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Bulky Monodentate Phosphoramidites in Palladium-Catalyzed Allylic Alkylation Reactions: Aspects of Regioselectivity and Enantioselectivity

Maarten D. K. Boele,[a] Paul C. J. Kamer,[a] Martin Lutz,[b] Anthony L. Spek,[b] Johannes G. de Vries,[c] Piet W. N. M. van Leeuwen,*[a] and Gino P. F. van Strijdonck[a]

Abstract: A series of bulky monodentate phosphoramidite ligands, based on biphenol, BINOL and TADDOL backbones, have been employed in the Pd-catalysed allylic alkylation reaction. Reaction of disodium diethyl 2-methyl malonate with monosubstituted allylic substrates in the presence of palladium complexes of the phosphoramidite ligands proceeds smoothly at room temperature. The regioselectivities observed depend strongly on the leaving group and the geometry of the allylic starting compounds. Mono-coordination occurs when these ligands are ligated in [Pd(allyl)(X)] complexes (allyl = C_3H_5, 1-$CH_3C_3H_4$, 1-$C_6H_5C_3H_4$, 1,3-$(C_6H_5)_2C_3H_3$; X = Cl, OAc). The solid-state structure determined by X-ray diffraction of [Pd(C_3H_5)(**1**)(Cl)] reveals a non-symmetric coordination of the allyl moiety, caused by the stronger *trans* influence of the phosphoramidite ligand relative to X^-. In all of these complexes, the *syn*,*trans* isomer is the major species present in solution. Because of fast isomerisation and high reactivity of the *syn*,*cis* complex, the major product formed upon alkylation is the linear product, especially for monosubstituted phenylallyl substrates in the presence of halide counterions. In the case of biphenol- and BINOL-based phosphoramidites, however, a strong memory effect is observed when 1-phenyl-2-propenyl acetate is employed as the substrate. In this case, nucleophilic attack competes effectively with the isomerisation of the transient cinnamylpalladium complexes. The asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate afforded the chiral product in up to 93% *ee*. Substrates with smaller substituents gave lower enantioselectivities. The observed stereoselectivity is explained in terms of a preferential rotation mechanism, in which the product is formed by attack on one of the isomers of the intermediate [Pd{1,3-$(C_6H_5)_2C_3H_3$}(L)(OAc)] complex.

Keywords: alkylation · asymmetric catalysis · homogeneous catalysis · ligand design · palladium

Introduction

Allylic-substitution reactions are currently among the most important and widely studied catalytic reactions in organic synthesis. Especially in the last decade, enormous progress has been made in gaining insight in the factors that determine the outcome of the reaction, such as the metal, the structure of the allyl substrate, ligand or nucleophile and the nature of the solvent.[1–4]

The vast majority of the studies reported apply palladium as the metal catalyst of choice. A plethora of ligands has been designed and employed, mainly with phosphorus and/or nitrogen donor atoms. Especially the asymmetric allylic alkylation has received broad attention (Scheme 1).[1–6] Excellent enantioselectivities have been obtained when C_2 symmetrical diphosphines were used, as demonstrated by Trost et al.[1,6] The observed stereoselectivities for these and other systems can often be explained by the concept of a "chiral pocket".[7–10] The chiral induction stems from the selective clockwise or anticlockwise rotation of the allyl moiety in this pocket upon nucleophilic attack to form the product η^2-alkene complex.

The potential of other classes of ligands has been recognised in recent years. These include chiral P–N ligands, as was demonstrated by Pfaltz and Helmchen, who employed chiral phosphinooxazoline ligands possessing C_1 symmetry.[5,11–18] The difference in donor properties of the coordinating phosphorus and nitrogen atoms offered the possibili-

[a] Dr. M. D. K. Boele, Dr. P. C. J. Kamer, Prof. Dr. P. W. N. M. van Leeuwen, Dr. G. P. F. van Strijdonck
University of Amsterdam
van't Hoff Institute for Molecular Sciences
Nieuwe Achtergracht 166, 1018 WV Amsterdam (Netherlands)
Fax: (+31) 20-525-5604
E-mail: pwnm@science.uva.nl

[b] Dr. M. Lutz, Prof. Dr. A. L. Spek
University of Utrecht
Bijvoet Center for Biomolecular Research
Utrecht (Netherlands)

[c] Prof. Dr. J. G. de Vries
DSM Research B.V., Postbus 18
6160 MD, Geleen (Netherlands)

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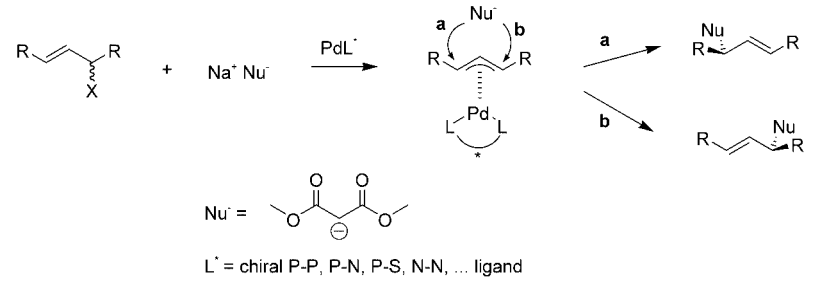
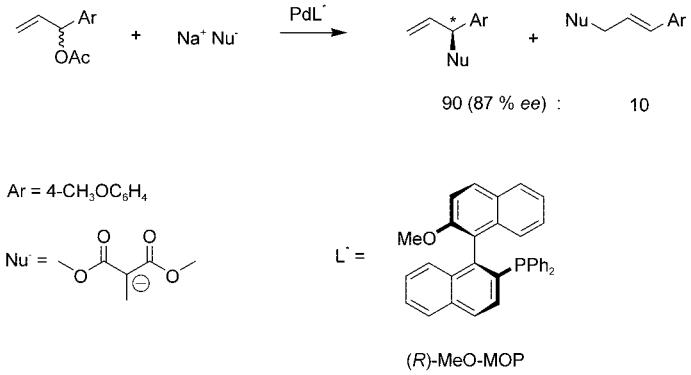


Scheme 1. Asymmetric palladium-catalysed allylic alkylation of a symmetrically substituted allyl substrate.

ty of directing the site of nucleophilic attack to the allylic carbon atom *trans* to phosphorus. This is caused by the larger *trans* influence exerted by P relative to N, thereby rendering the carbon atom *trans* to phosphorus more electrophilic.[14,19–22] Other bidentate P–N ligands, such as planar, chiral ferrocenyl derivatives, have also been successfully employed, with high regio- and stereoselectivities.[23]

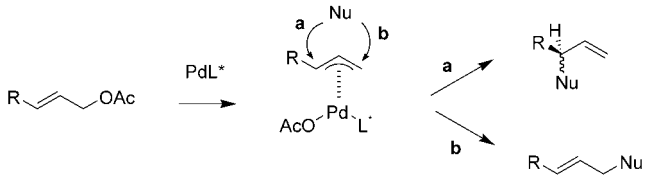
The number of chiral monodentate ligands that have been studied in palladium-catalysed asymmetric allylic transformations is rather limited. The reports on application of chiral monodentate ligands in the allylic alkylation deal almost without exception with chiral phosphines.[24–32] In most cases the enantioselectivities obtained are at best in the same range as those observed for bidentate analogues.[26] Among the most prominent examples of successful monodentate ligands are the so-called MOP-type ligands (Scheme 2), introduced by Hayashi and co-workers.[30,33] It



Scheme 2. [Pd((*R*)-MeO-MOP)]-catalysed regioselective and enantioselective alkylation of 1-substituted cinnamyl derivatives.

was shown that MOP ligands give very selective and active catalysts in the asymmetric Pd-catalysed reduction of allylic esters with formic acid.[27,30] Application of these ligands in allylic alkylation revealed several interesting features with respect to the regioselectivity of unsymmetrically substituted allyl groups (Scheme 3). With the use of MeO-MOP, the reaction of 1-aryl-2-propenyl acetate derivatives with the sodium salt of dimethyl 2-methyl malonate resulted in formation of the branched product in 90% regioselectivity, with an *ee* of 87% (Ar = 4-$CH_3OC_6H_4$, Scheme 2).[34]

Thus, directing the site of nucleophilic attack by a difference in donor properties could be accomplished by the use of mixed donor ligands or by the use of bulky, monodentate ligands. We have described the application of bulky, monodentate phosphoramidite ligands in the Suzuki and the Heck reaction.[35] These ligands were shown to have properties that distinguish them from most ligands used to date. The most

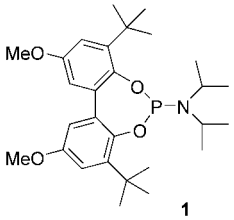


Scheme 3. Asymmetric palladium-catalysed allylic alkylation of an unsymmetrically substituted allyl substrate and a monodentate ligand.

important feature is the bulkiness of the ligand, resulting in enforced mono-coordination to palladium, which leads to enhanced reaction rates. Because of these interesting complexation characteristics, we decided to study bulky phosphoramidites in the palladium-catalysed allylic alkylation reaction, both the non-asymmetric and asymmetric variant. In the last few years a revival has taken place in the use of chiral monodentate ligands for asymmetric reactions.[36] In most cases, however, these ligands are relatively small and more than one ligand coordinates to the metal centre. The few early examples of the use of phosphoramidites as ligands include the hydroformylation.[37] An important breakthrough demonstrating the value of chiral phosphoramidites has been accomplished by Feringa and co-workers. They successfully applied this class of ligands in the copper-catalysed asymmetric 1,4-addition.[38] More recently, it has been shown that monodentate phosphoramidites can function as effective chiral ligands in other metal-catalysed reactions such as hydrogenations,[39,40] hydrosilylations[41] and hydrovinylations.[42] Despite the recent increase in interest for phosphoramidites as auxiliaries in catalysis, very few applications in palladium-catalysed allylic subtitution have been reported yet.[43] Several groups have exemplified the potential of chiral phosphoramidites in copper-catalysed allylic alkylations, which proceed through a mechanism (predominantly S_N2' from σ-allyl complexes) different from that of the palladium-catalysed reaction. The application of phosphoramidites in iridium-catalysed allylic alkylations has been reported.[44] The reaction was proposed to proceed through σ-allyl complexes as well and resulted in enantioselectivities of up to 93% with very high regioselectivity to the branched product (>99%). In this paper, we present the results we obtained in testing bulky phosphoramidites in palladium-catalysed allylic alkylations of several allylic substrates.[35] The ligand effects on regio- and enantioselectivity are described, together with the observation of a large regiochemical memory effect, and its implications for asymmetric transformations.

Results and Discussion

Ligand synthesis: Several bulky phosphoramidites, based on bulky biphenol, binaphthol or TADDOL backbones were prepared. These can be easily synthesised by published methods[37,45,46] and possess modular properties, allowing fine-tuning of their steric and electronic characteristics. An overview of the ligands we applied in the present studies of the palladium-catalysed allylic alkylation is shown here.



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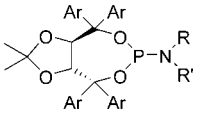
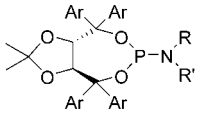
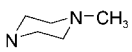


(*R,R*)-TADDOL deriv.

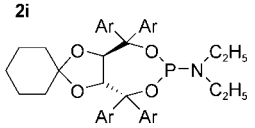


(*S,S*)-TADDOL deriv.

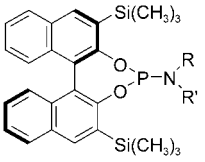
ligand	2a	2b	2c	2d	2e	2f
R =	CH_3	C_2H_5	CH_3	CH_3	$CH(CH_3)_2$	C_2H_5
R' =	CH_3	C_2H_5	(*R*)-$CH(CH_3)Ph$	(*S*)-$CH(CH_3)Ph$	$CH(CH_3)_2$	C_2H_5
Ar =	3,5-$(CH_3)_2C_6H_3$	3,5-$(CH_3)_2C_6H_3$	3,5-$(CH_3)_2C_6H_3$	3,5-$(CH_3)_2C_6H_3$	Ph	2-Naphthyl

ligand	2g	2h
NR =		
NR' =		
Ar =	3,5-$(CH_3)_2C_6H_3$	3,5-$(CH_3)_2C_6H_3$

2i

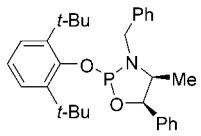


Ar = 3,5-$(CH_3)_2C_6H_3$



(*R*)-BINOL deriv.

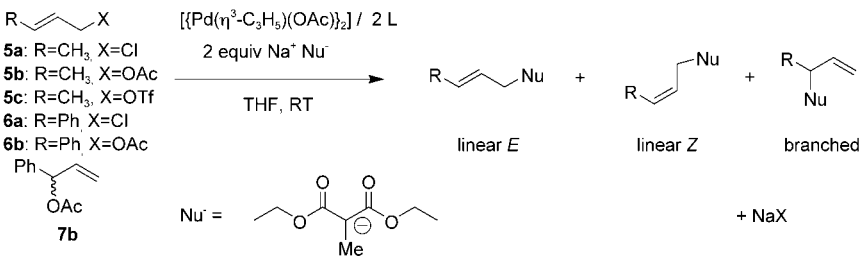
ligand	3a	3b
R =	C_2H_5	CH_3
R' =	C_2H_5	(*R*)-$CH(CH_3)Ph$



4

Allylic alkylation reactions: Phosphoramidite **1** was tested in the palladium-catalysed allylic alkylation reaction of different monosubstituted allylic substrates. From these reactants, three different isomeric products can be formed (see Scheme 4). The linear product, arising from nucleophilic attack on the nonsubstituted terminus of the allyl moiety, can be formed in *E* (*trans*) or *Z* (*cis*) geometry. Attack on the substituted site of the allyl results in formation of the chiral, branched product. The results for the catalytic reaction of crotyl acetate ((*E*)-3-methyl-2-propenyl acetate, **5b**), cinnamyl acetate ((*E*)-3-phenyl-2-propenyl acetate, **6b**) and *rac*-α-vinyl benzylacetate (1-phenyl-2-propenyl acetate, **7b**) and the corresponding chlorides, disodium diethyl 2-methyl malonate are shown in Table 1.

