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Better Performance of Monodentate *P*-Stereogenic Phosphanes Compared to Bidentate Analogues in Pd-Catalyzed Asymmetric Allylic Alkylations

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Keywords: Palladium / Allylic compounds / Asymmetric catalysis / Nucleophilic substitution

The cationic allylpalladium complexes **3a**–**3f**, **4a**, **4e**, **5e** of type $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)P_2]PF_6$ were synthesized using a group of monodentate *P*-stereogenic phosphanes, P=PPhRR′ (**a**–**f**) and diphosphanes $(PhRPCH_2)_2$ (**1a**, **1e**) or $PhRPCH_2Si(Me)_2CH_2PPhR$ (**2e**). The analogous cationic complexes with the disubstituted allyl group (η^3-1,3-Ph_2-C_3H_3) and monodentate phosphanes were not isolated as stable solids; only [PdCl(η^3-1,3-Ph_2-C_3H_3)P] (**6a**, **6d**) were obtained. Palladium allyl complexes were screened as precatalysts in the allylic substitution of *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) and (*E*)-3-acetoxy-1-phenyl-1-propene (**III**) with dimethyl malonate as the nucleophile. The various catalytic precursors showed a wide range of activity and selectivity. The bismonodentate phosphane complexes **3** are more active than the bidentate analogues. With regard to the regioselectivity, precursors containing monodentate phosphanes favour the formation of the linear product in the allylic substitution of cinnamyl acetate (**III**) compared with those containing bidentate phosphanes. With substrate **I**, compounds with the diphosphanes **1a** and **1e**, containing a five-membered chelate ring, gave low enantioselectivities (less than 10 % *ee*), but those with the diphosphane **2e**, forming a six-membered chelate ring or with two monodentate phosphanes, afforded products with moderate enantioselectivity under standard conditions (*ee* up to 74 %). The results show that the performance of precursors containing monodentate phosphanes was superior to those containing bidentate ligands in both activity and selectivity.

Introduction

Palladium-catalyzed asymmetric allylic substitution has been thoroughly investigated in recent years. A large number of ligands containing mainly phosphorus-, nitrogen- or sulfur-coordinating atoms have been prepared and tested in catalysis.[1,2] In particular, the use of *P*-stereogenic phosphanes has been widely studied, initially with limited success, like those obtained with (*R*,*R*)-DIPAMP.[3] Today, however, several *P*-stereogenic monodentate or bidentate phosphanes produce good results in the benchmark allylic alkylation of 1,3-diphenylallyl acetate (see examples in Table 1 and in ref.[2]).

The reaction is characterized by a well-established generic catalytic cycle involving an oxidative addition step followed by a nucleophilic attack on an allylpalladium(II) intermediate. It is normally assumed that the resting state of the process is the allylpalladium intermediate but recent findings have improved our understanding of the reaction. These include the observation of allyl-bridged dinuclear palladium(I) complexes formed by the interaction of the Pd^0 and allyl-Pd^{II} species of the standard catalytic cycle,[4] careful kinetic studies of the ion-pair implications when different stabilizing anions are present,[5] observations of the chloride effect in both systems, the consequences of strong regioretention in the allylic substitution[6] and the nonequivalence of the catalytic precursors prepared using mixtures of $[PdCl(\mu\text{-}Cl)(allyl)]_2$ plus ligand or ionic $[Pd(allyl)(ligand)_2]X$ compounds.[7] Impressive turnover numbers have been obtained using chiral diphosphite ligands in the allylic alkylation and amination of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene,[8a] and the origin of enantioselectivities has been explored using a library of phosphite-phosphoramidite ligands.[8b] Furthermore, the cationic nature of the palladium allyl intermediates allowed the use of mass spectrometric screening (ESI-MS) to evaluate the enantioselectivity of a chiral catalyst or to measure the discrimination power of several chiral ligands in a single experiment.[9] Other metals have also been used successfully in allylic substitution reactions: for example, high regioselectivity and enantioselectivity have been obtained with Ir complexes containing a single phosphoramidite ligand.[10]

The effect of monodentate phosphanes on the regioselectivity and enantioselectivity of symmetric and asymmetric allylic substrates has been studied in some detail. For example, some monodentate phosphoramidites show over 90 % *ee* in the allylic alkylation of 1,3-diphenylallyl acetate.[19] In the regioselectivity for asymmetric substrates like (*E*)-3-

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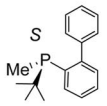
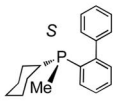
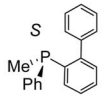
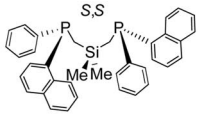
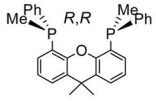
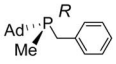
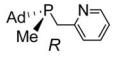
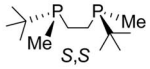
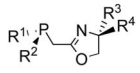
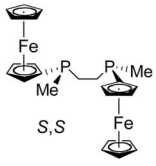
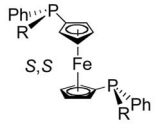
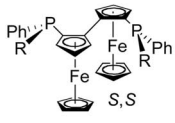
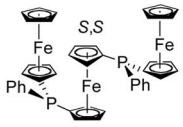
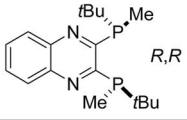
Table 1. Asymmetric allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate catalyzed by Pd/*P*-stereogenic phosphane complexes.[a]

Entry	Ligand	*t* (h)	Conv. (%)	*ee* (%)
1 ref. 11		15	> 99	81 (–)[b]
2 ref. 11		105	> 99	96 (–)[b]
3 ref. 11		17	> 99	0 (–)
4 ref. 12		4	> 99	27 (*R*)
5 ref. 13		6	96	85 (*R*)
6 ref. 14		2.5	91	74 (*R*)
7 ref. 14		0.1	93	44 (*R*)
8 ref. 14		16	96	88 (*S*)
9 ref. 14		16	99	96 (*S*)
10 ref. 15		1	99	95 (*S*)
11 ref. 16		2-48	82	77 (*R*)
12 ref. 17		2-48	87	88 (*R*)
13 ref. 17		2-48	84	81 (*R*)
14 ref. 18		1	85	92 (*R*)

[a] Reaction conditions were not the same for all the entries. The results shown are the best reported for each ligand. [b] Absolute configuration not reported.

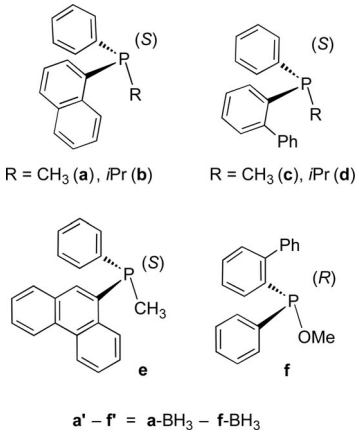
acetoxy-1-phenyl-1-propene (cinnamyl acetate), the linear product of substitution is usually favoured. However, if PCy_3 is used the stereochemistry of the starting allylic acetate is retained ("memory effect").[20] This effect is also observed when MOP is used.[21] With monodentate diamidophosphites[22] or 9-PBN[23] the *ee* obtained in the benchmark reaction can be 97%. When it is possible to compare the results of palladium catalysts stabilized by a bidentate or two monodentate phosphanes containing the same substituents, the rate observed is usually faster in the systems that contain monodentate ligands, whereas the selectivity is similar in both cases.[14] When the palladium/monodentate phosphane ratio is reduced to 1:1 the enantioselectivity of the reaction severely decreases.[14,24] In this reaction the 3,5-dialkylphenyl effect has also been observed, which increases the *ee* in the alkylation of cyclohexenyl acetate by 20%.[25]

In this study we have applied cationic palladium complexes containing two monodentate or a bidentate *P*-stereogenic phosphane as catalytic precursors in the allylic substitution reaction of *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) and (*E*)-3-acetoxy-1-phenyl-1-propene (**III**) with dimethyl malonate as the nucleophile. From the results of activity and selectivity it has been possible to compare the performance of catalytic systems containing monodentate phosphanes with those containing bidentate phosphanes with analogous substituents at the phosphorus atoms.

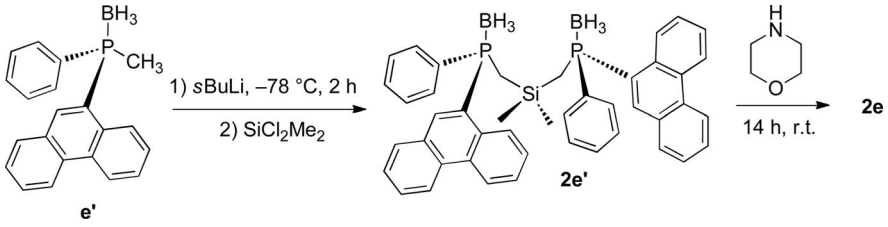
Results and Discussion

Ligand Synthesis

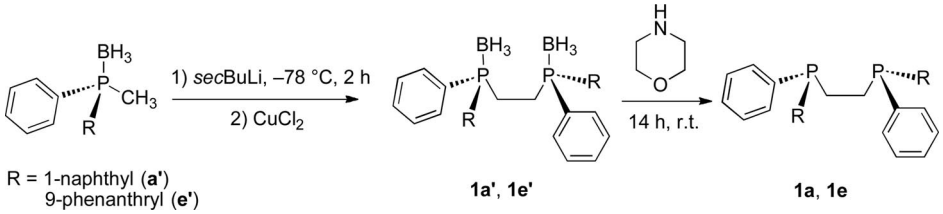
Monodentate *P*-stereogenic phosphanes **a**–**f** have already been described (Scheme 1).[26] From borane-protected methylphosphanes **a**′, **c**′ and **e**′ diphosphanes were prepared by the activation of a methyl proton by *sec*-BuLi, followed by a coupling reaction using $CuCl_2$, or directly with $SiCl_2Me_2$. Both methods have been described elsewhere.[27–30]



Scheme 1. Monodentate phosphanes **a**–**f**, the corresponding borane-protected phosphanes are indicated with primes.



