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Full Paper

Chiral P–P Ligands

Diphosphorus Ligands Containing a P-Stereogenic Phosphane and a Chiral Phosphite or Phosphorodiamidite – Evaluation in Pd-Catalysed Asymmetric Allylic Substitution Reactions

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Abstract: The synthesis of 14 new optically pure C_1-symmetric phosphane–phosphinite (**1**–**4**), phosphane–phosphite (**5**–**9**) and phosphane–phosphorodiamidite (**10**–**14**) ligands is reported. The ligands were prepared through the condensation of (2-hydroxyphenyl)phenylphosphanes PPh(2-PhOH)R (R = Me, *t*Bu and Ph) with chlorodiisopropylphosphane (**1** and **2**), chlorodiphenylphosphane (**3** and **4**), the chlorodioxaphosphepine derived from both enantiomers of 1,1′-bi-2-naphthol (**5**–**9**) and the chlorodiazaphosphepine derived from both enantiomers of *N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (**10**–**14**) in the presence of a base. With these ligands, cationic Pd complexes of the type $[Pd(\eta^3\text{-}C_4H_7)(PP')]PF_6$ (Pd**1**–Pd**14**) were obtained and characterised; the crystal structures of Pd**1**, Pd**2** and Pd**13** were obtained. In solution, the complexes are present as mixtures of two diastereomers because of the lack of symmetry of the ligand and the presence of the methallyl group. The Pd complexes catalyse the allylic alkylation with dimethyl malonate and the amination with benzylamine of the model substrate *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**). For the alkylation, full conversions and good enantioselectivities (up to 96 % *ee* with Pd**14**) were observed.

Introduction

Chiral phosphorus-based ligands have dominated asymmetric transition-metal homogeneous catalysis for more than 50 years.[1] Many of the most successful ligands are C_2-symmetric diphosphanes,[2] which were initially thought to be superior ligands to monophosphanes or C_1-symmetric ligands as the reduced number of intermediates and transition states in each step of a catalytic cycle would lead to higher enantioselectivities and simpler analysis of the results.

However, a much more complicated picture has now emerged. Although certain structural motifs lead to especially active and enantioselective ligands,[3] there will clearly never be a "universal ligand" suitable for all reactions and substrates. Therefore, all possible sources of structural diversity have been explored actively for the last two decades, and old dogmas and preconceptions have been revised or abandoned.[3,4] Nowadays, very active and enantioselective catalysts can contain ligands that are not phosphanes but possess one or more P–heteroatom bonds,[5] including many monophosphorus ligands.[6] It is also widely accepted that the previously ubiquitous C_2-symmetric diphosphorus ligands (PP) are not better per se than their C_1-symmetric counterparts (PP′).[5a,5c,7] Finally, a strong resurgence of P-stereogenic ligands has also occurred.[4b,8] The extraordinary activity in the area of ligand design is understandable for the ever-increasing demand of optically pure compounds in pharmaceutical, agrochemical and other fields and is evident from the number of recent reviews[5b,7,9] and monographs[4] about the synthesis of chiral phosphorus-based ligands.

Only a few C_1-symmetric diphosphorus ligands containing both a P-stereogenic phosphane and another phosphorus donor unit with a P–heteroatom bond have been reported.[10]

We have been working on the synthesis and catalytic applications of many chiral mono- and bidentate aminophosphane,[11] phosphinite,[12] phosphite[13] and phosphorodiamidite[14] ligands in several catalytic reactions. We have also been working on the synthesis and catalytic applications of P-stereogenic ligands.[12a,12b,15]

Therefore, it was deemed interesting to devote some effort to merge both areas of our previous research and prepare a few PP′ (P = P-stereogenic phosphane; P′ = phosphinite, phosphite or phosphorodiamidite) ligands and evaluate their catalytic potential. In this paper, we describe the synthesis of these ligands and their derived Pd complexes as well as their application as catalyst precursors in allylic substitution reactions.

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Results and Discussion

Ligand Synthesis

Upon analysing the possible routes to obtain modular P-stereogenic PP′ ligands with an appropriate bridge to form bidentate ligands, it was concluded that a relatively easy way would be the condensation reaction between an electrophilic chlorophosphorus precursor and a configurationally stable P-stereogenic 2-hydroxyphenylphosphane in the presence of base. Such reactions would yield PP′ ligands with rigid 2-oxyphenyl bridges between the two phosphorus atoms (Scheme 1).

An early paper of Pringle and Baker[16] described the preparation of one such ligand (see later), whereas Pizzano and co-workers have used this scaffold to prepare a series of phosphane–phosphite ligands and used them in Rh-[10f,10g,10l,17] and Ir-catalysed[10i,18] hydrogenations and in Rh-catalysed hydroformylation;[10l] however, only a few of their ligands possess a P-stereogenic phosphane moiety.

The required P-stereogenic 2-hydroxyphenylphosphanes are accessible as optically pure compounds by the well-known Jugé–Stephan method[19] starting from oxaphospholidine–borane **A**. Therefore, we started by reproducing the work of Stephan and co-workers,[20] who described the preparation of 2-hydroxyphenylphosphinite–borane **B**, and we obtained 2-hydroxyphenylphosphane **C**·BH_3 by treatment with excess methyllithium (Scheme 2).

A solution of **B** was also treated with excess *tert*-butyllithium to afford the corresponding 2-hydroxyphenylphosphane–borane **C′**·BH_3. It has to be noted that it is very difficult[21] to introduce the *tert*-butyl group to a phosphane through the Jugé–Stephan method. However, in this case, it seems that the presence of an oxygen-containing group at the *ortho* position relative to the P atom facilitates the organolithium attack.[21a,21c] Phosphane–boranes **C**·BH_3 and **C′**·BH_3 were deboronated by treatment with tetrafluoroboric acid to yield the free phosphinophenols **C** and **C′** as air-sensitive semisolids. The absolute configurations of the phosphorus atoms, expected to be *S*, could be verified by the crystal structures of the Pd complexes of the ligands (described below). The preparation of the achiral phosphinophenol **C″** was not required because it is commercially available. To complete the synthesis of the ligands, phosphinophenols **C**–**C″** were treated with the appropriate chlorophosphorus precursors (either commercially available or described previously)[14] in the presence of amines as detailed in the Experimental Section. After the removal of the ammonium salts by filtration and exhaustive drying under vacuum, the desired PP′ ligands were finally obtained as pasty solids. The ligands prepared in the present work are shown in Figure 1.

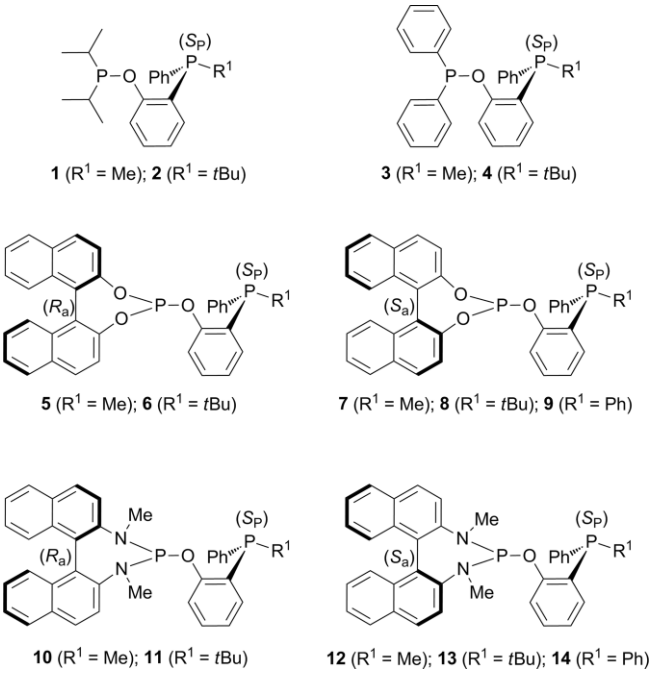
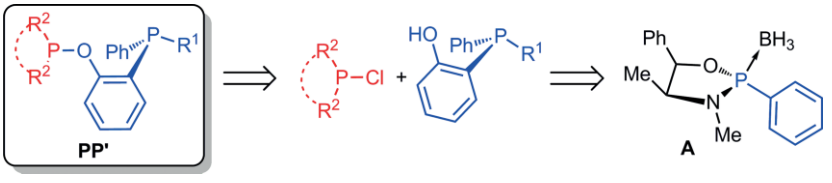
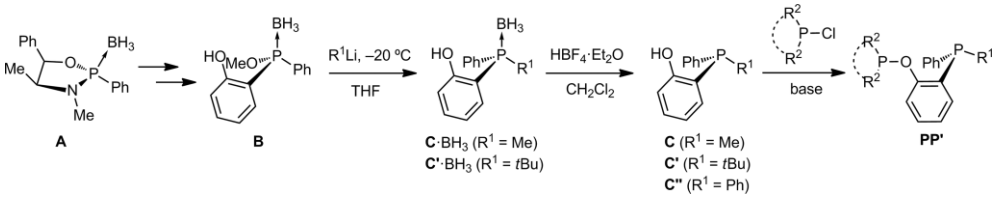


Figure 1. Prepared PP′ ligands **1**–**14**.

To the best of our knowledge, all of the prepared ligands are new except ligand **9**, which was described by Baker and Pringle[16] and used by Pizzano and co-workers in Rh-catalysed hydrogenation.[17b] The ligands were characterised by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which supported the structures depicted in Figure 1. In general, two doublets ($^4J_{P,P}$ = 0–41 Hz) were observed in the $^{31}P\{^1H\}$ NMR spectra, and the coupling



Scheme 1. Retrosynthetic route to the PP′ ligands.

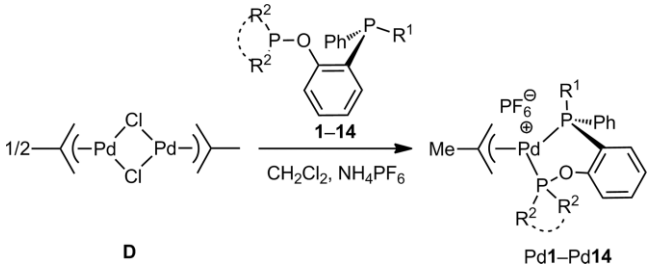


Scheme 2. Preparation of PP′ ligands **1**–**14**.

constants are strongly dependent on the ligand. The coupling constants for the phosphane–phosphinite ligands **1**–**4** are rather small (0–4 Hz), but those for phosphane–phosphite ligands **5**–**9** are much larger (15–42 Hz), whereas those for the phosphane–phosphorodiamidite ligands **10**–**14** have intermediate values (7–16 Hz). As expected,[14a] small differences in the $^{31}P\{^1H\}$ NMR chemical shifts for each of the members in the diastereomeric pairs **5**/**7**, **6**/**8**, **10**/**12** and **11**/**13** could be spotted. In the ^1H NMR spectra of phosphane–phosphorodiamidite ligands **10**–**14**, two doublets appeared for the two inequivalent N–Me groups coupled to the phosphorus atom, as previously reported for related compounds.[14a] A more thorough characterisation was not possible owing to the rapid degradation of the ligands by oxidation, hydrolysis, or both if they were not kept under a protective nitrogen atmosphere. Therefore, the ligands were not stored but used immediately for complexation to Pd as described in the following section.

Preparation of Pd Complexes

The reaction of the Pd dimer **D** with 2 equiv. of ligand in dichloromethane in the presence of excess ammonium hexafluorophosphate[12b,12c] yielded the expected cationic complexes of the type $[Pd(\eta^3\text{-}C_4H_7)(PP')]PF_6$ (Pd**1**–Pd**14**) as white or pale yellow solids after workup (Scheme 3).



Scheme 3. Preparation of Pd complexes Pd**1**–Pd**14**.

