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P-Stereogenic monophosphines in Pd-catalysed enantioselective hydrovinylation of styrene

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ABSTRACT

Two groups of *P*-stereogenic monodentate phosphines containing pendant groups bearing functionalities capable of having secondary interactions, PArPhR (Ar = 2-[(2′,6′-dimethoxy)-1,1′-biphenylyl] and R = OMe (**6**) or Me (**8**)) and PMeR(CH_2R') (**13**, R = *t*-Bu or **14** R = Fc and R′ = $SiMe_3$ (**a**), $SiMe_2Ph$ (**b**) or CH_2(2-naphthyl) (**c**)) have been prepared in enantiomerically pure form by the Jugé and Evans methodologies and characterised, including the crystal structure for the borane adduct of **12b**. Reaction of the phosphines with the Pd dimer [Pd(η^3-2-Me-allyl)(μ-Cl)]$_2$ produced neutral allylic complexes **C** [PdCl(η^3-2-Me-C_3H_4)P*], which have been characterised in solution and shown to be a mixture of isomers with different absolute configuration at the Pd atom. After abstraction of the chloride ligand by $AgBF_4$, the solutions of cationic complexes have been used as catalyst precursors in the hydrovinylation of styrene under mild conditions. Very good activities (up to 1015 h^{-1}), moderate to good selectivities to 3-phenyl-1-butene and low to moderate enantioselectivities (<45% ee) have been found. Deep differences in the activity and enantioselectivity have been found depending on the structure of the ligand. In spite of that the results did not permit to confirm the improvement of the selectivities of the reaction by stabilization of the catalyst through secondary coordination with the potentially hemilabile ligands.

1. Introduction

Catalytic activation and incorporation of simple inorganic and organic molecules into complex organic frameworks without waste generation constitutes one of the main research areas in chemistry. In this context, the hydrovinylation reaction can be defined as an heterodimerisation between ethylene gas and an activated olefin, usually styrene (and other vinylarenes) or norbornene [1], catalysed by a transition metal complex [2,3]. Scheme 1 shows the hydrovinylation of the model substrate, styrene, and some of the byproducts often encountered.

Typically encountered side reactions include dimerisation of either ethylene or styrene and isomerisation of the 3-phenyl-1-butene to the more stable 3-phenyl-2-butenes. The second process can be minimised by stopping the reaction before total consumption of styrene.

Since a stereogenic carbon atom is created, the reaction is amenable to enantiocontrol [4,5]. Hydrovinylation has much interest in enantioselective synthesis because it provides a short route to 2-arylpropionic acids, the most important family of nonsteroidal antiinflammatory drugs, including naproxen or ibuprofen [6,7]. More recently it has also been employed in the stereoselective construction of benzylic all-carbon quaternary stereocentres [8–10], a structural motif present in pharmacologically important compounds, and in the short synthesis of natural products [11,12]. In spite of its enormous potential and its long history [13,14], hydrovinylation is still an underused reaction even in the synthesis of fine chemicals. This is due to the presence of many side reactions, as shown in Scheme 1, which requires a subtle fine tuning of the catalyst to obtain good selectivity [3].

Although some work has been carried out with complexes of cobalt [15–20] and ruthenium [21], most of the studies on enantioselective hydrovinylation have been performed using Ni(II) and Pd(II) organometallic precursors [3,5]. It has been traditionally accepted that the mechanism involves an extremely reactive unsaturated cationic nickel or palladium hydride as true catalyst, which coordinates and inserts styrene, giving a η^3-benzylic intermediate. Ethylene coordination, insertion into the metal-carbon bond and β-elimination releases the product and regenerates the hydride closing the catalytic cycle [3]. It must be noted, however, that the presence of the metal hydride intermediate in nickel based systems has been recently questioned by a theoretical study of RajanBabu and

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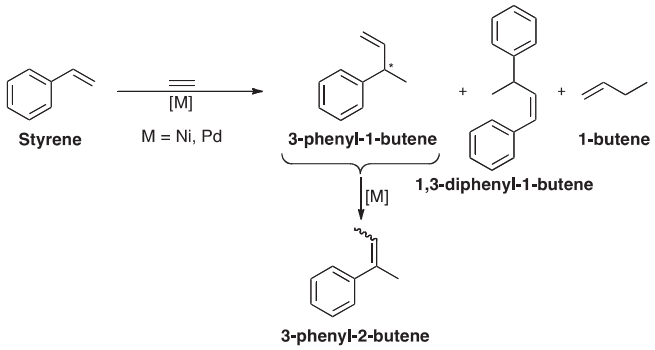


Scheme 1.

coworkers [22], who suggest a direct β-H transfer instead of a β-elimination. With palladium systems the isomerization of the product of codimerization has been observed and therefore a metal hydride intermediate fits adequately the experimental results. A particularity of Ni and Pd systems is that active catalysts only admit monodentate phosphorus ligands, since diphosphines and other bidentate ligands inhibit the reaction. This implies that a single monodentate ligand is responsible for the challenging task of controlling both the chemo- and enantioselectivity.

To circumvent this difficulty, several approaches such as pure steric shielding [1,23,24] or the dendritic effect [25–27] have been applied but the most successful has been the use of ligands possessing pendant groups capable of interacting with and stabilising the metal centre [28,29]. This strategy has been intensively pursued by RajanBabu [1,22,30–33], Leitner [34–37] and Zhou [8,38] employing Ni systems. A limitation of Ni-based systems is that to obtain high chemo- and enantioselectivities the reactions have to be carried out at very low temperatures, except for the less reactive substrates [8]. It must be noted that a recent contribution of Leitner and coworkers [37] describes a highly enantioselective Ni system for the hydrovinylation of vinylarenes at room temperature with a finely tuned phosphoramidite ligand, highlighting the importance of hemilabile interactions.

Pd-based catalysts have the advantage of operating at room temperature, constituting a promising alternative. Our group [24,26,27,39–41] and others [23] have been studying the hydrovinylation reaction using palladium π-allylic complexes with several types of monodentate *P*-stereogenic ligands as precatalysts. This is an interesting class of ligands to be explored in hydrovinylation since the close proximity of the stereogenic phosphorus to the metallic centre can provide high enantioselectivities as shown by Vogt and coworkers [23] and by us [24,26,27].

With the aim of exploring the effect of potential secondary interactions on Pd-catalysed enantioselective hydrovinylation of styrene, in this contribution we describe the preparation of several new *P*-stereogenic phosphines with different electronic properties bearing functionalities capable of having secondary interactions, like methoxy substituents or aryl groups. The comparison with the catalytic results obtained using similar phosphines lacking the potentially secondary coordination moieties could shed light on the importance of the intramolecular secondary coordination. Our recent experience with phosphines bearing pendant functionalities, discarded the use of isolated double bonds or carbonyl fragments [41].