(1)



(2)

Cu^{II}-promoted oxidative coupling is widely used [Equation (1)]. Careful adjustment of the excess of the alkyllithium compound is needed to ensure that mixtures of the desired diphosphane and the starting monophosphane are not obtained. The preparation of **1a′** and **1e′** was successful, but we were unable to obtain the pure diphosphane containing the *o*-biphenylyl group, possibly because this group is more sterically demanding. Several signals between –27 and +35 ppm were observed in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture from **c′**, indicating the decomposition of the phosphane.

By the methodology depicted in Equation (2) the diphosphanes containing 1-naphthyl (**2a**) and 9-phenanthryl (**2e**) groups were obtained in excellent yields. Phosphanes **1a** and **2a** have already been reported by Mezzetti and coworkers.[29,30]

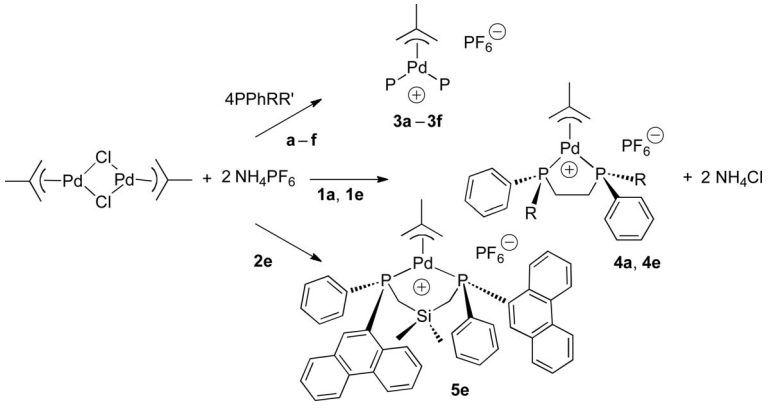
The mixtures can be purified by column chromatography. Starting from monodentate phosphanes of the *S*-absolute configuration, the diphosphanes **1** and **2** are expected to retain the same configuration (*S*,*S*) as reported for analogous ligands. The diastereomeric ratio of around 98:2 was improved by a single recrystallization. The crystal structure of allyl complex **3e** (vide infra) confirms the configuration of the stereogenic phosphorus atoms proposed for **1e**.

Preparation of Allyl Palladium Complexes

Reaction of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ with the appropriate amount of ligand (**a**–**f**, **1a**, **1e** and **2e**) in the presence of an excess of ammonium hexafluorophosphate afforded ionic allylic palladium complexes of the general formula $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(P_2)]PF_6$ (see **3a**–**3f**, **4a**, **4e**, **5e** in Scheme 2). The yields were in the range 40–60%. These compounds are soluble in coordinating solvents (acetonitrile, acetone, DMF), but only scarcely soluble in noncoordinating solvents such as toluene, chloroform or dichloromethane. Complexes **3c**, **3d** and **3f** containing phosphanes with the 2-biphenylyl substituent decomposed in solution, precluding the acquisition of their ^{13}C NMR spectra.

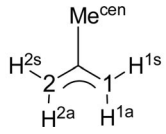
All these complexes were fully characterized by the usual techniques (see Exp. Section). From IR spectroscopy data, the most interesting absorption is the C–C stretch of the allylic moiety: for these complexes, one signal of medium intensity is observed in the range 1440–1420 cm^{-1}. As expected, the intense ν(P–F) vibration band is present at 750 ± 5 cm^{-1}.

Since all the allylic complexes contain two stereogenic phosphorus atoms with the same absolute configuration, the PdP_2 fragment displays C_2 symmetry. Accordingly, only



Scheme 2.

one isomer is expected to appear in solution, as was confirmed by ^{31}P NMR spectroscopy. However, because the C_2 symmetry is lost in the presence of the allyl ligand, two coupled signals are observed in all compounds showing a second-order effect.[31a] Interestingly, one of the doublets shows a considerable broadening, enhanced in nonpolar solvents, as was also reported by Filipuzzi et al.[31b] (see Supporting Information). This broadening is more pronounced in the complexes of the more crowded phosphanes, in accordance with the different lability of each ligand. ^1H NMR spectroscopic data were acquired in $CDCl_3$ or [D_6]-acetone at room temperature. The spectra revealed a single stereoisomer, showing different chemical shifts for the two halves of the symmetric allyl group ($H_{anti} \neq H_{anti}'$; $H_{syn} \neq H_{syn}'$). The signals of the *anti* protons appeared as doublets because of the coupling with the phosphorus atom in the *trans* position. Table 2 and Table 3 list relevant ^{31}P NMR and ^1H NMR spectroscopic data. ^{13}C NMR spectra show the same pattern: the terminal allylic atoms appear as doublets because of the coupling with the phosphorus atom in the *trans* position, and only complex **4a** shows coupling with both the *trans*- and *cis*-phosphorus atoms (see Supporting Information). The maximum differences between the chemical shifts of the terminal allylic carbon atoms are less than 3 ppm. Other effects of the allyl fragment include the nonequivalence of the two methyl groups in the silyl linker of the bridge in **5e**, and the nonequivalence of the pair of protons of each methylene bridge in the other diphosphanes.



Some ^1H 2D NOESY experiments were performed at room temperature to examine the nuclear Overhauser effects between different protons and proton-exchange processes. The most relevant NOE interactions were observed between the *syn* and *anti* protons of each terminal allyl carbon, and also between the *syn* protons and the central methyl-allyl group. No contacts were found between the phosphanes and the allylic protons. Furthermore, no off-diagonal exchange signals were observed and therefore no interconversion between the allyl protons was detected under the conditions of measurement.

When ^{13}C NMR spectra of **3c**, **3d** and **3f** containing the phosphanes with the 2-biphenylyl substituent were recorded an unexpected number of low intensity signals appeared. Proton spectra showed the decomposition of the initial complex after a few hours, suggesting the decoordination of one phosphane. This process would be favoured with the more sterically demanding phosphanes and is supported by the different pattern of the ^{31}P signals of the two phosphanes in several ionic complexes of type **3**.

Acceptable crystals for X-ray determination were obtained for complex **4e**. The data obtained for the organometallic cation were sufficient to establish the atom connectivity although disordered CH_2Cl_2 and toluene molecules are

Table 2. ^{31}P NMR and selected ^1H NMR spectroscopic data[a] (δ in ppm, J [Hz]) for complexes [Pd(η^3-(2-Me-C_3H_4))P_2]PF_6.

Complex	$\delta^{31}P$	P–CH_n	P–X–CH_3	allyl CH_3	*syn*	*anti*
3a	–0.4	1.74	–	1.65	3.53	3.65
	(d, 38.4)	(d, 8.0)			(s, br.)	(d, 10.0)
	2.2	1.97	–		3.74	3.34
	(d, 38.4)	(d, 8.0)			(s, br.)	(d, 9.6)
3b	21.3	1.20 –	0.24, 0.47	1.89	3.96	3.60
	(d, 32.4)	1.72 (m)	(d, 14.8),		(s, br.)	(d, 9.6)
			(d, 14.8)			
	24.2		0.59, 0.67		4.43	3.48
	(d, 32.9)		(dd, 14.0, 6.8),		(s, br.)	(d, 9.2)
			(dd, 14.4, 6.4)			
3c[b]	10.5	0.98	–	1.95	3.54	3.14
	(d, 39.5)	(d, 7.8)			(s, br.)	(d, 9.2)
	12.4	1.33	–		3.75	3.00
	(d, 39.5)	(d, 7.7)			(s, br.)	(d, 9.1)
3d[c]	39.4	1.26 –	0.61 –	2.20	4.13	3.60
	(d, 31.0)	1.68 (m)	0.91 (m)		(s, br.)	(d, 9.5)
	40.0				4.42	3.36
	(d, 31.0)				(s, br.)	(d, 8.8)
3e	0.5	1.80	–	1.81	3.76	3.78
	(d, 37.8)	(d, 8.0)			(s, br.)	(d, 10.0)
	3.7	2.09	–		3.92	3.47
	(d, 37.8)	(d, 7.6)			(s, br.)	(d, 9.6)
3f[d]	120.7	–	3.11	1.61	3.71	1.96
	(d, 53.9)		(d, 10.4)		(s, br.)	(d, 8.8)
	124.7	–	3.21		3.85	2.38
	(d, 53.9)		(d, 10.0)		(s, br.)	(d, 8.8)

[a] $CDCl_3$, 298 K, ^{31}P NMR and ^1H NMR spectra measured at 101.2 and 400.1 MHz, respectively. [b] ^1H NMR spectra measured in CD_3COCD_3 and at 250.1 MHz. [c] ^1H NMR spectra measured at 250.1 MHz. [d] ^1H NMR spectra measured at 500.1 MHz.

Table 3. ^{31}P NMR and selected ^{1}H NMR spectroscopic data[a] (δ in ppm, J [Hz]) for complexes [Pd(η^3-(2-Me-C_3H_4))(P–P)]PF_6.