The characterisation of solutions of the complexes by multinuclear ($^{31}P\{^1H\}$, ^1H, and in some cases $^{13}C\{^1H\}$) NMR spectroscopy revealed duplicate peaks indicative of the existence of two diastereoisomeric species owing to the lack of C_2 symmetry of the bidentate ligand and the presence of the η^3-methallyl moiety, as previously observed for neutral complexes of the type $[Pd(\eta^3\text{-}C_4H_7)Cl(P)]$ (P = chiral monophosphorus ligand).[12a,12c,14a,14c,22] The integration of the $^{31}P\{^1H\}$ and ^1H NMR spectra allowed the estimation of the diastereomeric ratio for each complex. There does not seem to be a simple correlation between the structures of the complexes and their diastereomeric ratios, which varied from 1:1 (Pd**2**, Pd**4**, Pd**7**, Pd**12** and Pd**14**) to a maximum of 1:2.7 for Pd**5**. In the $^{31}P\{^1H\}$ NMR spectra, two sharp pairs of doublets, one for each diastereomer, are indicative of AX spin systems. The $^2J_{P,P'}$ values are in the range previously reported for related compounds[14d,23] and follow the same trends as the $^4J_{P,P'}$ values for the free ligands. The ^{31}P coordination chemical shifts (CCS, defined as $\delta_{complex} - \delta_{free\ ligand}$) of the phosphane fragments are approximately +30 ppm for the complexes, as expected. In contrast, the other phosphorus moiety shows a larger sensitivity to coordination. The CCS values are approximately +40 ppm for phosphinite complexes Pd**1**–Pd**4**, +2 ppm for phosphite complexes Pd**5**–Pd**9** and −15 ppm for phosphorodiamidite complexes Pd**10**–Pd**14**. The shielding of the P atom of the phosphorodiamidite upon coordination is probably due to the low σ donation of this part of the ligand and has been reported for the complexation of other chiral phosphorodiamidite ligands.[14,24]

In ^1H NMR spectra, two sets of peaks associated with the aliphatic protons of each ligand are observed (see Experimental Section and Table S1 of the Supporting Information for details). For Pd**10**–Pd**14** bearing the phosphane–phosphorodiamidite ligands, two pairs of doublets, one for each isomer, account for the methyl groups of the diazaphosphepine part of the ligand. Interestingly, the $^3J_{H,P}$ coupling constants are clearly different for the two methyl groups of each isomer (ca. 10 and 15 Hz), and the same can be observed in the $^{13}C\{^1H\}$ NMR spectra, in which $^2J_{C,P} \approx 12$ and 30 Hz. This suggests that the amino groups have a different orientation in solution with respect to the P–Pd bond, as observed in the solid state (vide infra) and for previously reported related compounds.[14d,24,25]

For the methallyl group, the ^1H NMR spectra (Table S1) confirm the presence of two diastereomers. Hence, two singlets at δ = 1.3–2.0 ppm account for the methyl group, whereas two sets of four peak in the range δ = 2.3–4.8 ppm can be assigned to the four protons of the methallyl group. As expected,[14a,14d,22,23] the *anti* protons usually appear at higher fields (δ = 2.3–3.8 ppm) as doublets with coupling constants of ca. 10 Hz owing to the coupling with the phosphorus atom at the relative *trans* position. In a few cases, they appear as doublets of doublets, also coupled to the phosphorus atom at the *cis* position. At lower fields (δ = 3.6–4.8 ppm), two sets of *syn* protons appear as broad singlets, doublets, doublets of doublets or multiplets. For these protons, the coupling constants are smaller, as commonly found for comparable systems.[14a,14d,22,23] In the $^{13}C\{^1H\}$ NMR spectra (Table S1), the methylene termini of the methallyl groups appeared as doublets or doublets of doublets owing to the coupling with one or two phosphorus atoms, respectively. The difference in the chemical shifts, which has been used to evaluate the asymmetry of the allyl bonding,[26] ranged from 2.5 ppm for one of the isomers of Pd**3** to 13.6 ppm for one of the isomers of Pd**2**.

For Pd**1**, Pd**2** and Pd**13**, single crystals suitable for X-ray diffraction studies were obtained by layering hexane on solutions of the complexes in dichloromethane. For all of these complexes, the structures are composed of discrete molecules of the cationic complex, hexafluorophosphate anions and dichloromethane molecules as well as adventitious water molecules for Pd**13** separated by van der Waals distances. It is interesting to note that only one diastereomer was found in all of the crystals analysed. Representations of the molecular structures of Pd**1** and Pd**2** and a selection of bond lengths and angles are given in Figure 2.

For both structures, the palladium atom sits in a distorted square-planar geometry, coordinated to the two phosphorus atoms and to the terminal C atoms of the methallyl moiety. The metric parameters are in the ranges expected for cationic allylpalladium complexes.[12b,14d,22] For both structures, the Pd–

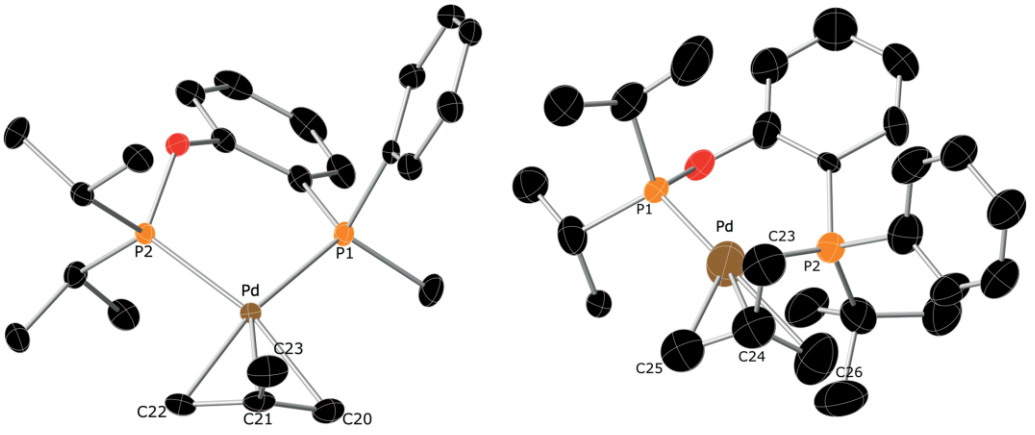


Figure 2. ORTEP representations (thermal ellipsoids drawn at 50 % of probability level, H atoms and PF_6^- anions removed for clarity) of Pd**1** (left) and Pd**2** (right). Distances [Å] and angles [°] for Pd**1**: Pd–P(1) 2.2904(6), Pd–P(2) 2.2510(6), Pd–C(20) 2.206(3), Pd–C(21) 2.212(2), Pd–C(22) 2.159(2), C(20)–C(21) 1.402(4), C(21)–C(22) 1.419(4), P(1)–Pd–Pd(2) 92.11(2), P(2)–Pd–C(22) 97.92(7), C(22)–Pd–C(20) 67.19(10), C(20)–Pd–P(1) 102.67(8); for Pd**2**: Pd–P(1) 2.232(2), Pd–P(2) 2.286(3), Pd–C(24) 2.087(10), Pd–C(25) 2.299(12), Pd–C(26) 2.552(12), C(24)–C(25) 1.366(17), C(24)–C(26) 1.447(17), C(24)–C(23) 1.365(15), P(1)–Pd–Pd(2) 94.67(9), P(1)–Pd–C(25) 125.6(3), C(25)–Pd–C(26) 61.1(4), C(26)–Pd–P(2) 76.4(3).

C_{allyl} distance *trans* to the phosphinite moiety is longer than the Pd–C_{allyl} distance *trans* to the phosphane moiety, especially for Pd**2**. The same trend has been found for comparable complexes.[27]

The X-ray structure of the phosphane–phosphorodiamidite complex Pd**13** is depicted in Figure 3.

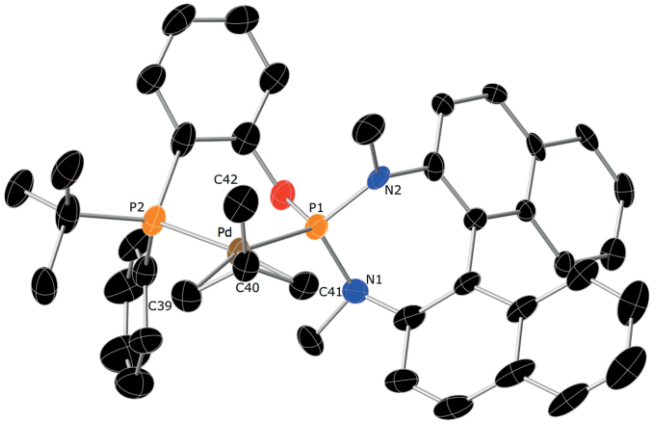


Figure 3. ORTEP representation (thermal ellipsoids drawn at 50 % of probability level, H atoms, water molecules and the PF_6^- anion removed for clarity) of Pd**13**. Distances [Å] and angles [°]: Pd–P(1) 2.2568(13), Pd–P(2) 2.3192(14), Pd–C(39) 2.177(5), Pd–C(40) 2.189(6), Pd–C(41) 2.158(6), C(39)–C(40) 1.428(9), C(40)–C(41) 1.376(8), C(40)–C(42) 1.517(9), P(1)–N(1) 1.683(4), P(1)–N(2) 1.656(5), P(1)–Pd–P(2) 91.60(5), P(2)–Pd–C(39) 104.10(18), C(39)–Pd–C(41) 66.6(2), C(41)–Pd–P(1) 97.63(16), ΣN(1) 346.7, ΣN(2) 357.1.

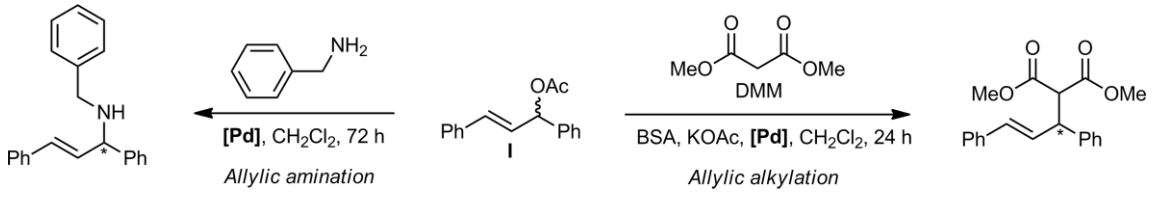
The complex has a distorted square-planar geometry around the palladium atom, and the coordination positions are occupied by the two phosphorus atoms of the ligand and the two terminal atoms of the methallyl fragment. The distances and angles are similar to those for comparable complexes.[14d] The Pd–C_{allyl} distance *trans* to the phosphorodiamidite fragment is longer than the Pd–C_{allyl} distance *trans* to the phosphane moiety, as observed for complexes containing comparable phosphane–phosphoramidite ligands.[27] The two P–N bond lengths are different and in the range found for similar compounds.[14a,14c,14d] The values suggest a partial double-bond character, as found in related complexes.[14d] The sums of the bond angles around both nitrogen atoms are close to 360°; therefore, the coordination is close to planarity, as occurs for related complexes.[14d,25] The torsion angle of the binaphthyl group is 59.14°.

It is interesting to note that the longest Pd–C_{allyl} distance in all the three crystal structures is always in the *cis* position with respect to the P-stereogenic phosphane group.

Pd-Catalysed Allylic Substitution

The performance of the ligands **1**–**14** was tested in Pd-catalysed asymmetric allylic substitution reactions with the model substrate *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) and the cationic palladium complexes Pd**1**–Pd**14** (Scheme 4).

The studied allylic substitutions involved alkylation with the C-nucleophile derived from dimethyl malonate (DMM) in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and potassium acetate and amination with benzylamine. The obtained results are given in Table 1.



Scheme 4. Allylic substitution reactions of **I** catalysed by Pd**1**–Pd**14** complexes.

Table 1. Results of asymmetric allylic substitutions of **I** with Pd**1**–Pd**14**.

Entry[a]	Pd complex	Alkylation Conv. [%][b]	*ee* [%][c]	Amination Conv. [%]b	*ee* [%][c]
1	Pd**1**	>99	9 (*S*)	40	<5
2	Pd**2**	>99	5 (*S*)	20	8 (*S*)
3	Pd**3**	>99	11 (*R*)	10	<5
4	Pd**4**	>99	45 (*R*)	17	18 (*S*)
5	Pd**5**	>99	80 (*R*)	<5	–
6	Pd**6**	>99	94 (*R*)	<5	–
7	Pd**7**	>99	66 (*S*)	<5	–
8	Pd**8**	>99	81 (*S*)	<5	–
9	Pd**9**	>99	88 (*S*)	<5	–
10	Pd**10**	>99	82 (*R*)	31	18 (*S*)
11	Pd**11**	>99	56 (*R*)	40	37 (*S*)
12	Pd**12**	>99	73 (*S*)	61	42 (*R*)
13	Pd**13**	>99	50 (*S*)	70	39 (*R*)
14	Pd**14**	>99	96 (*S*)	80	70 (*R*)

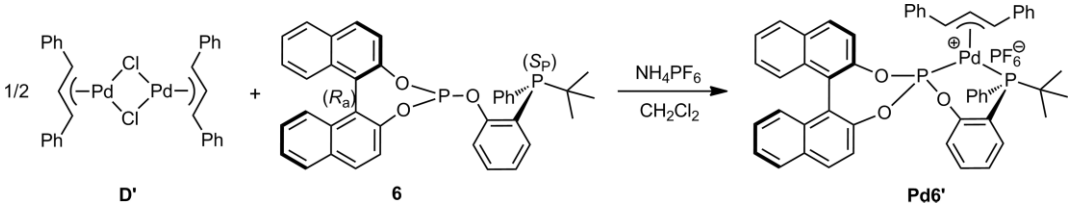
[a] Conditions for allylic alkylations with DMM: Pd complex (0.01 mmol), **I** (1 mmol), dimethyl malonate (3 mmol), BSA (3 mmol) and KOAc (1 mg) in CH_2Cl_2 (5 mL) at r.t. for 24 h; for allylic aminations with benzylamine: Pd complex (0.01 mmol), **I** (1 mmol) and benzylamine (3 mmol) in CH_2Cl_2 (5 mL) at r.t. for 72 h. [b] Conversion percentage expressed as **I** consumption, determined by NMR spectroscopy and HPLC. [c] Enantiomeric excesses determined by HPLC.