In all experiments, more than 95% conversion was obtained within two hours. The regioselectivity observed in the allylic alkylation appears to be largely dependent on the anionic counterion present. For crotyl chloride (**5a**), the branched and linear *E* product are formed in equal amounts (43%), together with a minor amount of the *Z* product. Upon changing to crotyl acetate (**5b**), the regioselectivity shifts dramatically towards the linear *E* product (84%, entry 2). This change in regioselectivity is accompanied by a drop in reaction rate. When 20 equivalents of tetra-*n*-butylammonium chloride are added, the high selectivity towards the branched product is restored, resulting in an even slightly higher percentage of branched alkene (57%). A similar trend is observed when the methyl substituent is replaced by the larger phenyl group, although in this case the overall formation of the *E* linear product is much more favoured than for the crotyl substrates (entries 5–7). No formation of the *Z* alkene is observed for the cinnamyl substrate (**6**). This is in accordance with observations in other studies.[19] The addition of bromide results in an increase of the amount of branched product formed. Fur-



Scheme 4. Allylic alkylation of monosubstituted allyl substrates.

Table 1. Catalytic alkylation of monosubstituted allyl compounds **5**–**7** with disodium diethyl 2-methyl malonate using $[\{Pd(\eta^3\text{-}C_3H_5)(OAc)_2\}_2]$/**1**.[a]

	Substrate	X	R	TOF[b]	Linear *E* [%]	Linear *Z* [%]	Branched [%]
1	**5a**	Cl	CH_3	180	43	14	43
2	**5b**	OAc	CH_3	122	84	8	8
3	**5c**	OTf	CH_3	n.d.	58	11	31
4[c]	**5b**	OAc	CH_3	174	40	3	57
5	**6a**	Cl	C_6H_5	284	91	0	9
6	**6b**	OAc	C_6H_5	56	97	0	3
7[c]	**6b**	OAc	C_6H_5	113	99	0	1
8	**7b**	OAc	1-C_6H_5	202	33	0	67
9[c]	**7b**	OAc	1-C_6H_5	307	84	0	16

[a] Reaction conditions: Pd/1/allylic substrate/nucleophile = 1:1:100:200; [Pd] = 10 mM in THF. Reaction time is 2 h. Selectivity after final conversion, determined by GC with dihexyl ether as internal standard. [b] Initial turnover frequency, determined after 5 mins. [c] 20 equivalents (to Pd) of $(n\text{Bu})_4\text{NCl}$ added.

thermore, for the phenyl-substituted allyl substrate, the allylic substitution displays a large memory effect. Thus, the alkylation of α-vinylbenzyl acetate **7b** yields a product mixture in which 67 % of the branched product is formed, compared to only 3 % starting from the isomeric linear substrate (entries 6 and 8). This memory effect largely disappears when extra halide is added to the reaction mixture (entry 9).

To gain more insight into the origin of the observed regioselectivity, stoichiometric allylic alkylation reactions were also carried out. In the stoichiometric reactions, the complex geometries have fully equilibrated to their thermodynamic ratios prior to alkylation. Therefore the regioselectivity observed in these alkylations will reflect the thermodynamic composition of the [Pd(allyl)(**1**)(X)] complexes, provided that the nucleophilic attack is faster than isomerisation of the Pd–allyl complex. Recent research into the regioselectivity of stoichiometric allylic alkylation with complexes with bidentate ligands has shown that the *syn* complex reacts mainly towards the linear *E* product, with formation of small quantities of the branched product. The isomeric *anti* complex reacts to the branched product or the linear *Z* product.[14,47–49] The reactions were performed by addition of a large excess of disodium diethyl 2-methyl malonate to a solution of the [Pd(allyl)(**1**)(X)] complex (X = Cl, OAc). The results of the stoichiometric alkylation reactions are shown in Table 2.

The observed selectivities in the stoichiometric alkylation differ significantly from those obtained from the catalytic

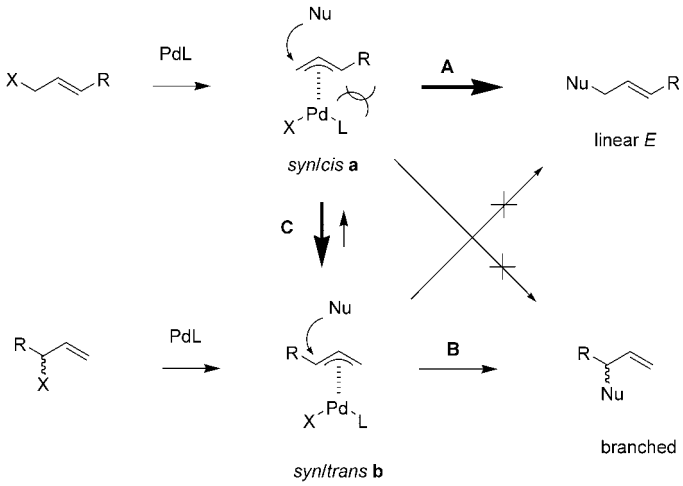
Table 2. Stoichiometric alkylation of $[Pd(3\text{-}RC_3H_4)(\mathbf{1})(X)]$ with disodium diethyl 2-methyl malonate.[a]

	Substrate	X	R	Linear *E* [%]	Linear *Z* [%]	Branched [%]
1	**5a**	Cl	CH_3	39	8	53
2	**5b**	OAc	CH_3	37	8	55
3[b]	**5b**	OAc	CH_3	31	3	66
4	**6a**	Cl	C_6H_5	94	0	6
5	**6b**	OAc	C_6H_5	83	0	17
6[b]	**6b**	OAc	C_6H_5	98	0	2

[a] Reaction conditions: Pd/nucleophile = 1:50; [Pd] = 10 mM in THF. Selectivity determined by GC. [b] 20 equivalents (to Pd) of $(n\text{Bu})_4\text{NCl}$ added.

experiments. For the stoichiometric reactions, the regioselectivity obtained when the crotyl complexes are applied is relatively insensitive to the counterion present (Table 2, entries 1–3). This is in sharp contrast to the catalytic reactions (Table 1, entries 1–4), in which the presence of halide is required for formation of the branched alkene. Stoichiometric reactions with the corresponding cinnamyl complexes result in similar observations. Thus, the application of [Pd(cinnamyl)(**1**)(OAc)] yields linear the *E* and branched product in a 83:17 ratio (entry 5), whereas in the catalytic reaction the branched product is formed in only 3 % (see Table 1). The results from the stoichiometric experiments with halide present do not deviate significantly from those of the catalytic reactions, resulting in high selectivity towards the linear product.

The observed trends can be explained as follows. From the principle of microscopic reversibility it follows that the oxidative addition (being the reverse reaction of reductive elimination) of allylic compounds to Pd^0 containing monodentate phosphorous ligands occurs in a *cis* fashion. Thus, the initial complexes formed from crotyl or cinnamyl substrates will have the substituent on the allyl moiety and the ligand in a *cis* relationship (see Scheme 5).[50–53] Since in the



Scheme 5. Possible explanation for regioselectivity observed in palladium-catalysed allylic alkylation in the presence of monodentate phosphoramidites.

NMR spectra only the *syn*,*trans* complexes (**b**) are observed (vide infra), we conclude that this is the most stable complex geometry. Therefore, the initially formed *syn*,*cis* complexes **a** will isomerise to the corresponding *trans* complex, by means of a pseudorotation mechanism.[1,54–56] The observed regioselectivity during catalysis will depend on the rate of this isomerisation, the equilibrium constant of the equilibrium **C** between **a** and **b** (Scheme 5) and the rate of nucleophilic attack (**A** and **B**). It has been shown by several groups that the addition of halide anions can accelerate dynamic processes in Pd(π-allyl) complexes considerably.[47,57–59] Since attack of the nucleophile will mainly occur on the allyl terminus *trans* to phosphorus (which has a much larger *trans* influence than the anionic ligand),[60] the *syn*,-

trans complex **b** will mainly react to the branched product (route **B**). The presence of halide counterions (Cl or Br) enhances the rate of isomerisation and therefore the amount of branched product formed. The isomerisation **C** from the initially formed *cis* complex **a** in the case of the [Pd(RC_3H_4)(**1**)(OAc)] complexes is slower compared to the halide-containing intermediates, resulting in formation of a larger amount of the linear (*E*) product through pathway **A**. This is what is observed for crotyl substrates.

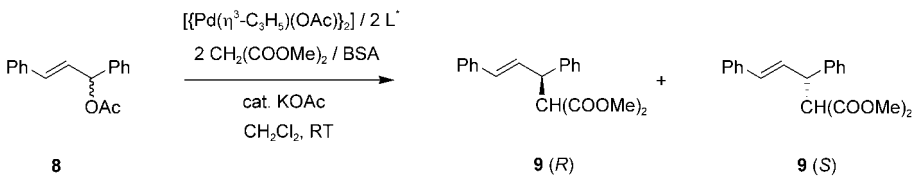
For the phenyl-substituted substrates, the situation is slightly different. Similar to the crotyl substrates, the isomerisation **C** in the cinnamylpalladium complexes will be relatively slow when OAc^- is the counterion. This is confirmed by the presence of the strong memory effect: when the 3-phenyl-substituted substrate **7b** is employed, which initially forms the *trans* complex (**b**), a high selectivity towards the branched product is observed. In contrast, the 1-acetoxy substrate (**6b**) will form the *cis* isomer (**a**) and therefore mainly reacts towards the linear product. The presence of halide enhances the rate of isomerisation between the *cis* and *trans* complexes drastically, resulting in faster isomerisation relative to nucleophilic attack. In this situation, the linear (*E*) product is formed predominantly. However, since only the *trans* complex is observed in NMR spectra, this implies that for cinnamyl complexes the *cis* complex reacts with higher rate than the corresponding *trans* complex, resulting in the predominant formation of linear product. Being higher in energy (and thus unfavoured in the equilibrium mixture), the energy barrier of the *cis* complex for nucleophilic attack is apparently lower than that of the *trans* complex, resulting in higher reaction rates and higher selectivity to the linear product isomer. Additionally, the increased steric hindrance of the phenyl group at the substituted allyl terminus hampers attack of the nucleophile on this carbon atom. Nucleophilic attack on this position is not favoured by electronic factors either, which render the unsubstituted terminus more electrophilic.[48] Therefore, a preference for the linear product exists when employing cinnamyl substrates. Because of the large *trans* influence of the phosphoramidite ligand, this product will be formed through the *cis* isomer (route **A** in Scheme 5).

These conclusions are supported by the observations in the stoichiometric reactions. If the isomerisation of the [Pd(cinnamyl)(**1**)(X)] (X = Cl, Br) complexes is very fast compared to nucleophilic attack, the stoichiometric reactions should not deviate significantly from the results obtained in the catalytic reactions. This is indeed what we have found (Tables 1 and 2). When no halide is present, more of the branched product is formed, due to the slower *cis/trans* isomerisation.

In summary, halides enhance the rate of isomerisation in [Pd(allyl)(**1**)(X)] complexes, resulting in more rapid equilibration of the isomeric complexes from the initially formed *syn,cis* to the more stable *syn,trans* form. The latter isomer reacts mainly to the branched product. Therefore, the branched product is formed in excess when crotyl substrates are employed in the presence of halide counterions. In contrast, when phenyl-substituted allyl substrates are used the *cis* isomer reacts at a much higher rate than the *trans* complex ($k_A \gg k_B$ in Scheme 5), resulting in the formation of mainly linear product, despite the fact that it is present in only very small quantities under equilibrium conditions. Only when the branched α-vinylbenzyl acetate **7b** is employed in the absence of halide anions, a significant amount of the branched product is formed, due to slow isomerisation.

Asymmetric allylic alkylations: It is clear that phosphoramidite ligands are a useful class of ligands for palladium-catalysed allylic alkylation reactions. Moreover, the possibility of regioselective nucleophilic attack on the substituted allyl terminus enables the enantioselective formation of the (chiral) branched product. Therefore, we tested chiral phosphoramidites in the asymmetric variant of the allylic alkylation reaction of both symmetric and nonsymmetric substrates.

First the alkylation of 1,3-diphenyl-2-propenyl acetate (**8**) with dimethyl malonate anion as the nucleophile (Scheme 6) was tested. Thus, 1 mol% [Pd(C_3H_5)(μ-OAc)]$_2$ and two



8 **9** (*R*) **9** (*S*)

Scheme 6. Asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate (**8**).

equivalents of ligand were stirred at room temperature for 15 minutes before the reaction was started. The nucleophile was formed in situ by addition of BSA (*N,O*-bis(trimethylsilyl) acetamide) and a catalytic amount of KOAc. The results of the catalytic reactions are shown in Table 3.