Complex	$\delta^{31}P$	P–CH_2–	–Si–CH_3	allyl CH_3	H_{syn}	H_{anti}
4a	44.2	2.38–2.59	–	1.71	4.11	3.27
	(d, 29.7)	(m, 2 H)			(s, br.)	(d, 10.4)
	45.6	3.14–3.30			4.54	2.95
	(d, 29.7)	(m, 2 H)			(s, br.)	(d, 10.0)
4e	44.7	2.40–2.70	–	1.69	4.11	3.31
	(d, 29.8)	(m, 2 H)			(s, br.)	(d, 9.6)
	45.4	3.18–3.33			4.52	3.03
	(d, 29.98)	(m, 2 H)			(s, br.)	(d, 10.0)
5g[b]	12.2	2.36–2.44	–0.56	1.78	3.63	3.46
	(d, 47.9)	(m)			(t, br., 4.0)	(d, 10.4)
	13.4		–0.48		3.79	3.23
	(d, 47.6)				(t, br., 4.0)	(d, 10.0)

[a] $CDCl_3$, 298 K, ^{31}P NMR and ^{1}H NMR spectra recorded at 101.2 and 400.1 MHz, resectively. [b] Measured in CD_3COCD_3.

included in the crystal. The ORTEP representation of the cation is given in Figure 1. Table 4 contains selected bond lengths and angles. Pd–P and Pd–C allylic bond lengths were in good agreement with other π-allylic Pd^{II} complexes containing either two monodentate or one bidentate phosphane and the 2-Me-allyl fragment reported in the literature.[32]

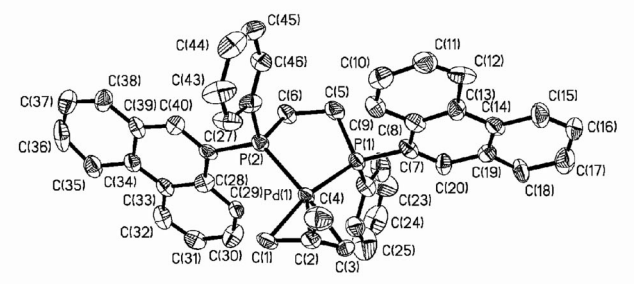


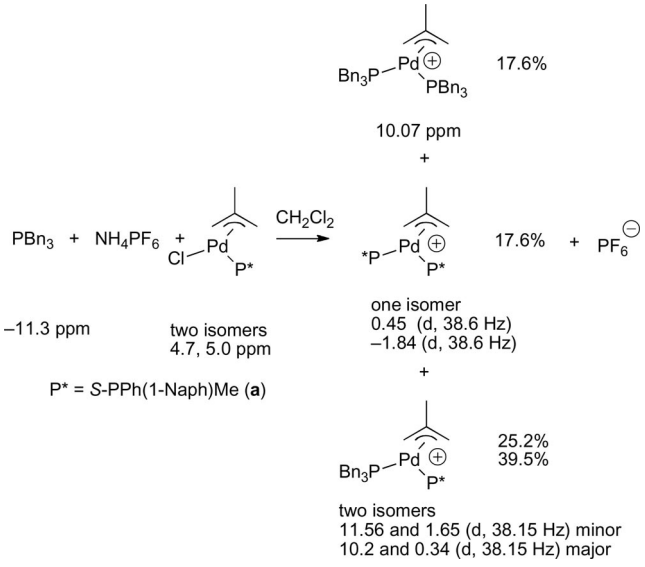
Figure 1. ORTEP view of the molecular structure of **4e**. Hydrogen atoms, solvents and hexafluorophosphate anion have been omitted for clarity.

Table 4. Selected bond lengths [Å] and angles [°] for complex **4e**.

Pd(1)–C(3)	2.135(9)		
Pd(1)–C(1)	2.158(10)	C(3)–Pd(1)–C(1)	67.8(4)
Pd(1)–C(2)	2.178(9)	P(1)–Pd(1)–P(2)	87.11(9)
Pd(1)–P(1)	2.285(2)	C(1)–C(2)–C(3)	115.6(9)
Pd(1)–P(2)	2.297(2)		
P(1)–C(5)	1.826(10)		
P(2)–C(6)	1.817(10)		
C(1)–C(2)	1.402(14)		
C(2)–C(3)	1.425(13)		
C(2)–C(4)	1.436(16)		
C(5)–C(6)	1.575(15)		

Combination of Phosphanes

Heterocombinations of monodentate chiral phosphonites with achiral phosphites or phosphanes[33] and chiral phosphoramidites with achiral phosphanes[34] improved the conversion and enantioselectivity in the Rh-catalyzed hydrogenation reactions compared to the systems formed by homocombination of two chiral ligands. This strategy has been further extended.[35] The relative amounts of the complexes present in solution was investigated in one case[33] and the ratio between the two homocombinations and the heterocombination observed was 1:1:16. We have checked the combination of the chiral phosphane **a** and tribenzylphosphane in detail, and the result is shown in Scheme 3. All the possible combinations of cationic complexes were observed by ^{31}P NMR spectroscopy. The two isomers of the complex corresponding to the heterocombination of ligands accounted for 65% of the mixture. The precipitate from toluene solutions mainly contained the achiral ligand homocombination and the heterocombination. Finally, by pentane precipitation we separated the chiral ligand homocombination, which was only slightly contaminated by the other complexes. The amount of the precursor containing the heterocombination of ligands was too small to be used in catalysis and no further essays were performed.

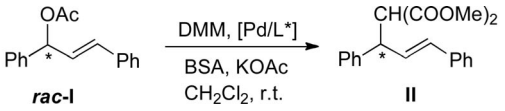


Scheme 3. Relative amounts of homo-/heterocombination of palladium allyl complexes type **3** with a 1:1 ratio of PBn_3 and **a** phosphanes.

Palladium-Catalyzed Asymmetric Allylic Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene (*rac*-I)

Palladium complexes **3**, **4** and **5** were tested as precatalysts in the allylic alkylation of *rac*-**I**, the model substrate

for the allylic substitution processes. This group of complexes was suitable for the comparison of the importance of the metallacycle size and the consequences of the monodentate or bidentate nature of the ligands (electronically analogous) and their influence on the activity and selectivity of the process. The fragment PdP_2 displays C_2 symmetry in all complexes.



***rac*-I** **II**

Complexes of type **3** with two monodentate phosphanes showed higher activity than those we observed with dithioethers or bis(oxazolines), and similar activity to that reported for phosphane-oxazolines[37] or phosphane-phosphoramidite ligands[38] (entries 1–6, Table 5). Complexes **4** and **5** containing bidentate phosphanes showed lower rates of reaction, which is consistent with the findings of Imamoto[14] and Mezzetti.[12] Complex **3e**, which contains two monodentate phosphanes, showed a higher selectivity than **4e** or **5e**, which have the same group of substituents at the phosphorus atom. Complexes **4** containing a five-membered metallic cycle gave almost racemic mixtures of the substitution products, as reported by Bosnich,[3] who used bis aryl-substituted phosphanes. The results showed a clear dependence of the enantioselectivity on the phosphorus substitution in the MePhPR series. The enantiomeric excesses follow the trend: 2-biphenylyl < 1-naphthyl < 9-phenanthryl (entries 1, 3 and 5, respectively). The increase of steric hindrance of the sp^3 arm is more sensitive. When the methyl group (entry 3 phosphane *S*-**c**) was substituted by a methoxy (entry 6 phosphane *R*-**f**) or an isopropyl group (entry 4 phosphane *S*-**d**) the *ee* improved but the direction of the asymmetric induction was inverted for the more hindered isopropylphosphanes (entries 1 vs. 2 and 3 vs. 4). The origin of this inversion must be produced in the very crowded allyl intermediate that could not be isolated since the crystal structures of the phosphane–boranes **c** and **d** do not show any remarkable differences.[26] For this reason the neutral allylic complex [PdCl(η^3-2-Me-C_3H_4)(**f**)] was tested as a precursor in the reaction (entries 7 and 8). It showed a lower but still remarkable *ee* and an initially lower rate of reaction, as expected for the less favoured initial nucleophilic attack on a neutral intermediate. The reorganization of the neutral complex [PdCl(η^3-2-Me-C_3H_4)(**f**)] affording cationic species that may be suitable as catalytic precursors can be considered.[39] Similar results have been reported when the ratio Pd/L is reduced to 1:1, with a severe decrease of the *ee*.[24]

Table 5. Results of asymmetric allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**) with dimethyl malonate catalyzed by type **3**, **4** and **5** complexes.[a]

Entry	Complex	*t* [h]	Conversion [%][b]	*ee* [%][c]
1	**3a**	1	>99.0	28 (*R*)
2	**3b**	1	92.6	45 (*S*)
3	**3c**	1	89.5	8 (*R*)
4	**3d**	1	87.5	14 (*S*)
5	**3e**	1	>99.0	68 (*R*)
6	**3f**	1	>99.0	74 (*S*)
7	[PdCl(allyl)(**f**)]	1	<2.0	– (–)
8	[PdCl(allyl)(**f**)]	24	>99.0	60 (*S*)
9	**4a**	1	2.0	– (–)
10	**4a**	24	>99.0	5 (*S*)
11	**4e**	1	4.1	– (–)
12	**4e**	24	>99.0	8 (*R*)
13	**5a**[d]	4	99	27 (*R*)
14	**5e**	1	12.3	58 (*R*)
15	**5e**	24	>99.0	60 (*R*)

[a] Catalytic conditions: 0.02 mmol of [Pd], complex **3**, **4** or **5**, 1 mmol of *rac*-1,3-diphenyl-2-propenyl acetate, 3 mmol of dimethyl malonate, 3 mmol of BSA and a catalytic amount of KOAc in 4 mL of CH_2Cl_2. [b] Conversion percentage based on the substrate. [c] Enantiomeric excesses determined by HPLC with a Chiralcel-OD column. Absolute configuration, in parentheses, determined by optical rotation: ref.[36] [d] Ref.[12]

Preparation of η^3-1,3-Diphenylallyl Palladium Complexes

The synthesis of palladium η^3-1,3-diphenylallyl bisphosphane intermediates were attempted by reaction among the palladium dimer, monodentate phosphane and NH_4PF_6.[40] Only neutral [PdCl(η^3-1,3-diphenylallyl)(P)] complexes were obtained. The use of an excess of phosphane and $AgPF_6$ did not afford any stable species. Possibly, the more sterically demanding 1,3-diphenylallyl group hinders the stabilization of the desired ionic compounds. The neutral complexes were fully characterized by the usual techniques.