All of the complexes were active in the allylic alkylations and provided complete conversions in 24 h with 1 % of complex. A wide range of *ee* values (5–96 %) was obtained, in line with the results for other C_1-symmetric diphosphorus ligands.[10d,27,28] The complexes with phosphane–phosphinite ligands, containing only the phosphorus atom as a stereogenic element (Table 1, Entries 1–4), led to the lowest enantioselectivities, and Pd**4** achieved a moderate value of 45 % *ee* (Table 1, Entry 4). The results with the other complexes with two stereogenic elements (Table 1, Entries 5–14) allow the discussion of the match–mismatch effects between them. A general trend is that the enantioselectivities are considerably higher than those for complexes containing phosphane–phosphinite ligands, and this highlights the efficiency of the 1,1′-binaphthyl unit as a chiral inductor. Indeed, most of the ligands give very enantioselective systems that afford similar or better results than those with other phosphane–phosphite[10d,28a] or phosphane–phosphoramidite ligands[27] except Pd**7**, Pd**11** and Pd**13** (Table 1, Entries 7, 11 and 13). There is a match–mismatch effect between the absolute configurations of the 1,1′-bi-2-naphthyl fragment of the phosphite or phosphorodiamidite moiety and the stereogenic phosphorus atom. Clearly, the matched combination corresponds to the (R_a,S_P) ligands (cf. Table 1, Entries 5 vs. 7, 6 vs. 8, 10 vs. 12 and 11 vs. 13). The absolute configurations of the alkylation product are controlled by the absolute configuration of the phosphite or phosphorodiamidite part of the ligand; therefore, (R_a) ligands preferentially produce the (*R*)-alkylation product (Table 1, Entries 5, 6, 10 and 11), whereas (S_a) ligands give the (*S*)-alkylation product (Table 1, Entries 7–9 and 12–14). The same fact was observed by van Leeuwen and co-workers[10d] for related phosphane–phosphite ligands with a more flexible bridge. The only relevant difference between the P-stereogenic phosphane–phosphite (Table 1, Entries 5–9) and phosphane–phosphorodiamidite (Table 1, Entries 10–13) complexes is that the complexes bearing the *t*Bu-containing phosphanes are more selective than the Me counterparts for the former (cf. Table 1, Entries 5 vs. 6 and 7 vs. 8), whereas the trend is the opposite for the latter (cf. Table 1, Entries 10 vs. 11 and 12 vs. 13). The best results were obtained with Pd**6**, Pd**9** and Pd**14** (Table 1, Entries 6, 9 and 14), the latter two of which contain an achiral phosphane moiety.

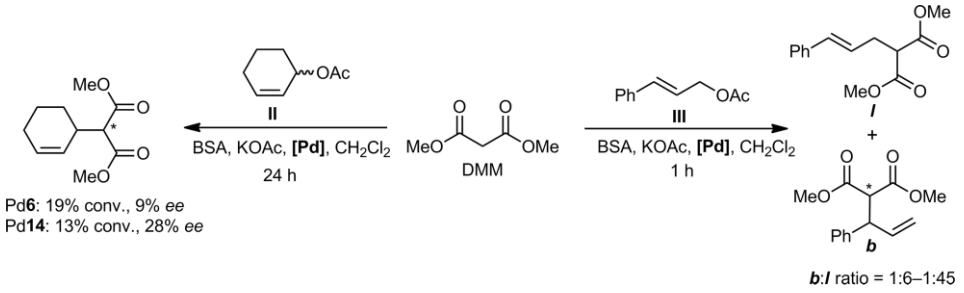
Palladium complexes Pd**1**–Pd**14** were also tested in the allylic amination of **I** with excess benzylamine. The systems are much slower in the allylic amination than in the alkylation, as reported for related phosphite–phosphoramidite ligands,[29] and the complexes with phosphane–phosphite ligands are totally inactive (Table 1, Entries 5–9). The other complexes led to low or moderate conversions at best. The complexes with phosphane–phosphinite ligands gave very poor enantioselectivities (Table 1, Entries 1–4), whereas those with phosphane–phosphorodiamidite ligands (Table 1, Entries 10–14) were slightly better. Complex Pd**14**, containing an achiral phosphane moiety, is clearly the best of the series in terms of activity and enantioselectivity. In this case, (R_a) ligands gave preferentially the (*S*) amination product, which is the same sense of induction as in the alkylation reaction, as the amination product has the opposite absolute configuration to the alkylation product owing to a change of priority of the groups in the Cahn–Ingold–Prelog (CIP) rules.

To help to rationalise the absolute configurations of the substitution products of **I**, complex Pd**6′**, bearing ligand **6** and the 1,3-diphenylallyl moiety, was prepared and characterised (Scheme 5).

This complex is one of the intermediates in the substitution of **I** with ligand **6**. In solution, it is present as a mixture of two diastereomers in a 1:3.5 ratio, whereas this ratio was 1:2.3 for Pd**6**. Unfortunately, we were unable to obtain any crystals of Pd**6′** suitable for X-ray diffraction. From the crystal structure data of Pd**1**, Pd**2** and Pd**13**, it seems that the phosphane (P) part exerts a lower *trans* influence than the other phosphorus moiety (P′). In principle, this means that the most electrophilic carbon atom of the allyl group and the one that will be preferentially attacked by the nucleophile will be the one at the *cis* position relative to the phosphane part. We assumed that the



Scheme 5. Preparation of complex Pd**6′**.



Scheme 6. Allylic alkylation of **II** and **III** catalysed by Pd complexes.

same trends would apply to the 1,3-diphenylallyl complexes and performed PM3-level calculations of the energies of the diastereomers of Pd**6′**, Pd**8′**, Pd**9′** and Pd**14′** (see Supporting Information). The absolute configuration of the substitution product resulting from the attack of the nucleophile at the allylic carbon atom *cis* to the phosphane moiety in the most stable isomer is coherent with the absolute configuration of the major enantiomer obtained experimentally.

We also studied the alkylations of cyclohexen-3-yl acetate (**II**) and cinnamyl acetate (**III**) with DMM (Scheme 6).

The more enantioselective catalysts Pd**6** and Pd**14** were chosen to study their potential in the alkylation of substrate **II**. As very low conversions and enantioselectivities were found within 24 h of reaction time, no more catalytic runs with this substrate were carried out. Finally, some of the complexes were tested in the alkylation of **III**. The complexes led to full conversions at 1 h reaction times, but, as expected,[12b] the achiral linear alkylation product (***l***) was favoured over the branched isomer (***b***). The full results can be found in Table S2 of the Supporting Information.

Conclusions

The preparation of 14 new, chiral phosphane–phosphinite, phosphane–phosphite and phosphane–phosphorodiamidite ligands has been reported. Most of them bear a stereogenic phosphorus atom and have been conveniently prepared by a condensation reaction between a phosphinophenol and a chlorophosphorus precursor. Many of the ligands include phosphite and phosphorodiamidite parts with a chiral 1,1′-binaphthyl moiety. The ligands have been designed to have one or two stereogenic elements to increase their modularity and to study the influence of the different combinations on the catalysis.

The cationic Pd complexes of the ligands with η^3-methallyl coligands have been prepared and characterised in solution by NMR spectroscopy and also by X-ray crystallography for Pd**1**, Pd**2** and Pd**13**. They are good catalytic precursors for allylic substitutions (alkylation with DMM and amination with benzylamine) with substrates **I**, **II** and **III**. In the alkylation of **I**, all of the complexes gave full conversion to the alkylation product after 24 h, and very high enantioselectivities (up to 95 % *ee*) were obtained with Pd**6** and Pd**14**. The stereochemical course of the reaction is coherent with the nucleophilic attack at the allylic carbon atom in *cis* position relative to the phosphane. Some match–mismatch effects have been identified, and it is the absolute configuration of the 1,1′-binaphthyl-based phosphite or phosphorodiamidite part of the ligand that dictates the absolute configuration of the alkylation product, but the phosphane part also has some influence on the level of enantioselection.

Given the results presented here and the high modularity of the ligands, we are currently preparing new ligands of the same type and using them and the reported ones in new catalytic reactions. The results of these studies will be reported in due course.

Experimental Section

General Data: All compounds were prepared under a purified nitrogen atmosphere by standard Schlenk and vacuum-line techniques. The solvents were obtained from a solvent-purification system or purified by standard procedures[30] and kept under nitrogen. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and HSQC ^{1}H–^{13}C NMR spectra were recorded with 300 and 400 MHz spectrometers with $CDCl_3$ as the solvent. The protons of the BH_3 moieties of the phosphane–boranes appeared in the aliphatic region of the spectra as very broad bands and have not been assigned. For the Pd complexes, ma and mi refer to the major and minor diastereomers of the complexes, respectively. The IR spectra were recorded with samples in KBr, and the main absorption bands are expressed in cm^{-1}. High-resolution mass spectrometry analyses were performed with electrospray ionisation. The optical rotations were measured at room temperature with a sodium lamp at the sodium D-line wavelength (589.592 nm). In all cases, the solvent was CH_2Cl_2, and the concentration was 1 g/100 mL. The allylic substitution reactions of **I** were analysed with an HPLC instrument equipped with a multidiode array detector and fitted with an OD-H chiral column. The eluent was a 95:5 *n*-hexane/*i*PrOH mixture. The allylic alkylations of **II** and **III** were analysed by GC with a chromatograph equipped with a capillary column with He as the carrier gas and a flame-ionisation detector (FID). Phosphinite–borane **B** [prepared from **1**,[19] which was prepared from (1*R*,2*S*)-(–)-ephedrine],[20] phosphane–borane **C**·BH_3,[20] the chlorodiazaphosphosphepine derived from *N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine,[14] Pd dimers **D**[31] and **D′**[32] and substrates **I**[33] and **III**[34] were prepared by literature procedures, whereas other reagents were used as received from commercial suppliers. CCDC 1461787 (for Pd**1**), 1461788 (for Pd**2**) and 1461789 (for Pd**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

(*S*)-(*tert*-Butyl)(2-hydroxyphenyl)phenylphosphane–Borane (C′·BH_3): Phosphinite–borane **B** (528 mg, 2.1 mmol) was dissolved in diethyl ether (30 mL), and the mixture was cooled to –30 °C. A 1.6 M

solution of *t*BuLi (3.1 mL, 5.0 mmol) was added by syringe, and the mixture was stirred for 1 h and left to warm to room temperature. Water (20 mL) was added carefully, the biphasic mixture was extracted with diethyl ether (3 × 10 mL), and the combined organic phases were washed with water (20 mL). The final organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was removed under vacuum to furnish the title product as an oil, yield 553 mg (97 %). ^{1}H NMR (400 MHz): δ = 8.06 (s, br, 1 H), 7.79–7.74 (m, 2 H), 7.51–7.37 (m, 4 H), 7.24–7.19 (m, 1 H), 6.98 (ddd, J = 8.4, 5.2, 1.2 Hz, 1 H), 6.88 (tm, J = 6.8 Hz, 1 H), 1.38 (d, $^3J_{H,P}$ = 14.8 Hz, 9 H) ppm. ^{13}C{^{1}H} NMR (101 MHz): δ = 161.8–109.9 (C, CH, Ar), 32.2 (d, $^1J_{C,P}$ = 32.7 Hz, C), 26.7 (d, $^2J_{C,P}$ = 3.0 Hz, 3 × CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +26.6 (d, br, $^1J_{B,P}$ = 71.0 Hz) ppm. HRMS: calcd. for $C_{16}H_{21}BOP$ [M – H]$^+$ 271.1417; found 271.1406. $[\alpha]_D$ = +140.8 (CH_2Cl_2, c = 1). HPLC analysis with a chiral column indicated that the compound was essentially enantiopure (see HPLC trace in the Supporting Information).