2. Results and discussion

2.1. Ligand synthesis

Among the several methods available to prepare optically pure *P*-stereogenic ligands [42], we selected the routes devised by Jugé [43] and by Evans [44] to prepare two distinct sets of optically pure *P*-stereogenic phosphines.

In previous studies on hydrovinylation [26,27,40] we found that, among the diarylalkyl phosphines studied, those bearing a 2-biphenylyl group led to the highest enantioselectivities. We reasoned that phosphines with the same substituent but containing methoxy groups may improve these results by intramolecular secondary coordination of the oxygen atom to the metallic centre. To this aim, we prepared 2-bromo-(2′,6′-dimethoxy)-1,1′-biphenyl (**1**), following slightly modified procedures (Scheme 2) [45,46].

This compound was easily lithiated at low temperature and installed at the phosphorus atom by nucleophilic attack on oxazaphospholidine **3**, following the standard Jugé procedure (Scheme 3) [43].

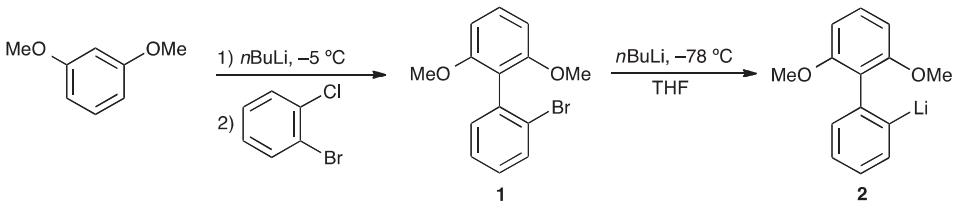
Aminophosphine-borane **4** was obtained as a diastereomerically pure compound according to NMR spectroscopy and was subjected without purification to acidic methanolysis, affording phosphinite-borane **5**. From this precursor, methylphosphine-borane **7** was easily obtained by substitution of the methoxy group by methyllithium. Phosphinite-borane **5** and phosphine-borane **7** were quantitatively deboronated by neat morpholine giving the desired ligands **6** and **8** as white solids after column chromatography to remove the morpholine-borane adduct.

In order to prepare electron-rich phosphines, we subjected dimethylphosphine-boranes **9** and **10** to the desymmetrisation protocol with *s*-BuLi/(−)-sparteine, a method originally developed by Evans and coworkers [44] and already used by us (Scheme 4) [47].

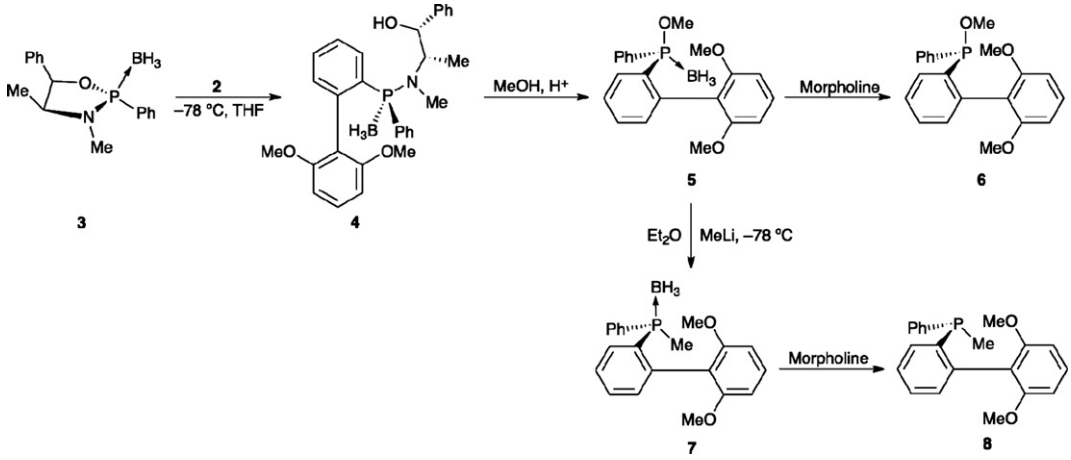
With this procedure, we obtained phosphine-boranes **11** and **12** after electrophilic quenching of the carbanions with chlorosilanes. HPLC analysis of the crude phosphine-boranes revealed very high (>97%) enantiomeric excesses for compounds of the *t*-Bu series, **11**. In contrast, compounds **12a** and **12b** were formed in 80 and 82% ee respectively, whereas **12c** was found to be enantiopure. The optical purity of **12b** could be easily increased by recrystallisation. The results suggest that the ferrocenyldimethylphosphine-borane (**10**) is a less selective substrate for the enantioselective deprotonation compared to **9** although the value of the enantioselectivity also depends on the electrophile.

We were able to obtain the crystal structure of optically pure phosphine **12b**, which confirmed the expected *S* configuration of the phosphorus atom, as shown in Fig. 1.

The distances and angles of **12b** are close to other reported phosphine-boranes [26,40,48]. The Cp rings of the ferrocenyl



Scheme 2.



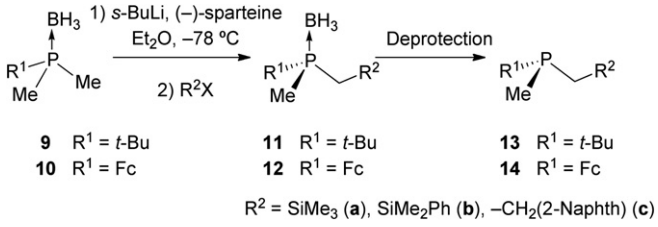
Scheme 3.

substituent are present in eclipsed conformation as observed in other ferrocenylphosphine-boranes [49,50].

Given the electron-rich character phosphine-boranes **11** and **12**, the deprotection was carried out with tetrafluoroboric acid followed by neutralisation [51], a procedure that worked efficiently for **11a**, **11c**, **12a** and **12c**. In contrast, the $-SiMe_2Ph$ group present in phosphine-boranes **11b** and **12b** was partially cleaved with the acidic treatment giving back the starting material **9** and **10** respectively. For this reason, **11b** and **12b** were deprotected with DABCO in refluxing toluene. The free phosphines **13** and **14** were found to be very sensitive to oxidation and therefore they were immediately complexed to palladium without isolation. Phosphines **13** and **14** were designed to incorporate pendant aryl moieties susceptible to interact with the unsaturated Pd centre during the catalysis. Phosphines **13a** and **14a**, without possibility of such interactions were prepared for comparison purposes.

A list of the ^{31}P NMR data of phosphine-boranes, free phosphines, phosphine selenides and Pd-allylic complexes (*vide infra*) is given in Table 1.