^{1}H NMR signals from the $CDCl_3$ solution of complex **6a** at room temperature showed broad, poorly defined signals. Therefore, spectra were recorded at temperatures ranging from 25 to –40 °C (see Supporting Information). In contrast, the spectrum of compound **6d** is well defined at room temperature.

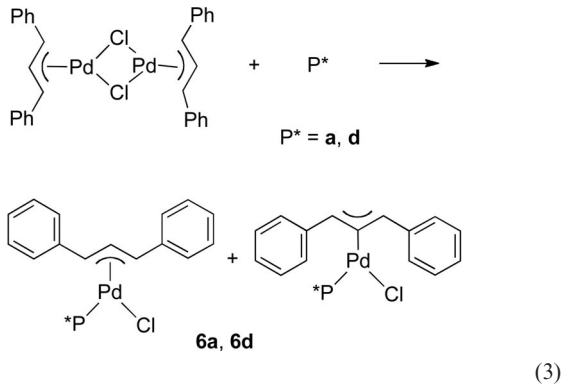
1D and 2D NMR spectroscopic data indicate that the number of isomers observed in these solutions are limited to those with the phenyl groups of the allyl ligand in *syn*-positions.[40,41] So, two isomers were observed in complexes **6a** and **6d** in the relative proportions shown in Table 6 [Equation (3)]. ^{31}P NMR spectra of both complexes show two signals, which is consistent with the presence of the two isomers. Discrimination between them increases with the size of the phosphane (**6d** > **6a**), but it is similar to that observed in the analogous [PdCl(η^3-2-Me-C_3H_4)(P)] complexes.[26] NOESY spectra showed dynamic exchange between the groups of hydrogen atoms. In particular, the exchange between *anti*-allylic protons of the two isomers indicates that the allyl pseudorotation is the main operating mechanism of exchange.[42]

A set of signals is observed for each isomer. The central allylic hydrogen appears as a triplet at a lower field than the terminal allylic hydrogen atoms. In addition, the *anti*-allylic hydrogen atom located on the carbon atom *trans* to the phosphorus atom appears (coupled with the central hydrogen and phosphorus atoms) at lower fields than those in the *cis* position (which are only coupled to the central hydrogen atom). This is also observed for similar compounds.[14]

Table 6. ^{31}P NMR and selected allyl ^{1}H NMR and ^{13}C NMR spectroscopic data[a] (δ in ppm, J [Hz]) for complexes [PdCl(η^3-1,3-$Ph_2C_3H_3$)(P)] **6a** and **6d**.

Complex	^{31}P NMR δ	^{1}H NMR *anti-t*P	^{1}H NMR *anti-c*P	^{1}H NMR *central*	^{13}C NMR *anti-t*P	^{13}C NMR *anti-c*P	^{13}C NMR *central*
6a							
(253 K) major							
1.2	7.8	5.44 (dd, 13.5, 10)	4.08 (d, 11)	6.19 (ps-t, 11.5)	97.7 (d, 25.2)	58.6 (s)	109.1 (s)
minor							
1	7.7	5.49 (dd, 13.5, 10)	3.97 (d, 11.5)	–6.34 (ov.)	96.7 (d, 25.2)	59.2 (s)	108.4 (s)
6d							
(298 K) major							
1.4	33.6	4.75 (ps-t, 10.5)	3.88 (d, 11)	6.21 (ps-t, 12)	98.1 (d, 24.4)	80.0 (s)	106.8 (s)
minor							
1	31.4	4.88 (ps-t, 10.5)	3.57 (d, 11)	6.13 (ps-t, 12)	96.2 (d, 25.2)	80.3 (s)	107.4 (s)

[a] $CDCl_3$, ^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectra measured at 101.2, 500 and 100.6 MHz, respectively; ps-t: pseudo triplet, ov.: overlapped.



(3)

^{13}C chemical shifts for the allylic carbon atoms show that the central atom resonates at a lower field than the terminal ones and that the carbon atom located at a position *trans* to phosphorus is less shielded than the *cis* atom, and is coupled to the phosphorus atom. Compared with the analogous [PdCl(η^3-2-Me-C_3H_4)(P)] complexes,[26] the carbon atoms *trans* to phosphorus are about 10 ppm more deshielded in the diphenylallyl complexes. Complex **6d** shows a large shift to lower fields in the allylic carbon atom *cis* to phosphorus, possibly as a result of the proximity of the *o*-phenyl group of the phosphane, as reflected in the crystal structure (see below).

Suitable crystals for X-ray diffraction measurements were obtained from dichloromethane solutions of **6d** by slow diffusion of hexane at 4 °C (Figure 2).

The crystal structure shows only the diastereoisomer with *R* configuration at the palladium centre with the substituted allyl ligand in *syn*,*syn* geometry. The palladium atom shows a distorted square-planar coordination, bonded to one chlorine ligand, one phosphorus ligand and the three allylic carbon atoms (Table 7). The position of the

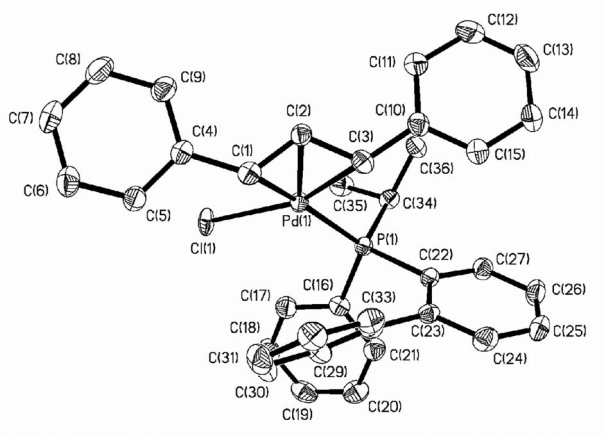


Figure 2. ORTEP view of the molecular structure of **6d**. Hydrogen atoms have been omitted for clarity.

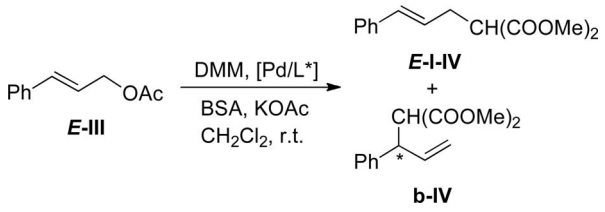
allylic ligand with respect to the plane defined by the palladium, chlorine and phosphorus atoms is heavily distorted: C(3) lies –0.021 Å away from the plane, while C(1) is at 0.577 Å, probably because of the disposition of the biphenyl substituent of the coordinated phosphane. This distortion is similar to those observed in the [Pd(η^3-1,3-$Ph_2C_3H_3$)(PPh_3)$_2$]$^+$ cation.[43] However, in the crystal structure of the analogous [PdCl(η^3-2-Me-C_3H_4)(P(*i*Pr)(*o*-Ph_2)-Ph)] complex,[26] the allyl moiety (C1 and C3) remains in the plane defined by the same three atoms. These features suggest that the steric hindrance of the P(*i*Pr)(*o*-Ph_2)Ph phosphane blocks the formation of the [Pd(η^3-1,3-$Ph_2C_3H_3$)P_2]$^+$ cation. The difference between the two Pd–C bond lengths, *trans* to the P and *trans* to the Cl atom (2.253 vs. 2.194 Å), indicates a major *trans* influence of the phosphane ligand, and consequently a different double bond character of the C(1)–C(2) and C(2)–C(3) allylic bonds (see Table 7).

Table 7. Selected bond lengths [Å] and bond angles [°] for **6d**.

Pd(1)–Cl(1)	2.4202(10)	Cl(1)–Pd(1)–P(1)	103.22(4)
Pd(1)–P(1)	2.3308(11)	C(1)–Pd(1)–C(3)	66.41(15)
Pd(1)–C(1)	2.253(4)	C(2)–Pd(1)–P(1)	138.24(11)
Pd(1)–C(2)	2.180(4)	C(2)–Pd(1)–Cl(1)	117.43(11)
Pd(1)–C(3)	2.194(4)	C(1)–C(2)–C(3)	119.7(4)
C(1)–C(2)	1.387(6)		
C(2)–C(3)	1.429(6)		

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-3-Acetoxy-1-phenyl-1-propene (III)

In order to compare the regioselectivity of the allylic alkylation reaction catalyzed by these palladium complexes, the substrate (*E*)-3-acetoxy-1-phenyl-1-propene (**III**) was used (Table 8). The reaction for this substrate was faster than for **I** and total conversion was achieved in less than one hour. The main difference was that for **III** a similar activity was observed with catalytic precursors containing bidentate phosphanes (4 and 5, entries 14–16) and those stabilized by monodentate phosphanes (3, entries 1–6). A short induction time for the activation of the catalytic precursor is necessary (entries 1 and 2, 7 and 8 or 9 and 10) as indicated by the colour change from pale yellow to orange. A similar induction time was observed when the catalytic precursor was prepared in a ratio Pd/ligand: 1:1 (entries 7 and 8). Furthermore, the initially inactive neutral allylic complex [PdCl(η^3-2-Me-C_3H_4)(**a**)] achieved complete conversion in 45 min (entries 9 and 10). Only the neutral complex, which contained the most hindered phosphane (**d**), showed limited activity (entries 12 and 13).