(*S*)-(2-Hydroxyphenyl)methylphenylphosphane (C): Phosphane–borane **C**·BH_3 (310 mg, 1.2 mmol) was dissolved in dichloromethane, and the solution was cooled to 0 °C. HBF_4·Et_2O (0.87 mL, 6.3 mmol) was added rapidly by syringe, the mixture was vigorously stirred for 1 h and deoxygenated thoroughly, and a saturated aqueous $NaHCO_3$ solution (10 mL) was added carefully. The organic layer was transferred to another flask, washed with thoroughly with deoxygenated water, dried with anhydrous sodium sulfate, filtered and brought to dryness under vacuum. The title product was obtained as an air-sensitive colourless oil, yield 200 mg (73 %). The characterisation data of this compound agreed with the data reported previously.[10f,35]

(*S*)-(*tert*-Butyl)(2-hydroxyphenyl)phenylphosphane (C′): The procedure was the same as that used to obtain **C**. From phosphane–borane **C′**·BH_3 (1000 mg, 3.7 mmol) and HBF_4·Et_2O (2.3 mL, 16.7 mmol), the title product was obtained as a colourless oil, yield 860 mg (90 %). The characterisation data of this compound agreed with the values reported previously.[36] ^{1}H NMR (400 MHz): δ = 7.74–7.70 (m, 2 H), 7.67–7.64 (m, 1 H), 7.30–7.28 (m, 2 H), 7.25–7.23 (m, 3 H), 6.96–6.92 (m, 1 H), 1.28 (d, $^3J_{H,P}$ = 13.6 Hz, 9 H) ppm. ^{13}C{^{1}H} NMR (101 MHz): δ = 161.0–115.3 (C, CH, Ar), 31.4 (d, $^1J_{C,P}$ = 7.8 Hz, C), 28.5 (d, $^2J_{C,P}$ = 13.8 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = –19.0 (s) ppm.

Compound 1: Hydroxyphosphane **C** (345 mg, 1.5 mmol) was dissolved in toluene (20 mL), and triethylamine (0.3 mL, 2.2 mmol) was added rapidly by syringe. To this mixture, a solution of chlorodiisopropylphosphane (0.24 mL, 1.5 mmol) in toluene (15 mL) was added dropwise over 15 min, and the suspension was stirred for 1 h. The ammonium salts were removed by filtration, and the filtrate was brought to dryness to afford the title product as a pasty, white solid, yield 445 mg (90 %). ^{1}H NMR (400 MHz): δ = 7.43–7.35 (m, 3 H), 7.30–7.27 (m, 3 H), 7.26–7.23 (m, 1 H), 7.10 (ddd, J = 7.6, 4.4, 1.6 Hz, 1 H), 6.95 (tm, J = 7.6 Hz, 1 H), 1.90 (m, 1 H), 1.68 (m, 1 H), 1.54 (d, $^3J_{H,P}$ = 4.4 Hz, 3 H), 1.17 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 10.8, 6.8 Hz, 3 H), 1.07 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 16.0, 7.6 Hz, 3 H), 0.94 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 16.0, 7.2 Hz, 3 H), 0.82 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 11.2, 6.8 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +145.1 (s), –37.5 (s) ppm.

Compound 2: The procedure was the same as that used to obtain **1**. From hydroxyphosphane **C′** (284 mg, 1.1 mmol), the title product was obtained as a white, pasty solid, yield 387 mg (94 %). ^{1}H NMR (400 MHz): δ = 7.52 (dt, J = 7.6, 2.0 Hz, 1 H), 7.41–7.35 (m, 3 H), 7.27–7.22 (m, 4 H), 6.94 (td, J = 7.6, 1.2 Hz, 1 H), 2.01 (m, 1 H), 1.88 (m, 1 H), 1.23 (d, $^3J_{H,P}$ = 12.4 Hz, 9 H), 1.18 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 11.2, 7.2 Hz, 3 H), 1.05 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 15.6, 7.2 Hz, 3 H), 0.86 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 15.6, 7.2 Hz, 3 H), 0.75 (dd, $^3J_{H,P}$, $^3J_{H,H}$ = 11.6, 7.2 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +145.9 (d, $^4J_{P,P}$ = 1.1 Hz), +2.0 (d, $^4J_{P,P}$ = 1.1 Hz) ppm.

Compound 3: The procedure was analogous to that used to obtain **1**. From hydroxyphosphane **C** (130 mg, 0.60 mmol) and chlorodiphenylphosphane (0.11 mL, 0.6 mmol), the title product was obtained as a white, pasty solid, yield 201 mg (84 %). ^{1}H NMR (400 MHz): δ = 7.80–7.73 (m, 2 H), 7.72–7.68 (m, 1 H), 7.61–7.48 (m, 4 H), 7.45–7.17 (m, 9 H), 7.15–7.10 (m, 1 H), 7.01 (tm, J = 7.6 Hz, 1 H), 6.92 (t, br, J = 7.2 Hz, 1 H), 1.52 (d, $^2J_{H,P}$ = 4.4 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +108.2 (d, $^4J_{P,P}$ = 2.1 Hz), –38.2 (s) ppm.

Compound 4: The procedure was the same as that used to obtain **3**. From hydroxyphosphane **C′** (242 mg, 0.94 mmol), the title product was obtained as a white, pasty solid, yield 396 mg (95 %). ^{1}H NMR (400 MHz): δ = 7.64–7.57 (m, 3 H), 7.37–7.33 (m, 6 H), 7.30–7.20 (m, 8 H), 7.11 (m, 1 H), 7.04 (td, J = 7.6, 1.2 Hz, 1 H), 1.24 (d, $^3J_{H,P}$ = 12.4 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +108.6 (d, $^4J_{P,P}$ = 3.6 Hz), +0.8 (d, $^4J_{P,P}$ = 3.4 Hz) ppm.

Compound 5: Hydroxyphosphane **C** (179 mg, 0.83 mmol) was dissolved in toluene (20 mL), and triethylamine (0.2 mL, 1.5 mmol) was added rapidly by syringe. To this mixture, a solution of the chlorodioxaphosphepine derived from (*R*)-(+)-1,1′-bi(2-naphthol)[37] (291 mg, 0.83 mmol) in toluene (10 mL) was added dropwise over 15 min, and the suspension was stirred for 1 h. The ammonium salts were removed by filtration, and the filtrate was brought to dryness to afford the title product as a white solid, yield 343 mg (78 %). ^{31}P{^{1}H} NMR (162 MHz): δ = +143.37 (d, $^4J_{P,P}$ = 20.1 Hz), –36.50 (d, $^4J_{P,P}$ = 20.2 Hz) ppm.

Compound 6: The procedure was the same as that used to obtain **5**. From hydroxyphosphane **C′** (245 mg, 0.95 mmol), the title product was obtained as a white solid, yield 409 mg (75 %). ^{1}H NMR (400 MHz): δ = 7.31–7.09 (m, 10 H), 7.04 (dd, J = 8.0, 4.0 Hz, 1 H), 6.86–6.78 (m, 5 H), 6.74–6.68 (m, 2 H), 6.64–6.55 (m, 3 H), 0.88 (d, $^3J_{H,P}$ = 12.4 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +144.31 (d, $^4J_{P,P}$ = 41.5 Hz), +1.30 (d, $^4J_{P,P}$ = 41.3 Hz) ppm.

Compound 7: The procedure was the same as that used to obtain **5** but with the chlorodioxaphosphepine derived from (*S*)-(–)-1,1′-bi(2-naphthol). From hydroxyphosphane **C** (378 mg, 1.75 mmol), the title product was obtained as a white solid, yield 770 mg (83 %). ^{1}H NMR (400 MHz): δ = 7.99 (d, J = 8.8 Hz, 1 H), 7.93 (t, J = 8.4 Hz, 1 H), 7.91 (t, J = 8.8 Hz, 1 H), 7.55 (d, J = 8.8 Hz, 1 H), 7.52 (d, J = 8.8 Hz, 1 H), 7.47–7.41 (m, 4 H), 7.38 (d, J = 6.8 Hz, 2 H), 7.31–7.25 (m, 6 H), 7.22–7.08 (m, 4 H), 1.57 (d, $^2J_{H,P}$ = 4.0 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +143.45 (d, $^4J_{P,P}$ = 16.7 Hz), –37.38 (d, $^4J_{P,P}$ = 16.7 Hz) ppm.

Compound 8: The procedure was the same as that used to obtain **7**. From hydroxyphosphane **C′** (379 mg, 1.47 mmol), the title product was obtained as a white solid, yield 660 mg (78 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 8.00 (d, J = 8.8 Hz, 1 H), 7.83 (t, J = 8.8 Hz, 2 H), 7.81–7.63 (m, 3 H), 7.66 (t, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 1 H), 7.39 (dd, J = 8.4, 4.4 Hz, 1 H), 7.34–7.29 (m, 2 H), 7.27–7.18 (m, 5 H), 7.15–7.02 (m, 3 H), 7.02 (t, J = 6.8 Hz, 1 H), 1.42 (d, $^3J_{H,P}$ = 12.4 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = +142.33 (d, $^4J_{P,P}$ = 28.8 Hz), +0.80 (d, $^4J_{P,P}$ = 29.0 Hz) ppm.

Compound 9: The procedure was the same as that used to obtain **7**. From hydroxyphosphane **C″** (242 mg, 0.87 mmol), the title product was obtained as a white solid, yield 480 mg (93 %). The characterisation data of this compound agreed with the values reported previously.[16] ^{1}H NMR (400 MHz): δ = 7.87 (d, J = 8.8 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.68 (d, J = 8.8 Hz, 1 H), 7.38–7.23 (m, 16 H), 7.21–7.12 (m, 4 H), 6.99 (t, J = 7.2 Hz, 1 H),

6.70 (ddd, *J* = 7.6, 4.0 Hz, 1.6 1 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +143.21 (d, $^{4}J_{P,P}$ = 14.7 Hz), –16.00 (d, $^{4}J_{P,P}$ = 14.7 Hz) ppm.

Compound 10: Hydroxyphosphane **C** (134 mg, 0.62 mmol) was dissolved in toluene (20 mL), and triethylamine (0.2 mL, 1.5 mmol) and 4-dimethylaminopyridine (DMAP, 2 mg, 0.016 mmol) were added rapidly. To this mixture, a solution of the chlorodiazaphosphepine derived from (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine[14d] (0.62 mmol) in toluene (10 mL) was added dropwise over 15 min, and the suspension was stirred for 1 h. The ammonium salts were removed by filtration, and the filtrate was brought to dryness to afford the title product as a white solid, yield 311 mg (90 %). ^{1}H NMR (400 MHz): δ = 7.93–7.84 (m, 4 H), 7.60 (d, *J* = 8.8 Hz, 1 H), 7.49 (d, *J* = 8.8 Hz, 1 H), 7.41–7.30 (m, 2 H), 7.27–7.10 (m, 11 H), 6.98–6.95 (m, 2 H), 3.06 (d, $^{3}J_{H,P}$ = 13.6 Hz, 3 H), 2.89 (d, $^{3}J_{H,P}$ = 9.6 Hz, 3 H), 1.35 (d, $^{2}J_{H,P}$ = 4.4 Hz, 3 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +170.59 (d, $^{4}J_{P,P}$ = 7.0 Hz), –37.86 (d, $^{4}J_{P,P}$ = 6.8 Hz) ppm.

Compound 11: The procedure was the same as that used to obtain **10**. From hydroxyphosphane **C**′ (206 mg, 0.80 mmol), the title product was obtained as a white solid, yield 450 mg (94 %). ^{1}H NMR (400 MHz): δ = 8.07–7.82 (m, 5 H), 7.71–7.58 (m, 3 H), 7.49–7.32 (m, 5 H), 7.29–6.98 (m, 8 H), 3.09 (d, $^{3}J_{H,P}$ = 12.0 Hz, 3 H), 3.03 (d, $^{3}J_{H,P}$ = 14.0 Hz, 3 H), 1.03 (d, $^{3}J_{H,P}$ = 12.4 Hz, 9 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +172.16 (d, $^{4}J_{P,P}$ = 16.0 Hz), +0.23 (d, $^{4}J_{P,P}$ = 15.9 Hz) ppm.