^{31}P data of compounds **5**–**8** is very similar to analogous compounds having an unsubstituted biphenylyl group [40]. The value of the $^{31}P-^{77}Se$ coupling constants of phosphine selenides are used to compare the σ-donor capacity of phosphorus ligands (for example 712 Hz for PCy_3 and 760.3 Hz for PPh_3) [52–56], although this method is not free from steric interference [55]. We easily prepared the selenides of some of the trialkylphosphines by direct treatment with elemental selenium. Comparison between J_{P-Se} of the selenides of **9-Se** and **10-Se**, **13a-Se** and **14a-Se** or **13b-Se** and **14b-Se** reflects the higher σ-donation of the phosphorus for phosphines containing the *tert*-butyl group (**9**) compared to those containing the ferrocenyl group (**10**). Given one of these substituents, the TMS group (**a**) is more σ-basic than the dimethylphenylsilyl group (**b**). Taken together, the effect of both substituents determine the following order of s-donation capacity for the ligands: **13a** > **13c** ~ **14a** > **13b** > **14c** > **14b**.



Scheme 4.

2.2. Allylpalladium complexes

Neutral allylic Pd complexes [PdCl(η^3-2-Me-C_3H_4)P*] were easily prepared by mixing 2 equivalents of the free phosphine with one equivalent of dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl-Cl)]$_2$ (Scheme 5).

After solvent removal, complexes **C** were obtained pure as solids or oils, which were indefinitely stable in air. Complexes **C13b** and **C14b** were contaminated with DABCO and DABCO·BH_3 according to ^1H NMR spectra. Complex **C14b**, dissolved in dichloromethane, could be purified by treatment with diluted aqueous hydrochloric acid, which removed DABCO, followed by column chromatography (SiO_2), which allowed the separation of DABCO·BH_3. When the same treatment was attempted with **C13b**, the complex decomposed to palladium black. Therefore, although the crude complex could be characterised by NMR (*vide infra*), it was not used in catalysis.

The most informative technique of characterisation was NMR spectroscopy. ^{31}P (Table 1) and ^1H NMR spectra of **C** showed the expected presence of two isomers (R_{Pd} and S_{Pd}) interconverting in solution. The isomeric ratios as well as selected ^1H NMR and ^{13}C NMR data are collected in Table 1S and Table 2S respectively (see Supporting information).

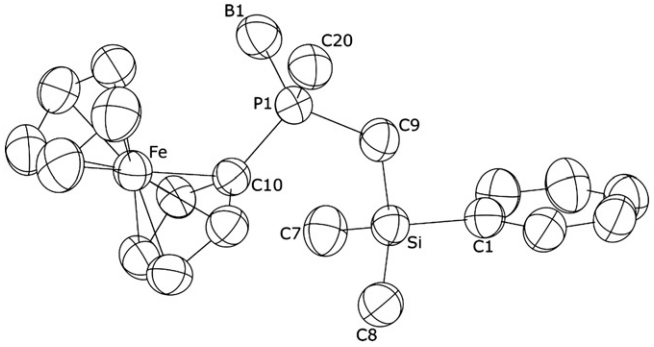


Fig. 1. ORTEP view (thermal ellipsoids drawn at the 50% probability level) of phosphine-borane **12b**. Hydrogen atoms have been omitted for clarity. Selected distances (Å): P1-B1, 1.910 (5); P1–C9, 1.799(4); P1–C10, 1.776(3); P1–C20, 1.810(4); Si–C1, 1.892 (3), Si–C7, 1.844(5); Si–C8, 1.849(4). Selected angles (°): B1–P1–C9, 109.9(3); B1–P1–C10, 111.5(2); B1–P1–C20, 113.4(2).

Table 1
^{31}P NMR data[a] ($CDCl_3$, 298 K, 101 MHz, δ in ppm, J in Hz) for phosphine-boranes, free phosphines, phosphine selenides and Pd-allylic complexes.

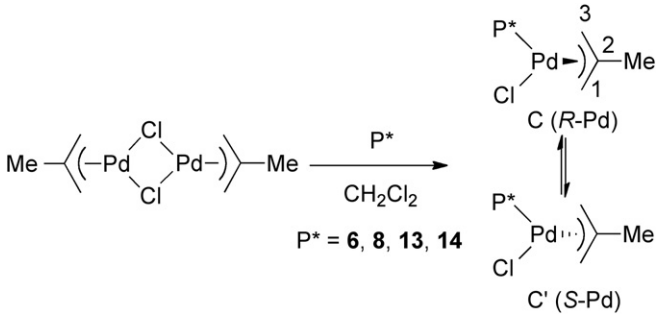
Compound	$\delta(^{31}P)$ P–BH_3	$\delta(^{31}P)$ free P	$\delta(^{31}P)$ P=Se	J_{P-Se}	$\delta(^{31}P)$ [Pd] Isomeric ratio
5, **6**, **C6**	107.2 (*bs*, d, 79.6)	+112.1	–[b]	–[b]	120.8, 120.6 60/40
7, **8**, **C8**	10.7 (*bs*, d, 68.6)	−33.9	–[b]	–[b]	5.3 100/0
9a, **9-Se**	20.5 (*q*, 58.8)	−28.3	39.2	689.8	–
9b, **10-Se**	0.0 (*q*, 55.9)	−56.9	11.5	702.7	–
11a, **13a**, **13a-Se**, **C13a**[c]	23.6 (*q*, 63.6)	−22.6	41.6	680.8	21.2, 21.9 50/50
11b, **13b**, **13b-Se**, **C13b**	24.0 (*q*, 68.8)	−23.2	39.5	704.9	21.9, 21.8 62/38
11c, **13c**, **C13c**	25.2 (*q*, 54.7)	−15.4	48.9	692.1	28.7, 28.3 55/45
12a, **14a**, **14a-Se**, **C14a**	2.9–4.6 (*m*)	−51.3	14.5	695.6	−4.9, −5.2 53/47
12b, **14b**, **14b-Se**, **C14b**	4.6 (*q*, 57.7)	−52.1	12.8	720.9	−3.9, −4.6 57/43
12c, **14c**, **14c-Se**, **C14c**[c]	1.7–2.3 (*m*)	−46.1	21.8	710.3	1.0, 0.2 50/50

[a] Multiplicity: *bs*, broad signal; *d*, doublet; *m*, multiplet; *s*, singlet; *q*, quadruplet.
[b] Not measured.
[c] Signals of both isomers of the complex not experimentally related.

Unexpectedly, a single set of signals was observed for complex **C8** at room temperature. It is possible that in this case both signals appeared overlapped since in **C6** they were observed at 120.8 and 120.6 ppm, furthermore an incomplete group of very small signals were observed in the proton spectra probably accounting for the minor isomer. For the rest of compounds, two ^{31}P signals and duplicity of allylic C and H resonances was observed. A moderate discriminating effect is observed with similar ligand **6**. In the case of ligands **13** and **14**, the highest discrimination is reached with ligands **13b** and **14b**, bearing a dimethylphenylsilyl moiety.