All precursors favoured the formation of the linear product, but the amount of branched compound **b-IV** obtained with type-**4** precursors (entries 14 and 15) was larger than the amount obtained with types **3** or **5** (Table 8). The bite angle of bidentate ligands strongly affects the regioselectivity. Van Leeuwen et al. studied the palladium-catalyzed allylic alkylation of 2-hexenyl acetate, and showed that the increase in the bite angle of the diphosphanes leads to the increase in the proportion of the linear isomer.[44] When the phosphane substituents are analogous, the pure steric interaction of the diphosphane and the allyl fragment determines the outcome.[44] Our results with complexes **4** and **5** follow the same trend. The selectivity observed with compounds **3**, which contain two monodentate phosphanes, can be explained in the same way, bearing in mind that the coordination of two bulky monodentate phosphanes will produce large P–Pd–P angles. For example the angles for palladium allyl bis(triphenylphosphane) complexes are

Table 8. Results obtained in the allylic alkylation of (*E*)-3-acetoxy-1-phenyl-1-propene (III) with dimethyl malonate catalyzed by type **3**, **4** and **5** complexes.[a]

Entry	Complex	*t* [min]	Conv. [%][b]	Branched/linear[c]
1	**3a**	10	6.2	–[e]
2	**3a**	20	>99.0	1:15
3	**3b**	60	>99.0	1:>20
4	**3c**	60	>99.0	1:15
5	**3e**	60	>99.0	1:16
6	**3f**	60	>99.0	1:>20
7[d]	[PdCl(allyl)(**a**)]	30	37.2	1:17
8[d]	[PdCl(allyl)(**a**)]	45	>99.0	1:16
9	[PdCl(allyl)(**a**)]	30	4.0	–[e]
10	[PdCl(allyl)(**a**)]	45	>99.0	1:18
11	[PdCl(allyl)(**b**)]	60	>99.0	1:>20
12	[PdCl(allyl)(**d**)]	60	<2.0	–[e]
13	[PdCl(allyl)(**d**)]	150	10.0	–[e]
14	**4a**	60	86.2	1:9
15	**4e**	60	>99.0	1:8
16	**5e**	60	85.1	1:13

[a] Reaction conditions: 0.02 mmol of palladium complex, 1 mmol of cinnamyl acetate, 3 mmol BSA and a catalytic amount of KOAc in 4 mL of CH_2Cl_2. [b] Conversion percentage based on the substrate, determined by GC. [c] Branched/linear ratio of isomers obtained by GC. [d] Palladium precursor obtained by reaction of the [PdCl(allyl)(phosphane)] complex with $AgBF_4$ in the presence of cinnamyl acetate. [e] The small conversion observed precludes the formulation of a confident ratio of isomers.

100.0°.[43,45] The low amounts of branched product obtained precluded the measurement of enantiomeric excesses. A similar range of selectivity was observed when bulky monodentate phosphoramidites were used.[19]

When the cationic precursor species were obtained from [PdCl(η^3-2-Me-C_3H_4), **a**], where the ratio Pd/P was 1:1, the reaction was slower (entries 1, 2, 7, 8) but the regioselectivity was similar. The use of the neutral complexes (Pd/P = 1:1) as precursors led to the same regioselectivity as that observed for the cationic complexes **3** (Pd/P = 1:2).

Conclusions

In summary, we have obtained a group of cationic palladium compounds **3**, **4** and **5** containing *P*-stereogenic monodentate and bidentate phosphanes that have two different aryl substituents at each phosphorus atom. The different labilities of the two coordinated phosphorus atoms were dependent on the size of the substituents, as is clearly demonstrated by comparing the ^{31}P NMR spectra of the complexes in which a methyl group was substituted by an isopropyl group or in the sequence **3a**, **3c**, **3e** (see Supporting Information).

All the cationic complexes were tested in Pd-catalyzed allylic substitution reactions. The alkylation of 3-acetoxy-1-phenyl-1-propene showed that the monodentate ligands favour the formation of the linear product. When alkylation was tested with *rac*-3-acetoxy-1,3-diphenyl-1 propene some noteworthy results were obtained. Complexes **3** containing two monodentate phosphanes were more active than **4** and **5**.

With regard to the asymmetric induction, the enantioselectivity with catalysts **3** increases with the size of the substituents of the phosphane, achieving the best result of 74% *ee* with the phosphinite ligand **f**. The sequence of *ee* observed was as follows: P(2-biphenylyl)PhMe (**3c**, 8%), P(2-biphenylyl)Ph(*i*Pr) (**3d**, 14%), P(2-biphenylyl)Ph(OMe) (**3f**, 74%), P(2-biphenylyl)(*t*Bu)Me (81%)[11] and P(2-biphenylyl)CyMe (96%).[11] This sequence illustrates the diversity and subtlety of factors determining the discrimination ability of apparently similar ligands. The lack of enantioselectivity observed for bidentate ligands with an ethylene bridge (**1a** and **1e**) is similar to the results reported for DIPAMP,[3] all of which contain two different aryl substituents. However, with the same bridge but with methyl and *tert*-butyl substituents, 88% *ee* has been obtained,[14] and with a completely planar bridge, 92% *ee* has been reported.[18] In both cases bisalkylaryl-monodentate or bidentate phosphanes gave the best selectivities. Bidentate ligands with three atoms in the bridge (**2**) showed a similar discrimination ability to that obtained with monodentate phosphanes.

The results of this study confirm that *P*-stereogenic monodentate phosphanes show higher activity and an analogous or better discrimination ability than bidentate phosphanes in the catalytic asymmetric allylic substitution reaction.

Experimental Section

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. $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ and $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ were prepared as described previously.[40,46] The routine ^1H, ^{13}C and ^{31}P NMR spectra were recorded with a Varian XL-500 or Mer-400 MHz (^1H NMR, standard $SiMe_4$), Varian Gemini (^{13}C NMR, 50.3 MHz, standard $SiMe_4$) and Bruker DRX-250 (^{31}P NMR, 101.2 MHz) spectrometer 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 with the following spectrometers: FTIR Nicolet 520, FTIR Nicolet Impact 400, FTIR Avatar 330 and FTIR Nicolet 5700. FAB mass chromatograms were obtained with a Fisons V6-Quattro instrument. The routine GC analyses were performed with 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 with 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 with a Waters 717 plus autosampler chromatograph with a Waters 996 multidiode array detector, fitted with a Chiracel OD-H chiral column (25 cm × 0.46 cm). The eluent, in all the determinations, was a mixture of *n*-hexane/*i*PrOH, 95:5. Optical rotations were measured with a Perkin–Elmer 241MC spectropolarimeter at 23 °C. Enantiomeric excesses were determined by GC with 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 Científicotècnics of the Universitat Rovira i Virgili with an Eager 1108 microanalyzer.

Synthesis

(*S*,*S*)-1,2-Bis[(1-naphthyl)phenylphosphanyl]ethane–Borane(*P*) (*S*,*S*)-1a′: The phosphane–borane **(*S*)-a′** (0.816 g, 3.1 mmol) was dissolved in THF (30 mL) and the solution was cooled to –78 °C. *Sec*-butyllithium (2.9 mL of a 1.3 M solution in hexane/cyclohexane, 3.7 mmol) was added by syringe and the mixture was stirred for 2 h. A precooled (–78 °C) suspension of $CuCl_2$ (1.25 g, 9.2 mmol) in THF (50 mL) was added and the mixture was warmed slowly to room temperature. A HCl solution (1 M, 10 mL) was added and the mixture was extracted with ethyl acetate. The combined organic fractions were washed with a 10% NaOH solution (3 × 10 mL) and eventually with an ammonia solution. The organic fraction was washed with brine and dried with anhydrous sodium sulfate. Filtration and evaporation of the solvent furnished the product as a white foam that could appear contaminated with small amounts of the methylmonophosphane–borane **(*S*)-a′** (<10%). The monosubstituted product was removed by flash chromatography (SiO_2, CH_2Cl_2). Combined yield 0.800 g (99%). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 0.20–2.10 (s, br., 6 H), 2.60 (s, br., 4 H), 7.37–7.98 (m, 24 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 298 K): δ = 20.2 (d, J_{CP} = 37.5 Hz, CH_2), 125.2–134.8 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +18.6 (s, br.) ppm.

(*S*,*S*)-1,2-Bis[(9-phenanthryl)phenylphosphanyl]ethane–Borane(*P*) (1/2), (*S*,*S*)-1e′: This diphosphane–borane was obtained by the same method as that used for **(*S*,*S*)-1a′**. From **(*S*)-e′** (0.942 g, 3 mmol), the desired product was obtained as a white foam that could appear contaminated with the monophosphane–borane **(*S*)-e′** (<15%). Combined yield 0.795 g (79%). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K: δ = 0.60–2.10 (s, br., 6 H), 2.65 (s, br., 4 H), 7.00–8.88 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +21.0 (s, br.) ppm.

(*S*,*S*)-2,2-Dimethyl-1,3-bis[(9-phenanthryl)phenylphosphanyl]-2-silapropane–Borane(*P*) (1/2) (*S*,*S*)-2e′: The phosphane–borane **(*S*)-e′** (0.628 g, 2.0 mmol) was dissolved in THF (5 mL) and cooled to –78 °C. *sec*-Butyllithium (1.70 mL of a 1.3 M solution in hexane/cyclohexane, 2.2 mmol) was added and the solution was stirred for 2 h. Dichlorodimethylsilane (0.129 g, 1 mmol) was quickly added by syringe and the mixture was warmed slowly to room temperature. A HCl solution (1 M, 10 mL) was added and the THF was removed. The aqueous suspension was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were washed with brine and dried with anhydrous sodium sulfate and filtered. Evaporation of the solvent yielded the title compound as a yellowish foam that could appear contaminated with the monophosphane–borane **(*S*)-e′** (<10%). Combined yield 0.650 g (95%). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = –0.31 (s, 6 H), 0.20–1.80 (s, br., 6 H), 1.60–2.15 (s, br., 4 H), 7.29–8.75 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +14.3 (s, br.) ppm.