Compound 12: The procedure was the same as that used to obtain **10** but with the chlorodiazaphosphepine derived from (*S*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine. From hydroxyphosphane **C** (162 mg, 0.75 mmol), the title product was obtained as a white solid, yield 371 mg (89 %). ^{1}H NMR (400 MHz): δ = 8.00 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.88 (d, *J* = 3.2 Hz, 1 H), 7.86 (d, *J* = 2.8 Hz, 1 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.62 (d, *J* = 9.2 Hz, 1 H), 7.46–7.32 (m, 4 H), 7.28–7.10 (m, 6 H), 7.07–6.95 (m, 3 H), 3.09 (d, $^{3}J_{H,P}$ = 9.6 Hz, 3 H), 3.05 (d, $^{3}J_{H,P}$ = 14.0 Hz, 3 H), 1.47 (d, $^{2}J_{H,P}$ = 4.0 Hz, 3 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +172.71 (d, $^{4}J_{P,P}$ = 11.0 Hz), –37.38 (d, $^{4}J_{P,P}$ = 11.0 Hz) ppm.

Compound 13: The procedure was the same as that used to obtain **12**. From hydroxyphosphane **C**′ (206 mg, 0.80 mmol), the title product was obtained as a white solid, yield 380 mg (79 %). ^{1}H NMR (400 MHz): δ = 7.57 (dd, *J* = 8.8, 0.8 Hz, 1 H), 7.45–7.39 (m, 4 H), 7.26–7.21 (m, 4 H), 7.12 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1 H), 6.93 (ddt, *J* = 8.0, 4.4, 0.8 Hz, 1 H), 6.90–6.61 (m, 8 H), 6.58 (td, *J* = 7.2, 1.2 Hz, 1 H), 2.73 (d, $^{3}J_{H,P}$ = 9.2 Hz, 3 H), 2.62 (d, $^{3}J_{H,P}$ = 14.0 Hz, 3 H), 0.91 (d, $^{3}J_{H,P}$ = 12.0 Hz, 3 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +171.34 (d, $^{4}J_{P,P}$ = 8.9 Hz), –0.67 (d, $^{4}J_{P,P}$ = 8.9 Hz) ppm.

Compound 14: The procedure was the same as that used to obtain **12**. From hydroxyphosphane **C**″ (223 mg, 0.80 mmol), the title product was obtained as a white solid, yield 408 mg (82 %). ^{1}H NMR (400 MHz): δ = 7.92 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 7.41–7.10 (m, 19 H), 6.97 (t, *J* = 6.8 Hz, 1 H), 6.75 (dd, *J* = 6.8, 4.8 Hz, 1 H), 2.92 (d, $^{3}J_{H,P}$ = 13.2 Hz, 3 H), 2.89 (d, $^{3}J_{H,P}$ = 8.8 Hz, 3 H) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +170.48 (d, $^{4}J_{P,P}$ = 10.2 Hz), –17.51 (d, $^{4}J_{P,P}$ = 10.5 Hz) ppm.

Complex Pd1: Phosphane–phosphinite **1** (195 mg, 0.59 mmol), Pd dimer **D** (92 mg, 0.23 mmol) and NH_4PF_6 (191 mg, 1.17 mmol) were suspended in dichloromethane (20 mL), and the suspension was stirred vigorously for 2 h. Water (20 mL) was added, and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic phase was washed with water, dried with anhydrous Na_2SO_4 and filtered, and the solvent was removed under vacuum. The crude product was recrystallised in dichloromethane/hexane to yield the title product as a white solid, yield 210 mg (71 %). Diastereomeric ratio: 1:1.8. IR: $\tilde{\nu}$ = 2970, 2929, 1591, 1468, 1436, 1267, 1207, 1028, 899, 891, 839 [$\nu(PF_6^-)$], 774, 736, 558 cm^{-1}. ^{1}H NMR (400 MHz): δ = 7.61 (t, *J* = 7.6 Hz, 2 H), 7.51–7.30 (m, 11 H, Ar), 7.23–7.18 (m, 5 H, Ar), 4.50 (t, *J* = 4.0 Hz, 1 H, ma), 4.47 (t, *J* = 3.6 Hz, 1 H, mi), 4.35 (t, *J* = 4.4 Hz, 1 H, ma), 4.31 (t, *J* = 4.4 Hz, 1 H, mi), 3.39 (d, *J* = 10.4 Hz, 1 H, ma), 3.34 (d, *J* = 10.0 Hz, 1 H, mi), 2.99 (d, *J* = 10.0 Hz, 1 H, mi), 2.88 (d, *J* = 10.0 Hz, 1 H, ma), 2.46–2.23 (m, 4 H, ma + mi), 2.29 (d, $^{2}J_{H,P}$ = 9.6 Hz, 3 H, ma), 2.24 (d, $^{2}J_{H,P}$ = 9.2 Hz, 3 H, mi), 1.89 (s, 3 H, ma), 1.84 (s, 3 H, mi), 1.22 (dd, $^{3}J_{H,P}$, $^{3}J_{H,H}$ = 16.4, 7.2 Hz, 3 H, ma), 1.15 (dd, $^{3}J_{H,P}$, $^{3}J_{H,H}$ = 18.4, 11.2 Hz, 3 H, ma), 1.08 (dd, $^{3}J_{H,P}$, $^{2}J_{H,H}$ = 7.2, 1.6 Hz, 3 H, mi), 1.03 (dd, $^{3}J_{H,P}$, $^{2}J_{H,H}$ = 7.6, 3.2 Hz, 3 H, mi), 0.98 (dd, $^{3}J_{H,P}$, $^{3}J_{H,H}$ = 19.6, 7.2 Hz, 3 H, ma), 0.91 (dd, $^{3}J_{H,P}$, $^{3}J_{H,H}$ = 16.8, 7.2 Hz, 3 H, mi), 0.85 (dd, $^{3}J_{H,P}$, $^{2}J_{H,H}$ = 16.0, 6.8 Hz, 3 H, ma) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz): δ = 158.3–123.0 (C, CH, Ar), 73.7 (dd, $^{2}J_{C,P}$ = 30.5, 3.1 Hz, CH_2, ma), 73.3 (dd, $^{2}J_{C,P}$ = 31.4, 2.2 Hz, CH_2, mi), 64.6 (dd, $^{2}J_{C,P}$ = 30.2, 2.1 Hz, CH_2, mi), 64.2 (d, $^{2}J_{C,P}$ = 30.2 Hz, CH_2, ma), 32.5 (d, $^{1}J_{C,P}$ = 11.3 Hz, CH, mi), 32.3 (d, $^{1}J_{C,P}$ = 10.3 Hz, CH, ma), 30.5 (d, $^{1}J_{C,P}$ = 24.1 Hz, CH, mi), 30.2 (d, $^{1}J_{C,P}$ = 25.3 Hz, CH, mi), 24.2 (s, CH_3, mi), 24.1 (s, CH_3, Ma), 17.8–16.5 (m, 8 × CH_3, ma + mi), 16.1 (d, $^{1}J_{C,P}$ = 28.3 Hz, CH_3, mi), 15.0 (d, $^{1}J_{C,P}$ = 29.1 Hz, CH_3, ma) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +190.81 (d, $^{2}J_{P,P}$ = 63.7 Hz, ma), +190.41 (d, $^{2}J_{P,P}$ = 63.8 Hz, mi), –6.49 (d, $^{2}J_{P,P}$ = 63.7 Hz, ma), –7.49 (d, $^{2}J_{P,P}$ = 63.7 Hz, mi) ppm. $C_{23}H_{33}F_6OP_3Pd$ (638.82): calcd. C 43.24, H 5.21; found C 42.81, H 5.69.

Complex Pd2: The procedure was the same as that used to prepare Pd**1**. From ligand **2** (180 mg, 0.48 mmol) and Pd dimer **D** (76 mg, 0.19 mmol), the product was obtained as a white solid, yield 230 mg (89 %). Diastereomeric ratio: 1:1. IR: $\tilde{\nu}$ = 2966, 2873, 1591, 1466, 1434, 1265, 1201, 1097, 1074, 1028, 899, 878, 839 [$\nu(PF_6^-)$], 773, 747, 699, 558, 518 cm^{-1}. ^{1}H NMR (400 MHz): δ = 7.76–7.42 (m, 2 H, Ar), 7.59–7.42 (m, 10 H, Ar), 7.22–6.99 (m, 6 H, Ar), 4.36 (d, *J* = 3.6 Hz, 2 H), 4.34 (m, 1 H), 3.64 (t, *J* = 4.4 Hz, 1 H), 3.42 (d, *J* = 10.0 Hz, 1 H), 2.90 (d, *J* = 10.0 Hz, 1 H), 2.87 (d, *J* = 10.0 Hz, 1 H), 2.61 (m, 1 H), 2.48 (m, 2 H), 2.38 (d, *J* = 11.6 Hz, 1 H), 2.36 (m, 2 H), 1.86 (s, 3 H), 1.54 (s, 3 H), 1.48–1.26 (m, 12 H), 1.42 (d, $^{3}J_{H,P}$ = 16.8 Hz, 9 H), 1.35 (d, $^{3}J_{H,P}$ = 16.4 Hz, 9 H), 1.19–1.07 (m, 12 H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz): δ = 159.2–115.0 (C, CH, Ar), 77.8 (dd, $^{2}J_{C,P}$ = 31.8, 3.1 Hz, CH_2), 76.1 (dd, $^{2}J_{C,P}$ = 31.1, 2.9 Hz, CH_2), 64.2 (dd, $^{2}J_{C,P}$ = 28.3, 1.7 Hz, CH_2), 62.9 (dd, $^{2}J_{C,P}$ = 28.5, 1.6 Hz, CH_2), 35.6 (d, $^{1}J_{C,P}$ = 22.0 Hz, C), 34.8 (d, $^{1}J_{C,P}$ = 22.6 Hz, C), 32.5 (d, $^{1}J_{C,P}$ = 12.6 Hz, 2CH), 31.2 (d, $^{1}J_{C,P}$ = 27.3 Hz, CH), 30.8 (d, $^{1}J_{C,P}$ = 27.1 Hz, CH), 28.4 (d, $^{2}J_{C,P}$ = 2.3 Hz, 3 × CH_3), 28.3 (d, $^{2}J_{C,P}$ = 2.5 Hz, 3 × CH_3), 23.72 (s, CH_3), 23.69 (s, CH_3), 18.2 (d, $^{2}J_{C,P}$ = 5.6 Hz, CH_3), 18.0 (d, $^{2}J_{C,P}$ = 4.9 Hz, CH_3), 17.8 (s, CH_3), 17.5 (d, $^{2}J_{C,P}$ = 5.5 Hz, CH_3), 17.4 (d, $^{2}J_{C,P}$ = 6.6 Hz, CH_3), 17.1 (s, CH_3), 16.7 (d, $^{2}J_{C,P}$ = 2.7 Hz, CH_3), 16.2 (s, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz): δ = +186.54 (d, $^{2}J_{P,P}$ = 59.6 Hz), +185.67 (d, $^{2}J_{P,P}$ = 59.8 Hz), +25.06 (d, $^{2}J_{P,P}$ = 59.6 Hz), +23.72 (d, $^{2}J_{P,P}$ = 59.6 Hz) ppm. $C_{26}H_{39}F_6OP_3Pd$ (680.90): calcd. C 45.86, H 5.77; found C 47.13, H 6.61.