Use of TADDOL-based phosphoramidites in the asymmetric alkylation of 1,3-diphenyl-2-propenyl acetate resulted in excellent yields and good enantioslectivity of the product in most cases. Thus, employing (*R,R*)-**2b** as the chiral auxiliary, product **9** was obtained in 89% *ee*, with *S* configuration. Lowering the reaction temperature improved the enantioselectivity marginally, to 90% (entry 4), but the conversion was incomplete in this case. Reaction with the corresponding ligand with the opposite stereochemistry in the TADDOLate backbone results in the same *ee*, with the opposite enantiomer (*R*) formed in excess (entry 5). Changing the structure of the backbone at the remote acetal moiety (ligand **2i**) resulted in a decrease of the enantioselectivity to 81% (entry 6). This can be explained by the fact that the cyclohexyl group slightly distorts the adjacent ring structure, and hence affects the geometry of the aryl substituents. Variation of the aryl moieties also has a large influence on the stereochemical outcome of the reaction: both the 2-naphthyl- (**2f**) and phenyl-containing (**2e**) ligands give rise to

Table 3. Asymmetric allylic alkylation of **8** with dimethyl malonate in the presence of phosphoramidite ligands **2**–**4**.[a]

	Ligand	*T* [°C]	Yield[b] [%]	*ee* (config)[c] [%]
1	**4**	25	65	68 (*R*)
2	(*R*)-**3b**	25	n.d.	67 (*R*)
3	(*R*,*R*)-**2b**	25	>99	89 (*S*)
4	(*R*,*R*)-**2b**	0	87	90 (*S*)
5	(*S*,*S*)-**2b**	25	>99	90 (*R*)
6	(*R*,*R*)-**2i**	25	70	81 (*S*)
7	(*R*,*R*)-**2f**	25	86	61 (*S*)
8	(*R*,*R*)-**2e**	25	>99	73 (*S*)
9	(*R*,*R*)-**2g**	25	n.d.	83 (*S*)
10	(*R*,*R*)-**2a**	25	n.d.	88 (*S*)
11	(*R*,*R*,*S*)-**2d**	25	>99	92 (*S*)
12	(*R*,*R*,*R*)-**2c**	25	>99	87 (*S*)
13	(*S*,*S*,*S*)-**2d**	25	>99	87 (*R*)
14	(*S*,*S*,*R*)-**2c**	25	98	93 (*R*)
15[d]	(*R*,*R*)-**2b**	25	>99	66
16[e]	(*R*,*R*)-**2b**	25	34	85 (*S*)

[a] Reaction conditions: Pd/ligand/allyl/dimethyl malonate/BSA = 1:2:100:150:150 in CH_2Cl_2. Catalyst incubation time is 15 mins, reaction time 16 h. [b] Based on conversion of the acetate, determined by GC with dihexyl ether as internal standard; n.d. = not determined. [c] Determined by HPLC (Daicel OD). [d] Reaction carried out in THF with disodium diethyl 2-methyl malonate as the nucleophile. [e] 20 equivalents (to Pd) of $(n\text{Bu})_4\text{NBr}$ added.

lower *ee*'s than the 3,5-dimethylphenyl group (entries 7 and 8).

The structure of the amino group in the ligand has a much less pronounced influence on the enantioselectivity (entries 9–14). The piperazine-substituted ligand **2g** gives lower *ee*. In the case of the *N*,α-dimethylbenzylamino substituent, the possibility of chiral cooperativity effects arises. Such effects, although not extremely large, have been observed for these ligands in asymmetric intramolecular Heck reactions.[35] In the asymmetric alkylations, a positive effect is observed when the amine moiety and the TADDOLate backbone have the opposite configuration (entry 11 and 14). The latter determines the absolute configuration and enantioselectivity of the reaction to a large extent (Table 3), but a further increase to 93% *ee* is observed when ligand (*S*,*S*,*R*)-**2c** is used (entry 14). Changing the nucleophile to disodium diethyl 2-methyl malonate in THF has a strong detrimental effect on the level of stereocontrol (entry 15). The addition of extra halide anions lowers both the product yield and *ee* (entry 16).

To gain insight into the coordination mode of the bulky phosphoramidite ligands during the catalytic reaction, we tested the dependence of the observed enantioselectivity in the reaction of **8** with dimethyl malonate on the enantiopurity of the ligand employed. Such relationships have been shown to give important information on the nature of the catalytically active species as bis-ligand complexes often show nonlinear effects.[52,53] The results for ligand **2b** are shown in Figure 1. Within experimental error, the stereochemical outcome of the reaction is linearly correlated to the *ee* of the ligand. Therefore, a reaction mechanism in which the active catalytic species has only one chiral ligand coordinated to the Pd centre is most likely, as also observed for the enantioselective Heck cyclisations,[35,61,62] but an accidental linear behaviour for a bis-ligand complex remains feasible.

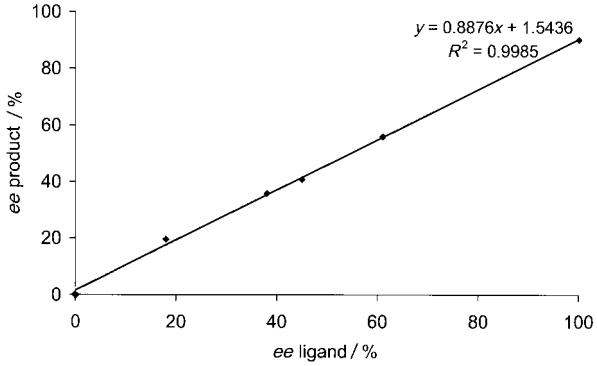


Figure 1. Correlation between the enantiopurity of ligand **2b** and the enantioselectivity in the reaction of **8** to **9**.

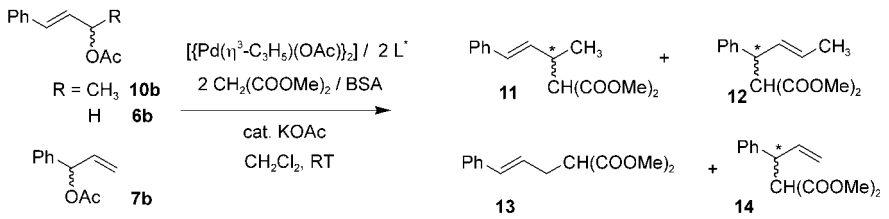
As was demonstrated, bulky phosphoramidites can steer the regioselectivity of monosubstituted allylic compounds towards the chiral, branched product. Therefore, we also probed these TADDOL-based ligands in the asymmetric allylic alkylation of other prochiral, nonsymmetrically substituted substrates. The results of the reactions performed with *rac*-1-phenyl-2-propenyl acetate (α-vinylbenzyl acetate **7b**), *rac*-1-phenyl-3-but-1-enyl acetate (1-methyl-3-phenylallyl acetate **10**) and cinnamyl acetate (**6b**) with dimethyl malonate in dichloromethane at room temperature are shown in Table 4.

Table 4. Asymmetric allylic alkylation of **6b**, **7b** and **10b** with dimethyl malonate using phosphoramidite ligands **2b** and **3b**.[a]

	Substrate	*T* [°C]	Ligand	Yield[b] [%]	Regioselectivity[c]	*ee*[d] [%]
1	**10b**	25	(*R*,*R*)-**2b**	>95	>99:1 (**11**:**12**)	32
2	**7b**	25	(*R*,*R*)-**2b**	>99	94:6	18
3	**7b**	0	(*R*,*R*)-**2b**	79	94:6	25
4[e]	**7b**	25	(*R*,*R*)-**2b**	>99	98:2	n.d.
5	**6b**	25	(*R*,*R*)-**2b**	>99	98:2	n.d.
6	**7b**	25	(*R*)-**3b**	>99	26:74	7

[a] Reaction conditions: Pd/ligand/allyl substrate/dimethyl malonate/BSA = 1:2:100:150:150 in CH_2Cl_2. Catalyst incubation time is 15 mins, reaction time 16 h. [b] Based on conversion of the acetate, determined by GC with dihexyl ether as internal standard. [c] Lineair/branched ratio, determined by GC. [d] Determined by HPLC (Daicel OD), n.d. = not determined. [e] 20 equivalents (to Pd) of $(n\text{Bu})_4\text{NBr}$ added.

As for most ligands reported,[1] the high level of enantioselectivity obtained for the 1,3-diphenylallyl substrate (**8**) drops dramatically when allylic substrates containing smaller substituents are employed. Thus, reaction of **10b** with dimethyl malonate in the presence of ligand (*R*,*R*)-**2b** results in complete regioselective formation of the product stemming from nucleophilic attack at the methyl-substituted allyl terminus (**11**) in 32% *ee* (Scheme 7, Table 4 entry 1), compared to 89% *ee* for diphenylallyl substrate **8**. Moreover, the strong regiochemical memory effect observed when ligand **1** was employed for the alkylation of substrate **7b** (Table 1) is not found for the TADDOL-based chiral phos-

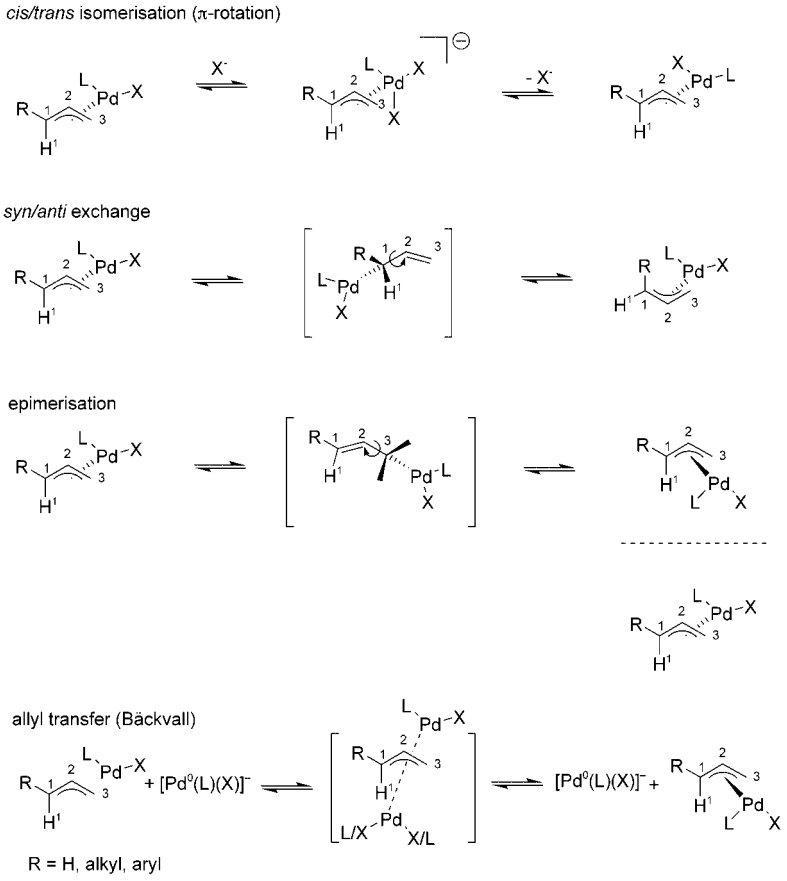


Scheme 7. Palladium-catalysed allylic alkylation with unsymmetrically substituted allyl substrates.

phoramidites (Table 4, entries 2–5). Apparently, for all nonsymmetrically substituted allyl substrates, the isomerisation and/or the relative reactivity of the transient [Pd(allyl)(**2**)] complexes largely favours reaction from the electronically and sterically less stable isomer bearing the phenyl substituent *cis* to the bulky ligand. In the case of cinnamyl derivatives this results in the formation of mainly linear (nonchiral) product. When BINOL-based ligand (*R*)-**3b** is used, the regiochemical selectivity for the branched product is higher again. This ligand is expected to have steric properties that are similar to those of ligand **1**, because of the resemblance of the backbones in both ligands. Nevertheless, the enantioselectivity observed for the reaction of (*R*)-**3b** is very low, also relative to the enantioselectivity obtained for (*R*)-**3b** in the alkylation of 1,3-diphenylallyl acetate **8** (7% vs 67% *ee* for the latter compound). Possibly, the diminished steric constraints reduce the steric interactions that discriminate the two possible pathways upon allyl rotation. The reason for this remarkable influence of the ligand backbone on the regioselectivity (i.e. the memory effect) is unclear at present.

Complex synthesis and characterisation: To investigate the coordination behaviour of the bulky phosphoramidites in more detail, we synthesised various [Pd(allyl)(L)(X)] (allyl = C_3H_5, $C_6H_5C_3H_4$, 1,3-$(C_6H_5)_2C_3H_3$; L = bulky phosphoramidite, X = Cl, OAc) complexes and studied them using NMR spectroscopy. The chloride-containing complexes could readily be obtained by reaction of the ligand with 0.5 equivalents of the corresponding [{Pd(allyl)(μ-Cl)}$_2$] dimer, which yielded the desired complexes in near-quantitative yields. The acetate complexes were prepared from the [{Pd(allyl)(OAc)}$_2$] dimer, which was prepared from the chloro dimer by reaction with AgOAc. These complexes appeared to be less stable than their chloro analogues and were therefore not isolated.