(*S*,*S*)-1,2-Bis[(1-naphthyl)phenylphosphane]ethane (*S*,*S*)-1a: The diphosphane–borane **(*S*,*S*)-1a′** (0.263 g, 0.5 mmol) was dissolved in degassed morpholine (15 mL) and stirred for 14 h at room temperature. The morpholine was removed and the pasty residue was passed through a short column of alumina with toluene as eluent. Evaporation of toluene furnished the free diphosphane as a white pasty solid; yield 0.120 g (48%). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 2.06–2.36 (br., s, 4 H), 7.16–8.48 (m, 24 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = –23.4 (s) ppm.

(*S*,*S*)-1,2-Bis[(9-phenanthryl)phenylphosphanyl]ethane (*S*,*S*)-1e: This diphosphane–borane was obtained by the same method as that used for **(*S*,*S*)-1a**. From **(*S*,*S*)-1e′** (0.795 g, 1.27 mmol), the desired product was obtained as a white pasty solid that could appear con-

taminated with the methylmonophosphane **(*S*)-e** (<10%). Combined yield 0.356 g (47%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 2.10–2.78 (br., s, 4 H), 7.16–8.48 (m, 24 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K): δ = –26.9 (s) ppm.

(*S*,*S*)-2,2-Dimethyl-1,3-bis[(9-phenanthryl)phenylphosphanyl]-2-silapropane (*S*,*S*)-2e: This diphosphane–borane was obtained by the same method as that used for **(*S*,*S*)-1a**. From **(*S*,*S*)-2e′** (0.650 g, 0.95 mmol), the free diphosphane was obtained as a viscous oil that could appear contaminated with the monophosphane **(*S*)-e** (<15%). Combined yield 0.234 g (38%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = –0.05 (s, 6 H), 0.90–0.95 (m, 4 H), 7.20–8.69 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = –32.9 (s) ppm.

(η^3-2-Methylallyl)bis[(*R*)-methyl(1-naphthyl)phenylphosphane]palladium(II) Hexafluorophosphate (3a): The phosphane **(*S*)-a** (0.299 g, 1.19 mmol) was dissolved in CH_2Cl_2 (20 mL). Ammonium hexafluorophosphate (0.278 g, 1.71 mmol) and the palladium dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.112 g, 0.28 mmol) were added and the yellow solution was stirred for 1 h. Water (20 mL) was added and the resulting mixture was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were washed with water and dried with sodium sulfate. The solvent was then removed and the resulting yellowish foam was suspended in pentane, filtered and washed with more pentane. The product was finally obtained as a yellow solid; yield 0.310 g (66%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.65 (s, 3 H), 1.74 (d, J = 8.0 Hz, 3 H), 1.97 (d, J = 8.0 Hz, 3 H), 3.34 (d, J = 9.6 Hz, 1 H), 3.53 (s, 1 H), 3.65 (d, J = 10.0 Hz, 1 H), 3.74 (s, 1 H), 6.96–8.10 (m, 24 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 13.6 (d, J_{CP} = 28.2 Hz, CH_3), 15.0 (d, J_{CP} = 28.2 Hz, CH_3), 23.5 (s, CH_3), 74.3 (d, J_{CP} = 28.2 Hz, CH_2), 76.1 (d, J_{CP} = 29.7 Hz, CH_2), 125.2–138.3 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = –0.4 (d, J = 38.4 Hz, 1 P), +2.2 (d, J = 38.4 Hz, 1 P) ppm. $C_{38}F_6H_{37}P_3Pd$ (807,03): calcd. C 56.56, H 4.62; found C 57.16, H 5.04.

(η^3-2-Methylallyl)bis[(*R*)-isopropyl(1-naphthyl)phenylphosphane]-palladium(II) Hexafluorophosphate (3b): This complex was obtained by the same method as that used for **3a**. From **(*S*)-b** (0.200 g, 0.72 mmol), ammonium hexafluorophosphate (0.168 g, 1.03 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.068 g, 0.17 mmol), the title complex was obtained as a red solid; yield 0.125 g (42%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 0.24 (d, J = 14.8 Hz, 3 H, br.), 0.47 (d, J = 14.8 Hz, 3 H, br.), 0.59 (dd, J = 14.0, 6.8 Hz, 3 H), 0.67 (dd, J = 14.4, 6.4 Hz, 3 H), 1.20–1.72 (m, 2 H), 1.89 (s, 3 H), 3.48 (d, J = 9.2 Hz, 1 H), 3.60 (d, J = 9.6 Hz, 1 H) ppm. 3.96 (s, 1 H), 4.43 (s, 1 H), 7.02–8.12 (m, 24 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 18.4 (d, J_{CP} = 3.8 Hz, CH_3), 18.5 (s, CH_3), 19.2 (d, J_{CP} = 6.9 Hz, CH_3), 19.6 (d, J_{CP} = 8.4 Hz, CH_3), 23.1 (s, CH_3), 25.2–25.8 (br., CH), 75.4 (d, J_{CP} = 26.6 Hz, CH_2), 125.4–137.6 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +21.3 (d, J = 32.4 Hz, 1 P), +24.2 (d, J = 32.9 Hz, 1 P) ppm. $C_{42}F_6H_{45}P_3Pd$ (863.14): calcd. C 58.45, H 5.26; found C 58.55, H 5.82.

(η^3-2-Methylallyl)bis[(*R*)-methyl(9-phenanthryl)phenyphosphane]-palladium(II) Hexafluorophosphate (3e): This complex was obtained by the same method as that used for **3a**. From the phosphane **(*S*)-e** (0.442 g, 1.47 mmol), ammonium hexafluorophosphate (0.343 g, 2.10 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.138 g, 0.35 mmol), the desired compound was obtained as a red solid; yield 0.330 g (52%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.80 (d, J = 8.0 Hz, 3 H), 1.81 (s, 3 H), 2.09 (d, J = 7.6 Hz, 3 H), 3.47 (d, J = 9.6 Hz, 1 H), 3.76 (s, 1 H), 3.78 (d, J = 10.0 Hz, 1 H) ppm. 3.92 (s, 1 H), 7.01–8.53 (m, 28 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 14.3 (d, J_{CP} = 27.4 Hz, CH_3), 16.1 (d, J_{CP} = 28.2 Hz, CH_3), 23.7 (s, CH_3), 74.2 (d, J_{CP} = 28.9 Hz, CH_2), 76.4 (d, J_{CP} = 29.0 Hz, CH_2), 122.6–138.3 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +0.5 (d, J = 37.9 Hz, 1 P), +3.7 (d, J = 37.7 Hz, 1 P) ppm. $C_{46}F_6H_{41}P_3Pd$ (907.15): calcd. C 60.90, H 4.56; found C 60.13, H 5.33.

(η^3-2-Methylallyl)bis[(*R*)-(2-biphenylyl)methylphenylphosphane]-palladium(II) Hexafluorophosphate (3c): This complex was obtained by the same method as that used for **3a**. From the phosphane **(*S*)-c** (0.539 g, 1.95 mmol), ammonium hexafluorophosphate (0.454 g, 2.79 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.183 g, 0.46 mmol), the product was obtained as a red solid; yield 0.485 g (62%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 0.98 (d, J = 7.8 Hz, 3 H), 1.33 (d, J = 7.7 Hz, 3 H), 1.95 (s, 3 H), 3.00 (d, J = 9.1 Hz, 1 H), 3.14 (d, J = 9.2 Hz, 1 H), 3.54 (s, 1 H), 3.75 (s, 1 H), 6.86–8.17 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, CD_3COCD_3, 298 K): δ = +10.5 (d, J = 39.5 Hz, 1 P), +12.4 (d, J = 39.5 Hz, 1 P) ppm. $C_{42}F_6H_{41}P_3Pd$ (859.11): calcd. C 58.72, H 4.81; found C 59.27, H 4.98 H.

(η^3-2-Methylallyl)bis[(*R*)-(2-biphenylyl)isopropylphenylphosphane]-palladium(II) Hexafluorophosphate (3d): This complex was obtained by the same method as that used for **3a**. From the phosphane **(*S*)-d** (0.140 g, 0.46 mmol), ammonium hexafluorophosphate (0.0937 g, 0.57 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.0442 g, 0.11 mmol), the title product was isolated as a yellow solid; yield 0.100 g (50%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): δ = 0.61–0.91 (m, 12 H), 1.26–168 (m, 2 H), 2.20 (s, 3 H), 3.36 (d, J = 8.8 Hz, 1 H), 3.60 (d, J = 9.5 Hz, 1 H), 4.13 (s, 1 H), 4.42 (s, 1 H), 6.79–7.48 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, CD_3COCD_3, 298 K): δ = +39.4 (d, J = 31.0 Hz, 1 P), +40.0 (d, J = 31.0 Hz, 1 P) ppm. $C_{46}F_6H_{49}P_3Pd$ (915.21): calcd. C 60.37, H 5.40; found C 60.77, H 5.94.

(η^3-2-Methylallyl)bis[(*S*)-(2-biphenylyl)methoxyphenylphosphane]-palladium(II) Hexafluorophosphate (3f): This complex was obtained by the same method as that used for **3a**. From the phosphinite **(*R*)-f** (0.265 g, 0.99 mmol), ammonium hexafluorophosphate (0.231 g, 1.42 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.093 g, 0.24 mmol), the desired complex was obtained as a red solid; yield 0.233 g (58%). ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K): δ = 1.61 (s, 3 H), 1.96 (d, J = 8.8 Hz, 1 H), 2.38 (d, J = 8.8 Hz, 1 H), 3.11 (d, J = 10.4 Hz, 3 H), 3.21 (d, J = 10.0 Hz, 3 H), 3.71 (s, 1 H), 3.84–3.86 (m, 1 H), 6.81–7.62 (m, 28 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +120.7 (d, J = 53.9 Hz, 1 P), +124.7 (d, J = 53.9 Hz, 1 P) ppm. $C_{38}F_6H_{37}O_2P_3Pd$ (839.03): calcd. C 54.40, H 4.44; found C 57.00, H 5.19.

