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Structural control in palladium(II)-catalyzed enantioselective allylic alkylation by new chiral phosphine-phosphite and pyridine-phosphite ligands

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Abstract

The ligands 6-[(diphenylphosphanyl)methoxy]-4,8-di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene, **1**, (*S*)-4-[(diphenylphosphanyl)methoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4*a*′]-dinaphthalene, (*S*)-**2**, and (*S*)-4-[(diphenylphosphanyl)methoxy]-2,6-bis-trimethylsilanyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene, (*S*)-**3**, (*S*)-2-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yloxymethyl)pyridine, (*S*)-**4**, and (*S*)-2-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yloxy)pyridine, (*S*)-**5**, have been easily prepared.

The cationic complexes $[Pd(\eta^3\text{-}C_3H_5)(L\text{–}L')]CF_3SO_3$ (L–L′ = **1**–(*S*)-**5**) and $[Pd(\eta^3\text{-}PhCHCHCHPh)(L\text{–}L')]CF_3SO_3$ (L–L′ = (*S*)-**2**–(*S*)-**4**) were synthesized by conventional methods starting from the complexes $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and $[Pd(\eta^3\text{-}PhCHCHCHPh)Cl]_2$, respectively. The behavior in solution of all the π-allyl- and π-phenylallyl-(L–L′)palladium derivatives **6**–**14** was studied by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR and 2D-NOESY spectroscopy. As concerns the ligands (*S*)-**4** and (*S*)-**5**, a satisfactory analysis of the structures in solution was possible only for palladium–allyl complexes $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{4})]CF_3SO_3$, **11**, and $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{5})]CF_3SO_3$, **12**, since the corresponding species $[Pd(\eta^3\text{-}PhCHCHCHPh)((S)\text{-}\mathbf{4})]CF_3SO_3$, **13**, and $[Pd(\eta^3\text{-}PhCHCHCHPh)((S)\text{-}\mathbf{5})]CF_3SO_3$, **14**, revealed low stability in solution for a long time. The new ligands (*S*)-**2**–(*S*)-**5** were tested in the palladium-catalyzed enantioselective substitution of (1,3-diphenyl-1,2-propenyl)acetate by dimethylmalonate. The precatalyst $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{2})]CF_3SO_3$ afforded the allyl substituted product in good yield (95%) and acceptable enantioselectivities (71% e.e. in the *S* form). A similar result was achieved with the precatalyst $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{3})]CF_3SO_3$. The nucleophilic attack of the malonate occurred preferentially at allylic carbon far from the binaphthalene moiety, namely *trans* to the phosphite group. When the complexes containing ligands (*S*)-**4** and (*S*)-**5** were used as precatalysts, the product was obtained as a racemic mixture in high yield. The number of the configurational isomers of the Pd-allyl intermediates present in solution in the allylic alkylation and the relative concentrations are considered a determining factor for the enantioselectivity of the process.

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1. Introduction

Palladium-catalyzed allylic substitution provides an effective route for enantioselective carbon–carbon bond formation, under mild conditions.[1] Consequently, there is considerable interest in this research area and a number of groups have synthesized several chiral ligands, which have achieved good asymmetric inductions.[2]

Phosphorus–phosphorus, phosphorus–nitrogen and nitrogen–nitrogen chelating ligands have been successfully used in these reactions. Generally, much lower enantiomeric excess was observed for ligands with small substituents and low steric bulk. Helmchen et al.[2l] achieved enantioselectivities of 99% in the allylic substitution of acyclic substrates using (phosphanyl)-dihydrooxazoles as ligands. Extensive research by Trost's group has led to many applications of the allylic alkylation in organic synthesis.[3] Pfaltz et al.[2e] achieved good results (97% e.e., 97% yield) in the alkylation of racemic 1,3-diphenyl-2-propenyl acetate using substituted bis(oxazoline) ligands.

However, the origin of the observed enantioselectivity, in the above-mentioned catalytic processes, is still under discussion and indications about the features that the chiral coordinated ligands in the catalyst should have to achieve high enantiomeric excess are ambiguous.

With regard to the mechanism of the Pd-catalyzed enantioselective allylic alkylation, two steps are very important in order to induce enantiodiscrimination: (i) the activation of the allylic substrate by the Pd^0-ligand complex with formation of the Pd^0-olefin intermediate; and (ii) the attack of the nucleophile on the Pd-(η^3-allyl) cation. Several studies deal with the factors determining the enantioselectivity of these reaction steps.[4] Recently, to understand how the nucleophile can discriminate between the allylic carbon atoms (C1 and C3), Osborn, van Leeuwen et al.[5] introduced the concept of preferential rotation (PR).

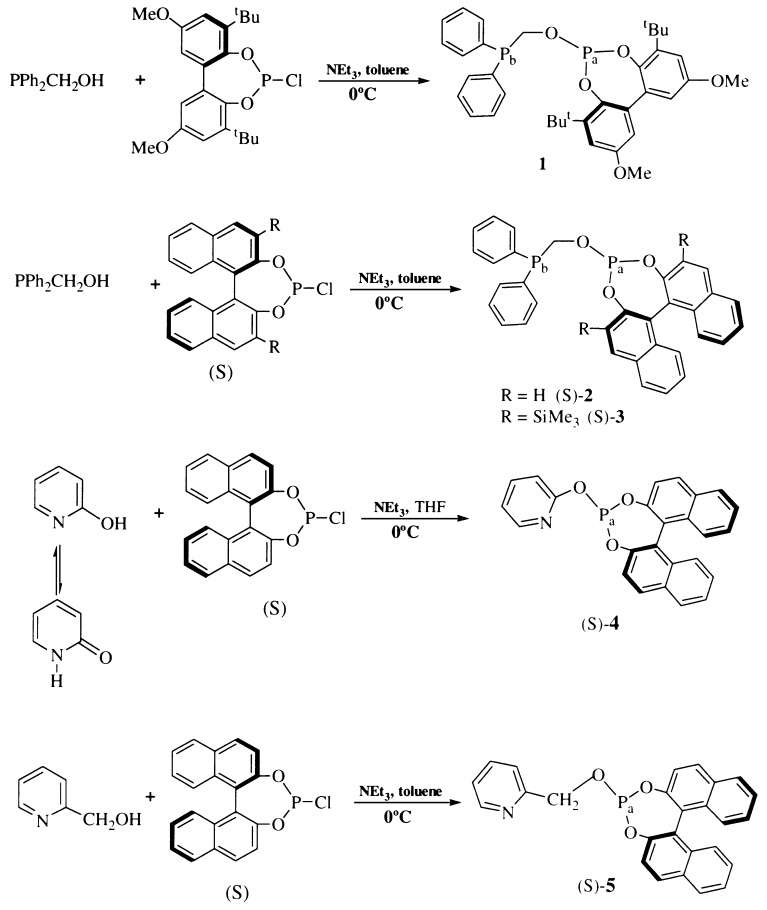
Here we report the results of a study on the preparation and applications of a new series of phosphine-phosphite and pyridine-phosphite ligands in the allylic alkylation reactions. The aim was to gain an insight into the possible correlation between the intermediate palladium and allyl isomers containing the chiral bidentate ligand and the enantiodiscrimination of the nucleophilic attack. As far as we know, this is the first example in which chiral phosphine–phosphite and pyridine–phosphite mixed ligands are used in Pd-catalyzed enantioselective allylic alkylation.