The differences in the chemical shifts of allylic protons and carbons between isomers in complex **C6** reach 0.6 and 2.9 ppm in ^{1}H and ^{13}C NMR respectively. These differences are much smaller for complexes **C13** and **C14**. In ^{13}C NMR the C1 carbon (*trans* to the phosphine) is shifted downfield in complexes **C6** and **C8** compared to complexes **C13** and **C14**, in all cases highly deshielded (~25 ppm) compared to the corresponding C3 carbon, *cis* to the phosphine. As observed in similar complexes [28,40,57], both the carbon and H atoms *trans* to the phosphorus were coupled to the phosphorus atom.

Complexes **C13** or **C14** present one or two methylene groups in the phosphine part. Due to the stereogenic phosphorus atom, the protons of each group are diastereotopic and hence chemically and



Scheme 5.

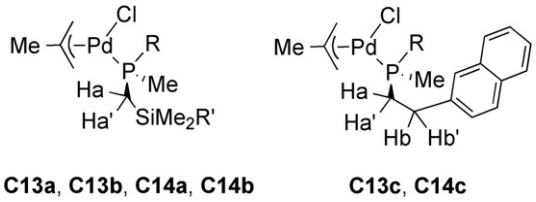


Fig. 2. Diastereotopic CH_2 protons.

magnetically inequivalent, coupling to each other and to the phosphorus atom (Fig. 2). An additional complication is the presence of two isomers of the complex, which duplicates the number of signals. The observed patterns are listed in Table 3S.

Phase-sensitive NOESY experiments on some of the complexes were carried out to study the mechanism of interconversions between isomers. The usual η^3- η^1- η^3 and the allyl pseudorotation mechanisms were observed although interestingly for complex **C14b** only the η^3- η^1- η^3 mechanism could be detected.

2.3. Styrene hydrovinylation

Neutral allylic Pd complexes are suitable precatalysts for styrene hydrovinylation [40,41]. The activation of these complexes was carried out with one equivalent of $AgBF_4$ in the presence of styrene, giving solutions containing [PdL(η^3-2-Me-C_3H_4)P*]BF_4 (L = styrene or solvent). These solutions were immediately introduced into an autoclave and pressurised with ethylene. The results obtained after GC analysis of at least two runs are listed in Table 2.

Comparison between precatalysts containing diarylphosphines (entries 1–4) and those with trialkylphosphines (entries 5–9) shows that the latter are much more active, probably due to the extra stabilisation of the cationic palladium hydride species by the more bulky and basic trialkylphosphines.

Within the group of diarylphosphines (entries 1–4), the introduction of methoxy groups in the biphenylyl substituent causes a severe drop in the activity (*cf.* entry 1 with entry 2 and entry 3 with entry 4), probably due to steric and secondary interaction effects. More interesting are the differences on the enantioselectivity. Whereas with the precursors bearing the methylphosphines the presence of the methoxy groups completely destroys the chiral induction (*cf.* entries 3 with 4), in the methylphosphinite pair the

Table 2
Hydrovinylation of styrene catalysed by [PdL(η^3-2-Me-C_3H_4)P*]BF_4 precursors[a].

Entry	Precursor	Time, h	Conversion[b], %	Codimers[c], %	Selectivity[d]	TOF[e], h^{-1}	ee, %
1	**C6**	3	8.5	8.4	99.1	29	45 (*R*)
2[f]	**C15**	1	18.1	17.7	95.9	178	12 (*R*)
3	**C8**	3	10.7	10.6	96.3	35	<5 (–)
4[f]	**C16**	1	10.5	10.0	97.2	100	23 (*S*)
5	**C13a**	3	96	94	83	322	<5 (–)
6	**C13c**	1	100	99	67	1015	35 (*R*)
7[g]	**C14a**	3	85	85	74	283	20 (*R*)
8	**C14b**	3	72	71	84	241	35 (*R*)
9	**C14c**	3	50	49	92	145	17 (*R*)

[a] Conditions: 25 °C, 15 bar of initial pressure of ethylene in 10 ml of CH_2Cl_2. Ratio styrene/Pd: 1000/1.
[b] Conversion of starting styrene.
[c] Total amount of codimers.
[d] % of 3-phenyl-1-butene/codimers.
[e] TOF calculated as the total amount of phenylbutenes formed.
[f] Complexes **C15** and **C16** are similar to **C6** and **C8** respectively but bearing an unsubstituted 2-biphenylyl group in the phosphine, the data has been taken from our previous report [40].
[g] The phosphine used to prepare the complex had a 80% ee.

effect is inverse (*cf.* entries 1 with 2), enhancing the enantiomeric excess and making **C6** a moderately enantioselective catalyst. The absolute configuration of the 3-phenyl-1-butene in entries 1 and 2 is opposite to that of entry 4 as expected due to the opposite absolute configuration at the phosphorus atom.

In the trialkylphosphine series, precursor and **C14a** (entry 7), without possibility of secondary interactions, is faster than the other catalysts bearing the ferrocenyl substituent. Precursor **C13c** (entry 6), which is extraordinarily active, quantitatively consumes the styrene in 1 h and leads to noticeable isomerisation. We do not have any explanation for this fact. Although all the systems favour the *R* enantiomer of 3-phenyl-1-butene, some interesting observations can be made. Entries 5 and 6 show that while **C13a**, bearing a pendant TMS group, is a very poor chiral inductor, **C13c**, with a pendant 2-naphthyl group, gives much better enantioselectivity. In contrast, entries 7–9 show that both **C14a** and **C14c** are equivalent in terms of enantioselectivity, a result that is improved by **C14b**. All the trialkylphosphines have the same absolute configuration at the P atom leading to the same sense in the chiral induction due to the preferential coordination of styrene by one of its enantiotopic faces. In spite of that, an interesting modulation of the enantioselectivity is observed possibly due to secondary coordination interactions between the Pd centre and aromatic rings. This effect is more pronounced in the phosphines bearing the *tert*-butyl group.

3. Conclusions

A family of [PdCl(η^3-2-Me-C_3H_4)P*] complexes containing two types of new enantiopure *P*-stereogenic ligands have been prepared and characterised. The cationic derivatives obtained after extraction of the coordinated chloride by a silver salt have been used in the catalytic hydrovinylation of styrene. Good activities and regioselectivities towards 3-phenyl-1-butene have been found. In contrast, the enantioselectivities have remained low to moderate, which requires further work on ligand design. Some interesting trends in the enantioselectivities have been identified. In general, except for **C13a**, the increase of the bulkiness of the ligands diminishes the activity of the catalysts, an effect that is more pronounced in the diarylphosphine series. For the diarylphosphines, either enhancement (**C6**) or destruction (**C8**) of the enantioselectivity has been observed whereas for the trialkylphosphines a low to moderate increase on the enantioselectivity has been found.