For the nonchiral ligand **1**, the complex [Pd(C_3H_5)(**1**)(Cl)] can exist as two enantiotopic isomers (possible conformers arising from different orientations within the ligand excluded): the complex with the allyl "up" (also called *exo*) or, alternatively, "down" (*endo*).[55] These two isomers are enantiomers in the case of the C_3H_5 ligand and any other C_{2v} symmetric allyl moiety. As expected, the ^{31}P NMR spectrum showed only one sharp resonance at $\delta = 140.1$ ppm ($CDCl_3$, 20 °C). Addition of an extra 0.5 equivalents of ligand did not change the spectrum for the complex, but only resulted in the appearance of the signal of uncoordinated phosphoramidite (153.3 ppm). Inspection of the corresponding ^{1}H NMR spectrum revealed that all allyl protons are inequivalent, showing slightly broadened signals at room temperature. This confirms that only one ligand coordinates to the Pd centre. The broadening of the allyl signals can be explained by slow *syn*/*anti* exchange through the well-known η^3-η^1-η^3 mechanism (Scheme 8, R = H). The exchange is faster for the allyl protons with the lowest shifts in the ^{1}H NMR spectrum. Cooling down to −20 °C resulted in sharpening of the allyl resonances, while the peak in the ^{31}P NMR spectrum broadened significantly. Phosphorus decoupling of the



Scheme 8. Possible isomerisation mechanisms in [Pd(allyl)(L)(X)] complexes.

proton spectrum resulted in the change of the two apparent triplets stemming from the allyl moiety into two doublets. Therefore, these two signals can be attributed to the protons being *trans* to the phosphoramidite ligand. This implies that the *syn/anti* exchange is faster for the protons situated *cis* to the phosphorus donor. On further cooling, the phosphorus resonance decoalesces into two broad singlets of approximately equal intensity (1:0.9 at −70 °C). This decoalescence is accompanied by broadening of the isopropyl protons from the amine moiety of the ligand in the ^{1}H NMR spectrum. The two observed different species at low temperature are likely to arise from the two different orientations of the biphenyl backbone of the ligand. When rotation around the C–C axis is restricted, the ligand becomes chiral due to atropisomery, giving rise to two diastereomers in the palladium–allyl complex.

We were able to grow crystals of [Pd(C_3H_5)(**1**)(Cl)] by slow evaporation of a solution of the complex in hexanes. X-ray crystal structure determination revealed that the compound crystallises as a racemate in the centrosymmetric space group $P2_1/c$. As a consequence of the disordered allyl group both diastereomers (in the crystal no biphenyl rotation will take place) are present in a 1:1 ratio. The structure of the (*S*)-isomer (allyl up) is shown in Figure 2 and confirms the mono-coordination of the bulky ligand to the palladium centre. The nonsymmetric environment of the allyl moiety is reflected in the bond lengths observed in the solid-state structure (see Table 5). The allyl ligand was refined with a disorder model. In this model the end carbon atoms remain on the same position. The observed significantly dissymmetric character of the allyl group is thus reliably determined; the Pd–C bond *trans* to the phosphoramidite ligand is longer than the one at the *cis* position (2.1809(19) Å vs 2.150(2) Å respectively, see Table 5) and is caused by the stronger *trans* influence of the phosphorusamidite relative to the chloride.[63] Due to the disorder of the allyl group the C–C distances are less accurately determined. The length of the C–C bond within the allyl group *trans* to phosphorus atom is 1.350(6) Å and shows significantly more double bond character than the other C–C bond, which is 1.437(5) Å. Nucleophilic attack will take place preferentially on the *trans* terminus, which is more electrophilic. Remarkably, this difference is reversed (although smaller) for the *R* isomer in the crystal structure. This reversed order has been observed before in allyl complexes bearing bidentate phosphinyloxazoline ligands[18] or monodentate phosphines.[63] In addition, sterically the *trans* site seems more favourable for attack, since there is virtually no steric hindrance present on this side of the allyl, as can be seen from the crystal structure. This effect will be even more important for monosubstituted allyl substrates, since the substituents on the newly formed sp^3 carbon atom have to bend backwards during the reaction, into the relative empty space around the chloride ligand.

Table 5. Selected distances [Å] and bond angles [°] from the crystal structure of [Pd(C_3H_5)(**1**)(Cl)].[a]

Pd(1)–C(1)	2.1809(19)	Pd(1)–Cl(1)	2.3598(5)
Pd(1)–C(2)(*R*)	2.174(4)	C(2)(*R*)–C(1)	1.411(5)
Pd(1)–C(2)(*S*)	2.159(4)	C(2)(*R*)–C(3)	1.383(5)
Pd(1)–C(3)	2.150(2)	C(2)(*S*)–C(1)	1.350(5)
Pd(1)–P(1)	2.2960(5)	C(2)(*S*)–C(3)	1.437(5)
Cl(1)-Pd(1)-P(1)	96.828(17)	Cl(1)-Pd(1)-C(1)	92.09(6)
P(1)-Pd(1)- C(3)	103.62(6)		

[a] C(3)(*R*) and C(3)(*S*) belong to two different disorder components.

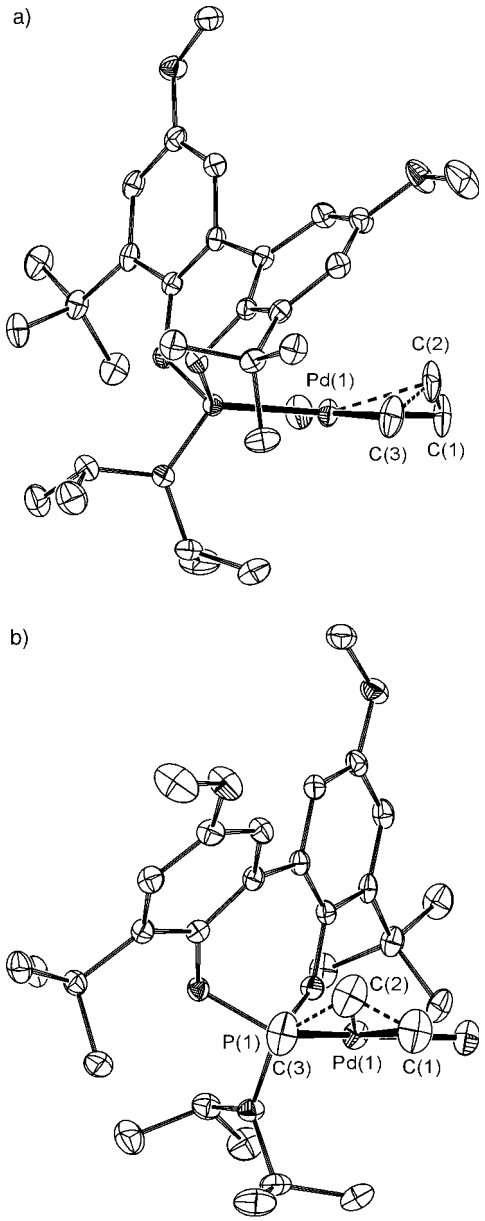


Figure 2. Molecular structure of [(*S*)-Pd($C_6H_5C_3H_4$)(**1**)(Cl)]: side-view (top) and front-view (bottom).

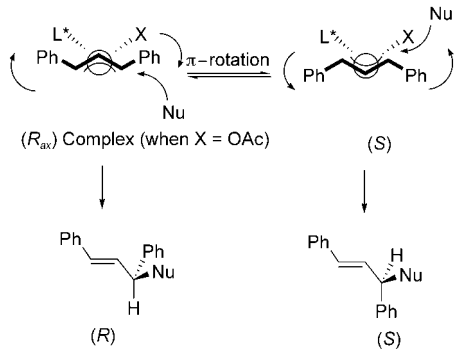
Complexes bearing unsymmetrically substituted allyl moieties have a larger number of possible isomers than the unsubstituted ones. For the cinnamyl-containing palladium complex for example, eight different isomers can be envisaged (again assuming fast rotation around the Pd–P axis): the *syn*,*trans*-, *syn*,*cis*-, *anti*,*trans*- and *anti*,*syn* complexes, each having two enantiomers. However, in the case of nonchiral phosphoramidite **1**, the monosubstituted allyl com-

plexes show a behaviour similar to the unsubstituted complexes. [Pd(1-$C_6H_5C_3H_4$)(**1**)(Cl)] has four different allyl resonances in the ^{1}H NMR spectrum at room temperature. From the P–H and H–H couplings observed on the hydrogen atom attached to the benzylic carbon atom (^3J(P,H) = 14 Hz, ^3J(H,H) = 15 Hz) in this complex we conclude that the prefered geometry of the cinnamyl is *trans* with respect to the phosphorus atom and *syn* to the central allyl hydrogen atom. No other complexes are observed, as is confirmed by ^{31}P NMR spectroscopy, which shows one signal at 141.4 ppm. This confirms the assumption that the allyl moiety will orient itself in a fashion in which it experiences the least steric hindrance, that is, *trans*,*syn* to the bulky ligand. This is also the electronically most stable isomer. The signals of the two protons on the nonsubstituted terminus of the allyl ligand are very broad at room temperature, indicating *syn*/*anti* exchange. No *syn*/*anti* isomerisation is observed for the other side of the allyl over a temperature range of −50 °C to +55 °C. The acetato complexes showed similar behaviour. Upon addition of an excess of ligand to a solution of [Pd($CH_3C_3H_4$)(**1**)(OAc)], prepared in situ, no changes in the the ^{1}H NMR spectrum were observed, and only the signal of free **1** appeared in the ^{31}P NMR spectrum. Therefore we conclude that also in the [Pd(allyl)(L)(OAc)] complexes only one phosphoramidite ligand is coordinated to palladium.

Next, the behaviour of complexes bearing chiral bulky phosphoramidites was studied. The [Pd(C_3H_5){(*R*,*R*)-**2b**}(Cl)] complex appeared to be present as two diastereomers, as indicated by the presence of two resonances in the ^{31}P NMR spectrum (δ = 119.3 and 117.3 ppm, CD_2Cl_2, −20 °C). The ratio of the two diastereomers is temperature dependent, ranging from 2.7:1 at −50 °C to 1.5:1 at 20 °C. On further increasing the temperature, coalescence starts to occur. Unfortunately we were unable to determine the coalescence temperature due to decomposition of the complex above 60 °C ($CDCl_3$). Also in the ^{1}H NMR spectrum, the presence of the two diastereomers was observed. Overlap of the signals of the ligand and the allyl hampered complete assignment of all the resonances, but by means of 2D NMR (GHSQC) spectroscopy we were able to confirm that both species are π-allyl complexes. Because of the chirality of the ligand, the two isomers stemming from the different orientation of the allyl fragment are diastereomers, one with the allyl group in the *endo* position and one with it in the *exo* position. The analogous complex [Pd(1,3-(C_6H_5)$_2$$C_3H_3$){(*R*,*R*)-**2b**}(Cl)], bearing the 1,3-diphenylallyl moiety, showed only one signal (δ = 119.4 ppm in $CHCl_3$) in the ^{31}P NMR spectrum over a broad temperature range (−60 to 40 °C). In the ^{1}H NMR spectrum, only one isomer was observed (> 95 %) as judged from the presence of two allyl signals (the third resonance is obscured by overlap with signals of the ligand). No significant change was observed in the ^{1}H NMR spectrum upon variation of the temperature either. This suggests the presence of only one major diastereomer in solution for [Pd(1,3-(C_6H_5)$_2$$C_3H_3$){(*R*,*R*)-**2b**}(Cl)]. Unfortunately, we were unable to obtain crystals suitable for X-ray analysis of allyl complexes with **2** as the ligand to confirm the complex geometry.

Origin of enantioselectivity: From the NMR studies of the [Pd(1,3-diphenylallyl)((*R*,*R*)-**2b**)(Cl)] complex, it is concluded that the complex exists mainly as one isomer. Based on steric considerations, we assume that the *syn*,*syn* geometry of the 1,3-diphenylallyl moiety is largely favoured. In this case, two isomeric complexes can be envisaged: one with the chirality from the [Pd(allyl)(L*)(X)] complex with *S* configuration and one with the opposite *R* configuration. These complexes can interconvert (epimerise) through π rotation (see Scheme 8). Semi-empirical modelling studies (PM3(tm) level) did not enable us to determine which of the diastereomers is thermodynamically the most stable and thus corresponds to the one observed by NMR spectroscopy. However, assuming that nucleophilic attack will take place *trans* to the phosphorus atom,[13,15,17,64] the reactive complex should be the one with the allyl fragment coordinated in an *R* configuration when employing the (*S*,*S*)-TADDOLate backbone (see Table 3, entry 4).