2. Results and discussion

2.1. Synthesis of ligands

Syntheses of ligands **1**–(*S*)-**5** are outlined in Scheme 1. Ligand **1** was easily prepared by reaction of diphenylhydroxymethylphosphine (Ph_2PCH_2OH) with 1 equivalent of 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene, in the presence of NEt_3, in toluene at 0°C. Following the same synthetic procedure, ligand (*S*)-**2** was obtained using Ph_2PCH_2OH and (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene as starting materials.

Ligands **1** and (*S*)-**2** were isolated as white solids, air sensitive in the solid state and in solution. The ligand **1** is not chiral owing to the low rotational energy barrier of the biphenyl moiety, also when the two *o*-phenolic oxygen atoms are bound to phosphorus atom. However, **1** was used since the NMR characterization of the allylic palladium isomers formed in solution containing



Scheme 1.

this ligand, gave a helpful insight into the NMR study of all the other allylic palladium systems with coordinated ligands (*S*)-**2**–(*S*)-**5**.

The enantiopure *ortho*-bis(trimethylsilyl)substituted dinaphthalene derivative ligand (*S*)-**3** was obtained similarly to **1** and (*S*)-**2** starting from *o*-$SiMe_3$-substituted (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene which was prepared as described by van Leeuwen et al.[6]

Ligand (*S*)-**4** was obtained as a white solid by reaction of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene with 2-hydroxypyridine (1:1 = equivalent ratio) in THF solution, as described above for ligand **1**. From the crude resulting white powder, ligand (*S*)-**4** was obtained, as a pure sample and in low yield, by extraction with a mixture of toluene:hexane (1:3). Most probably, the low yield could be ascribed to the presence of a keto–enolic tautomerism[7] (Scheme 1) involving the reactant 2-hydroxypyridine.

Ligand (*S*)-**5** was obtained from the 2-hydroxymethylpyridine and (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene. The ligand was isolated as a white solid, stable in argon atmosphere.

Selected $^{31}P\{^1H\}$ and ^1H NMR resonances for ligands **1**–(*S*)-**5** are reported in Tables 1 and 2.

Table 1
$^{31}P\{^{1}H\}$ NMR data for compounds **1**–**14**[a]

Compound	Conformer	$^{31}P\{^{1}H\}$ P_a[b]	P_b[b]	$^{2}J_{PaPb}$
1[c]		134.8(s)	-13.5(s)	
2[c]		140.2(s)	-12.7(s)	
3[c]		135.6(s)	-14.6(s)	
4[c]		145.3(s)		
5[c]		139.6(s)		
6[d]	*exo*	163.5(d)	60.4(d)	71
7[d]	*exo*	170.5(d)	55.3(d)	73
	endo	170.6(d)	56.7(d)	74
8[d]	*exo syn-syn*	161.6(d)	49.1(d)	97
	endo syn-anti	160.7(d)	47.9(d)	99
9[d]	*exo*	164.5(d)	58.9(d)	70
	endo	163.5(d)	58.2(d)	70
10[d]	*exo syn-syn*	157.2(d)	49.5(d)	93
	endo syn-anti	159.6(d)	48.3(d)	92
11[d]	*exo*	135.6(s)		
	endo	135.4(s)		
12[d]	*exo*	148.5(s)		
	endo	148.2(s)		
13[d]		125.2(br s)		
14[d]		143.5(br s)		

[a] Chemical shifts, δ, are reported in ppm and coupling constants, $^{2}J_{PaPb}$, in Hz. [b] P_a= Phosphite, P_b= Phosphine. [c] in C_6D_6 solution. [d] in $CDCl_3$ solution.

2.2. Palladium η^3-allyl complexes

The cationic complexes $[Pd(\eta^3\text{-}C_3H_5)(L\text{–}L')]\ CF_3SO_3$ [L–L′ = **1**–(*S*)-**5**] were synthesized in high yields by reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with the corresponding chiral ligand L–L′, in a 1:2 molar ratio, in the presence of $AgCF_3SO_3$ (Pd:Ag = 1:1).[8] In a similar way, the complexes $[Pd(\eta^3\text{-}PhCHCHCHPh)(L\text{–}L')]CF_3SO_3$ were prepared from $[Pd(\eta^3\text{-}PhCHCHCHPh)Cl]_2$ and the bidentate ligands L–L′ [(*S*)-**2**–(*S*)-**4**].

All the π-allyl- and π-phenylallyl-(L–L′)palladium derivatives **6**–**14** were obtained as yellow solids, soluble in chlorinated solvents, acetone and methanol; in acetone solutions they are 1:1 electrolytes.

Tables 1 and 2 show selected $^{31}P\{^{1}H\}$ and ^{1}H resonances of complexes **6**–**14**, respectively.

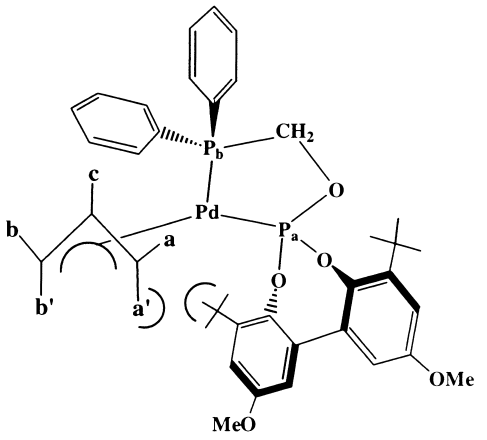
The $^{31}P\{^{1}H\}$ NMR spectrum, in $CDCl_3$ solution, of complex $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})]CF_3SO_3$, **6**, shows two doublets centered at δ 163.5 and 60.4 ppm with coupling constants $^{2}J_{P_aP_b}$ of 71 Hz, relative to the phosphite (P_a) and the phosphine (P_b) fragment of the bidentate ligand, respectively.