Therefore, the results did not allow to confirm the improvement of the selectivities of the reaction by stabilization of the catalyst through secondary coordination with the methoxy groups or aryl fragments in the ligands prepared.

4. Experimental section

4.1. General data

All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. The routine ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on either a Varian XL-500 or Mer-400 MHz (^{1}H, standard $SiMe_4$), Varian Inova 300 (^{13}C, 75.4 MHz, ^{1}H, standard $SiMe_4$) and Bruker DRX-250 (^{31}P, 101.2 MHz) spectrometers in $CDCl_3$ unless otherwise specified. Chemical shifts were reported downfield from standards. The two-dimensional experiments were carried out with a Bruker DMX-500 or a Varian XL-500 instrument. IR spectra were recorded on the spectrometers: FT-IR Nicolet 520 and FT-IR Nicolet 5700; only the stretching bands assigned to the allyl group are given [58]. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. The routine GC analyses were performed on a Hewlett–Packard 5890 Series II gas chromatograph (50-m Ultra 2 capillary column 5% phenylmethylsilicone and 95% dimethylsilicone) with a FID detector. The GC/MS analyses were performed on a Hewlett–Packard 5890 Series II gas chromatograph (50-m Ultra 2 capillary column) interfaced to a Hewlett–Packard 5971 mass selective detector. HPLC analyses were carried out in a Waters 717 plus autosampler chromatograph with a Waters 996 multidiode array detector, fitted with a Chiralcel OD-H chiral column. The eluent, in all the determinations, was a mixture n-hexane/*i*-PrOH 95:5. Optical rotations were measured on a Perkin Elmer 241 MC spectropolarimeter at 23 °C. Enantiomeric excesses were determined by GC on a Hewlett–Packard 5890 Series II gas chromatograph (30-m Chiraldex DM column) with a FID detector. Elemental analyses were carried out by the Serveis Cientificotècnics of the Universitat Rovira i Virgili and of Universitat de Barcelona. Phosphine-borane **13c** had already been reported by us [47].

4.2. Synthesis of ligands

4.2.1. 2-Bromo-2′,6′-dimethoxybiphenyl (*1*)

m-dimethoxybenzene (4.00 ml, 4.22 g, 30.6 mmol) was dissolved in 60 ml of dry THF and cooled to −5 °C. *n*-BuLi (19.2 ml of 1.6 M solution, 30.8 mmol) was added by syringe and after 15 min the solution was allowed to warm to room temperature. After 5 h of stirring, the suspension was cooled to 0 °C and *o*-bromochlorobenzene (3 ml, 4.96 g, 25.6 mmol), dissolved in 20 ml of THF, was slowly added during a period of 30 min and the resulting solution was stirred for 15 min. Methanol (0.5 ml) was added and the brownish solution immediately became yellow. This solution was concentrated under reduced pressure and diethyl ether (100 ml) and water (100 ml) were added. The layers were separated and the aqueous phase was extracted with diethyl ether (2 × 50 ml). The combined organic extracts were washed once with brine (50 ml), dried with anhydrous sodium sulphate and concentrated under reduced pressure to yield a yellow solid. This solid was recrystallised in CH_2Cl_2/diethyl ether to yield the desired product. Yield: 3.7 g (49%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 3.73 (*s*, 6H), 6.65 (*d*, 2H, J = 8.4 Hz), 7.19–7.25 (*m*, 2H), 7.31–7.36 (*m*, 2H), 7.65 (*dd*, 1H, J = 8.0 Hz, 1.2 Hz) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 56.8 (CH_3), 104.9 (CH), 126.0–158.5 (C, CH, Ar) ppm.

4.2.2. (1R,2S)-2-{[(S)-(2-(2′,6′-Dimethoxybiphenylyl))phenylphosphanyl] methylamino}-1-phenylpropan-1-ol-P-borane (*4*)

1 (10.11 g, 34.5 mmol) was dissolved in 100 ml of dry THF and cooled to −78 °C. *n*-BuLi (22.5 ml of 1.6 M solution, 36.0 mmol) was added by syringe. After 2 h, to ensure the complete lithiation, the suspension was warmed to −20 °C and cooled again to −78 °C. A solution of **3** (8.55 g, 30.0 mmol) was dissolved in 30 ml of THF, cooled to −78 °C and added slowly to the suspension of **2**. The mixture was allowed to warm to room temperature overnight. Water (25 ml) was added and the organic solvents were removed in vacuo. The obtained suspension was extracted with dichloromethane (3 × 30 ml) and the combined organic fractions were washed with water (100 ml). The final organic fraction was dried with sodium sulphate, filtered and concentrated. The desired product was obtained as a white powder. Yield: 13.51 g (90%). ^{31}P{^{1}H} NMR (101.3 MHz, CD_3COCD_3, 298 K): δ = +70.4 (*bs*) ppm. ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 0.00–1.80 (*m*, *bs*, 3H), 0.97 (*d*, 3H, J = 6.9 Hz), 2.65 (*d*, 3H, J = 7.8 Hz), 3.50 (*s*, 3H), 3.70 (*s*, 3H), 3.90 (*m*, 1H), 4.84 (*d*, 1H, J = 3.6 Hz), 6.33 (*d*, 1H, J = 8.3 Hz), 6.42 (*d*, 1H, J = 8.3 Hz), 6.65 (*d*, 1H, J = 8.3 Hz), 7.13–7.48 (*m*, 14H, Ar) ppm. ^{13}C{^{1}H} NMR (50.0 MHz, $CDCl_3$, 298 K): δ = 9.6 (*d*, CH_3, J_{CP} = 4.6 Hz), 30.6 (*s*, CH_3), 56.6 (*d*, CH, J_{CP} = 9.1 Hz), 53.9 (*s*, CH_3), 54.3 (*s*, CH_3), 77.7 (*d*, CH, J_{CP} = 2.3 Hz), 102.0–156.7 (*m*, C, CH, Ar) ppm.