Pd3: The procedure was the same as that used to prepare Pd**1**. From ligand **3** (200 mg, 0.50 mmol) and Pd dimer **D** (78 mg, 0.20 mmol), the product was obtained as a white solid, yield 215 mg (76 %). Diastereomeric ratio: 1:1.3. IR: $\tilde{\nu}$ = 3064, 3009, 2916, 1590, 1466, 1437, 1386, 1265, 1199, 1128, 1103, 1079, 1027, 999, 894, 839 [$\nu(PF_6^-)$], 777, 741, 693, 587, 558, 518, 475 cm^{-1}. ^{1}H NMR (400 MHz): δ = 7.62–7.23 (m, Ar), 6.74 (m, Ar), 4.58 (t, *J* = 3.6 Hz, 1 H, mi), 4.55 (t, *J* = 4.0 Hz, 1 H, ma), 4.37 (t, *J* = 4.0 Hz, 1 H, mi), 4.30 (t, *J* = 4.0 Hz, 1 H, ma), 3.48 (d, *J* = 10.0 Hz, 1 H, ma), 3.41 (d, *J* = 10.8 Hz, 1 H, mi), 3.21 (d, *J* = 10.0 Hz, 1 H, ma), 2.97 (d, *J* = 10.0 Hz, 1 H, mi), 2.35 (d, $^{2}J_{H,P}$ = 9.6 Hz, 3 H, ma), 2.34 (d, $^{2}J_{H,P}$ = 9.6 Hz, 3 H, mi), 1.96 (s,

3 H, mi), 1.79 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 155.7–119.1 (C, CH, Ar), 72.4 (d, $^2J_{C,P}$ = 34.0 Hz, CH_2, ma), 72.0 (d, $^2J_{C,P}$ = 23.8 Hz, CH_2, mi), 69.45 (d, $^2J_{C,P}$ = 26.3 Hz, CH_2, mi), 69.37 (d, $^2J_{C,P}$ = 28.3 Hz, CH_2, ma), 24.2 (s, CH_3, mi), 24.1 (s, CH_3, ma), 15.2 (d, $^1J_{C,P}$ = 27.1 Hz, CH_3, mi), 14.3 (d, $^1J_{C,P}$ = 28.4 Hz, CH_3, ma) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +151.53 (d, $^2J_{P,P}$ = 68.5 Hz, mi), +150.56 (d, $^2J_{P,P}$ = 68.2 Hz, ma), –5.06 (d, $^2J_{P,P}$ = 68.0 Hz, ma), –5.87 (d, $^2J_{P,P}$ = 68.8 Hz, mi) ppm. $C_{29}H_{29}F_6OP_3Pd$ (706.86): calcd. C 49.28, H 4.14; found C 49.64, H 4.58.

Complex Pd4: The procedure was the same as that used to prepare Pd**1**. From ligand **4** (150 mg, 0.34 mmol) and Pd dimer **D** (53 mg, 0.13 mmol), the product was obtained as a white solid, yield 157 mg (81 %). Diastereomeric ratio: 1:1. IR: $\tilde{\nu}$ = 3061, 2960, 2865, 1590, 1567, 1466, 1436, 1398, 1369, 1310, 1264, 1197, 1104, 1073, 1026, 999, 831 [$\nu(PF_6^-)$], 773, 746, 694, 588, 558, 519, 481 cm^{-1}. ^1H NMR (400 MHz): δ = 7.78–7.32 (m, 31 H, Ar), 7.17–7.07 (m, 4 H, Ar), 6.91–6.84 (m, 3 H, Ar), 4.44–4.40 (m, 2 H), 4.14 (t, *J* = 4.0 Hz, 1 H), 3.91 (dd, *J* = 5.6, 4.0 Hz, 1 H), 3.48 (d, *J* = 12.4 Hz, 1 H), 3.45 (d, *J* = 10.4 Hz, 1 H), 2.95 (d, *J* = 10.8 Hz, 1 H), 2.81 (d, *J* = 9.6 Hz, 1 H), 1.81 (s, 3 H), 1.75 (s, 3 H), 1.49 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H), 1.43 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 156.6–116.9 (C, CH, Ar), 74.6 (dd, $^2J_{C,P}$ = 33.5, 3.0 Hz, CH_2), 70.8 (dd, $^2J_{C,P}$ = 28.0, 2.9 Hz, CH_2), 68.4 (dd, $^2J_{C,P}$ = 28.0, 2.5 Hz, CH_2), 35.0 (d, $^1J_{C,P}$ = 21.7 Hz, C), 34.2 (d, $^1J_{C,P}$ = 22.0 Hz, C), 28.17 (d, $^2J_{C,P}$ = 6.9 Hz, 3 × CH_3), 28.11 (d, $^2J_{C,P}$ = 6.9 Hz, 3 × CH_3), 23.96 (s, CH_3), 23.86 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +148.71 (d, $^2J_{P,P}$ = 65.8 Hz), +148.45 (d, $^2J_{P,P}$ = 65.9 Hz), +29.74 (d, $^2J_{P,P}$ = 65.8 Hz), +28.39 (d, $^2J_{P,P}$ = 65.8 Hz) ppm. $C_{32}H_{35}F_6OP_3Pd$ (748.94): calcd. C 51.32, H 4.71; found C 53.15, H 5.47.

Complex Pd5: The procedure was the same as that used to prepare Pd**1**. From ligand **5** (300 mg, 0.57 mmol) and Pd dimer **D** (86 mg, 0.22 mmol), the product was obtained as a white solid, yield 270 mg (73 %). Diastereomeric ratio: 1:2.7. IR: $\tilde{\nu}$ = 3068, 1619, 1591, 1509, 1464, 1437, 1321, 1264, 1223, 1184, 1068, 959, 841 [$\nu(PF_6^-)$], 774, 750, 695, 608, 558, 500 cm^{-1}. ^1H NMR (400 MHz): δ = 8.17–8.13 (m, Ar), 8.09–7.98 (m, Ar), 7.79–7.75 (m, Ar), 7.62–7.30 (m, Ar), 7.24–7.15 (m, Ar), 7.07–6.98 (m, Ar), 4.45 (d, *J* = 9.6 Hz, 1 H, mi), 4.25 (d, *J* = 8.8 Hz, 1 H, ma), 3.73 (d, *J* = 4.4 Hz, 2 H, ma + mi), 3.62 (d, *J* = 16.8 Hz, 1 H, ma), 3.12 (d, *J* = 8.8 Hz, 1 H, mi), 3.00 (dd, *J* = 10.4, 2.8 Hz, 1 H, ma), 2.63 (d, br, *J* = 11.6 Hz, 1 H, mi), 2.39 (d, $^2J_{H,P}$ = 10.0 Hz, 3 H, ma), 2.38 (d, $^2J_{H,P}$ = 10.0 Hz, 3 H, mi), 1.91 (s, 3 H, mi), 1.66 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 153.5–119.2 (C, CH, Ar), 75.5 (dd, $^2J_{C,P}$ = 46.0, 3.7 Hz, CH_2, ma), 73.2 (dd, $^2J_{C,P}$ = 47.9, 3.8 Hz, CH_2, mi), 69.8–69.4 (m, 2 × CH_2, ma + mi), 24.0 (s, CH_3, ma), 23.8 (s, CH_3, mi), 14.0 (d, $^1J_{C,P}$ = 28.9 Hz, CH_3, mi), 13.2 (d, $^1J_{C,P}$ = 28.8 Hz, CH_3, ma) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +145.71 (d, $^2J_{P,P}$ = 102.5 Hz, mi), +145.64 (d, $^2J_{P,P}$ = 102.9 Hz, ma), –4.21 (d, $^2J_{P,P}$ = 102.9 Hz, ma), –4.90 (d, $^2J_{P,P}$ = 102.7 Hz, mi) ppm. $C_{37}H_{31}F_6O_3P_3Pd$ (836.96): calcd. C 53.10, H 3.73; found C 52.78, H 4.46.

Complex Pd6: The procedure was the same as that used to prepare Pd**1**. From ligand **6** (380 mg, 0.66 mmol) and Pd dimer **D** (105 mg, 0.27 mmol), the product was obtained as a white solid, yield 331 mg (70 %). Diastereomeric ratio: 1:1.8. IR: $\tilde{\nu}$ = 3068, 2957, 2869, 1619, 1590, 1509, 1464, 1434, 1400, 1322, 1264, 1225, 1184, 1068, 958, 927, 842 [$\nu(PF_6^-)$], 773, 696, 609, 558 cm^{-1}. ^1H NMR (400 MHz): δ = 8.25–8.02 (m, Ar), 7.89–7.87 (m, Ar), 7.78–6.80 (m, Ar), 4.29 (d, *J* = 8.8 Hz, 1 H, mi), 3.83 (d, *J* = 17.2 Hz, 1 H, Ma), 3.68–3.59 (m, 3 H, 2 × ma + mi), 3.10 (d, *J* = 8.0 Hz, 1 H, ma), 2.65 (d, *J* = 8.8 Hz, 1 H, mi), 2.47 (d, *J* = 16.4 Hz, 1 H, mi), 1.93 (s, 3 H, mi), 1.57 (d, $^3J_{H,P}$ = 17.2 Hz, 9 H, ma), 1.49 (d, $^3J_{H,P}$ = 16.4 Hz, 9 H, mi), 1.48 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 154.7–115.7 (C, CH, Ar), 78.9 (dd, $^2J_{C,P}$ = 46.4, 2.3 Hz, CH_2, ma), 75.9 (d, $^2J_{C,P}$ = 48.5 Hz, CH_2, mi), 70.1 (dd, $^2J_{C,P}$ = 27.4, 7.5 Hz, CH_2, mi), 69.5 (dd, $^2J_{C,P}$ = 25.9, 7.1 Hz, CH_2, ma), 36.0 (d, $^1J_{C,P}$ = 21.3 Hz, C, ma), 35.4 (d, $^1J_{C,P}$ = 22.9 Hz, C, mi), 28.3 (d, $^2J_{C,P}$ = 6.5 Hz, 3 × CH_3, mi), 28.2 (d, $^2J_{C,P}$ = 6.6 Hz, 3 × CH_3, ma), 23.7 (s, CH_3, ma), 23.6 (s, CH_3, mi) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +144.42 (d, $^2J_{P,P}$ = 97.8 Hz, ma), +143.67 (d, $^2J_{P,P}$ = 98.7 Hz, mi), +29.52 (d, $^2J_{P,P}$ = 98.8 Hz, mi), +28.76 (d, $^2J_{P,P}$ = 97.2 Hz, ma) ppm. $C_{40}H_{37}F_6O_3P_3Pd$ (879.04): calcd. C 54.65, H 4.24; found C 54.23, H 5.06.

Complex Pd7: The procedure was the same as that used to prepare Pd**1**. From ligand **7** (400 mg, 0.75 mmol) and Pd dimer **D** (123 mg, 0.31 mmol), the product was obtained as a white solid, yield 398 mg (77 %). Diastereomeric ratio: 1:1. IR: $\tilde{\nu}$ = 3066, 2957, 2924, 1619, 1591, 1509, 1464, 1437, 1322, 1264, 1224, 1185, 1128, 1068, 958, 919, 832 [$\nu(PF_6^-)$], 774, 741, 695, 608, 558, 500 cm^{-1}. ^1H NMR (400 MHz): δ = 8.24–8.02 (m, 4 H, Ar), 7.73–7.18 (m, 17 H, Ar), 4.79 (d, *J* = 7.6 Hz, 1 H), 4.53 (d, *J* = 8.0 Hz, 1 H), 3.79–3.64 (m, 3 H), 3.32 (d, *J* = 15.6 Hz, 1 H), 3.07 (d, *J* = 9.6 Hz, 1 H), 2.69 (d, *J* = 7.2 Hz, 1 H), 2.43 (d, $^2J_{H,P}$ = 9.6 Hz, 3 H), 2.35 (d, $^2J_{H,P}$ = 9.6 Hz, 3 H), 1.97 (s, 3 H), 1.68 (s, 3 H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +146.20 (d, $^2J_{P,P}$ = 103.2 Hz), +145.87 (d, $^2J_{P,P}$ = 102.7 Hz), –3.99 (d, $^2J_{P,P}$ = 103.2 Hz), –5.42 (d, $^2J_{P,P}$ = 102.9 Hz) ppm. HRMS: calcd. for $C_{37}H_{31}O_3P_2Pd$ [M – PF_6]$^+$ 691.0777; found 691.0793.