The ^{1}H 2D-NOESY spectrum leads to the assignment of the proton signals. The H_c proton shows two NOEs with H_a and H_b (Fig. 1), that are related by further cross-peaks with $H_{a'}$ and $H_{b'}$, respectively. We have assigned $H_{a'}$ as belonging to the allylic site *cis* to the phosphito group by the strong cross-peak with the *t*-butyl protons. On the other hand, the absence of any cross-peak between H_a and the *t*-butyl hydrogens led us to conclude that the *t*-butyl group is lying below the coordination plane supporting the structure depicted in Fig. 1.

Table 2
^{1}H NMR data for compounds **1**–**14**[a]

Compound	Conformer	H_c	H_a	H_b	$H_{a'}$	$H_{b'}$	others
1[b]							1.28(s, $(CH_3)_3$-C), 1.09(s, $(CH_3)_3$-C), 3.85(s, O-CH_3), 3.83(s, O-CH_3)
2[b]							4.69(m, H_A-C-H_B); 4.41(m, H_A-C-H_B)
3[b]							5.02(m, H_A-C-H_B), 4.23(m, H_A-C-H_B), 0.62(s, $(CH_3)_3$-Si), 0.58(s, $(CH_3)_3$-Si)
4[b]							8.24(d, H_o-py)
5[b]							8.36(d, H_o-py), 5.18(m, H_A-C-H_B), 5.04(m, H_A-C-H_B)
6[c]	***exo***	5.53(m)	5.05(t)	4.34(br t)	3.38(t)	3.06(br t)	1.29(s, $(CH_3)_3$-C), 1.17(s, $(CH_3)_3$-C), 3.86(s, O-CH_3), 3.84(s, O-CH_3), 5.06(m, H_A-C-H_B), 4.86(m, H_A-C-H_B)
7[c]	***exo***	5.50(m)	4.96(t)	4.43(br t)	3.58(t)	3.53(br t)	5.09(m, H_A-C-H_B), 5.02(m, H_A-C-H_B)
	endo	5.75(m)	5.07(t)	4.51(br t)	3.40(t)	3.07(br t)	5.07(m, H_A-C-H_B), 5.04(m, H_A-C-H_B)
8[c]	***exo syn-syn***	6.45 (m)	6.09 (t)	5.85 (br t)			4.82(m, H_A-C-H_B), 4.86(m, H_A-C-H_B)
	endo syn-anti	6.87 (m)	5.33 (t)	6.24(br t)			5.12(m, H_A-C-H_B), 4.74(m, H_A-C-H_B)
9[c]	***exo***	5.63(m)	5.11(t)	3.77(br t)	3.24(t)	2.75(br t)	5.09(m) H_A-C-H_B), 4.84(m, H_A-C-H_B), 0.16(s, $(CH_3)_3$-Si), 0.04(s, $(CH_3)_3$-Si)
	endo	5.48(m)	5.14(t)	3.89(br t)	3.47(t)	2.88(br t)	5.01(m, H_A-C-H_B), 4.68(m, (H_A-C-H_B), 0.14(s, $(CH_3)_3$-Si), 0.06(s, $(CH_3)_3$-Si)
10[c]	***exo syn-syn***	6.66(t)	5.50(dd)	5.20(br t)			4.87(m) H_A-C-H_B), 4.66(m, H_A-C-H_B), 0.42(s, $(CH_3)_3$-Si), 0.21(s, $(CH_3)_3$-Si)
	endo syn-anti	6.80(t)	5.75(dd)	6.10(br t)			4.78(m) H_A-C-H_B), 4.55(m, H_A-C-H_B), 0.49(s, $(CH_3)_3$-Si), 0.12(s, $(CH_3)_3$-Si)
11[c]	***exo***	5.23(m)	5.11(t)	3.15(br t)	4.16(t)	3.11(br t)	9.09(d, H_o-py), 5.35(m, H_A-C-H_B), 5.25(m, H_A-C-H_B)
	endo	5.19(m)	4.08(t)	2.78(br t)	3.06(t)	2.59(br t)	9.02(d, H_o-py), 5.31(m, H_A-C-H_B), 5.28(m, H_A-C-H_B)
12[c]	***exo***	5.78(m)	5.04(t)	3.09(br t)	4.39(t)	3.07(br t)	9.07(d, H_o-py), 5.32(m, H_A-C-H_B), 5.23(m, H_A-C-H_B)
	endo	5.46(m)	4.12(t)	2.58(br t)	3.01(t)	2.53(br t)	8.99(d, H_o-py), 5.28(m, H_A-C-H_B), 5.18(m, H_A-C-H_B)

[a] Chemical shifts, δ, are reported in ppm.[b] in C_6D_6 solution. [c] in $CDCl_3$ solution.



exo – **6**

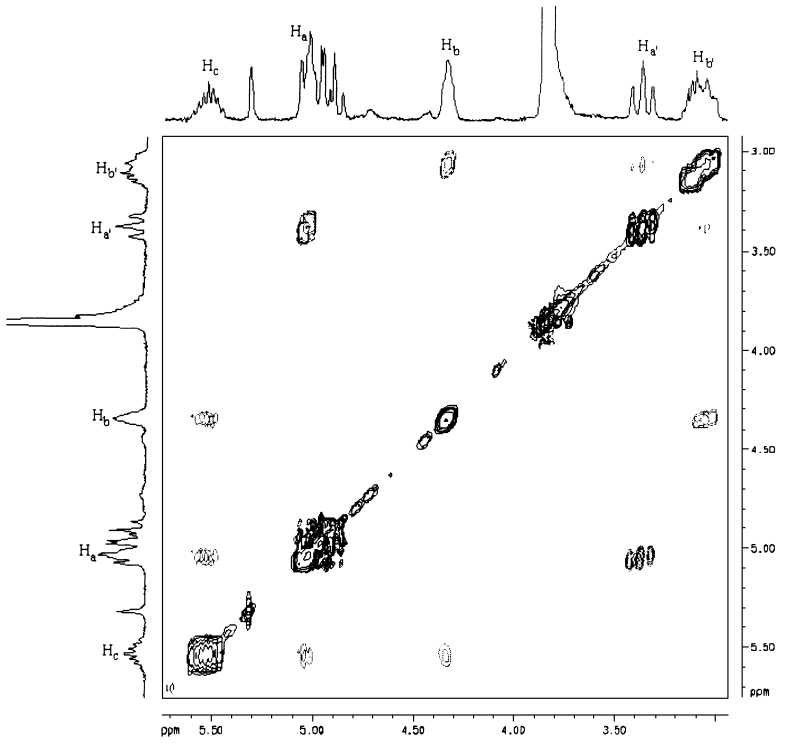


Figure 1. Allyl section of the phase-sensitive ^{1}H 2D-NOESY spectrum for the *exo*-isomer **6**