*4.2.3. (R)-(2-(2′,6′-Dimethoxybiphenylyl))methoxy-phenylphosphine-P-borane (**5**)*

Compound **4** (13.50 g, 27.0 mmol) was dissolved in 200 ml of dry methanol and cooled to 0 °C. Sulphuric acid (1.51 ml, 2.78 g, 27.0 mmol) was rapidly added and the mixture was left stirring overnight. Removal of the solvent furnished a pasty solid, which was suspended in 100 ml of ethyl acetate causing the precipitation of (−)-ephedrine sulphate, which was filtered out. The solvent was removed and the oil obtained was treated several times with diethyl ether, which dissolved the desired compound. Concentration furnished again a pasty solid, which was recrystallised in CH_2Cl_2/ethanol to yield the title product as a white solid. Yield: 3.08 g (30%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +107.2 (*d*, *bs*, J = 79.6 Hz) ppm. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.25–1.20 (*m*, *bs*, 3H), 3.33 (*s*, 3H), 3.41 (*s*, 3H), 3.57 (*d*, 3H, J = 12.0 Hz), 6.26 (*d*, 1H, J = 8.4 Hz), 6.38 (*d*, 1H, J = 8.0 Hz), 7.11–7.58 (*m*, 9H, Ar), 8.13–8.19 (*m*, 1H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 53.9 (*d*, CH_3, J_{CP} = 4.6 Hz), 55.1 (*s*, CH_3), 55.2 (*s*, CH_3), 102.7–158.1 (*m*, C, CH, Ar) ppm. $C_{21}H_{24}BO_3P$: calcd. C 68.88, H 6.61; found C 68.63, H 6.57. $[a]_D$ (c = 0.9, CH_2Cl_2): +28.4°.

*4.2.4. (S)-(2-(2′,6′-Dimethoxybiphenylyl))methylphenyl-phosphine-P-borane (**7**)*

Compound **5** (0.732 g, 2.0 mmol) was dissolved in 20 ml of dry diethyl ether and cooled to −20 °C. Methyllithium (2.00 ml of 1.6 M solution, 3.2 mmol) was added rapidly by syringe and the mixture was left stirring for 30 min and then allowed to warm to room temperature. Water was carefully added and the mixture was extracted with diethyl ether (3 × 30 ml). The combined organic extracts were washed with water (100 ml), the final organic fraction was dried with anhydrous sodium sulphate, filtered and concentrated to dryness furnishing the product as a white powder. Yield: 0.271 g (39%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +10.7 (*d*, *bs*, J = 68.6 Hz) ppm. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.20–2.10 (*m*, *bs*, 3H), 1.53 (*d*, 3H, J = 10.0 Hz), 3.21 (*s*, 3H), 3.58 (*s*, 3H), 6.27 (*d*, 1H, J = 8.4 Hz), 6.49 (*d*, 1H, J = 8.4 Hz), 7.07–7.55 (*m*, 9H, Ar), 8.07–8.13 (*m*, 1H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 10.8 (*d*, CH_3, J_{CP} = 41.3 Hz), 55.1 (*s*, CH_3), 55.4 (*s*, CH_3), 103.1–158.0 (*m*, C, CH, Ar) ppm. $C_{21}H_{24}BO_2P$: calcd. C 72.02, H 6.91; found C 72.43, H 7.05.

*4.2.5. (R)-(2-(2′,6′-Dimethoxybiphenylyl))methoxy-phenylphosphine (**6**)*

Phosphinite-borane **5** was dissolved in degassed morpholine and stirred for 14 h at room temperature. The morpholine was removed in vacuo and the pasty residue was dissolved into a small amount of toluene and eluted through a short column of alumina, with toluene as eluent. Concentration to dryness quantitatively furnished the desired phosphinite as a colourless oil. $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +112.1 ppm ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 3.24 (*s*, 3H), 3.52 (*d*, 3H, J = 15.0 Hz), 3.81 (*s*, 3H), 6.41 (*d*, 1H, J = 8.4 Hz), 6.66 (*d*, 1H, J = 8.2 Hz), 7.14–7.44 (*m*, 9H, Ar), 7.68–7.70 (m, 1H, Ar) ppm.

*4.2.6. (S)-(2-(2′,6′-Dimethoxybiphenylyl))methylphenylphosphine (**8**)*

The same method used to deboronate **5** was employed. The desired product was obtained quantitatively as a white solid. $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = −33.9 ppm ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.44 (*d*, 3H, J = 4.4 Hz), 3.43 (*s*, 3H), 3.76 (*s*, 3H), 6.48 (*d*, 1H, J = 8.4 Hz), 6.64 (*d*, 1H, J = 8.4 Hz), 7.17–7.41 (m, 10H, Ar) ppm.

*4.2.7. General procedure for enantioselective deprotonation of dimethylphosphine-boranes **9**–**10***

(−)-Sparteine (5.53 g, 23.6 mmol) was dissolved in diethyl ether (20 ml) and cooled to −78 °C. *s*-BuLi (18.2 ml of a 1.3 M solution, 23.6 mmol) was added by syringe and the mixture stirred for 30 min at −78 °C. A solution of dimethylphosphine-borane **9** (23.6 mmol) was added by syringe and the mixture was stirred for 3 h at −78 °C. At the same temperature, the solution was quenched with the desired electrophile (35.4 mmol). The reaction mixture was allowed to warm to room temperature overnight and then hydrolysed with 20 ml of water. The mixture was washed with a solution of HCl (0.5 M, 3 × 10 ml). The combined organic layers were dried with sodium sulpate, filtered, and the resulting solution concentrated in vacuo. The remaining residue was purified by chromatography on silica gel and/or by recrystallisation.

4.2.8. (S)-Tert-butyl(2,2-dimethyl-2-sila-1-propyl) methylphosphine-P-borane (11a)

The crude product was purified by recrystallisation in dichloromethane/diethyl ether to afford the title compound as a white powder. Yield: 3.85 g (80%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +23.6 (*q*, J_{PB} = 63.6 Hz) ppm. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ = 0.18 (*s*, 9H), 0.72–0.85 (*m*, 2H), 1.11 (*d*, 9H, J = 13.6 Hz), 1.20 (*d*, 3H, J = 10.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ = 0.8 (*s*, CH_3), 7.7 (*d*, CH_3, J_{CP} = 57.5 Hz), 7.8 (*s*, CH_2), 25.5 (*s*, CH_3) ppm. $C_9H_{26}BPSi$ (204.17): calcd. C 52.94, H 12.83; found C 50.93, H 13.55. $[\alpha]_D$ (c = 0.3, $CHCl_3$): −8.9.

