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Effect of chelating *vs.* bridging coordination of chiral short-bite P–X–P (X = C, N, O) ligands in enantioselective palladium-catalysed allylic substitution reactions †

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The chiral short-bite ligands (R_a,R_a)-bis(dinaphthylphosphonito)methane, (R_a,R_a)-**1**, (R_a,R_a)-bis-dinaphthyl-pyrophosphite, (R_a,R_a)-**2**, (S_c)-bis(diphenylphosphino)-*sec*-butylamine, (S_c)-**3**, (R_a,R_a)-bis(dinaphthylphosphonito)-phenylamine, (R_a,R_a)-**4a**, (R_a,R_a,S_c)-bis(dinaphthylphosphonito)-*sec*-butylamine, (R_a,R_a,S_c)-**4b**, and (R_a,S_c)-(dinaphthylphosphonito)(diphenylphosphino)-*sec*-butylamine, (R_a,S_c)-**5**, have been synthesised. The cationic palladium–allyl mononuclear chelate, [Pd(η^3-PhCHCHCHPh)(μ-L–$L_{short\text{-}bite}$)]PF_6 [L–$L_{short\text{-}bite}$ = (S_c)-**3**, (R_a,R_a)-**4a**, (R_a,R_a,S_c)-**4b** and (R_a,S_c)-**5** for complexes **8**, **9**, **10** and **11**, respectively] and binuclear bridged [Pd(η^3-PhCHCHCHPh)-(μ-R_a,R_a-**2**)]$_2$(PF_6)$_2$, **12**, have been isolated. The short-bite chiral ligands synthesised have been tested in the palladium–allyl catalysed substitution reaction of 1,3-diphenylallyl acetate with dimethyl malonate. The catalytic system was studied, in solution, by a multinuclear NMR technique. In the catalytically active species formed with (R_a,R_a)-**2** ligand, [Pd(η^3-PhCHCHCHPh)(R_a,R_a-**2**)]$_2$(PF_6)$_2$, **12**, the palladium(II) centres are bridged by two ligands which are forced to adopt a nearly *cis*-coordination to allow coordination of the allyl-moiety. Semiempirical calculations on a biphenyl-model molecule, similar to the species **12**, indicate that this situation induces a strain and rigid conformation in the chiral ligands, which produce differences in the terminal allyl carbon atoms. As consequence, the catalytic product was obtained with an enantiomeric excess of 57.1% in the *S* form. A low e.e. value was obtained when the (R_a,R_a)-**1**, (S_c)-**3**, (R_a,R_a)-**4a**, (R_a,R_a,S_c)-**4b** and (R_a,S_c)-**5** ligands have been tested in the same palladium-catalysed reaction.

Introduction

Short-bite ligands have been widely used in organometallic chemistry owing to their structural features.[1] In fact, they are bidentate ligands in which the donor-atoms are separated by one spacer atom, as C, N, O, S, and are able to give, by co-ordination to a metal centre, either chelated mononuclear or bridged binuclear complexes.[1] In the mononuclear complexes, the short-bite ligand forms a strained four-membered ring with a very small bite angle; in the binuclear complexes, two metal centres are held in close proximity by the features of the bridging short-bite ligand. For the latter coordination mode, novel modes of substrate activation, as a consequence of cooperative interactions between the metal centres, can be achieved.[2] Owing to these properties, both mononuclear and binuclear complexes, containing short-bite ligands, have been found to act as homogeneous catalysts.[3]

Among the short-bite ligands, the bis(diphenylphosphino)-methane (dppm) and analogous 1,1-diphosphines,[1a,c,4] the bis(diphenylphosphino)methylamine (dppma)[1e,f,5] and the 2-(diphenylphosphino)pyridine (Ph_2PPy)[1b,d,6] have been widely studied and have shown great versatility either to bridge metal centres or to display chelating behaviour.

As far as we know, the only chiral optically pure short-bite ligands reported in literature are **A**–**C**.[7]

Among them only the diphosphines MiniPHOS **A** were explored as catalyst precursors in asymmetric catalysis, affording excellent enantioselectivity in representative reactions.[7]

Either the conformational rigidity of the highly strained four-membered ring formed by chelation, or the cooperative interaction between metal centres in the binuclear complexes can promote beneficial effects in the asymmetric C–C formation catalysis.[3d] On this basis, we started with the synthesis of new ligands, with structural features analogous to dppm, dppma, and Ph_2PPy, containing the chiral moiety –P(binaphthyl) instead of $–PPh_2$. In a subsequent step of the work, we explored the coordinating properties of the synthesised ligands toward palladium(II)–allyl substrates. This study was preliminary to the use of such systems, containing palladium(II)–allyl-substrates and the chiral P–X–P (X = C, N, O) short-bite ligands, in conventional palladium-catalysed asymmetric allylic alkylation reactions. The work was focused to have insight on the effect of chelating or bridging coordination mode of P–X–P short-bite ligand in the palladium-catalysed allylic substitution reactions.