The ^{1}H NMR spectrum shows well-defined proton signals belonging only to one species and the $^{31}P\{^{1}H\}$ NMR spectrum presents only one pair of doublet resonances, confirming the presence in solution of one species. By ^{1}H 2D-NOESY analysis, this species was assigned as the *exo*-conformer and is further supported by the absence of any exchange cross-peak. The presence of one stable isomer in solution could be ascribed to the high steric hindrance of the *t*-butyl groups

in the *ortho*-position in the biphenol fragments. These groups, located below the Pd–allyl coordination plane, avoid any possible rotation around the Pd–η^1-allyl bond as expected in any exchange mechanism.

The assignment of all proton signals for the complex **6**, where only the *exo*-isomer is present in solution, allowed us to elucidate all the species present in solution for complexes **7**–**10**.

As far as compound [Pd(η^3-C_3H_5)((S)-**2**)]CF_3SO_3, **7**, is concerned, the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, shows two pairs of doublets relative to the phosphite (δ 170.6 ppm, $J_{P_bP_a} = 74$ Hz and δ 170.5 ppm, $J_{P_bP_a} = 73$ Hz) and the phosphine (δ 56.7 ppm, $J_{P_bP_a} = 74$ Hz and δ 55.3 ppm, $J_{PbPa} = 73$ Hz) moieties of coordinated ligand (*S*)-**2** in the *exo*- and *endo*-isomers present in solution in a ratio of 1:0.8. 2D-NOESY NMR spectroscopy enabled us to assign the allyl hydrogens resonances for the two isomers. As shown previously for **6**, the central allylic proton H_c presents two NOE cross-peaks with H_a and H_b that are related to $H_{a'}$ and $H_{b'}$, respectively. Phase-sensitive NOEs provides exchange information between the allyl resonances in the *endo*- and *exo*-isomers. As shown in Fig. 2, we find exchange cross-peaks between H_c^* and H_c, H_b^* and $H_{b'}$, H_b and $H_{b'}^*$, $H_{a'}^*$ and $H_{a'}$, and H_a^* and H_a.

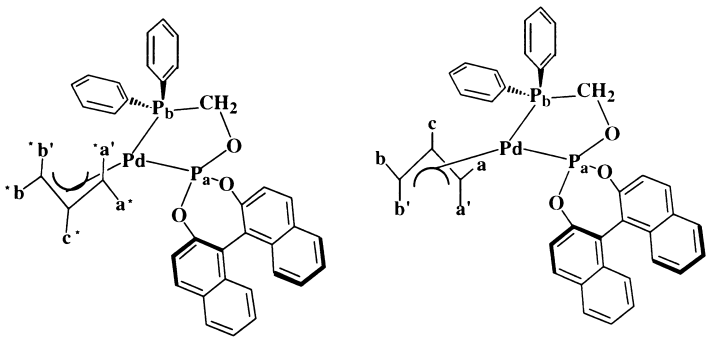
On the basis of the same conclusions reached by Pregosin et al.,[9] this process indicates an η^3-η^1-η^3 mechanism involving the opening of the Pd–C_a bond *cis* to the -PPh_2 group which is selective for the allylic carbon atom in the *trans* position to phosphito moiety since its *trans* influence is higher than that for the phosphine donor -PPh_2. $^{13}C\{^1H\}$ assignment of the allylic carbon atoms was performed by ^{13}C, ^1H correlation experiment [$^{13}C\{^1H\}$ δ ($CDCl_3$, 298 K): 123.5 ppm, C_c; 71.4 ppm, C_a; 72.9 ppm, C_b; 124.5 ppm, C_c^*; 71.2 ppm, C_a^*; 71.9 ppm, C_b^*]. In both isomers C_b lies slightly downfield compared to C_a and this is further evidence that C_b is the labile site in the allylic exchange as described above.

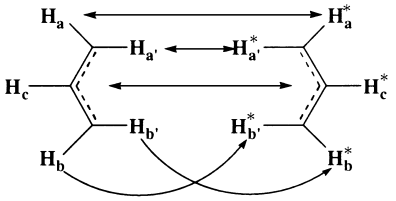
^1H and $^{31}P\{^1H\}$ NMR spectra of [Pd(η^3-PhCHCHCHPh)((S)-**2**)]CF_3SO_3, **8**, showed in solution the resonances relative to only two *exo syn–syn* and *endo syn–anti*-isomers confirming that the allylic rearrangement came from an η^3-η^1-η^3 mechanism. This feature is already known for compounds of this type.[9] Proton assignment of **8** was made possible by ^1H 2D-NOESY (see Table 2).

$^{13}C\{^1H\}$ assignment of the two isomers for complex **8** was performed by ^{13}C, ^1H correlation [$^{13}C\{^1H\}$ δ ($CDCl_3$, 298 K): 113.7 ppm, C_c; 90.9 ppm, C_a; 93.5 ppm, C_b; 111.0 ppm, C_c^*; 82.3 ppm, C_a^*; 98.0 ppm, C_b^*]. The two terminal allyl carbons C_a and C_b in the *endo syn–anti*-isomer have quite substantially different chemical shifts (C_a^* 82.3 ppm versus C_b^* 98.0 ppm), while in the *exo syn–syn* conformation the resonances have little difference, C_a 90.9 ppm versus C_b 93.5 ppm. Most probably, the high steric hindrance of the two allylic phenyl substituents in the *endo syn–anti* conformation led to this marked difference in chemical shifts.

The derivatives [Pd(η^3-C_3H_5)((S)-**3**)]CF_3SO_3, **9**, and [Pd(η^3-PhCHCHCHPh)((S)-**3**)] CF_3SO_3, **10**, were studied by NMR spectroscopy.