(η^3-2-Methylallyl){(*R*,*R*)-1,2-bis[(1-naphthyl)phenylphosphanyl]-ethane}palladium(II) Hexafluorophosphate (4a): The phosphane **1a** (0.110 g, 0.22 mmol) was dissolved in CH_2Cl_2 (10 mL). Ammonium hexafluorophosphate (0.059 g, 0.36 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.047 g, 0.12 mmol) were added and the mixture was stirred for 1 h. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic fraction was washed with water and dried with anhydrous sodium sulfate. The solvent was removed and the remaining yellowish foam was recrystallized from toluene/dichloromethane to yield the title product as a white crystalline solid; yield 0.110 g (57%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.71 (s, 3 H), 2.38–2.59 (m, 2 H), 2.95 (d, J = 10.0 Hz, 1 H), 3.14–3.30 (m, 2 H), 3.27 (d, J = 10.4 Hz, 1 H), 4.11 (s, 1 H), 4.54 (s, 1 H), 6.98–8.00 (m, 26 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$,

298 K): δ = 24.1 (s, CH_3), 26.6 (d, J_{CP} = 12.9 Hz, CH_2), 27.0 (d, J_{CP} = 12.9 Hz, CH_2), 69.8 (dd, J_{CP} = 29.8, 3.8 Hz, CH_2), 70.6 (dd, J_{CP} = 29.0, 3.8 Hz, CH_2), 124.1–138.2 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = +44.2 (d, J = 29.7 Hz, 1 P), +45.6 (d, J = 29.6 Hz, 1 P) ppm. $C_{37}F_6H_{35}P_3Pd$ (793.01): calcd. C 56.04, H 4.45; found C 58.28, H 5.08.

(η^3-2-Methylallyl){(*R*,*R*)-1,2-bis[(9-phenanthryl)phenylphosphanyl]-ethane}palladium(II) Hexafluorophosphate (4e): This complex was obtained by the same method as that used for **4a**. From the diphosphane **(*S*,*S*)-1e** (0.271 g, 0.45 mmol), ammonium hexafluorophosphate (0.147 g, 0.90 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.087 g, 0.23 mmol), the desired product was obtained as a pale yellow solid; yield 0.222 g (55%). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.69 (s, 3 H), 2.40–2.70 (m, 2 H), 3.03 (d, J = 10.0 Hz, 1 H), 3.18–3.33 (m, 2 H), 3.31 (d, J = 9.6 Hz, 1 H), 4.11 (s, 1 H), 4.52 (s, 1 H), 7.06–8.71 (m, 28 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 24.2 (s, CH_3), 26.6 (d, J_{CP} = 13.7 Hz, CH_2), 27.0 (d, J_{CP} = 13.7 Hz, CH_2), 70.2 (d, J_{CP} = 28.9 Hz, CH_2), 71.0 (d, J_{CP} = 29.8 Hz, CH_2), 122.7–138.3 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K): δ = +44.7 (d, J = 29.8 Hz, 1 P), +45.4 (d, J = 29.8 Hz, 1 P) ppm. $C_{46}F_6H_{39}P_3Pd$ (905.13): calcd. C 61.04, H 4.34; found C 62.96, H 4.51.

Crystal Structure Determination of 4e: Colourless crystals, suitable to perform X-ray diffraction studies, were obtained by slow diffusion of toluene over a solution of the complex in dichloromethane at 4 °C. $C_{50}H_{44}ClF_6P_3Pd$ (1/2 toluene, 1/2 CH_2Cl_2) M_r = 993.69 g mol^{-1}, orthorhombic, a = 19.9089(11) Å, b = 19.9089(11) Å, c = 66.178(5) Å, U = 22716(2) Å^3, T = 298(2) K, space group R_{32n}, Z = 18, 38579 reflections measured, 11451 unique (R_{int} = 0.1321), which were used in all calculations. The final $wR(F2)$ was 0.2402 (all data).

CCDC-753099 contains the supplementary crystallographic data for **4e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(η^3-2-Methylallyl){(*R*,*R*)-2,2-dimethyl-1,3-bis[(9-phenathryl)phenyl]-2-silapropane}palladium(II) Hexafluorophosphate (5e): This complex was obtained by the same method as that used for **4a**. From the diphosphane **(*S*,*S*)-2e** (0.200 g, 0.30 mmol), ammonium hexafluorophosphate (0.196 g, 1.20 mmol) and the dimer [PdCl(μ-Cl)η^3-(2-CH_3-C_3H_4)] (0.059 g, 0.15 mmol), the title complex was isolated as a white solid; yield 0.104 g (36%). ^1H NMR (400.1 MHz, CD_3COCD_3, 298 K): δ = –0.56 (s, 3 H), –0.48 (s, 3 H), 1.78 (s, 3 H), 2.36–2.55 (m, 4 H), 3.23 (d, 1 H, J = 10.0 Hz), 3.46 (d, 1 H, J = 10.4 Hz), 3.63 (t, 1 H, J = 4.0 Hz), 3.79 (t, 1 H, J = 4.0 Hz), 7.13–9.05 (m, 28 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100.0 MHz, CD_3COCD_3, 298 K): δ = –0.3 (s, CH_3), –0.2 (s, CH_3), 11.0–11.3 (m, 2CH_2), 23.5 (s, CH_3), 74.0 (d, J_{CP} = 32.7 Hz, CH_2), 76.6 (d, J_{CP} = 31.2 Hz, CH_2), 123.6–139.9 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, CD_3COCD_3, 298 K): δ = +12.2 (d, J = 47.9 Hz, 1 P), +13.4 (d, J = 47.6 Hz, 1 P) ppm. $C_{48}F_6H_{45}P_3PdSi$ (963.29): calcd. C 59.85, H 4.71; found C 60.05, H 4.35.

Chloro(η^3-1,3-diphenylallyl)[(*R*)-methyl(1-naphthyl)phenylphosphane]palladium(II) (6a): The phosphane **(*S*)-a** (0.140 g, 0.56 mmol) was dissolved in CH_2Cl_2 (10 mL). The dimer [PdCl(μ-Cl)(η^3-1,3-diphenylallyl)]$_2$ (0.181 g, 0.27 mmol) was added and the mixture was stirred for 1 h. The solvent was removed and the remaining yellowish foam was washed several times with pentane. Finally the yellow powder obtained was filtered and dried under vacuum; yield 0.150 g (46%). ^1H NMR (500.1 MHz, $CDCl_3$, 253 K): δ = P–CH_3 major 1.8 (d, 3 H, J = 9.0 Hz), minor 2.1 (d, 3 H, J = 9.0 Hz) ppm. Allyl system: see discussion. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 13.8 (s, CH_3), 14.1 (s, CH_3), 72.0 (s, CH_3), 96.6 (d, J_{CP} = 25.4 Hz, CH), 97.7 (d, J_{CP} = 25.4 Hz, CH), 108.4 (s, CH), 109.1 (s, CH), 124.8–138.1 (m, 1 C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (101.1 MHz, $CDCl_3$, 298 K): δ = 3.4 (b) ppm. $^{31}P\{^1H\}$ NMR (11.1 MHz, $CDCl_3$, 253 K): δ = 7.7 (45%), 7.8 (55%) ppm. $C_{32}ClH_{28}PPd$ (585.41): calcd. C 65.66, H 4.82; found C 65.90, H 5.30.

Chloro(η^3-1,3-diphenylallyl)[(*R*)-(2-biphenylyl)isopropylphenylphosphane]palladium(II) (6d): This complex was obtained by the same method as that used for **6a**. From the phosphane **(*S*)-d** (0.215 g, 0.706 mmol) and the dimer [PdCl(μ-Cl)(η^3-1,3-diphenylallyl)]$_2$ (0.235 g, 0.350 mmol), the desired product was obtained as a pale orange solid; yield 0.320 g (71%). IR: $\tilde{\nu}$ = 3056 ν(C–H), 3030 ν(C–H), 2984 ν(C–H), 2964 ν(C–H), 2928 ν(C–H), 1548, 1490, 1463, 1434, 1385, 1183, 1091, 761, 752, 738, 709, 697, 690, 649, 508 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$, 298 K): δ = P–C*H*–$(CH_3)_2$ major 1.48 (m), minor 2.55 (m), P–CH–(C*H*$_3)_2$ major 0.65, 0.88 (dd, J = 13, 7 Hz), minor 0.90, 1.1 (dd, J = 18.5, 7 Hz, 3 H) ppm. Allyl system: see discussion. $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 19.0 (d, J_{CP} = 43.5 Hz, CH_3), 19.5 (d, J_{CP} = 37.4 Hz, CH_3), 21.2 (d, J_{CP} = 6.1 Hz, CH_3), 21.6 (d, J_{CP} = 9.2 Hz, CH_3), 25.1 (d, J_{CP} = 20.6 Hz, CH), 27.1 (d, J_{CP} = 21.4 Hz, CH), 71.8 (s, CH), 72.3 (d, J_{CP} = 5.4 Hz, CH), 96.2 (d, J_{CP} = 25.2 Hz, CH), 98.1 (d, J_{CP} = 24.4 Hz, CH), 106.8 (d, J_{CP} = 4.6 Hz, CH), 107.4 (s, CH), 126.2–147.1 (C, CH, Ar) ppm. $^{31}P\{^1H\}$ NMR (11.1 MHz, $CDCl_3$, 298 K): δ = 31.4 (43%), 33.6 (57%) ppm. $C_{36}ClH_{34}PPd$ (639.50): calcd. C 67.62, H 5.36; found C 67.05, H 5.90.