*4.2.9. (S)-Tert-butyl(2-methyl-2-phenyl-2-sila-1-propyl) methylphosphine-P-borane (**11b**)*

The crude oil was purified by column chromatography (flash SiO_2, hexane/ethyl acetate 95:5) to afford the title compound as a white powder. Yield: 5.65 g (90%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ = +24.0 (*q*, J_{PB} = 68.8 Hz) ppm. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.50 (*s*, 3H), 0.56 (*s*, 3H), 1.00 (*d*, 3H, J = 11.2 Hz), 1.05 (*d*, 2H, J = 13.2 Hz), 1.13 (*d*, 9H, J = 13.2 Hz), 7.36–7.40 (*m*, 3H, Ar), 7.55–7.59 (*m*, 2H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −1.5 (*s*, CH_3), −0.4 (*d*, CH_3, J_{CP} = 2.0 Hz), 7.2 (*d*, CH_3, J_{CP} = 35.2 Hz), 7.6 (*d*, CH_2, J_{CP} = 20.1 Hz), 24.5 (*d*, CH_3, J = 2.0 Hz), 28.2 (*d*, C, J_{CP} = 33.2 Hz), 127.9 (Ar), 129.3 (Ar), 133.4 (Ar), 138.38 (Ar), 138.42 (Ar) ppm. MS (HR-ESI(+)): m/z 265.1699 $[M - H]^+$; 289.1678 $[M + Na]^+$. HPLC (hexane:2-propanol, 90:10), t_R: 7.95 min $C_{14}H_{28}BPSi$ (266.24): calcd. C 63.16, H 10.60; found C 62.95, H 11.43. $[\alpha]_D$ (c = 0.6, $CHCl_3$): +4.3°.

*4.2.10. (S)-Ferrocenyl(2,2-dimethyl-2-sila-1-propyl) methylphosphine-P-borane (**12a**)*

The crude product was purified by column chromatography (flash SiO_2, hexane/ethyl acetate 9:1 as eluent) to afford the title compound as an orange powder. Yield: 3.53 g (45%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +3.8 (*bs*) ppm. ^1H (400.1 MHz, $CDCl_3$, 298 K): δ = 0.06 (*s*, 9H), 1.07 (*d*, 2H, J = 15.0 Hz), 1.56 (*d*, 3H, J = 10.1 Hz), 4.28 (*s*, 5H), 4.30–4.32 (*m*, 1H), 4.40–4.42 (*m*, 2H), 4.49–4.51 (*m*, 1H) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 0.4 (*s*, CH_3), 15.2 (*d*, CH_3, J_{CP} = 40.1 Hz), 17.3 (*d*, CH_2, J_{CP} = 22.2 Hz), 69.5 (*s*, Cp), 69.75 (*m*, Cp), 70.9 (*d*, Cp, J_{CP} = 8.1 Hz), 71.1 (*d*, Cp, J_{CP} = 6.1 Hz), 72.1 (*d*, Cp, J_{CP} = 14.2 Hz) ppm. $C_{15}H_{26}FePBSi$ (332.09): calcd. C 54.25, H 7.89; found C 53.90, H 7.94. HPLC (hexane:2-propanol, 95:5), t_R: 10.66 min $[\alpha]_D$ (c = 0.3, $CHCl_3$): −10.0.

*4.2.11. (S)-Ferrocenyl(2-methyl-2-phenyl-2-sila-1-propyl) methylphosphine-P-borane (**12b**)*

The crude product was purified by recrystallisation in dichloromethane/hexane to afford the title compound as an orange powder. Yield: 8.37 g (90%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ = +4.59 (*q*, J_{PB} = 57.7 Hz) ppm. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.30 (*s*, 3H), 0.45 (*s*, 3H), 1.30 (*d*, 2H, J = 14.8 Hz), 1.41 (*d*, 3H, J = 10.1 Hz), 4.26 (*bs*, 6H), 4.38 (*bs*, 2H), 4.46 (*bs*, 1H), 7.35 (*bs*,

3H), 7.46–7.47 (*m*, 2H) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = −1.29 (*s*, CH_3), −1.22 (*s*, CH_3), 14.72 (*d*, CH_3, J_{CP} = 40.8 Hz), 17.0 (*d*, CH_2, J_{CP} = 25.4 Hz), 69.5 (*bs*, Cp), 69.7–69.8 (*m*, Cp), 70.9–71.1 (*m*, Cp), 72.0–72.2 (*m*, Cp), 127.9 (Ar), 129.3 (Ar), 133.4 (Ar), 138.3 (*m*, Ar) ppm. $C_{20}H_{28}BFePSi$ (394.15): calcd. C 60.95, H 7.16; found C 59.86, H 7.49. HPLC (hexane:2-propanol, 90:10), t_R: 11.91 min $[\alpha]_D$ (*c* = 0.6, $CHCl_3$): −3.4°.

4.2.12. Crystal structure determination of **12b**

Orange crystals, suitable to perform X-ray diffraction studies, were obtained by slow diffusion of hexane over a solution of **12b** in dichloromethane at room temperature. $C_{20}H_{28}BFePSi$ M_r = 394.14 gmol^{-1}, monoclinic, *a* = 9.014(6) Å, *b* = 11.641(7) Å, *c* = 10.499(4) Å, β = 109.55(2), *U* = 1038.2(10) Å^3, *T* = 298(2) K, space group $P2_1$, *Z* = 2, 7736 reflections measured, 4669 unique (R_{int} = 0.0407), which were used in all calculations. The final *w*R (*F*2) was 0.1196 (all data).

4.2.13. (S)-Ferrocenyl(2-(2-naphthyl)methyl)methylphosphine-P-borane (**12c**)

The crude oil was purified by column chromatography (flash SiO_2, hexane/ethyl acetate 1:9 as eluent) to afford the title compound as an orange solid. Yield: 5.67 g (60%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ = +1.7–2.3 (*m*) ppm. ^1H (400.1 MHz, $CDCl_3$, 298 K): δ = 1.56 (*d*, 3H, *J* = 10.0 Hz), 2.01–2.15 (*m*, 2H), 2.82–3.00 (*m*, 2H), 4.31 (*s*, 6H), 4.40–4.47 (*m*), 4.55–4.57 (*m*, 1H), 7.24–7.27 (*dd*, 1H, *J* = 8.0, 1.6 Hz), 7.40–7.47 (*m*, 2H), 7.57 (*bs*, 1H), 7.74–7.80 (*m*, 3H) ppm. $^{13}C\{^1H\}$ (100.6 MHz, $CDCl_3$, 298 K): δ = 10.8 (*d*, CH_3, J_{CP} = 40.1 Hz), 29.4 (*s*, CH_2), 30.8 (*d*, CH_2, J_{CP} = 35.4 Hz), 69.6 (*s*, Cp), 71.3–71.5 (*m*, Cp), 72.6 (*s*, Cp), 72.8 (*s*, Cp), 125.4 (*s*, Ar), 126.1 (*d*, Ar, J_{CP} = 3.3 Hz), 126.6 (*s*, Ar), 127.4 (*s*, Ar), 127.5 (*s*, Ar), 128.2 (*s*, Ar), 132.1 (*s*, Ar), 133.5 (*s*, Ar) ppm. $C_{23}H_{26}FeBP$ (400.08): calcd. C 69.05, H 6.55; found C 68.99, H 6.77. HPLC (hexane:2-propanol, 95:5), t_R: 8.27 min $[\alpha]_D$ (*c* = 0.6, $CHCl_3$): −5.4°.