We explain the observed enantioselectivities in terms of steric considerations. We assume a transition state that resembles more the η^2-alkene product complex rather than the π-allyl starting compound. Upon nucleophilic attack, the hybridisation of the carbon atom at which the new bond is formed changes from sp^2 to sp^3. The coordination mode of the allyl moiety changes from η^3 to η^2. To enable this, the pre (*R*)-allyl has to rotate in a clockwise fashion for the (R_{ax})-allyl complex, whereas the (S_{ax})-allyl complex will show counterclockwise rotation giving the *S* product (Scheme 9). Inspection of the complex structures obtained



Scheme 9. Pathways of nucleophilic attack on the trans-termini yielding the two enantiomers.

from modeling reveals that in the [Pd(1,3-(C_6H_5)$_2$$C_3H_3$){(*S*,*S*)-**2b**}(Cl)] complex, the ligand adopts a geometry in which the lower left side of the allyl group is shielded by one of the aryl groups of the ligand backbone (see Figure 3). This structure closely resembles the ligand conformation found in the X-ray structure elucidated of the related [{Pd(4-C_6H_4CN)(**2**)(μ-Br)}$_2$] complex.[35] Upon attack on the *S* isomer, the counterclockwise rotation moves the phenyl group at the sp^2-hybridised carbon atom in close proximity of this aryl group. In contrast, the clockwise rotation (from the *R* complex) will result in relief of steric interactions, since both sides of the product alkene rotate into less occupied space around the metal centre. Therefore, we

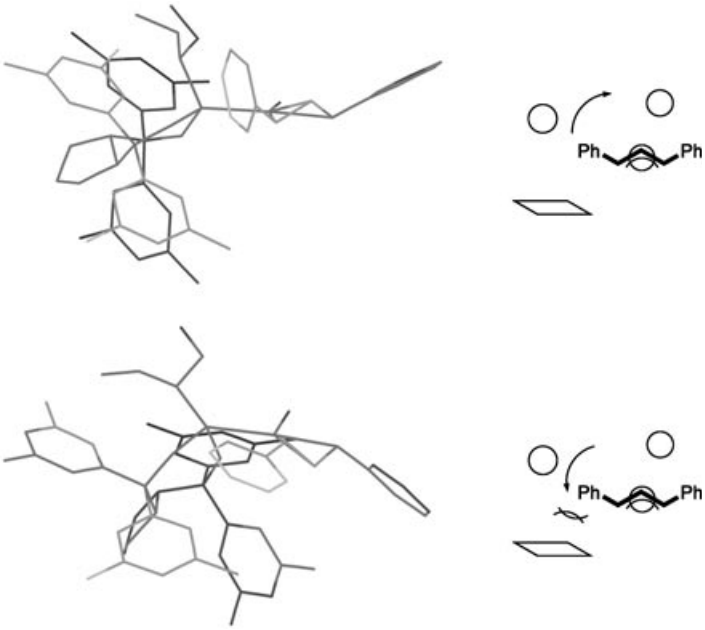


Figure 3. Modelled structure (PM3(tm)-level) of the two *syn*,*syn* [Pd{1,3-$(C_6H_5)_2C_3H_3$}{(*S*,*S*)-**2b**}(Cl)] complexes (left), schematically represented when viewed along the Pd–allyl axis on the right (the plane represents the aryl-fragment of the ligand blocking the allyl moiety upon rotation, empty circles represent minor steric interactions).

expect the clockwise rotation to be more facile, resulting in the formation of the *R* product, as is observed. This simple steric model is supported by the fact that replacement of the 3,5-dimethylphenyl groups in the TADDOLate ligands by other, less bulky aryl moieties results in a large decrease of stereoinduction, because of decreased steric interactions during the anticlockwise rotation of the alkene being formed, lowering the enantiodiscrimination. In this model, the amine functionality is not expected to have a large influence in the stereochemical outcome of the reaction, which is confirmed by experiment.

Changing the substrate from 1,3-diphenylallyl to the smaller 1-methyl-3-phenylallyl or even cinnamyl, also has a large detrimental effect on the observed *ee*'s (Table 4). The simple model presented above for the mechanism cannot fully account for this observation, since one would expect the enantioselectivity to be mainly dependent on the bulk of the substituent on the side of the allyl group *cis* to phosphorus and rather insensitive towards substitution on the *trans* carbon atom of the allyl moiety. Probably, the smaller bulk of the substituents bending backwards on the carbon atom on which the nucleophile attacks also plays an important role in interacting with the chirality of the ligand and thus preventing anticlockwise rotation.

Conclusion

Bulky monodentate phosphoramidite ligands can successfully be applied in the Pd-catalysed allylic alkylation reaction with carbon nucleophiles. The results obtained with these ligands show interesting features that differ considerably from the results generally obtained with symmetrical bidentate ligands, especially with respect to regioselectivity. From the studies on isolated complexes, it was concluded that in the allylpalladium complexes only one ligand can coordinate to the metal centre. Despite this monocoordination, high enantioselectivities can be obtained with bulky chiral phosphoramidites and disubstituted allyllic substrates. The *ee*'s are significantly lower for substrates with smaller substituents or non-symmetrically substituted allyl compounds.

Experimental Section

General remarks: All experiments were carried out under a purified nitrogen atmosphere by using standard Schlenk techniques unless noted otherwise. Solvents were purchased from Acros and dried prior to use. Toluene was distilled from sodium; THF, hexanes and diethyl ether from sodium/benzophenone ketyl and dichloromethane from calcium hydride. All amines employed were distilled from calcium hydride prior to use. Phosphorus trichloride was distilled prior to use and stored at −20 °C. Hexamethyl phosphoramide (HMPT), 1,8-bis(dimethylamino)naphthalene, *N*,*O*-bis(trimethylsilyl) acetamide (BSA), cinnamyl chloride and dimethyl malonate were purchased from Acros and used as received. Other allylic substrates were prepared following standard procedures.[65] The TADDOL-type backbones employed were synthesised according to literature procedures.[66,67] (*R*)-3,3′-Trimethylsilyl-1,1′-binaphtyl-2,2′-diol was synthesised as reported by Buisman et al.[68] *N*-Benzyl-(1*R*,2*S*)-norephedrine was synthesised by a literature procedure.[69] [{Pd(C_3H_5)(μ-Cl)}$_2$], [{Pd(cinnamyl)(μ-Cl)}$_2$] and [{Pd(1,3-diphenylallyl)(μ-Cl)}$_2$] were synthesised according to literature procedures.[70,71] Disodium diethyl 2-methyl malonate (0.5 M in THF) was prepared from diethyl 2-methyl malonate and NaH in THF at 0 °C. [{Pd(crotyl)(μ-OAc)}$_2$] was freshly prepared from the corrseponding chloride-bridged dimer and AgOAc (1.0 equiv) in the appropriate solvent, followed by filtration over Celite. NMR spectra were recorded on a Varian Mercury 300 (300.1 MHz) in $CDCl_3$ and are reported in ppm with tetramethylsilane (^{1}H and ^{13}C) and 85 % H_3PO_4 (^{31}P) as external standards. Thin-layer chromatography was carried out on Macherey-Nagel SIL G/UV plates of Kieselgel 60. Column chromatography was performed with silica 60 (SDS Chromagel, 70–200 μm). GC measurements were performed on a Shimadzu GC-17A apparatus (split/splitless, equipped with a F.I.D. detector and a BPX35 column (internal diameter of 0.22 mm, film thickness 0.25 μm, carrier gas 70 kPa He)) and an Interscience HR GC Mega 2 apparatus (J&W Scientific, DB-1 column, 30 m/inner diameter 0.32 mm/film thickness 3.0 μm, carrier gas 70 kPa He, F.I.D. detector). GC/MS measurements (E.I. detection) were performed on a HP 5890/5971 apparatus, equipped with a ZB-5 column (5 % cross-linked phenyl polysiloxane) with an internal diameter of 0.25 mm and film thickness of 0.25 μm. Melting points were measured on a Gallenkamp melting point apparatus and are reported uncorrected. HPLC measurements for determination of enantiomeric excesses were performed using a Gilson apparatus equipped with a Dynamax UV-1 absorbance detector. High-resolution mass spectra were recorded at the Department of Mass Spectroscopy at the University of Amsterdam using FAB$^+$ ionisation on a JEOL JMS SX/SX102A four sector mass spectrometer with 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Department of Microanalysis at the Rijksuniversiteit Groningen (The Netherlands).

(1*R*,7*R*)-4-Dimethylamino-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2a): (2*R*,3*R*)-*O*-isopropylidene-1,1,4,4-tetra(3,5-dimethylphenyl)threitol (300 mg, 0.52 mmol) was dried by dissolving the compound in toluene (5 mL) and evaporating evaporating thoroughly to dryness (3 times). Next, the diol was dissolved in toluene (20 mL). The solution was cooled to 0 °C and a solution of HMPT (113 μL, 0.62 mmol) together with 1*H*-tetrazole (ca. 1 mg) in toluene (5 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 2 h and subsequently refluxed for 24 h. After removal of the solvent in vacuo the resulting foamy solid was purified by column chromatography (hexanes/EtOAc/triethylamine, 95/5/

2.5 v/v/v) to yield the product as a white powder. Yield: 165 mg (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (s, 2H; Ar-H), 7.19 (s, 2H; Ar-H), 7.06 (s, 4H; Ar-H), 6.87 (s, 2H partial overlap; Ar-H), 6.86 (s, 2H partial overlap; Ar-H) 5.08 (dd, J = 3.3, 8.2 Hz, 1H; C*H*), 4.77 (d, J = 8.2 Hz, 1H; C*H*), 2.73 (d, ^3J(P,H) = 10.4 Hz, 6H; NCH_3), 2.29–2.26 (m, 24H; ArCH_3), 1.35 (s, 3H; OCCH_3), 0.28 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 147.2, 146.9, 142.0, 137.4, 137.0, 136.7, 136.4, 129.3, 129.0, 129.0, 128.8, 127.1, 126.8, 126.7, 125.3, 125.1, 111.8, 83.2, 83.0, 82.7, 81.8, 81.3, 81.2 (the area 83.2–81.2 ppm contains some extra resonances probably due to P–C coupling.) 35.5 (d, ^2J(P,C) = 19.5 Hz), 27.9, 25.7, 21.9, 21.8 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 139.7 ppm; HRMS: m/z calcd for $C_{41}H_{51}NO_4P$: 652.3556; found: 652.3557 $[M-H]^+$; elemental analysis calcd (%) for $C_{41}H_{50}NO_4P$: C 75.55, H 7.73, N 2.15; found: C 75.17, H 7.84, N 2.19.

(1*S*,7*S*)-4-Dimethylamino-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*S*,*S*)-2a): This compound was prepared as described above for (*R*,*R*)-**2a** from 2*S*,3*S*-*O*-isopropylidene-1,1,4,4-tetra(3,5-dimethylphenyl)threitol (500 mg, 0.86 mmol) and HMPT (188 μL, 1.03 mmol). Yield: 310 mg (55%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (s, 2H; Ar-H), 7.24 (s, 2H; Ar-H), 7.11 (s, 4H; Ar-H), 6.91 (s, 3H partial overlap; Ar-H), 6.88 (s, 1H partial overlap; Ar-H) 5.12 (dd, J = 3.3, 8.2 Hz, 1H; C*H*), 4.81 (d, J = 8.2 Hz, 1H; C*H*), 2.78 (d, ^3J(P,H) = 10.5 Hz, 6H; N(CH_3)$_2$), 2.33–2.30 (m, 24H; ArCH_3), 1.40 (s, 3H; OCCH_3), 0.33 ppm (s, 3H; OCCH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 139.7 ppm. HRMS: m/z calcd for $C_{41}H_{51}NO_4P$: 652.3556; found: 652.3533 $[M+H]^+$; elemental analysis calcd (%) for $C_{41}H_{50}NO_4P$: C 75.55, H 7.73, N 2.15; found: C 75.62, H 7.92, N 2.21.

(1*R*,7*R*)-4-Chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane: 2*R*,3*R*-*O*-isopropylidene-1,1,4,4-tetra(3,5-dimethylphenyl)threitol (3.50 g, 6.0 mmol) was dried by dissolving the compound in toluene (15 mL) and evaporating thoroughly to dryness (3 times). The diol was dissolved in toluene (60 mL) together with triethylamine (1.3 mL, 9 mmol) and cooled to −40 °C. Subsequently, a solution of phosphorus trichloride (0.66 mL, 7.5 mmol) and triethylamine (1.3 mL, 9 mmol) in toluene (20 mL) was added dropwise. After complete addition, the cooling bath was removed and the cloudy mixture slowly warmed to room temperature and stirred overnight. Next, the suspension was refluxed for 2 h and filtered under strict nitrogen atmosphere to remove the salts (Et_3N·HCl) formed. The resulting solution was evaporated in vacuo to yield a slightly yellow moisture-sensitive powder as the product. This was not purified further, but used immediately in the following reactions.

(1*R*,7*R*)-4-Diethylamino-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2b): A solution of diethylamine (0.54 mL, 5.3 mmol) and triethylamine (0.73 mL, 5.3 mmol) in toluene (20 mL) was added dropwise to a solution of (1*R*,7*R*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (2.3 g, 3.5 mmol) in toluene (75 mL) at 0 °C. After complete addition, the mixture was allowed to warm to room temperature and stirred for 2 h and subsequently stirred at 80 °C during 4 h. The resulting suspension was filtered under nitrogen and evaporated in vacuo. The resulting off-white powder was purified by column chromatography (hexanes/triethylamine 95/5 v/v). Yield: 2.10 g (88%) of white semi-crystalline powder; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 2H; Ar-*H*), 7.29 (s, 2H; Ar-*H*), 7.15 (s, 4H; Ar-*H*), 6.92–6.88 (m, 4H; Ar-*H*), 5.15 (dd, J = 8.3, 3.5 Hz, 1H; OC*H*), 4.75 (d, J = 8.3 Hz, 1H; OC*H*), 3.33 (dq, J = 11.0 (^3J(P,H)), 7.0 Hz, 4H; N(CH_2CH_3)$_2$), 2.35–2.33 (m, 24H; ArCH_3), 1.50 (s, 3H; OCCH_3), 1.25 (t, J = 7.0 Hz, 6H; N(CH_2CH_3)$_2$), 0.33 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} (75.5 MHz, $CDCl_3$) NMR: δ = 147.6, 147.2, 142.3, 137.3, 136.9, 136.7, 136.4, 129.2, 129.0, 128.9, 128.8, 127.2, 126.8, 126.7, 125.3, 111.4, 83.5, 83.1, 82.8, 81.4, 81.3, 81.2, 39.5, 39.2, 28.0, 27.2, 25.6, 21.9, 21.9, 15.7 ppm; ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$) NMR: δ = 141.5 ppm; HRMS (FAB^+): m/z calcd for $C_{43}H_{55}NO_4P$: 680.3869; found: 680.3856 $[M-H]^+$; elemental analysis calcd (%) for $C_{43}H_{54}NO_4P$: C 75.96, H 8.01, N 2.06; found: C 75.83, H 7.92, N 1.98.