Complex Pd8: The procedure was the same as that used to prepare Pd**1**. From ligand **8** (285 mg, 0.50 mmol) and Pd dimer **D** (72 mg, 0.18 mmol), the product was obtained as a white solid, yield 207 mg (65 %). Diastereomeric ratio: 1:2.3. IR: $\tilde{\nu}$ = 3065, 2961, 2869, 1619, 1590, 1509, 1464, 1435, 1400, 1368, 1322, 1263, 1223, 1184, 1068, 958, 836 [$\nu(PF_6^-)$], 774, 750, 696, 603, 558, 515 cm^{-1}. ^1H NMR (400 MHz): δ = 8.26–8.13 (m, Ar), 8.13–7.87 (m, Ar), 7.78–7.71 (m, Ar), 7.61–7.29 (m, Ar), 7.09–7.01 (m, Ar), 4.43 (d, *J* = 8.8 Hz, 1 H, ma), 4.21 (dd, *J* = 9.2, 2.4 Hz, 1 H, mi), 3.67 (s, br, 1 H, Ma), 3.47 (s, br, 1 H, mi), 3.36 (d, *J* = 16.4 Hz, 1 H, mi), 3.29 (d, *J* = 17.2 Hz, 1 H, ma), 3.09 (d, *J* = 10.0 Hz, 1 H, ma), 2.57 (dd, *J* = 10.0, 3.6 Hz, 1 H, mi), 1.83 (s, 3 H, mi), 1.63 (s, 3 H, Ma), 1.54 (d, $^3J_{H,P}$ = 17.2 Hz, 9 H, mi), 1.49 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 153.8–118.2 (C, CH, Ar), 75.4 (d, $^2J_{C,P}$ = 50.1 Hz, 2 × CH_2, ma + mi), 70.7 (d, $^2J_{C,P}$ = 20.9 Hz, CH_2, ma), 68.6 (d, $^2J_{C,P}$ = 19.9 Hz, CH_2, mi), 34.5 (d, $^1J_{C,P}$ = 20.5 Hz, C, mi), 34.2 (d, $^1J_{C,P}$ = 21.0 Hz, C, ma), 28.0 (d, $^2J_{C,P}$ = 6.9 Hz, 3 × CH_3, ma), 27.8 (d, $^2J_{C,P}$ = 6.5 Hz, 3 × CH_3, mi), 23.82 (s, CH_3, mi), 23.77 (s, CH_3, ma) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +146.99 (d, $^2J_{P,P}$ = 95.9 Hz, ma), +146.75 (d, $^2J_{P,P}$ = 96.7 Hz, mi), +32.10 (d, $^2J_{P,P}$ = 96.6 Hz, mi), +32.01 (d, $^2J_{P,P}$ = 96.1 Hz, ma) ppm. $C_{40}H_{37}F_6O_3P_3Pd$ (879.04): calcd. C 54.65, H 4.24; found C 54.53, H 4.71.

Complex Pd9: The procedure was the same as that used to prepare Pd**1**. From ligand **9** (320 mg, 0.54 mmol) and Pd dimer **D** (81 mg, 0.21 mmol), the product was obtained as a white solid, yield 303 mg (80 %). Diastereomeric ratio: 1:1.7. IR: $\tilde{\nu}$ = 3061, 1619, 1590, 1509, 1463, 1437, 1323, 1265, 1224, 1184, 1068, 958, 921, 841 [$\nu(PF_6^-)$], 774, 749, 695, 609, 558, 517 cm^{-1}. ^1H NMR (400 MHz): δ = 8.24–8.19 (m, Ar), 8.14–7.91 (m, Ar), 7.72–7.49 (m, Ar), 7.43–7.24 (m, Ar), 7.21–7.10 (m, Ar), 6.93–6.86 (m, Ar), 4.28 (d, *J* = 8.8 Hz, 1 H, mi), 4.10 (d, *J* = 8.8 Hz, 1 H, ma), 3.80 (d, *J* = 16.4 Hz, 1 H, ma), 3.74 (s, br, ma), 3.67 (s, br, mi), 3.33 (d, *J* = 16.4 Hz, 1 H, mi), 3.17 (dd, *J* = 10.4, 2.0 Hz, 1 H, ma), 2.78 (dd, *J* = 10.0, 2.0 Hz, 1 H, mi), 1.96 (s, 3 H, mi), 1.70 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 153.5–117.9 (C, CH, Ar), 75.2 (d, $^2J_{C,P}$ = 47.9 Hz, CH_2, mi), 70.4 (dd, $^2J_{C,P}$ = 28.0, 6.5 Hz, CH_2, ma), 70.0 (dd, $^2J_{C,P}$ = 28.6, 7.5 Hz, CH_2, mi), 24.06 (s, CH_3, ma), 23.95 (s, CH_3, mi) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +145.93 (d, $^2J_{P,P}$ = 100.9 Hz, ma), +145.66 (d, $^2J_{P,P}$ = 101.3 Hz, mi), +12.31 (d, $^2J_{P,P}$ = 101.4 Hz, mi), +11.48 (d, $^2J_{P,P}$ = 100.9 Hz, ma) ppm.

$C_{42}H_{33}F_6O_3P_3Pd$ (899.03): calcd. C 56.11, H 3.70; found C 55.47, H 3.5.

Complex Pd10: The procedure was the same as that used to prepare Pd**1**. From ligand **10** (320 mg, 0.57 mmol) and Pd dimer **D** (94 mg, 0.24 mmol), the product was obtained as a white solid, yield 315 mg (76 %). Diastereomeric ratio: 1:2.4. IR: $\tilde{\nu}$ = 3195, 3063, 2957, 1619, 1591, 1507, 1466, 1437, 1329, 1263, 1198, 1131, 1090, 1026, 944, 901, 843 [$\nu(PF_6^-)$], 751, 697, 633, 606, 558, 499 cm^{-1}. ^1H NMR (400 MHz): δ = 8.16–8.07 (m, Ar), 8.02–7.91 (m, Ar), 7.84–7.82 (m, Ar), 7.71–7.38 (m, Ar), 7.32–7.13 (m, Ar), 7.10–7.05 (m, Ar), 6.88–6.79 (m, Ar), 4.08 (d, J = 6.4 Hz, 1 H, mi), 3.78 (d, J = 4.8 Hz, 1 H, ma), 3.73 (m, 1 H, mi), 3.59 (d, J = 13.6 Hz, 1 H, ma), 3.38 (s, br, 1 H, ma), 3.31 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H, ma), 3.14 (d, $^3J_{H,P}$ = 10.8 Hz, 3 H, mi), 3.05 (d, J = 10.4 Hz, 1 H, ma), 2.89 (d, $^3J_{H,P}$ = 14.8 Hz, 3 H, mi), 2.84 (s, br, 1 H, mi), 2.73 (d, $^3J_{H,P}$ = 14.8 Hz, 3 H, ma), 2.49 (d, J = 9.6 Hz, 1 H, mi), 2.25 (d, $^2J_{H,P}$ = 9.2 Hz, 3 H, ma), 2.14 (d, $^2J_{H,P}$ = 9.2 Hz, 3 H, mi), 1.95 (s, 3 H, mi), 1.57 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 155.1–120.4 (C, CH, Ar), 73.8 (d, $^2J_{C,P}$ = 43.6 Hz, CH_2, mi), 65.16 (dd, $^2J_{C,P}$ = 30.0, 5.8 Hz, CH_2, ma), 65.11 (d, $^2J_{C,P}$ = 31.1 Hz, CH_2, mi), 39.58 (d, $^2J_{C,P}$ = 31.9 Hz, CH_3, ma), 39.54 (d, $^2J_{C,P}$ = 30.2 Hz, CH_3, mi), 35.92 (d, $^2J_{C,P}$ = 12.2 Hz, CH_3, ma), 35.84 (d, $^2J_{C,P}$ = 12.6 Hz, CH_3, mi), 24.0 (s, CH_3, ma), 23.9 (s, CH_3, mi), 13.4 (d, $^1J_{C,P}$ = 29.2 Hz, CH_3, mi), 12.5 (d, $^1J_{C,P}$ = 28.6 Hz, CH_3, ma) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +156.57 (d, $^2J_{P,P}$ = 85.2 Hz, mi), +155.95 (d, $^2J_{P,P}$ = 87.2 Hz, ma), –4.25 (d, $^2J_{P,P}$ = 87.2 Hz, ma), –5.92 (d, $^2J_{P,P}$ = 85.2 Hz, mi) ppm. HRMS: calcd. for $C_{39}H_{37}N_2OP_2Pd$ [M – PF_6]$^+$ 717.1410; found 717.1435.

Complex Pd11: The procedure was the same as that used to prepare **Pd1**. From ligand **11** (450 mg, 0.75 mmol) and Pd dimer **D** (118 mg, 0.30 mmol), the product was obtained as a white solid, yield 375 mg (69 %). Diastereomeric ratio: 1:2.1. IR: $\tilde{\nu}$ = 3063, 2959, 2870, 1619, 1591, 1507, 1466, 1434, 1329, 1262, 1198, 1091, 944, 876, 842 [$\nu(PF_6^-)$], 771, 748, 697, 633, 606, 558, 517 cm^{-1}. ^1H NMR (400 MHz): δ = 8.19–7.86 (m, Ar), 7.71–7.40 (m, Ar), 7.39–7.11 (m, Ar), 7.06–6.95 (m, Ar), 4.34 (d, J = 6.0 Hz, 1 H, mi), 3.91 (s, br, 1 H, mi), 3.68 (d, J = 15.2 Hz, 1 H, ma), 3.64 (dd, J = 9.2, 3.2 Hz, 1 H, ma), 3.34 (s, br, 1 H, ma), 3.28 (d, $^3J_{H,P}$ = 10.0 Hz, 3 H, ma), 3.17 (d, J = 10.0 Hz, 1 H, ma), 3.11 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H, mi), 3.01 (d, $^3J_{H,P}$ = 15.2 Hz, 3 H, mi), 2.82 (d, $^3J_{H,P}$ = 14.4 Hz, 3 H, ma), 2.45 (d, J = 9.2 Hz, 1 H, mi), 2.36 (d, J = 14.0 Hz, 1 H, mi), 1.97 (s, 3 H, mi), 1.52 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H, ma), 1.43 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H, mi), 1.33 (s, 3 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 156.3–121.8 (C, CH, Ar), 74.9 (d, CH_2, mi), 65.4 (dd, $^2J_{C,P}$ = 27.3, 5.2 Hz, CH_2, ma), 64.6 (d, $^2J_{C,P}$ = 27.8 Hz, CH_2, mi), 39.85 (d, $^2J_{C,P}$ = 30.1 Hz, CH_3, mi), 39.75 (d, $^2J_{C,P}$ = 31.9 Hz, CH_3, ma), 36.49 (d, $^2J_{C,P}$ = 11.3 Hz, CH_3, mi), 36.28 (d, $^2J_{C,P}$ = 11.2 Hz, CH_3, ma), 35.9 (d, $^1J_{C,P}$ = 21.1 Hz, C, ma), 35.2 (d, $^1J_{C,P}$ = 22.4 Hz, C, mi), 28.6 (d, $^2J_{C,P}$ = 7.0 Hz, 3 × CH_3, mi), 28.2 (d, $^2J_{C,P}$ = 6.6 Hz, 3 × CH_3, ma), 23.73 (s, CH_3, mi), 23.70 (s, CH_3, ma) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +153.98 (d, $^2J_{P,P}$ = 81.0 Hz, ma), +153.09 (d, $^2J_{P,P}$ = 80.7 Hz, mi), +27.73 (d, $^2J_{P,P}$ = 80.7 Hz, mi), +26.96 (d, $^2J_{P,P}$ = 81.0 Hz, ma) ppm. $C_{42}H_{43}F_6N_2OP_3Pd$ (905.12): calcd. C 55.73, H 4.79, N 3.09; found C 55.96, H 5.19, N 3.02.

Complex Pd12: The procedure was the same as that used to prepare **Pd1**. From ligand **12** (300 mg, 0.54 mmol) and Pd dimer **D** (84 mg, 0.21 mmol), the product was obtained as a white solid, yield 210 mg (58 %). Diastereomeric ratio: 1:1. IR: $\tilde{\nu}$ = 3064, 2962, 1619, 1592, 1507, 1467, 1438, 1329, 1275, 1200, 1090, 944, 843 [$\nu(PF_6^-)$], 740, 697, 633, 605, 558, 509 cm^{-1}. ^1H NMR (400 MHz): δ = 8.18–7.04 (m, 4 H, Ar), 8.03–7.88 (m, 4 H, Ar), 7.83–7.67 (m, 5 H, Ar), 7.62–7.33 (m, 16 H, Ar), 7.31–7.05 (m, 13 H, Ar), 4.76 (d, J = 6.0 Hz, 1 H), 4.50 (d, J = 4.0 Hz, 1 H), 3.67 (d, J = 14.0 Hz, 1 H), 3.53 (t, J = 4.4 Hz, 1 H), 3.38 (s, 1 H), 3.34 (d, J = 14.0 Hz, 1 H), 3.15 (d, J = 10.4 Hz, 1 H), 2.86 (d, $^3J_{H,P}$ = 14.8 Hz, 3 H), 2.68 (d, $^3J_{H,P}$ = 14.4 Hz, 3 H), 2.54 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H), 2.51 (d, J = 8.0 Hz, 1 H), 2.39 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H), 2.36 (d, $^2J_{H,P}$ = 10.0 Hz, 3 H), 2.30 (d, $^2J_{H,P}$ = 9.6 Hz, 3 H), 2.07 (s, 3 H), 1.66 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 154.6–121.3 (C, CH, Ar), 71.3 (d, $^2J_{C,P}$ = 39.9 Hz, CH_2), 71.2 (d, $^2J_{C,P}$ = 40.3 Hz, CH_2), 67.2 (d, $^2J_{C,P}$ = 35.0 Hz, CH_2), 65.0 (d, $^2J_{C,P}$ = 34.6 Hz, CH_2), 39.6 (d, $^2J_{C,P}$ = 31.8 Hz, CH_3), 39.4 (d, $^2J_{C,P}$ = 29.7 Hz, CH_3), 35.03 (d, $^2J_{C,P}$ = 11.8 Hz, CH_3), 35.00 (d, $^2J_{C,P}$ = 12.1 Hz, CH_3), 24.2 (s, CH_3), 24.1 (s, CH_3), 16.3 (d, $^1J_{C,P}$ = 28.8 Hz, CH_3), 14.8 (d, $^1J_{C,P}$ = 26.3 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +158.83 (d, $^2J_{P,P}$ = 84.6 Hz), +158.66 (d, $^2J_{P,P}$ = 85.2 Hz), –3.16 (d, $^2J_{P,P}$ = 84.7 Hz), –4.95 (d, $^2J_{P,P}$ = 85.1 Hz) ppm. HRMS: calcd. for $C_{39}H_{37}N_2OP_2Pd$ [M – PF_6]$^+$ 717.1410; found 717.1437.