The behavior in solution of complex **9** is similar to the corresponding complex [Pd(η^3-C_3H_5)((S)-**2**)]CF_3SO_3, **7**, since we found in $^{31}P\{^1H\}$ NMR spectrum two pair of doublets and the pattern for the allylic protons in the ^1H NMR spectrum indicative of the presence of the *exo*- and *endo*-isomers. As evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectra, complex **10** was present in solution like two different conformers. ^1H 2D-NOESY led us to assign all the proton resonances relative to the *exo*- and *endo*-isomers for complex **9** and to the two *exo syn–syn* and *endo syn–anti*-isomers for complex **10**. We gained further structural information from the cross-peaks between the Si–Me_3 group and the *ortho*-hydrogens in the phenyl substituents of the allyl moiety *cis* to the phosphito fragment.





H_b is trans to phosphite P_a, H_a is trans to phosphine P_b

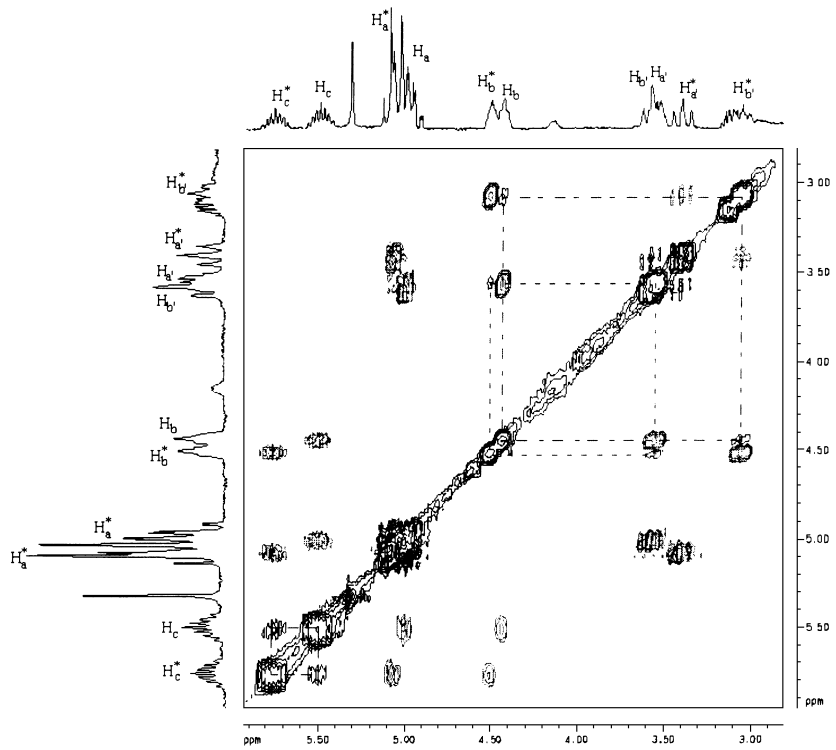


Figure 2. 2D-NOESY of **7** showing the various exchange peaks. The analysis of these data revealed selective exchange within the two *exo*- and *endo*-isomers

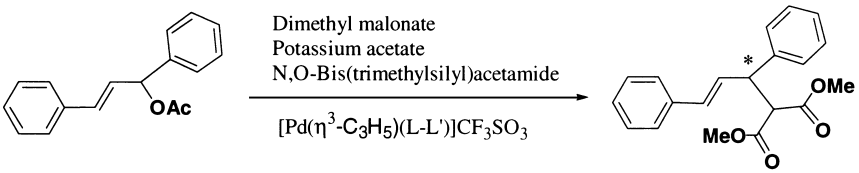
The ^{13}C and ^{1}H correlation allowed us to assign allylic carbon atoms for the isomers of complexes **9** and **10**. As regards the two isomers for the complex **9**, there is a small difference between the C_a and C_b chemical shifts [$^{13}C\{^{1}H\}$ δ ($CDCl_3$, 298 K): 124.9 ppm, C_c; 73.0 ppm, C_a; 71.7 ppm, C_b; 125.0 ppm, C_c^*; 72.6 ppm, C_a^*; 72.1 ppm, C_b^*], but the C_b resonance is at a higher field than C_a due to the steric hindrance of the *cis* $SiMe_3$ on C_a atom. $^{13}C\{^{1}H\}$ NMR chemical shifts (δ, in $CDCl_3$ at 298 K) relative to the two isomers of complex **10** are found as follows: 113.1 ppm, C_c; 92.7 ppm, C_a; 91.7 ppm, C_b; 112.7 ppm, C_c^*; 86.9 ppm, C_a^*; 98.9 ppm, C_b^*. As previously described for compound **8**, there is a marked chemical shifts difference between the two terminal allyl carbons C_a^* and C_b^* only in the the *endo syn–anti*-isomer of complex **10**.

With regard to ligands (*S*)-**4** and (*S*)-**5,** a satisfactory analysis of the structures in solution by 2D ^{1}H-NOESY technique has been possible only for palladium–allyl complexes [Pd(η^3-C_3H_5)((*S*)-**4**)]CF_3SO_3, **11**, and [Pd(η^3-C_3H_5)((*S*)-**5**)]CF_3SO_3, **12**, since the corresponding species [Pd(η^3-PhCHCHCHPh)((*S*)-**4**)]CF_3SO_3, **13**, and [Pd(η^3-PhCHCHCHPh)((*S*)-**5**)]CF_3SO_3, **14**, revealed a low stability in solution over a long time. For all these complexes, the lower field chemical shift of the *ortho*-proton of the pyridine is further evidence for the coordination of the pyridine nitrogen atom to the palladium center.[10] $^{31}P\{^{1}H\}$ NMR spectra of **11** and **12** species appear in any case as a broad signal showing that a fast equilibrium in the NMR time scale is taking place. This result is confirmed by ^{1}H NMR spectra, where similarly we find again a family of broad signals. 2D ^{1}H-NOESY has allowed us to identify in solution two different isomers with *exo*- and *endo*-conformation.

The NMR characterization in a solution of **13** and **14** has been possible only by ^{1}H NMR. The broadness of the signals in the $^{31}P\{^{1}H\}$ and ^{1}H NMR in a temperature range of 298–220 K indicated that exchange processes are present in solutions between all different conformations. The main reason for the speed of this exchange could be found in the absence of bulky substituents on the bound pyridine towards the *cis* allyl side that makes the pyridine unable to stop or even retard the rotation of the allyl around the Pd–C bond.

