H*); 2.42 major (d, $J_{P,H}$ = 17.2 Hz, 1 H, *anti-trans*-C*H*); 3.0 minor (d, $J_{P,H}$ = 16.4 Hz, 1 H, *anti-trans*-C*H*); 3.82 major (d, $J_{P,H}$ = Hz12 1 H, *syn-trans*-C*H*); 4.03 minor (d, $J_{P,H}$ = 10.4 Hz, 1 H, *syn-trans*-C*H*); 6.85–7.90 (m, 36 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 122.6 major (s, allyl-*C*H_3); 30.8, 36.0 43.3 (s, C3, C4, C2 Ad); 58.9 major (s, *cis*-*C*H_2); 77.2 major (*trans*-*C*H_2 ov. $CDCl_3$); 78.5 (s, *C*1O Ad); 120.1–133.8 (*C* and *C*H Naph); 147.6 (s, *C*OP); 151.9 (s, *C*O Ad) ppm. $C_{94}H_{88}ClO_6PPd$: calcd. C 75.95, H 5.97; found C 72.64, H 6.24. HR-MS/ESI: *m*/*z* calcd. 1449.5353 [M – Cl]$^+$; found 1449.5376.

Chloro(η³-2-Me-allyl){tris[(*R*)-2′-(1-adamantyl ester)-1,1′-binaphthyl-2-yl]phosphite}palladium(II) (Pd5): The procedure was the same as described above. From [{PdCl(η³-2-Me-allyl)}$_2$] (19.7 mg, 0.05 mmol) and **5** (144 mg, 0.105 mmol), the title product was obtained as a white solid, yield 109 mg (70%). Isomer ratio observed in solution 2.5:1. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 1118.0 (major), 118.86 (minor) ppm. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 10.85 major (s, 1 H, *anti-cis* C*H*); 1.14 major (s, 3 H, allyl-CH_3); 1.23–1.78 (m, 45 H, major and minor adamantyl protons; ov. minor 1 H, *anti-cis* C*H*; ov. minor 3 H, allyl-CH_3; ov. major and minor 1 H, *syn-cis* C*H*); 1.87 major (d, $J_{P,H}$ = 16 Hz, 1 H, *anti-trans*-C*H*); 3.13 minor (d, $J_{P,H}$ = 16 Hz, 1 H, *anti-trans*-C*H*); 3.86 major (d, $J_{P,H}$ = 12.0 Hz, 1 H, *syn-trans*-C*H*); 4.29 minor (d, $J_{P,H}$ = 12.0 Hz, 1 H, *syn-trans*-C*H*); 6.73–7.90 (m, 36 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 122.7 major (s, allyl-*C*H_3); 27.6, 36.1, 37.9, 40.5 (s, C3, C4, C2, C1 Ad); 57.4 major (s, *cis*-*C*H_2); 80.7 major (d, $J_{P,C}$ = 50 Hz, *trans*-*C*H_2); 118.8–133.4 (s, *C* and *C*H Binaph); 146.9 (s, *C*OP); 147.0 (s, *C*O Ad); 175.6 (s, *C*OO) ppm. $C_{97}H_{88}ClO_9PPd$: calcd. C 74.18, H 5.65; found C 74.19, H 6.50. HR-MS/ESI: *m*/*z* calcd. 1533.5201 [M – Cl]$^+$; found 1533.5214.

General Procedure for Asymmetric Hydrovinylation: Hydrovinylation reactions were carried out in a stainless-steel autoclave fitted with an external jacket connected to an ethanol bath and temperature controlled using a thermostat to ±0.5 °C. The internal temperature was controlled with a thermocouple. The suitable amounts of the chosen neutral complex **Pd1**–**Pd5**, styrene (20 mmol) and $AgBF_4$ (1.1 molar equiv.) with respect to the amount of Pd were dissolved in dichloromethane (15 mL) and stirred for 10 min sheltered from light. After removing the formed AgCl by filtration, the solution was placed by syringe into the autoclave, which had been purged by successive vacuum/nitrogen cycles and thermostatted to 25 °C. Ethylene was admitted until a pressure of 16 bar was reached. After the selected time, the autoclave was slowly depressurised and a 10% aqueous NH_4Cl solution (10 mL) was added. The mixture was stirred for 10 min to quench the catalyst. The organic layer was separated, dried with Na_2SO_4, filtered through a plug of SiO_2 and subjected to GC analysis to determine the distribution of the products and the enantiomeric excess with 30 m Agilent HP 5 and Astec Chiraldex DM columns.

General Procedure for Asymmetric Hydrogenation: A solution of [Rh(cod)$_2$]BF_4 or [Rh(cod)$_2$]OTf (0.015 mmol) and the monophosphite (0.03 mmol) in dry CH_2Cl_2 (4 mL) was introduced into a stainless-steel autoclave and stirred for 10 min. Dimethyl itaconate (1.5 mmol) was added with a cannula and the autoclave was then filled with the desired hydrogen pressure. After 24 h (or 48 h), the autoclave was opened and the reaction mixture was concentrated to dryness, dissolved in *n*-hexane and passed over a silica gel pad. Samples were analysed with a gas chromatograph equipped with a chiral column.

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