(1*S*,7*S*)-4-Diethylamino-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*S*,*S*)-2b): This compound was prepared as described for (*R*,*R*)-**2b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 2H; Ar-*H*), 7.21 (s, 2H; Ar-*H*), 7.05 (s, 4H; Ar-*H*), 6.86–6.82 (m, 4H; Ar-*H*), 5.08 (dd, J = 8.3, 3.5 Hz, 1H; OC*H*), 4.67 (d, J = 8.3 Hz, 1H; OC*H*), 3.26 (dq, J = 11.0 (^3J(P,H)), 7.0 Hz, 4H; N(CH_2CH_3)$_2$), 2.30–2.26 (m, 24H; ArCH_3), 1.42 (s, 3H; OCCH_3), 1.17 (t, J = 7.0 Hz, 6H; N(CH_2CH_3)$_2$), 0.25 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 147.6, 147.2, 142.4, 137.3, 136.9, 136.7, 136.4, 129.2, 129.0, 128.8, 128.8, 127.2, 126.8, 125.3, 111.4, 83.5, 83.1, 82.8, 81.4, 81.3, 81.2, 39.3 (d, ^2J(P,C) = 22.0 Hz), 28.0, 25.6, 21.8, 15.7, 15.6 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 141.5 ppm; HRMS (FAB^+): m/z calcd for $C_{43}H_{55}NO_4P$: 680.3869; found: 680.3856 $[M+H]^+$; elemental analysis calcd (%) for $C_{43}H_{54}NO_4P$: C 75.96, H 8.01, N 2.06; found: C 75.86, H 8.22, N 2.20.

(1*S*,7*S*)-4-(*N*-Methyl-*N*-(*R*)-1-phenylethylamino)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*S*,*S*,*R*)-2c): Prepared analogously to the synthesis of (*R*,*R*)-**2b** from (1*S*,7*S*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (2.6 mmol) and (*R*)-(+)-*N*,α-dimethylbenzylamine (0.47 mL, 3.2 mmol). The crude product was purified by extraction with hexanes (2×10 mL), followed by quick column chromatography (hexanes/triethylamine 95/5 v/v) to give a white foam as the product. Yield: 510 mg (27%); ^{1}H NMR (300 MHz): δ = 7.60–6.80 (m, 17H; Ar-*H*), 5.14 (dd, J = 8.2, 3.2 Hz, 1H; OC*H*), 4.70 (m, 1H; NC*H*), 4.65 (d, J = 8.2 Hz, 1H; OC*H*), 2.61 (d, J = 6.0 Hz, 3H; NCH_3), 2.34–2.18 (m, 24H; ArCH_3), 1.53 (d, J = 6.9 Hz, 3H; NCHCH_3), 1.47 (s, 3H; OCCH_3), 0.50 (s, 3H; OCCH_3); ^{13}C{^{1}H} (75.5 MHz, C_6D_6) NMR: δ = 148.7, 148.2, 148.1, 144.0, 144.0, 143.6, 143.1, 138.0, 137.6, 137.5, 137.0, 129.9, 129.6, 129.5, 128.9, 127.8, 127.7, 127.3, 126.2, 126.1, 112.1, 84.8, 83.7, 83.4, 82.6, 82.5, 82.5, 56.6 (d, ^2J(P,C) = 35.4 Hz), 29.8, 28.5, 27.6, 26.3, 26.0, 22.1, 22.0 (m), 19.5, 19.4, 12.0 ppm; ^{31}P{^{1}H} NMR (121 MHz): δ = 140.9 ppm; HRMS (FAB^+): m/z calcd for $C_{48}H_{57}NO_4P$: 742.4025; found 742.3993 $[M-H]^+$; elemental analysis calcd (%) for $C_{48}H_{56}NO_4P$: C 77.70, H 7.61, N 1.89; found: C 77.59, H 7.52, N 1.81.

(1*R*,7*R*)-4-(*N*-Methyl-*N*-(*R*)-1-phenylethylamino)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*,*R*)-2c): This compound was prepared similarly to the synthesis of (*S*,*S*,*R*)-**2c** from (1*R*,7*R*)-4-Chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane. Yield: 42%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.04 (m, 13H; Ar-*H*), 6.90–6.69 (m, 4H; Ar-*H*), 5.14 (dd, J = 8.3, 3.1 Hz, 1H; OC*H*), 4.85–4.72 (m, 1H; NC*H*(Ph)(Me)), 4.69 (d, J = 8.3 Hz, 1H; OC*H*), 2.57 (d, ^3J(P,H) = 6.9 Hz, 3H; NCH_3), 2.32–2.23 (m, 24H; Ar-CH_3), 1.58 (d, J = 7.2 Hz, 3H; NCHCH_3), 1.42 (s, 3H; OCCH_3), 0.28 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 147.5, 147.2, 143.2, 143.2, 142.6, 142.1, 137.4, 136.9, 136.8, 136.4, 129.3, 129.0, 128.9, 128.9, 128.3, 127.7, 127.2, 126.8, 125.3, 111.5, 83.4, 82.9, 82.7, 81.6, 81.5, 81.4, 55.3 (d, ^2J(P,C) = 35.4 Hz), 28.0, 26.5, 26.4, 25.7, 21.9, 21.8, 18.4, 18.4, 12.0 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 140.1 ppm; HRMS (FAB^+): m/z calcd for $C_{48}H_{57}NO_4P$: 742.4025; found: 742.4025 $[M-H]^+$; elemental analysis calcd (%) for $C_{48}H_{56}NO_4P$: C 77.70, H 7.61, N 1.89; found: C 77.02, H 7.87, N 1.95.

(1*R*,7*R*)-4-(*N*-Methyl-*N*-(*S*)-1-phenylethylamino)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*,*S*)-2c): This compound was prepared similarly to the synthesis of (*S*,*S*,*R*)-**2c** from (1*R*,7*R*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (0.81 mmol) and (*S*)-(−)-*N*,α-dimethylbenzylamine (141 μL; 0.97 mmol). Yield: 268 mg (45%); ^{1}H NMR (300 MHz, C_6D_6): δ = 8.00 (s, 2H; Ar-*H*), 7.71 (s, 2H; Ar-*H*), 7.58 (s, 4H; Ar-*H*), 7.46 (s, 1H; Ar-*H*), 7.44 (s, 1H; Ar-*H*), 7.22–7.07 (m, 4H; Ar-*H*), 6.77–6.70 (m, 4H; Ar-*H*), 5.84 (dd, J = 8.4, 3.9 Hz, 1H; OC*H*), 5.34 (d, ^3J(H,H) = 8.4 Hz, 1H; OC*H*), 4.84–4.75 (m, 1H; NC*H*(Me)(Ph)), 2.81 (d, ^3J(P,H) = 6.3 Hz, 3H; NCH_3), 2.18–2.07 (m, 24H; Ar-CH_3), 1.55 (s, 3H; OCCH_3), 1.48 (d, ^3J(H,H) = 6.9 Hz 3H; NCH(CH_3)(Ph)), 0.49 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 148.7, 148.1, 148.1, 144.0, 143.9, 143.5, 143.5, 143.1, 138.0, 137.6, 137.4, 137.4, 137.4, 137.0, 129.9, 129.6, 129.5, 128.9, 128.0, 127.8, 127.7, 127.4, 126.2 (partial overlap with residual solvent signal), 112.1, 84.7, 83.7, 83.4, 82.6, 82.5, 82.5, 56.6 (d, ^2J(P,C) = 35.4 Hz), 35.3 (m), 29.8, 28.5, 27.6 (m), 26.3, 26.0, 22.0 (m), 19.5, 12.0 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 140.8 ppm; HRMS (FAB^+): m/z calcd for $C_{48}H_{57}NO_4P$: 742.4025; found: 742.3996 $[M-H]^+$; elemental analysis calcd (%) for $C_{48}H_{56}NO_4P$: C 77.70, H 7.61, N 1.89; found: C 77.68, H 7.54, N 1.94.

(1*S*,7*S*)-4-(*N*-Methyl-*N*-(*S*)-1-phenylethylamino)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*S*,*S*,*S*)-2c): This compound was prepared similarly to the synthesis of (*S*,*S*,*R*)-**2c** from (1*S*,7*S*)-4-Chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (0.81 mmol) and (*S*)-(−)-*N*,α-dimethylbenzylamine (141 μL, 0.97 mmol). Yield: 261 mg (43 %); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.99 (s, 2H; Ar-*H*), 7.73 (s, 1H; Ar-*H*), 7.63 (s, 2H; Ar-*H*), 7.60 (s, 2H; Ar-*H*), 7.42 (d, J = 7.7 Hz, 2H; Ar-*H*), 7.22–7.11 (m, 4H; Ar-*H*), 6.79–6.70 (m, 4H; Ar-*H*), 5.83 (dd, J = 8.3, 3.8 Hz, 1H; OC*H*), 5.44 (d, ^3J(H,H) = 8.3 Hz, 1H; OC*H*), 4.91–4.83 (m, 1H; NC*H*), 2.77 (d, ^3J(P,C) = 7.1 Hz, 3H; NCH_3), 2.18–2.07 (m, 24H; Ar-CH_3), 1.53 (d, ^3J(H,H) = 7.1 Hz, 3H; NCH(CH_3)(Ph)), 1.52 (s, 3H; OCCH_3), 0.55 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 148.6, 148.1, 143.7, 143.6, 143.5, 143.1, 138.1, 137.6, 137.4, 137.0, 130.0, 129.8, 129.6, 129.4, 127.9, 127.3, 126.1, 112.3, 84.3, 83.8, 83.5, 83.1, 82.5, 82.4, 56.0 (d, ^2J(P,C) = 34.2 Hz), 35.3, 29.8, 28.4, 27.6, 27.6, 27.3, 27.2, 26.4, 26.0, 23.1, 22.0 (m), 19.0, 12.0 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 142.0 ppm; HRMS (FAB$^+$): m/z calcd for $C_{48}H_{57}NO_4P$: 742.4025; found: 742.4016 [M−H]$^+$; elemental analysis calcd (%) for $C_{48}H_{56}NO_4P$: C 77.70, H 7.61, N 1.89; found: C 77.83, H 7.68, N 1.84.

(1*R*,7*R*)-4-(Diisopropylamino)-9,9-dimethyl-2,2,6,6-tetraphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2e): This compound was prepared analogously to (*R*,*R*)-**2b** from (2*R*,3*R*)-*O*-isopropylidene-1,1,4,4-tetraphenylthreitol. Its observed spectroscopic characteristics matched previously reported data.[45]

(1*R*,7*R*)-4-Diethylamino-9,9-cyclohexyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2i): This compound was prepared analogously to (*R*,*R*)-**2b** from the corresponding TADDOL backbone. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (s, 2H; Ar-*H*), 7.23 (s, 2H; Ar-*H*), 7.15 (s, 2H; Ar-*H*), 7.04 (s, 2H; Ar-*H*), 6.84–6.80 (m, 4H; Ar-*H*), 4.97 (dd, J = 8.5, 3.5 Hz, 1H; OC*H*), 4.68 (d, 1H; J = 8.5 Hz, OC*H*), 3.22 (m, 4H; N(CH_2CH$_3$)$_2$), 2.28–2.25 (m, 24H; ArCH_3), 1.56–1.49 (m, 4H; OCCH_2), 1.28–1.12 (m, 4H; CH_2), 1.15 (t, 6H; J = 6.9 Hz, N(CH$_2$CH_3)$_2$), 0.55–0.45 (m, 1H; C*H*), 0.35–0.24 ppm (m, 1H; C*H*); ^{13}C{^{1}H} (75.5 MHz, $CDCl_3$) NMR: δ = 147.6, 147.4, 142.5, 142.1, 137.2, 136.8, 136.5, 136.2, 129.1, 128.8, 128.7, 128.6, 127.1, 126.9, 126.8, 125.4, 125.2, 112.1, 82.7, 82.4, 81.9, 81.5, 81.4, 41.9, 39.1 (d, J = 22.0 Hz), 37.5, 35.6, 25.4, 24.6, 24.3, 21.9, 15.6, 15.5, 11.4 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 141.4 ppm; HRMS (FAB$^+$): m/z calcd for $C_{46}H_{59}NO_4P$: m/z 720.4182; found: 720.4182 [M−H]$^+$; elemental analysis calcd (%) for $C_{46}H_{58}NO_4P$: C 76.74, H 8.12, N 1.95; found: C 76.65, H 8.06, N 1.88.