Complex Pd13: The procedure was the same as that used to prepare **Pd1**. From ligand **13** (150 mg, 0.25 mmol) and Pd dimer **D** (40 mg, 0.10 mmol), the product was obtained as a white solid, yield 122 mg (67 %). Diastereomeric ratio: 1:2. IR: $\tilde{\nu}$ = 3064, 2963, 1619, 1591, 1507, 1467, 1435, 1329, 1262, 1199, 1090, 943, 842 [$\nu(PF_6^-)$], 774, 750, 697, 601, 557, 518 cm^{-1}. ^1H NMR (400 MHz): δ = 8.15–8.05 (m, Ar), 7.99–7.90 (m, Ar), 7.86–7.81 (m, Ar), 7.73–7.66 (m, Ar), 7.58–7.41 (m, Ar), 7.31–7.07 (m, Ar), 4.57–4.53 (m, 2 H, ma + mi), 3.68 (d, J = 14.0 Hz, 1 H, ma), 3.33 (d, J = 14.0 Hz, 1 H, mi), 3.20–3.12 (m, 3 H, 2 × ma + mi), 2.84 (d, $^3J_{H,P}$ = 14.8 Hz, 3 H, mi), 2.65 (d, $^3J_{H,P}$ = 14.4 Hz, 3 H, ma), 2.38 (d, $^3J_{H,P}$ = 10.0 Hz, 3 H, ma), 2.22 (d, $^3J_{H,P}$ = 9.6 Hz, 3 H, mi), 2.03 (s, 3 H, mi), 1.61 (s, 3 H, ma), 1.50 (d, $^3J_{H,P}$ = 16.4 Hz, 9 H, mi), 1.47 (d, $^3J_{H,P}$ = 16.4 Hz, 9 H, ma) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 155.2–120.1 (C, CH, Ar), 73.4 (d, $^2J_{C,P}$ = 44.0 Hz, CH_2, ma), 67.5 (d, $^2J_{C,P}$ = 22.6 Hz, CH_2, ma), 39.2 (d, $^2J_{C,P}$ = 30.9 Hz, CH_3, ma), 35.1 (d, $^2J_{C,P}$ = 10.8 Hz, CH_3, ma), 32.9 (d, $^1J_{C,P}$ = 19.6 Hz, C, mi), 32.3 (d, $^1J_{C,P}$ = 19.4 Hz, C, ma), 27.4 (d, $^2J_{C,P}$ = 6.3 Hz, 3 × CH_3, mi), 27.1 (d, $^2J_{C,P}$ = 6.9 Hz, 3 × CH_3, ma), 23.9 (s, CH_3, ma), 23.8 (s, CH_3, mi) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +157.80 (d, $^2J_{P,P}$ = 77.6 Hz, ma), +154.36 (d, $^2J_{P,P}$ = 78.2 Hz, mi), +35.38 (d, $^2J_{P,P}$ = 78.2 Hz, mi), +35.34 (d, $^2J_{P,P}$ = 77.4 Hz, ma) ppm. $C_{42}H_{43}F_6N_2OP_3Pd$ (905.12): calcd. C 55.73, H 4.79, N 3.09; found C 53.22, H 5.01, N 3.08.

Complex Pd14: The procedure was the same as that used to prepare **Pd1**. From ligand **14** (320 mg, 0.52 mmol) and Pd dimer **D** (81 mg, 0.21 mmol), the product was obtained as a white solid, yield 303 mg (78 %). Diastereomeric ratio: 1:1. IR: $\tilde{\nu}$ = 3063, 1618, 1591, 1507, 1465, 1437, 1329, 1263, 1200, 1090, 944, 842 [$\nu(PF_6^-)$], 749, 697, 607, 558, 519 cm^{-1}. ^1H NMR (400 MHz): δ = 8.14 (d, J = 7.2 Hz, 1 H), 8.12 (d, J = 6.4 Hz, 2 H), 8.09 (d, J = 6.4 Hz, 1 H), 8.00 (d, J = 3.6 Hz, 1 H), 7.98 (d, J = 4.0 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.8 Hz, 1 H), 7.70 (q, J = 8.0 Hz, 2 H), 7.73–7.36 (m, 20 H, Ar), 7.32–7.16 (m, 17 H, Ar), 7.12–7.08 (m, 2 H, Ar), 6.79 (m, 2 H, Ar), 4.31 (d, J = 6.0 Hz, 1 H), 3.99 (dd, J = 7.2, 2.4 Hz, 1 H), 3.86 (d, J = 13.6 Hz, 1 H), 3.61 (t, J = 4.4 Hz, 1 H), 3.41 (s, br, 1 H), 3.32 (d, J = 13.6 Hz, 1 H), 3.22 (d, J = 10.4 Hz, 1 H), 2.99 (d, $^3J_{H,P}$ = 15.2 Hz, 3 H), 2.80 (d, $^3J_{H,P}$ = 14.8 Hz, 3 H), 2.74 (dd, J = 10.4, 2.0 Hz, 1 H), 2.56 (d, $^3J_{H,P}$ = 10.8 Hz, 3 H), 2.35 (d, $^3J_{H,P}$ = 10.4 Hz, 3 H), 2.02 (s, 3 H), 1.70 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 147.8–121.0 (C, CH, Ar), 39.8 (d, $^2J_{C,P}$ = 28.0 Hz, CH_3), 39.6 (d, $^2J_{C,P}$ = 31.2 Hz, CH_3), 34.7 (d, $^2J_{C,P}$ = 17.0 Hz, CH_3), 34.6 (d, $^2J_{C,P}$ = 17.0 Hz, CH_3), 24.2 (s, CH_3), 24.0 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +158.84 (d, $^2J_{P,P}$ = 84.7 Hz), +158.62 (d, $^2J_{P,P}$ = 83.3 Hz), +13.21 (d, $^2J_{P,P}$ = 83.3 Hz), 12.65 (d, $^2J_{P,P}$ = 84.7 Hz) ppm. $C_{44}H_{39}F_6N_2OP_3Pd$ (925.11): calcd. C 57.12, H 4.25, N 3.03; found C 56.14, H 4.56, N 3.03.

Complex Pd6′: The procedure was the same as that used to prepare **Pd1**. From ligand **6** (300 mg, 0.52 mmol) and Pd dimer **D′** (135 mg, 0.2 mmol), the product was obtained as a white solid,

yield 253 mg (62 %). Diastereomeric ratio: 1:3.5. IR: $\tilde{\nu}$ = 3057, 2957, 1596, 1470, 1430, 1183, 1070, 957, 848 [$\nu(PF_6^-)$], 745, 561 cm^{-1}. ^1H NMR (400 MHz): δ = 8.47–6.18 (m, 40 H, Ar), 6.06–5.90 (m, 4 H, 2 × ma + 2 × mi), 5.24–5.19 (m, 2 H, ma + mi), 1.43 (d, $^3J_{H,P}$ = 17.2 Hz, 9 H, ma), 1.08 (d, $^3J_{H,P}$ = 16.8 Hz, 9 H, mi) ppm. $^{13}C\{^1H\}$ NMR (101 MHz): δ = 154.8–118.5 (C, CH, Ar), 112.73 (d, $^2J_{C,P}$ = 7.9 Hz, CH), 112.60 (d, $^2J_{C,P}$ = 8.2 Hz, CH), 100.22 (d, $^2J_{C,P}$ = 4.5 Hz, CH), 99.86 (d, $^2J_{C,P}$ = 4.8 Hz, CH), 86.36 (d, $^2J_{C,P}$ = 10.5 Hz, CH), 86.13 (d, $^2J_{C,P}$ = 10.7 Hz, CH), 36.79 (d, $^1J_{C,P}$ = 19.7 Hz, C, mi), 36.72 (d, $^1J_{C,P}$ = 18.6 Hz, C, ma), 27.9 (d, $^2J_{C,P}$ = 6.2 Hz, 6 × CH_3, ma + mi) ppm. $^{31}P\{^1H\}$ NMR (162 MHz): δ = +139.57 (d, $^2J_{P,P}$ = 138.0 Hz, ma), +137.27 (d, $^2J_{P,P}$ = 144.5 Hz, mi), +29.87 (d, $^2J_{P,P}$ = 138.0 Hz, ma), +26.75 (d, $^2J_{P,P}$ = 144.3 Hz, mi) ppm. HRMS: calcd. for $C_{51}H_{43}O_3P_2Pd$ $[M - PF_6]^+$ 871.1716; found 871.1733.

Allylic Alkylations with Dimethyl Malonate: Under a nitrogen atmosphere, the appropriate Pd complex (0.01 mmol), the precursor **I**, **II** or **III** (1 mmol), dimethyl malonate (3 mmol), BSA (3 mmol) and KOAc (1 mg) were dissolved in dichloromethane (5 mL) in this precise order. The flask was covered with aluminium foil, and the mixture was stirred for the allotted time. To quench the reaction, diethyl ether (20 mL) and aqueous 10 % ammonium chloride solution (20 mL) were added. After extraction, the organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was removed in vacuo. The crude product was analysed by ^1H NMR spectroscopy to estimate the conversion. The crude product was dissolved in ethyl acetate, and the solution was passed through a column of silica to remove the metallic impurities. The eluent was removed in vacuo, and the residue was analysed by NMR spectroscopy and HPLC (alkylations of **I**) or GC (alkylations of **II** and **III**).

Allylic Amination of I with Benzylamine: Under a nitrogen atmosphere, the Pd complex (0.01 mmol), **I** (1 mmol) and benzylamine (3 mmol) were dissolved in dichloromethane (5 mL) in this precise order. The flask was covered with aluminium foil, and the mixture was stirred for 72 h. To quench the reaction, diethyl ether (20 mL) and aqueous 10 % ammonium chloride solution (20 mL) were added. After extraction, the organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was removed in vacuo. The crude product was analysed by ^1H NMR spectroscopy to estimate the conversion. The crude product was dissolved in ethyl acetate, and the solution was passed through a column of silica to remove the metallic impurities. The eluent was removed in vacuo, and the residue was analysed by NMR spectroscopy and HPLC.

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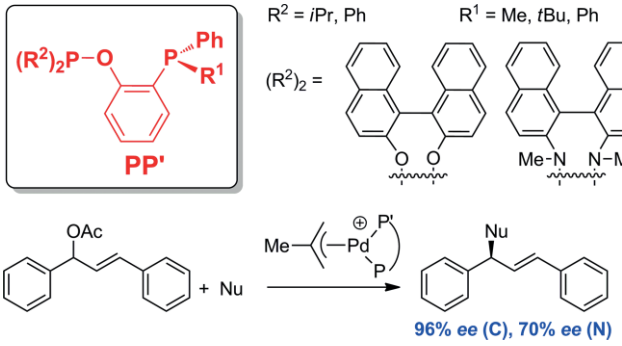
Chiral P–P Ligands



A series of C_1-symmetric diphosphorus ligands containing a P-stereogenic phosphane moiety are synthetized and characterized. The derived π-methallyl Pd complexes are used in catalytic allylic substitutions and provide good conversions and enantioselectivities.

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