2.3. Catalytic reactions

The new ligands (*S*)-**2**–(*S*)-**5** have been tested in the palladium-catalyzed enantioselective substitution of 1,3-diphenyl-1,2-propenyl acetate by dimethylmalonate as shown in Scheme 2.



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Scheme 2.

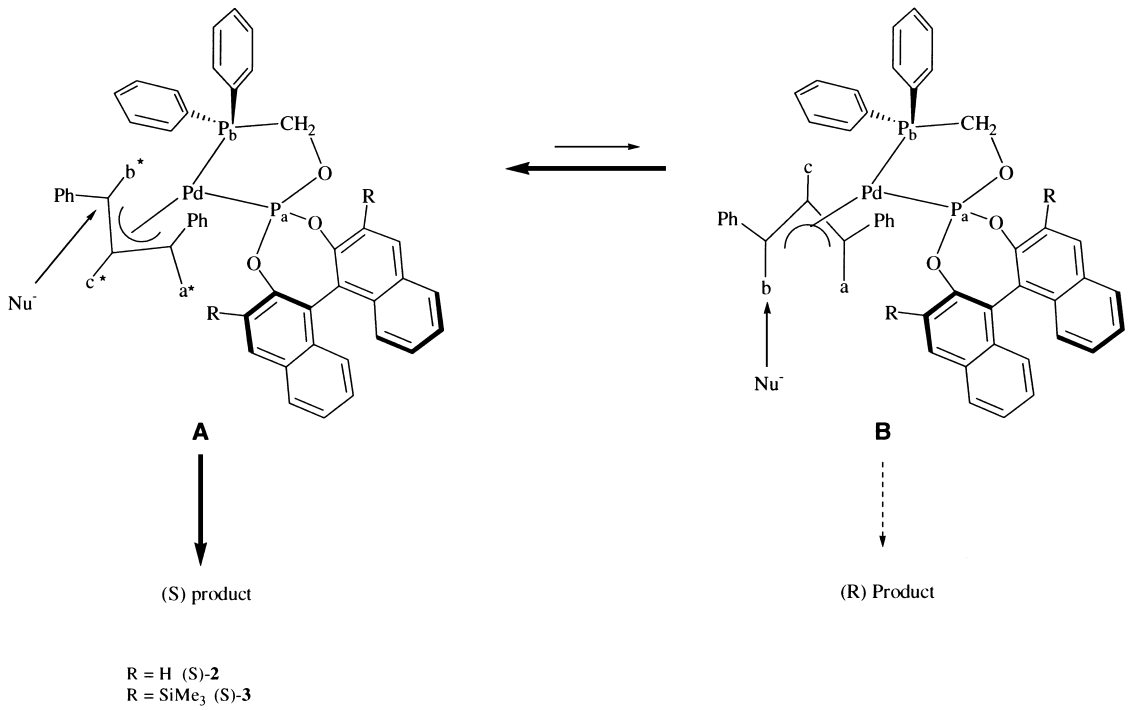
The mixture obtained by reaction of racemic (1,3-diphenyl-1,2-propenyl)acetate with the palladium catalyst [Pd(η^3-C_3H_5)((*S*)-**2**)]CF_3SO_3 in dichloromethane solution, followed by dimethylmalonate addition, was kept at 25°C for 16 h (Table 3: entry 1) under continuous stirring and afterwards afforded the allyl-substituted product in good yield (95%) and acceptable enantioselectivities (71% e.e. in the (*S*) form).

Table 3
Enantioselective allylic alkylation with $[(\eta^3\text{-}C_3H_5)Pd\ (L\text{–}L')]^+$ complexes (L–L′ = **2**–**5**) according to Scheme 3[a]

Entry	L-L'	Solvent	T (°C)	time	Yield[d]	e.e.%[e]
1	**2**	CH_2Cl_2	25	16 h	95	71 (S)
2	**2**	CH_2Cl_2	- 20	16 h	93	70 (S)
3	**2**	THF	25	16 h	94	69 (S)
4	**2**[b]	CH_2Cl_2	25	16 h	95	71 (S)
5	**2**[c]	CH_2Cl_2	25	16 h	95	71 (S)
6	**3**	CH_2Cl_2	25	32 h	95	68 (S)
7	**4**	CH_2Cl_2	25	16 h	94	0
8	**5**	CH_2Cl_2	25	16 h	95	0
9	**5**[b]	CH_2Cl_2	25	16 h	95	0

[a] 1 mol % of $[(\eta^3\text{-}C_3H_5)Pd(L\text{-}L')]CF_3SO_3$, 3 equiv. of $H_2C(COOMe)_2$, 3 equiv. of BSA, 1 mol % of KOAc, [b]catalyst prepared in situ from 0.5 mol % of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and 1.5 mol % of ligand, [c] using the PF_6 salt [d] Yield of analytically pure product after column chromatography [e] The e. e. conversion was determinated by ^1H NMR spectroscopy ($CDCl_3$/0.25 equiv $[Eu(hfc)_3]$; splitting of the signal for the left methoxy group).

The enantioselectivity is not significantly affected by any modification of the reaction conditions. Indeed, either the change of solvent from CH_2Cl_2 to THF, or temperature from 25 to –20°C, does not significantly modify the e.e. of the product (entry 2 and 3); a decrease of the temperature gives rise to a decrease of the product yield (entry 2). When the hexafluorophosphate complex $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{2})]PF_6$, instead of the corresponding CF_3SO_3 salt, was employed as catalyst, the enantiomeric excess and product yield were unchanged (entry 5). The absolute configuration of the product was determined from its specific rotation according to the literature data.[8] Use of the *ortho*-bis(trimethylsilyl)substituted binaphthalene derivative (*S*)-**3** does not significantly affect the enantiomeric excess and the yield of the catalytic reaction, even though the reaction is slower than with ligand (*S*)-**2** (entry 6). As evidenced by NMR spectroscopy, the *ortho*-trimethylsilyl substituent on the binaphthalene interacts with the phenyl ring of the allylic moiety coordinated to palladium(II); this implies a transition state of higher activation energy than for ligand (*S*)-**2**. However, the enantioselectivity of the allylic alkylation was not modified, indicating that nucleophilic attack of the malonate occurs, as for the ligand (S)-**2**, preferentially at the allylic carbon far from the binaphthalene moiety, namely *trans* to phosphite group in (*S*)-**3**, as reported in the NMR discussion. It has been demonstrated that the nucleophile preferentially attacks the allylic carbon atom with the longer Pd–C bond which is consequently more reactive. [2f,i,11] Elongation of the Pd–C bond is a consequence either of the *trans*-influence of the donor-atom in the *trans* position or of steric hindrance between the substituent at allylic terminal atoms and the coordinated chiral ligand. [2f,i,11] The results obtained using the ligand (*S*)-**3** indicate that, for



Scheme 3.

donor-atoms with a high *trans* influence, the steric factors are slightly important. Thus, with (*S*)-**2** or (*S*)-**3** ligands, the nucleophilic attack of the malonate occurs preferentially at the allylic carbon atom activated by the higher *trans*-effect of the phosphite than the phosphine group.