(1*R*,7*R*)-4-Diethylamino-9,9-dimethyl-2,2,6,6-tetra(2-naphthyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2f): The compound was prepared analogously to the 3,5-(CH$_3$)C$_6$H$_3$-substituted ligand ((*R*,*R*)-**2b**). Purification was done by column chromatography (SiO_2) twice using hexanes/Et$_3$N/CH$_2$Cl$_2$ (92.5/5.0/2.5 v/v) to yield the compound as a white solid (49 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1H; Ar-*H*), 8.21 (s, 1H; Ar-*H*), 8.12 (s, 1H; Ar-H), 8.05 (s, 1H; Ar-*H*), 7.91–7.41 (m, 24H; Ar-*H*), 5.53 (dd, J = 8.5, 3.6 Hz, 1H; OC*H*), 5.12 (d, J = 8.5 Hz, 1H; OC*H*), 3.37–3.28 (m, 4H; N(CH_2CH$_3$), 1.41 (s, 3H; OCCH_3), 1.21 (t, J = 6.9 Hz, 6H; N(CH$_2$CH_3)), 0.28 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 145.1, 144.3, 144.3, 140.2, 139.8, 133.3–133.0 (overlapping), 129.0–126.5 (overlapping), 112.5, 83.6, 82.4, 82.1, 82.0, 46.8, 44.5, 39.8, 39.5, 28.1, 25.9, 15.8 ppm; ^{31}P{^{1}H} NMR (121.5 MHz): δ = 141.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{51}H_{47}NO_4P$: 768.3243; found: 768.3235 [M−H]$^+$; elemental analysis calcd (%) for $C_{51}H_{46}NO_4P$: C 79.77, H 6.04, N 1.82; found: C 79.85, H 6.12, N 1.78.

(1*R*,7*R*)-4-*N*-(1-Aza-4-oxacyclohexyl)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2h): This compound was prepared analogously to the synthesis of (*R*,*R*)-**2b** from (1*R*,7*R*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (2.6 mmol) and morpholine (164 μL, 164 mg, 1.88 mmol). The crude product was purified by quick column chromatography (hexanes/triethylamine 95/5 v/v) to give a white foam as the product. Yield: 510 mg (27 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (s, 2H; Ar-*H*), 7.20 (s, 2H; Ar-*H*), 7.03 (s, 2H; Ar-*H*), 6.99 (s, 2H; Ar-*H*), 6.87–6.83 (m, 4H; Ar-*H*), 5.07 (dd, J = 8.4, 3.6 Hz, 1H; OC*H*), 4.73 (d, 1H; 8.3 Hz), 3.74–3.68 (m, 4H; N(CH_2CH$_2$)$_2$O), 3.35–3.33 (m, 2H; CH_2O), 3.21–3.18 (m, 2H; CH_2O), 2.28–2.26 (m, 24H; Ar-CH_3), 1.43 (s, 3H; OCCH_3), 0.29 ppm (s, 3H; OCCH_3); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 148.2, 147.9, 147.9, 143.1, 143.0, 138.1, 137.7, 137.4, 137.0, 130.0, 129.8, 129.7, 129.5, 127.8, 127.8, 126.0, 112.7, 83.9, 83.7, 83.6, 83.3, 82.5, 82.4, 68.2 (d, J = 4.9 Hz), 45.0 (d, J = 17.1 Hz), 35.3, 29.7, 28.3, 27.6, 26.5, 22.0, 21.8, 21.2, 19.3, 12.0 ppm; ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 138.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{43}H_{53}NO_5P$: 694.3661; found: 694.3670 [M−H]$^+$; elemental analysis calcd (%) for $C_{43}H_{52}NO_5P$: C 74.43, H 7.55, N 2.02; found: C 74.28, H 7.46, N 1.94.

(1*R*,7*R*)-4-*N*-(1-Aza-4-(*N*′-methyl)azacyclohexyl)-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R*,*R*)-2g): This compound was prepared analogously to the synthesis of (*R*,*R*)-**2b** from (1*R*,7*R*)-4-chloro-9,9-dimethyl-2,2,6,6-tetra(3,5-dimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (1.30 mmol) and 1-methylpiperazine (173 μL, 156 mg, 1.56 mmol). The crude product was purified by quick column chromatography (hexanes/triethylamine 95/5 v/v) to give a white foam as the product. Yield: 510 mg (27 %); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 148.4, 148.0, 148.0, 143.3, 143.2, 138.0, 137.6, 137.3, 129.9, 129.8, 129.7, 129.4, 127.8, 127.8, 126.1, 112.6, 84.0, 84.1, 83.7, 83.5, 83.4, 82.5, 82.4, 56.7, 47.1 (d, J = 7.3 Hz), 44.8 (d, J = 19.5 Hz), 35.3, 29.8, 28.3, 27.6, 26.5, 26.0, 21.9 (m), 12.0 ppm; HRMS (FAB$^+$): m/z calcd for $C_{44}H_{56}N_2O_4P$: 707.3978; found: 707.3986 [M−H]$^+$; elemental analysis calcd (%) for $C_{44}H_{55}N_2O_4P$: C 74.76, H 7.84, N 3.96; found: C 74.83, H 8.04, N 3.66.

***(R)*-*O*,*O*′-(1,1′)-Dinaphthyl-2,2′-diyl-3,3′-di(trimethylsilyl)phosphorchloridite**: (*R*)-3,3′-trimethylsilyl-1,1′-binaphtyl-2,2′-diol (1.00 g, 2.31 mmol) was azeotropically dried by dissolving it in anhydrous toluene (10 mL) followed by evaporation in vacuo of the solvent (2 times). The dry starting material was then dissolved in toluene (25 mL). PCl_3 (242 μL, 381 mg, 2.77 mmol) and triethylamine (1.3 mL, 0.93 g, 9.2 mmol) were dissolved in toluene (50 mL) and were added dropwise to the diol solution at 0 °C. After stirring overnight, the resulting suspension was stirred at 50 °C for 1 h. After cooling to room temperature, the suspension was filtered and the solvent evaporated to give a yellow, air-sensitive powder (^{31}P{^{1}H} NMR: δ = 176 ppm). This compound was not characterised further, but used immediately in further reactions.

***O*,*O*′-(1,1′)-Dinaphthyl-2,2′-diyl-3,3′-di(trimethylsilyl)-*N*,*N*-diethylphosphoramidite ((*R*)-3a)**: (*R*)-*O*,*O*′-(1,1′)-Dinaphthyl-2,2′-diyl-3,3′-di(trimethylsilyl)phosphorchloridite (546 mg, 1.10 mmol) was dissolved in toluene (25 mL) and cooled to 0 °C; then triethylamine (0.23 mL, 1.65 mmol) was added. Next, a solution of diethylamine (0.17 mL, 1.65 mmol) in toluene (20 mL) was added dropwise. After complete addition, the solution was warmed to room temperature and stirred for 2 h. Subsequently the cloudy mixture was stirred overnight at 75 °C. After cooling to room temperature the resulting suspension was filtered and all volatiles evaporated in vacuo. The crude product was washed with hexanes (2 × 15 mL) and purified by column chromatography (SiO_2, eluens EtOAc/Et$_3$N/PE = 5:5:90) to afford the product as a white powder. Yield: 110 mg (19 %). Precipitation from the hexane washing fractions yielded another 100 mg pure product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2H; J = 12.3 Hz, Ar-*H*), 7.89 (d, J = 8.1 Hz, 2H; Ar-*H*), 7.39–7.05 (m, 6H; Ar-*H*), 2.94 (br, 4H; NCH_2CH$_3$), 1.02 (br, 6H; NCH$_2$C H_3), 0.47 (s, 9H; Si(CH_3)$_3$), 0.41 ppm (s, 9H; Si(CH_3)$_3$); ^{13}C{^{1}H} (75.5 MHz, $CDCl_3$): δ = 154.1, 154.0, 137.0, 136.8, 134.3, 134.1, 132.9, 132.5, 131.0, 130.2, 128.5, 128.4, 127.1, 127.0, 126.4, 126.3, 124.6, 124.3, 122.9, 122.8, 121.3, 40.6 (m), 29.9, 15.7, 0.3, 0.2 ppm; ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$): δ = 150.2 ppm; HRMS: m/z calcd for $C_{30}H_{38}NO_2PSi_2$: 532.2257; found: 532.2274 [M−H]$^+$; elemental analysis calcd (%) for $C_{30}H_{38}NO_2PSi_2$: C 67.76, H 7.20, N 2.63; found: C 67.47, H 7.42, N 2.67.

***O*,*O*′-(1,1′-Dinaphthyl-2,2′-diyl-3,3′-di(trimethylsilyl))-*N*-methyl-*N*-(*R*)-1-phenylethylphosphoramidite ((*R*)-3b)**: This compound was prepared analogously to (*R*)-**3a** from (*R*)-*O*,*O*′-(1,1′)-dinaphthyl-2,2′-diyl-3,3′-di(trimethylsilyl)phosphorchloridite (546 mg, 1.10 mmol) and (*R*)-(+)-*N*,α-dimethylbenzylamine (0.22 g, 1.65 mmol). Purified by column chromatography (SiO_2, eluents EtOAc/Et$_3$N/PE = 2.5:5:92.5). Yield: 251 mg (38 %) of a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, 2H; J = 4.8 Hz, Ar-*H*), 7.88 (dd, J = 8.3, 1.1 Hz, 2H; Ar-*H*), 7.46–7.01 (m, 11H; Ar-*H*), 4.90 (m, 1H; NC*H*(Me)(Ph)), 2.13 (d, J = 4.3 Hz, 3H; NCH_3), 1.63 (d, J = 7.0 Hz, 3H; NCH(CH_3)), 0.44 (s, 9H; Si(CH$_3$)$_3$), 0.43 ppm (s, 9H; Si(CH$_3$)$_3$); ^{13}C{^{1}H} (75.5 MHz, $CDCl_3$): δ = 153.5 (d, J = 1.5 Hz), 142.0, 136.7, 16.6, 133.9, 133.7, 132.3, 131.9, 130.5, 129.8, 128.0, 127.8, 127.4, 126.8, 126.7, 126.5, 126.0, 124.2, 124.1, 122.5, 122.5, 121.1, 121.1,

56.1, 55.5, 45.3, 29.5, 27.5, 19.1, 19.0, 0.3, −0.2, −0.2 ppm; $^{31}P\{^1H\}$ (121.5 MHz, $CDCl_3$): $\delta = 145.6$ ppm; HRMS: *m/z* calcd for $C_{35}H_{40}NO_2PSi_2$: 594.2414; found: 594.2415 $[M-H]^+$; elemental analysis calcd (%) for $C_{35}H_{40}NO_2PSi_2$: C 70.79, H 6.79, N 2.36; found: C 70.49, H 7.04, N 2.45.

3-Benzyl-2-(2,6-di-*tert*-butylphenoxy)-4-(*S*)-methyl-5-(*R*)-phenyl-1,3,2-oxazaphospholidine (4): *N*-Benzyl-(1*R*,2*S*)-norephedrine (340 mg, 1.40 mmol) was dissolved in anhydrous toluene (40 mL). Separately, 2,6-di(*tert*-butyl)phenoxyphosphordichloridite (433 mg, 1.40 mmol)[37] was dissolved in anhydrous toluene (40 mL). Both solutions were slowly dropwise added, simultaneously, to a solution of triethylamine (3 mL) in toluene (40 mL) at −40 °C. Care was taken to ensure that the rate of addition of both reactant-containing solutions was as equal as possible. After complete addition, the resulting reaction mixture was warmed to room temperature and stirred for 48 h. The formed ammonium salts were filtered and the solvent removed in vacuo. This resulted in a yellowish powder as the crude product. Pure compound was obtained by crystallisation from diethyl ether, followed by washing of the formed crystals with cold diethyl ether (5 mL) and acetonitrile (2×5 mL). Yield: 365 mg (55%); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38$–7.34 (m, 12H; Ar-*H*), 6.99 (t, $J = 7.7$ Hz, 1H; Ar-*H*), 5.13 (d, $J = 6.0$ Hz, 1H; C*H*(Ph)O), 4.60 (dd, $J = 15.1$, 7.9 Hz, 1H; NC(*H*)(H)(Ph)), 4.09 (dd, $J = 23.2$, 7.9 Hz, 1H; NC(*H*)(H)(Ph)), 3.31 (m, 1H; C*H*(Me)N), 1.61 (s, 18H; $C(CH_3)_3$), 1.00 ppm (d, $J = 6.8$ Hz, 3H; $CH(CH_3)N$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 152.1$ (d, $J = 11.0$ Hz), 143.7, 139.3, 138.2, 128.9, 128.3, 128.1, 128.1, 127.9, 127.6, 126.7, 126.3, 122.7, 86.0 (d, $J = 12.2$ Hz), 55.2, 51.0 (d, $J = 30.5$ Hz), 35.8, 32.4, 15.6 ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 154.9$ ppm; HRMS: *m/z* calcd for $C_{30}H_{38}NO_2P$: 476.2718; found: 476.2746 $[M-H]^+$; elemental analysis calcd (%) for $C_{30}H_{38}NO_2P$: C 75.76, H 8.05, N 2.95; found: C 75.58, H 8.07, N 3.06.