Crystal Structure Determination for 6d: Orange crystals, suitable to perform X-ray diffraction studies, were obtained by slow diffusion of hexane over a solution of the complex in dichloromethane at 4 °C. $C_{36}H_{34}ClPPd$, M_r = 947.66 g mol^{-1}, orthorhombic, a = 12.991(3) Å, b = 13.684(3) Å, c = 16.864(3) Å, U = 2997.7(10) Å^3, T = 173 K, space group $P2_12_12_1$ (no. 19), Z = 4, 17564 reflections measured, 6129 unique (R_{int} = 0.0208), which were used in all calculations. The final $wR(F2)$ was 0.1062 (all data).

CCDC-753100 contains the supplementary crystallographic data for **6d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Selected ^{13}C NMR spectroscopic data of complexes **3**, **4** and **5**. Crystal data and structure refinement for **4e** and **6d**. ^1H NMR spectra of **6a** in $CDCl_3$ at different temperatures. $^{31}P\{^1H\}$ NMR spectra for selected palladium complexes.

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[1] a) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; b) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2943.
[2] Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297.
[3] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.
[4] C. Markert, M. Neuburger, K. Kulicke, M. Meuwly, A. Pfaltz, *Angew. Chem. Int. Ed.* **2007**, *46*, 5892–5895.
[5] L. A. Evans, N. Fey, J. N. Harvey, D. Hose, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne, G. J. J. Owen-Smith, M. Purdie, *J. Am. Chem. Soc.* **2009**, *131*, 14471–14473.

[6] a) P. Fristrup, T. Jensen, J. Hoppe, P. O. Norrby, *Chem. Eur. J.* **2006**, *12*, 5352–5360; b) C. Amatore, A. A. Bahsoun, A. Jutand, L. Mensah, G. Meyer, L. Ricard, *Organometallics* **2005**, *24*, 1569–1577.
[7] a) C. Amatore, A. Jutand, M. A. M'Barki, G. Meyer, L. Mottier, *Eur. J. Inorg. Chem.* **2001**, 873–880; b) T. Cantat, E. Génin, C. Giroud, G. Meyer, A. Jutand, *J. Organomet. Chem.* **2003**, *687*, 365–376.
[8] a) A. B. Castillo, I. Favier, E. Teuma, S. Castillón, C. Godard, A. Aghmiz, C. Claver, M. Gómez, *Chem. Commun.* **2008**, 6197–6199; b) E. Raluy, O. Pàmies, M. Diéguez, *Adv. Synth. Catal.* **2009**, *351*, 1648–1670.
[9] a) C. A. Müller, A. Pfaltz, *Angew. Chem. Int. Ed.* **2008**, *47*, 3363–3366; b) C. Markert, P. Rösel, A. Pfaltz, *J. Am. Chem. Soc.* **2008**, *130*, 3234–3235.
[10] a) S. Spiess, C. Welter, G. Franck, J. P. Taquet, G. Helmchen, *Angew. Chem. Int. Ed.* **2008**, *47*, 7652–7655; b) S. T. Madrahimov, D. Markovic, J. F. Hartwig, *J. Am. Chem. Soc.* **2009**, *131*, 7228–7229.
[11] H. Tsuruta, T. Imamoto, *Synlett* **2001**, 999–1002.
[12] R. M. Stoop, A. Mezzetti, *Organometallics* **1998**, *17*, 668–675.
[13] Y. Hamada, F. Matsuruta, M. Oku, K. Hatano, T. Shiori, *Tetrahedron Lett.* **1997**, *38*, 8961–8964.
[14] H. Danjo, M. Higuchi, M. Yada, T. Imamoto, *Tetrahedron Lett.* **2004**, *45*, 603–606.
[15] N. Oohara, K. Katagiri, T. Imamoto, *Tetrahedron: Asymmetry* **2003**, *14*, 2171–2175.
[16] U. Nettekoven, M. Widhalm, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry* **1997**, *8*, 3185–3188.
[17] U. Nettekoven, M. Widhalm, H. Kalchhauser, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *J. Org. Chem.* **2001**, *66*, 759–770.
[18] T. Imamoto, M. Nishimura, A. Koide, K. Yoshida, *J. Org. Chem.* **2007**, *72*, 7413–7416.
[19] M. D. K. Boele, P. C. J. Kamer, M. Lutz, A. L. Spek, J. G. de Vries, P. W. N. M. Leeuwen, G. P. F. van Strijdonck, *Chem. Eur. J.* **2004**, *10*, 6232–6246.
[20] A. J. Blacker, M. L. Clarke, M. S. Loft, J. M. J. Williams, *Org. Lett.* **1999**, *1*, 1969–1971.
[21] T. Hayashi, M. Kawatsura, Y. Uozumi, *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687.
[22] V. N. Tsarev, S. E. Lyubimov, A. A. Shiryaev, S. V. Zheglov, O. G. Bondarev, V. A. Davankov, A. A. Kabro, S. K. Moiseev, V. N. Kalinin, K. N. Gavrilov, *Eur. J. Inorg. Chem.* **2004**, 2214–2222.
[23] Y. Hamada, N. Seto, H. Ohmori, K. Hatano, *Tetrahedron Lett.* **1996**, *37*, 7565–7568.
[24] Y. Y. Yan, T. V. RajanBabu, *Org. Lett.* **2000**, *2*, 199–202.
[25] P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2004**, *23*, 2295–2304.
[26] A. Grabulosa, G. Muller, J. I. Ordinas, A. Mezzetti, M. Á. Maestro, M. Font-Bardia, X. Solans, *Organometallics* **2005**, *24*, 4961–4973.
[27] S. Jugé, M. Stephan, J. A. Laffitte, J. P. Genet, *Tetrahedron Lett.* **1990**, *31*, 6357–6360.
[28] T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 1635–1636.
[29] R. M. Stoop, C. Bauer, P. Setz, M. Wörle, T. Y. H. Wong, A. Mezzetti, *Organometallics* **1999**, *18*, 5691–5700.
[30] R. M. Stoop, A. Mezzetti, F. Spindler, *Organometallics* **1998**, *17*, 668–675.
[31] P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, *Helv. Chim. Acta* **2004**, *87*, 272–278.
[32] a) E. Cesarotti, M. Grassi, L. Prati, F. Demartin, *J. Organomet. Chem.* **1989**, *370*, 407–419; b) F. Ozawa, T. Son, S. Ebina, K. Osakada, A. Yamamoto, *Organometallics* **1992**, *11*, 171–176; c) J. Cermak, S. D. Perera, B. L. Shaw, M. Thornton-Pett, *Inorg. Chim. Acta* **1996**, *244*, 115–120; d) M. Lejeune, C. Jeunesse, D. Matt, N. Kyritsakas, R. Welter, J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.* **2002**, 1642–1650.
[33] M. T. Reetz, X. Li, *Angew. Chem. Int. Ed.* **2005**, *44*, 2959–2962.
[34] R. Hoen, J. A. F. Boogers, H. Bernsmann, A. J. Minnaard, A. Meetsma, T. D. Tiemersma-Wegman, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Angew. Chem. Int. Ed.* **2005**, *44*, 4209–4212.
[35] a) M. T. Reetz, O. Bondarev, *Angew. Chem. Int. Ed.* **2007**, *46*, 4523–4526; b) M. T. Reetz, M. Surowiec, *Heterocycles* **2006**, *67*, 567–574.
[36] U. Leutenegger, G. Umbricht, C. Fahrni, P. V. Matt, A. Pfaltz, *Tetrahedron* **1992**, *48*, 2143–2156.
[37] P. von Matt, A. Pfaltz, *Angew. Chem. Int. Ed. Engl.* **1994**, *32*, 566–568.
[38] J. Wassenaar, S. van Zutphen, G. Mora, P. Le Floch, M. A. Siegler, A. L. Spek, J. N. H. Reek, *Organometallics* **2009**, *28*, 2724–2734.
[39] a) E. Szuromi, H. Shen, B. L. Gooddall, R. F. Jordan, *Organometallics* **2008**, *27*, 402–409; b) R. M. Ceder, C. García, A. Grabulosa, F. Karipcin, G. Muller, M. Rocamora, M. Font-Bardía, X. Solans, *J. Organomet. Chem.* **2007**, *692*, 4005–4019.
[40] P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* **1995**, *78*, 265–284.
[41] O. Hoarau, H. Aiet-Haddou, J.-C. Daran, D. Cramailere, G. G. A. Balavoine, *Organometallics* **1999**, *18*, 4718–4723.
[42] Sometimes it is possible to observe this exchange by NMR spectroscopy as in: M. A. Pericàs, C. Puigjaner, A. Riera, A. Vidal-Ferran, M. Gómez, F. Jiménez, G. Muller, M. Rocamora, *Chem. Eur. J.* **2002**, *8*, 4164–4178; or it is not observed as in: D. Franco, M. Gómez, F. Jiménez, G. Muller, M. Rocamora, M. A. Maestro, J. Mahía, *Organometallics* **2004**, *23*, 3197–3209.
[43] C. Amatore, A. A. Bahsoun, A. Jutand, L. Mensah, G. Meyer, L. Ricard, *Organometallics* **2005**, *24*, 1569–1577.
[44] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **1998**, 25–27, and references cited therein.
[45] a) M. W. Baize, P. W. Blosser, V. Plantevin, D. G. Schimpff, J. C. Gallucci, A. Wojcicki, *Organometallics* **1996**, *15*, 164–173; b) S. Ogoshi, K. Tsutsumi, H. Kurosawa, *J. Organomet. Chem.* **1995**, *493*, C19–C21.
[46] W. T. Dent, R. Long, A. J. Wilkinson, *J. Chem. Soc.* **1964**, 1585–1588.

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