By using ligands (*S*)-**4** and (*S*)-**5** in the reaction reported in Scheme 2, product **15** was obtained as a racemic mixture in high yield (runs 7 and 8). Ligands (*S*)-**4** and (*S*)-**5** are bidentate P,N-ligands which afford mononuclear cationic allylic-palladium(II) chelated complexes by reaction with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in the presence of $AgCF_3SO_3$ salt. They contain the phosphite framework as (*S*)-**2** but, differently to (*S*)-**2**, a pyridine nitrogen atom instead of the PPh_2 fragment. Also in (*S*)-**4** and (*S*)-**5** the *trans*-influence of the phosphite is higher than that of the other donor group. Thus, the lack of enantiomeric excess using (*S*)-**4** and (*S*)-**5** must be a consequence of the presence of the pyridine instead of the PPh_2; the effect is not principally electronic (in this case the enantiomeric excess should be only modified) but due to smaller steric hindrance of the pyridine with respect to PPh_2. As deduced from NMR spectra, the allylic-intermediates $[Pd(PhCHCHCHPh)((S)\text{-}\mathbf{4})]^+$ and $[Pd(PhCHCHCHPh)((S)\text{-}\mathbf{5})]^+$, formed in the reaction course, assume four possible isomeric forms and undergo fast exchange processes. Under these conditions the steric effect in the nucleophilic attack by the malonate is low and the enantiodiscrimination is mastered. NMR spectra, in solution, of the complexes $[Pd(PhCHCHCHPh)((S)\text{-}\mathbf{4})]^+$ and $[Pd(PhCHCHCHPh)((S)\text{-}\mathbf{5})]^+$ support these assertions. Indeed, they give very broad signals in the temperature range 298–220 K indicating exchange processes between the four possible different configurational isomers (*syn–syn exo*, *syn–anti exo*, *syn–syn endo*, *syn–anti endo*). Pregosin et al.[12] showed, by a detailed NMR study, that the palladium–allyl cation, containing the PhCHCHCHMe allyl and the bidentate P,S-ligand (*R*)-2-ethylthio-1-(phenylethyl)-(*R*)-binaphthyl phosphite, forms in solution at least five components

which undergo selective exchange; they considered that the presence of much components in solution is the reason for the modest selectivities observed in the allylic alkylation by this P,S-ligand.

Differently from the complexes **13** and **14**, the intermediates [Pd(PhCHCHCHPh)((*S*)-**2**)]$^+$ and [Pd(PhCHCHCHPh)((*S*)-**3**)]$^+$, containing ligands (*S*)-**2** and (*S*)-**3**, which afford the highest enantioselectivity, exist in solution only as a couple of diastereomeric form (*syn–syn exo*; *syn–anti endo*) in the ratio of 1:0.8. As shown in Scheme 3, the nucleophilic attack occurs at the allyl carbon C_b *trans* to the phosphito group. The fact that the (*S*)-product is obtained as a major enantiomer indicates higher reactivity of the *endo syn–anti*-isomer **A** than the *exo syn–syn*-isomer **B**. It is important to consider that the observed e.e. for the allylation is different from the isomeric distribution of the intermediate allyl-complexes, indicating different rates for the nucleophilic attack at the carbon atom of diastereomeric forms. In conclusion, the number and the relative concentrations of the configurational isomers of the Pd–allyl complexes present in solution as intermediate in the allylic alkylation is a factor determining the enantioselectivity of the process. This aspect was previously also considered by Togni, Pregosin et al.[12,13]

Studies that consider ligands such as (*S*)-**4** and (*S*)-**5** containing bulky substituents on the pyridine ring are in progress, with the aim to further ascertain that the enantioselectivity of the process increases with a decrease in the number of Pd–allyl configurational isomers formed as a consequence of the steric requirements of the pyridine moiety.

3. Experimental

Published methods were used to prepare the compounds Ph_2PCH_2OH,[14] 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene,[15] (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene,[15] (*S*)-4-chloro-2,6-bis-trimethylsilanyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene,[6] [Pd(η^3-PhCHCHCHPh)(μ-Cl)]$_2$.[2f] All other reagents were purchased from Sigma–Aldrich and were used as supplied. Solvents were dried by standard procedures. All experiments were performed under purified argon. For column chromatography, silica gel 60 (220–440 mesh) purchased from Fluka was used. 1D and 2D NMR experiments were carried out using a Bruker AMX R300 spectrometer. ^{1}H NMR spectra were referenced to internal tetramethylsilane and ^{31}P{^{1}H} spectra to external 85% H_3PO_4. Standard pulse sequences were employed for ^{1}H–2D-NOESY,[16] ^{13}C, ^{1}H ,[17] ^{31}P, ^{1}H correlation studies.[18] The phase sensitive NOESY experiments used mixing times of 0.8 s. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

3.1. 6-[(Diphenylphosphanyl)methoxy]-4,8-di-tert-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[a,c]cycloheptene ***1***

A solution of Ph_2PCH_2OH (0.71 g, 3.28 mmol) and Et_3N (0.653 g, 6.57 mmol) in toluene (5 ml) was added dropwise to a solution of 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene (1.390 g, 3.28 mmol) in the same solvent (15 ml) at 0°C. The reaction mixture was stirred overnight at room temperature and then the precipitate of Et_3N·HCl formed was removed by filtration. The toluene was evaporated from the filtrate. The residue was washed with hexane (5 ml) and dried. A white solid was obtained in 90% yield (1.781 g, 2.95 mmol). Anal. calcd for $C_{35}H_{40}O_5P_2$: C, 69.76; H, 6.69. Found: C, 68.56; H, 6.63.