4.2.14. Deprotection of phosphine-boranes **11** and **12**

Method A: The phosphine-borane (**11a**, **11c**, **12a** or **12c**) was dissolved in dichloromethane and the solution cooled to −10 °C. 5 equivalents of $HBF_4{\cdot}OEt_2$ were added and the mixture was stirred for 1 h at room temperature. The completion of the deboronation and formation of the phosphonium salt was checked by ^{31}P NMR spectroscopy. The solution was treated with degassed, aqueous saturated solution of $NaHCO_3$ and stirred vigorously during 30 min ^{31}P NMR spectroscopy confirmed complete formation of the phosphine. The organic layer was separated, dried with sodium sulphate and filtered. This solution, containing the free phosphine, was immediately treated with the Pd dimer to form complexes **C**.

Method B: The phosphine-borane (**11b** or **12b**) and DABCO (10 equivalents) were dissolved in degassed toluene and heated to 90 °C during 6 h. The completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Once cold, this solution was treated with a CH_2Cl_2 solution of the Pd dimer to obtain the neutral complexes **C**.

4.3. Synthesis of palladium complexes

4.3.1. [PdCl(η^3-C_4H_7)(6)] (**C6**)

Phosphinite **6** (0.197 g, 0.56 mmol) was dissolved in 10 ml of anhydrous CH_2Cl_2. The dimer $[PdCl(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$ (0.181 g, 0.27 mmol) was added and the mixture was stirred for 1 h. The solvent was removed in vacuo and the remaining yellowish powder was washed several times with pentane. Finally, the obtained powder was filtered and dried under vacuum. NMR data of **C6** and the rest of Pd complexes are listed in Tables 1S–3S (Supporting information). Yield 0.28 g (91%). IR (KBr), ν (cm^{-1}): 1473, 1430. $C_{25}H_{28}ClO_3PPd$ (548.05): calcd. C 54.66, H 5.14; found C 54.33, H 5.08. MS (HR-ES(+)): *m*/*z* 513.0818 $[M - Cl]^+$. MS (HR-ES(+)): calcd. for $[M - Cl]^+$ *m*/*z* 513.0811, found 513.0818.

4.3.2. [PdCl(η^3-C_4H_7)(**8**)] (**C8**)

The same procedure used to prepare **C6** but using **8** was employed. Yield 80%. IR (KBr), ν (cm^{-1}): 1471, 1434. $C_{25}H_{28}ClO_2PPd$ (533.33): calcd. C 56.30, H 5.29; found C 56.60, H 5.10. MS (HR-ES (+)): calcd. for $[M - Cl]^+$ *m*/*z* 497.0862, found 497.0871.

4.3.3. [PdCl(η^3-C_4H_7)(**13a**)] (**C13a**)

The same procedure used to prepare **C6** but using **13a** was employed. Yield 90%. IR (KBr), ν (cm^{-1}): 1463, 1422. $C_{13}H_{30}ClPPdSi$ (387.31): calcd. C 40.31, H 7.81; found C 41.10, H 8.14.

4.3.4. [PdCl(η^3-C_4H_7)(**13b**)] (**C13b**)

The same procedure used to prepare **C6** but using **13b** (impurified with DABCO and $DABCO{\cdot}BH_3$) was employed. The crude complex was rapidly dissolved in anhydrous $CDCl_3$ and analysed by NMR. Attempts of purification resulted into deposition of Pd black.

4.3.5. [PdCl(η^3-C_4H_7)(**13c**)] (**C13c**)

The same procedure used to prepare **C6** but using **13c** was employed. The title product was recovered as an orange oil after concentration to dryness. IR (Nujol), ν (cm^{-1}): 1462. $C_{21}H_{30}ClPPd$, MS (HR-ES(+)): calcd. for $[M - Cl]^+$ *m*/*z* 419.1120, found 419.1126.

4.3.6. [PdCl(η^3-C_4H_7)(**14a**)] (**C14a**)

The same procedure used to prepare **C6** but using **14a** was employed. The title product was recovered as an orange oil after concentration to dryness. IR (Nujol), ν (cm^{-1}): 1460. $C_{19}H_{30}ClFePPdSi$, MS (HR-ES(+)): calcd. for $[M - Cl]^+$ *m*/*z* 479.0239, found 479.0237.

4.3.7. [PdCl(η^3-C_4H_7)(**14b**)] (**C14b**)

The same procedure used to prepare **C6** but using a solution of **14b** (impurified with DABCO and $DABCO{\cdot}BH_3$) in toluene was employed. The crude complex was dissolved in dichloromethane and rapidly washed with aqueous 10% solution of hydrochloric acid. The organic layer was separated, dried with Na_2SO_4, filtered and concentrated to dryness. The residue was purified by column chromatography (flash SiO_2, hexane/ethyl acetate 9:1 as eluent), yielding the title product as an orange oil after concentration to dryness. IR (KBr), ν (cm^{-1}): 1459. The value of the given elemental analysis is the best of several runs $C_{24}H_{32}ClFePPdSi$ (577.29): calcd. C 49.93, H 5.59; found C 46.13, H 5.89. MS (HR-ES(+)): calcd. for $[M - Cl]^+$ *m*/*z* 541.0395, found 541.0400.

4.3.8. [PdCl(η^3-C_4H_7)(**14c**)] (**C14c**)

The same procedure used to prepare C6 but using **14c** was employed. Yield 65%. IR (KBr), ν (cm^{-1}): 1413. $C_{27}H_{27}ClFePPd$ (580.19): calcd. C 55.90, H 4.69; found C 55.93, H 5.18.

4.4. General procedure for the enantioselective hydrovinylation of styrene

Hydrovinylation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to an ethanol bath and the temperature controlled using a thermostat to ±0.5 °C. Internal temperature was controlled with a termopar.

A mixture of the suitable neutral palladium complex **C** (0.045 mmol), $AgBF_4$ (8.8 mg, 0.045 mmol) and styrene (4.7 g, 45 mmol) in 10 ml of dry and freshly distilled dichloromethane was stirred for 5 min in the dark. After filtering off the AgCl formed, the solution was placed into the autoclave (which had been purged by

successive vacuum/nitrogen cycles and thermostated to 25 °C) by syringe. Ethylene was admitted until a pressure of 15 bar was reached. After the desired time, the autoclave was slowly depressurised and 10 ml of a 10% aqueous NH_4Cl solution was added. The mixture was stirred for 10 min in order 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 product distribution and the ee using 30 m (0.320 mm) Agilent HP5 and 30 m (0.25 mm) Astec Chiraldex DM Columns. The major components were also characterised by ^1H NMR.

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Appendix A. Supplementary material

CCDC-786189 contains the supplementary data for **12b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.034.

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