[Pd(C_3H_5)(1)(Cl)]: A Schlenk vessel was charged with $[\{Pd(allyl)(\mu\text{-}Cl)\}_2]$ (111 mg, 0.30 mmol) and phosphoramidite **1** (293 mg, 0.60 mmol). Next, dichloromethane (15 mL) was added and the resulting mixture was stirred for 30 min at room temperature. Evaporation of the solvent gave the product complex as a pale yellow microcrystalline powder in quantitative yield. Crystals suitable for an X-ray analysis were grown by slow evaporation of a solution of the compound in hexanes. ^1H NMR (300 MHz, CD_2Cl_2, 0 °C): $\delta = 6.92$ (brs, 2H; (L)Ar-*H*), 6.78 (brd, 2H; (L)Ar-*H*), 5.18–5.09 (m, 1H; (allyl)-H_{meso}), 4.41 (apparent t, $J = 8.8$ Hz, 1H; (allyl)-$H_{3,syn}$), 4.24–4.18 (m, 2H; $N(CHMe_2)_2$), 3.80 (s, 6H; OCH_3), 3.38 (apparent t, $J = 14.0$ Hz, 1H; (allyl)-$H_{3,anti}$), 3.24 (brd, $J = 5.7$ Hz, 1H; (allyl)-$H_{1,anti}$), 1.94 (d, $J = 12.2$ Hz, 1H; (allyl)-$H_{1,syn}$) 1.47 (s, 9H; $C(CH_3)_3$), 1.42 (s, 9H; $C(CH_3)_3$), 1.30 ppm (d, $J = 6.7$ Hz, 6H; $N(CH(CH_3)_2)_2$); $^{13}C\{^1H\}$ NMR(75.5 MHz,CD_2Cl_2, 0 °C): $\delta = 157.47$, 146.14, 143.85 (d, $J = 5.0$ Hz), 133.4, 132.96, 119.78 (d, $J = 9.7$ Hz), 116.75, 115.59, 81.44 (d, $J = 44.9$ Hz), 61.49, 57.73, 50.76 (d, $J = 12.1$ Hz), 37.78, 33.32, 26.59 ppm; ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 140.1$ ppm; HRMS (FAB^+): *m/z* calcd for $C_{31}H_{47}NO_4PPd$: 634.2277; found: 634.2297 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{31}H_{47}ClNO_4PPd$: C 55.53, H 7.07, N 2.09; found: C 55.39, H 7.12, N 2.03.

[Pd(crotyl)(1)(Cl)]: A Schlenk vessel was charged with $[\{Pd(crotyl)(\mu\text{-}Cl)\}_2]$ (37 mg, 0.09 mmol) and phosphoramidite (92 mg, 0.18 mmol). Next, dichloromethane (5 mL) was added and the resulting mixture was stirred for 30 min at room temperature. The dichloromethane was removed in vacuo and the resulting solid washed with two portions of diethyl ether (5 mL). After drying under vacuum the product complex was obtained as a beige microcrystalline powder in quantitative yield. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 6.96$ (brs, 2H; Ar-*H*), 6.78 (brs, 2H; Ar-*H*), 4.93 (brq, $J = 10.4$ Hz, 1H; allyl-H_{meso}), 4.33–4.24 (m, 2H; $N(CHMe_2)_2$), 4.16–4.05 (m, 1H; allyl-*H*), 3.80 (s, 6H; OCH_3), 3.06 (brs, 1H; allyl-*H*), 1.86 (brd, $J = 10.7$ Hz, 1H; allyl-*H*), 1.66–1.32 ppm (m, 33H; L + allyl-CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 155.83$, 144.51 (d, $J = 6.1$ Hz), 142.22, (d, $J = 4.9$ Hz), 131.9 (br), 131.5 (br), 117.25 (d, $J = 8.5$ Hz), 115.11, 113.98, 100.04, 99.54, 66.20, 56.10, 49.20 (d, $J = 13.4$ Hz), 36.17, 31.76, 25.01, 17.69 ppm (d, $J = 7.3$ Hz); ^{31}P NMR (CD_2Cl_2): $\delta = 143.6$ ppm; HRMS (FAB^+): *m/z* calcd for $C_{32}H_{49}NO_4PPd$: 648.2434; found: 648.2430 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{32}H_{49}ClNO_4PPd$: C 56.15, H 7.21, N 2.05; found: C 56.12, H 7.20, N 2.01.

[Pd(cinnamyl)(1)(Cl)]: A Schlenk vessel was charged with $[\{Pd(cinnamyl)(\mu\text{-}Cl)\}_2]$ (91 mg, 0.18 mmol) and phosphoramidite (172 mg, 0.36 mmol). Dichloromethane (10 mL) was added and the resulting mixture was stirred for 30 min at room temperature. Evaporation of the solvent gave the product complex as a yellow powder in quantitative yield. ^1H NMR (0 °C, CD_2Cl_2): $\delta = 7.30$ (brs, 5H; (cinnamyl)Ar-*H*), 6.96 (brs, 2H; (L)Ar-*H*), 6.80 (brs, 2H; (L)Ar-*H*), 5.50 (apparent double t, $J = 12.6$, 9.6 Hz, 1H; (cinnamyl)-H_{meso}), 4.91 (apparent t, $J = 14.1$ Hz, 1H; (cinnamyl)-H_3), 4.25 (heptet, $J = 6.5$ Hz, 2H; $N(CHMe_2)_2$), 3.80 (s, 6H; OCH_3), 3.24 (brd, $J = 6.5$ Hz, 1H; (cinnamyl)-H_{syn}), 2.16 (brd, 1H; (cinnamyl)-H_{anti}), 1.56 (s, 9H; $C(CH_3)_3$), 1.48 (s, 9H; $C(CH_3)_3$), 1.28 ppm (d, $J = 6.5$ Hz, 6H; $N(CH(CH_3)_2)_2$); $^{13}C\{^1H\}$ NMR: $\delta = 153.74$, 142.34, 140.33, 134.51 (d, $J = 9.7$ Hz), 130.37, 127.10, 126.71, 126.54, 126.49, 113.19, 111.82, 109.47 (d, $J = 9.0$ Hz), 54.13, 53.91, 47.69 (d, $J = 12.8$ Hz), 34.30, 30.13, 23.23 ppm; ^{31}P NMR (CD_2Cl_2): $\delta = 141.4$ ppm; HRMS (FAB^+): *m/z* calcd for $C_{37}H_{51}NO_4PPd$: 710.2590; found: 710.2601 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{37}H_{51}ClNO_4PPd$: C 59.52, H 6.88, N 1.88; found: C 59.61, H 6.82, N 1.93.

[Pd(C_3H_5){(*R*,*R*)-2b}(Cl)]: This compound was prepared as described for $[Pd(C_3H_5)(\mathbf{1})(Cl)]$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, mixture of isomers): $\delta =$ 144.12, 142.18, 142.11, 141.67, 138.38, 138.07, 137.58, 136.34, 129.73, 128.92, 128.80, 127.46, 127.05, 126.87, 126.37, 125.63, 125.10, 118.06, 117.87, 114.92, 89.33, 89.16, 86.61, 79.87, 79.23, 78.99, 78.52, 65.89, 62.82, 57.16, 55.12, 41.06, 27.16, 26.89, 26.67, 26.54, 21.46, 21.39, 21.22, 15.33, 14.91 ppm; ^{31}P NMR (MHz, −20 °C, CD_2Cl_2): $\delta = 119.25$ (major isomer), 117.32 ppm (minor isomer); HRMS (FAB^+): *m/z* calcd for $C_{46}H_{59}NO_4PPd$: 826.3216; found: 826.3198 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{46}H_{59}ClNO_4PPd$: C 64.04, H 6.89, N 1.62; found: C 64.10, H 6.82, N 1.58.

[Pd(1,3-diphenylallyl){(*R*,*R*)-2b}(Cl)]: A Schlenk vessel was charged with $[Pd(1,3\text{-diphenylallyl})(\mu\text{-}Cl)]_2$ (91 mg, 0.18 mmol) and phosphoramidite (*R*,*R*)-**2b** (172 mg, 0.36 mmol). Dichloromethane (10 mL) was added and the resulting mixture was stirred for 30 min at room temperature. Evaporation of the solvent gave the product complex as an orange/yellow microcrystalline powder in quantitative yield. The compound decomposed slowly in solution. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$–6.78 (m, 22H; Ar-*H*), 6.19 (t, $J = 12.9$ Hz, 1H), 5.90 (d, $J = 7.7$ Hz, 1H), 5.12 (d, $J = 7.5$ Hz, 1H), 4.30 (apparent t, $J = 13.0$ Hz, 1H), 2.92–2.82 (m, 3H), 2.50–2.17 (m, 27H), 1.59–1.51 (m, 2H), 0.63 (s, 3H), 0.50 (s, 3H), 0.45–0.41 ppm (m, 6H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 144.62$, 142.07, 141.68, 141.62, 139.50, 138.51, 137.42, 136.35, 135.97, 130.72, 129.53, 129.25, 128.77, 128.25, 128.20, 127.97, 127.84, 127.20, 125.73, 114.82, 107.27, 107.18, 94.40, 94.08, 90.06, 89.87, 85.93, 79.24, 78.44, 78.41, 71.39, 71.33, 39.82 (d, $J = 9.3$ Hz), 26.87, 26.54, 21.83, 21.50, 21.39, 21.17, 13.83 ppm; ^{31}P NMR: $\delta = 119.4$ ppm.

Allylic alkylation reactions

General procedure: A flame-dried Schlenk vessel was charged with freshly prepared stock-solutions in THF (1 mL per experiment) containing $[\{Pd(crotyl)(\mu\text{-}OAc)\}_2]$ (2.0 mg, 0.005 mmol) and ligand **1** (4.9 mg, 0.010 mmol, 2 equiv). Subsequently, the allylic substrate (1.0 mmol) and dihexyl ether (50 μL), as internal standard for GC measurements, were added and the reaction mixture was stirred for 15 min at room temperature. A solution of disodium diethyl 2-methyl malonate (4 mL, 2.0 mmol, 0.5 M) was added and the solution was stirred at room temperature. Aliquots were taken from the reaction mixture at certain time intervals, diluted with diethyl ether, washed with saturated aqueous ammonium chloride solution, dried over $MgSO_4$ and analysed by GC.

Asymmetric allylic alkylation reactions

General procedure: A flame-dried Schlenk vessel was charged with $[\{Pd(allyl)(\mu\text{-}OAc)\}_2]$ (2.0 mg, 0.005 mmol) and ligand (0.020 mmol, 4 equiv) through freshly prepared stock-solutions in CH_2Cl_2 (2 mL per experiment). Subsequently, the allylic substrate (1.0 mmol) and dihexyl ether (50 μL), as internal standard for GC measurements were added, followed by dimethyl malonate (171 μL, 1.5 mmol). This mixture was stirred at room temperature for 15 minutes. The reaction was started by addition of *N*,*O*-bis(trimethylsilyl) acetamide (371 μL, 1.5 mmol) and KOAc (1 mg). The reaction was monitored by GC and TLC. After the desired reaction time, the mixture was diluted with Et_2O (10 mL), washed with saturated ammonium chloride solution (5 mL) and dried over $MgSO_4$. Evaporation of the solvent gave crude product which was purified by flash column chromatography (SiO_2, eluents: EtOAc/hexanes = 1:3) to yield a colourless oil. The enantiomeric excess was deter-

mined by chiral HPLC (Daicel OD, *n*-hexane/2-propanol = 99.5:0.5, flow 0.5 mL min^{-1}, t_R (*R*) = 35.4, t_R (*S*) = 38.7 min, λ = 254 nm for the product from 1,3-diphenylallyl acetate).

Computational details: All calculations were performed on an SG workstation using the commercially available SPARTAN program (version 5.0.3.). The geometry optimisations were carried out on semi-empirical (PM3(tm)) level after optimisation using molecular mechanics (Sybyl force field), for the [Pd(allyl)(L)(Cl)] complexes, in which L is the structure of the ligand without the substituents on the acetal moiety in the backbone. The product η^2-alkene complexes were modelled by using $-CH(COOH)_2$ as the newly coupled fragment.

X-ray crystal structure determination of [Pd(C_3H_3)(1)(Cl)]: $C_{31}H_{47}ClNO_4PPd$, M_r = 670.52, pale yellow block, 0.30 × 0.30 × 0.15 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 10.9862(1), b = 16.6159(1), c = 18.1533(2) Å, β = 104.4576(3)°, V = 3208.86(5) Å^3; Z = 4, ρ = 1.388 g cm^{-3}; 41792 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and $Mo_{K\alpha}$ radiation (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (μ = 0.75 mm^{-1}, correction range 0.80–0.89). The reflections were merged using the program SORTAV,[72] resulting in 7358 unique reflections (R_{int} = 0.0493), of which 6093 were observed [$I > 2\sigma(I)$]. The structure was solved with automated Patterson methods using the program DIRDIF,[73] and refined with the program SHELXL97[74] against F^2 of all reflections up to a resolution of $(\sin\vartheta/\lambda)_{max}$ = 0.65 Å^{-1}. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. The allyl ligand was rotationally disordered over two conformations and was refined with a disorder model. There were 374 refined parameters, 0 restraints. *R* (obsd reflns): *R*1 = 0.0276, *wR*2 = 0.0711; *R* (all data): *R*1 = 0.0370, *wR*2 = 0.0762. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.1877P]$, where $P = (F_o^2 + 2F_c^2)/3$. GoF = 1.066. Residual electron density between −0.66 and 0.71 e Å^{-3}. The drawings, structure calculations and checking for higher symmetry was performed with the program PLATON.[75] CCDC-247629 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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