3.2. (S)-4-[(Diphenylphosphanyl)methoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4a′]dinaphthalene **2**

This compound was obtained by an analogous procedure to **1**, as a white solid, by reaction of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (0.612 g, 1.75 mmol) and Ph_2PCH_2OH (0.377 g, 1.75 mmol). Yield: 85% (0.789 g, 1.49 mmol). Anal. calcd for $C_{33}H_{24}O_3P_2$: C, 74.71; H, 4.56. Found: C, 73.52; H, 4.61.

3.3. (S)-4-[(Diphenylphosphanyl)methoxy]-2,6-bis-trimethylsilanyl-3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalene **3**

This compound was prepared by an analogous procedure to **1**, as a white solid, by reaction of (*S*)-4-chloro-2,6-bis-trimethylsilanyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (0.124 g, 2.50 mmol) and Ph_2PCH_2OH (0.540 g, 2.50 mmol). Yield: 90% (1.518 g, 2.25 mmol). Anal. calcd for $C_{39}H_{40}O_3P_2Si_2$: C, 69.41; H, 5.97. Found: C, 64.27; H, 5.89.

3.4. (S)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yloxymethyl)pyridine **4**

A solution of PyOH (0.166 g, 1.77 mmol) and Et_3N (0.358 g, 3.54 mmol) in THF (8 ml) was added dropwise to a solution of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (0.620 g, 1.77 mmol) in the same solvent (15 mL) at 0°C. The resulting solution was stirred overnight at room temperature and then the solvent was vacuum evaporated. The pure ligand **4** was extracted by toluene:hexane (1:3) from the resulting white powder. Yield 35% (0.253 g, 0.619 mmol). Anal. calcd for $C_{25}H_{16}NO_3P$: C, 73.35; H, 3.94; N, 3.42. Found: C, 73.61; H, 3.99; N, 3.46.

3.5. (S)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yloxy)pyridine **5**

This compound was obtained by an analogous procedure to **1**, as a white solid, by reaction of 2-(hydroxymethyl)pyridine (0.225 g, 2.06 mmol) and (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (0.723 g, 2.06 mmol). Yield: 90% (0.785 g, 1.85 mmol). Anal. calcd for $C_{26}H_{18}NO_3P$: C, 73.75; H, 4.29; N, 3.31. Found: C, 73.25; H, 4.23; N, 3.30.

3.6. $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})]CF_3SO_3$ **6**

The following procedure for the preparation of **6** is typical and it was used for the synthesis of all $[Pd(\eta^3\text{-}C_3H_5)(L\text{–}L')]CF_3SO_3$ complexes (L–L′ = **1**–**5**). A solution of **1** (0.457 g, 0.76 mmol) in CH_2Cl_2 (5 ml) was added to a stirred solution of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl]_2$ (0.111 g, 0.30 mmol) in the same solvent (15 ml). After ca. 30 min, $AgCF_3SO_3$ (0.156 g, 0.60 mmol) was added, and the precipitated AgCl filtered on Celite. The filtrate was vacuum reduced to ca. 3 ml and addition of hexane (20 ml) gave a yellow solid. Yield 80% (0.432 g, 0.48 mmol). Anal. calcd for $C_{39}H_{45}F_3O_8P_2PdS$: C, 52.09; H, 5.04. Found: C, 51.10; H, 5.07.

3.7. $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-}\mathbf{2})]CF_3SO_3$ **7**

Yellow powder. Yield 86%. Anal. calcd for $C_{37}H_{29}F_3O_6P_2PdS$: C, 53.73; H, 3.53. Found: C, 53.80; H, 3.55.

3.8. [Pd(η³-C₃H₅)((S)-3)]CF₃SO₃ 9

Yellow powder. Yield 83%. Anal. calcd for $C_{43}H_{45}F_3O_6P_2PdSSi_2$: C, 53.17; H, 4.67. Found: C, 53.20; H, 4.70.

3.9. [Pd(η³-C₃H₅)((S)-4)]CF₃SO₃ 11

White powder. Yield 80%. Anal. calcd for $C_{29}H_{21}F_3NO_6PPdS$**:** C, 49.34; H, 3.00; N, 1.98. Found: C, 49.20; H, 2.97; N, 1.95.

3.10. [Pd(η³-C₃H₅)((S)-5)]CF₃SO₃ 12

White powder. Yield 82%. Anal. calcd for $C_{30}H_{23}F_3NO_6PPdS$: C, 50.05; H, 3.22; N, 1.95. Found: C, 50.12; H, 3.26; N, 1.98.

3.11. [Pd(η³-PhCHCHCHPh)((S)-3)]CF₃SO₃ 10

In a similar manner to the preparation of **6**, [Pd(η³-PhCHCHCHPh)(L–L′)]CF_3SO_3 (L–L′ = **1**–**5**) complexes were prepared. Compound **10** was synthesized by reaction of [Pd(η³-PhCHCHCHPh)-(μ-Cl)]$_2$ (0.131 g, 0.20 mmol) and (*S*)-**3** (0.500 g, 0.49 mmol). Yield: 85% (0.382 g, 0.34 mmol). Anal. calcd for $C_{55}H_{53}F_3O_6P_2PdSSi_2$: C, 58.79; H, 4.75. Found: C, 58.84; H, 4.77.

3.12. [Pd(η³-PhCHCHCHPh)((S)-2)]CF₃SO₃ 8

Orange powder. Yield 82%. Anal. calcd for $C_{49}H_{37}F_3O_6P_2PdS$: C, 60.10; H, 3.81. Found: C, 60.17; H, 3.83.

3.13. [Pd(η³-PhCHCHCHPh)((S)-4)]CF₃SO₃ 13

Orange powder. Yield 81%. Anal. calcd for $C_{41}H_{29}F_3NO_6PPdS$: C, 57.39; H, 3.41; N, 1.63. Found: C, 57.22; H, 3.48; N, 1.65.

3.14. [Pd(η³-PhCHCHCHPh)((S)-5)]CF₃SO₃ 14

Orange powder. Yield 83%. Anal. calcd for $C_{42}H_{31}F_3NO_6PPdS$: C, 57.84; H, 3.58; N, 1.61. Found: C, 57.92; H, 3.53; N, 1.67.

3.15. Allylic alkylation

The procedure applied for allylic alkylation was the same as described by Pfaltz et al.[2e] In many cases [Pd(η³-C_3H_5)(L–L′)]CF_3SO_3 complexes [L–L′ = (*S*)-**2**–(*S*)-**5**] were used as catalyst precursors. For yields and enantiomeric excesses see Table 1.

Acknowledgements

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