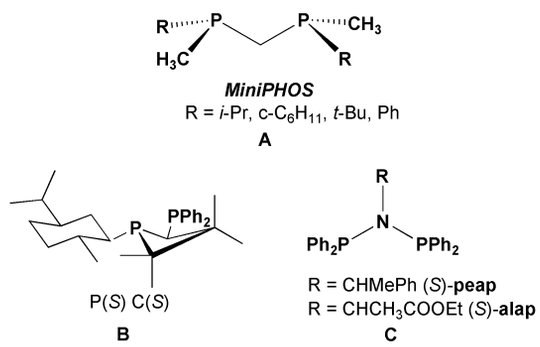

Chart 1

Results and discussion

Synthesis of the ligands

The new short-bite chiral ligands synthesised are reported in Fig. 1.

The synthesised ligands, in principle, should behave either as chelating, and originate four-membered metallacycles, or as bridging ligands to give bimetallic species. The different value

† Electronic supplementary information (ESI) available: Colour versions of Fig. 2 and Fig. 4. See http://www.rsc.org/suppdata/dt/b3/b309385a/

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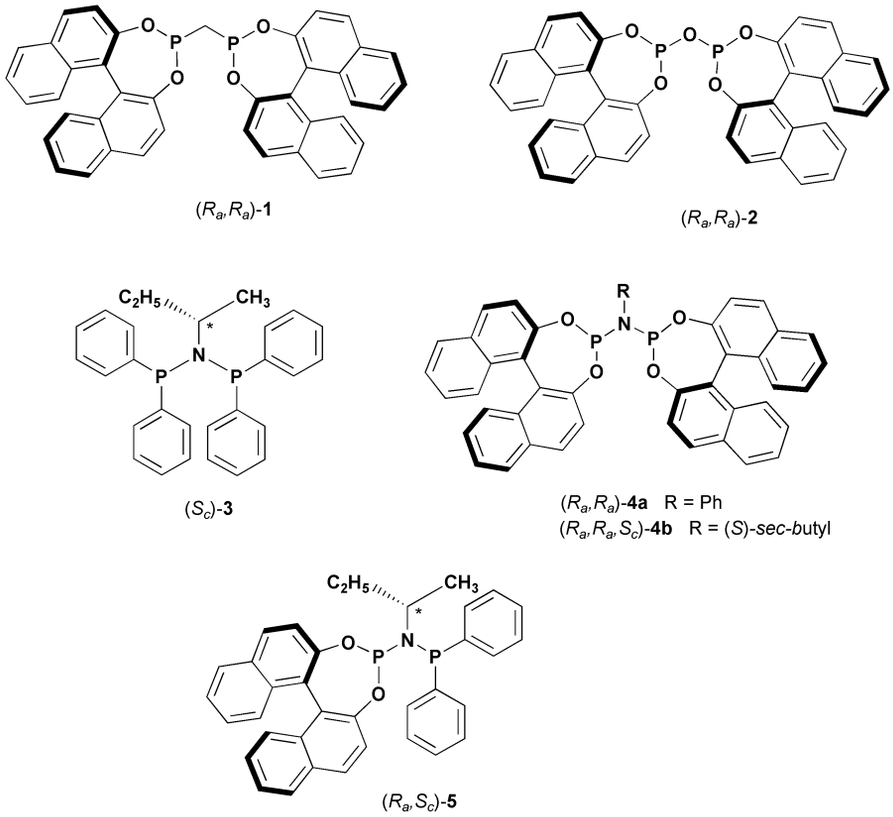


Fig. 1 Synthesised ligands.

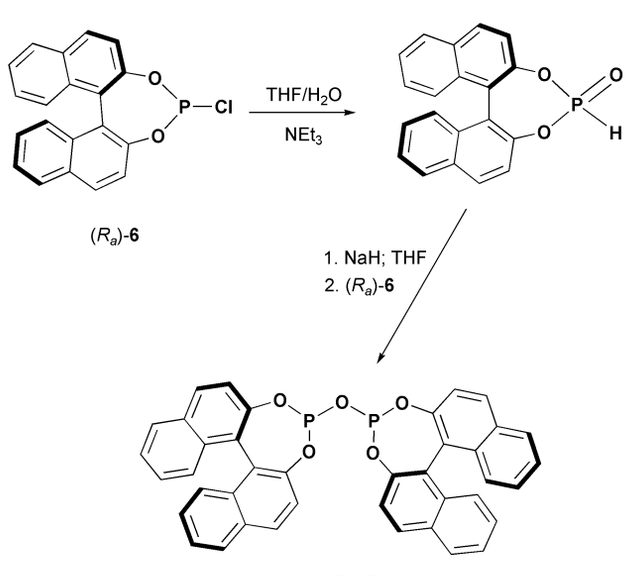
of the angle P–X–P (X = C, N, O) should be the factor determining their coordination mode.

The ligand (R_a,R_a)-**1** was easily obtained from the reaction of bis(dichlorophosphino)methane with (R_a)-binaphthol, in a molar ratio 1 : 2, in toluene, at room temperature, in the presence of an excess of NEt_3. It is a microcrystalline white solid, moderately stable in the air and in solution; its $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$, shows a singlet at δ 204.0.

We attempted the synthesis of a compound similar to 2-(diphenylphosphino)pyridine, Ph_2PPy, containing axial chirality at phosphorus substituents, following the method reported to obtain this short-bite ligand.[8] All the attempts to obtain it by reaction of 2-bromopyridine with n-BuLi, in THF at 173 K, and subsequently with the phosphorochloridite derived from (R_a)-binaphthol, (R_a)-**6**, failed and afforded to a mixture without the desired product. The major product shows in the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$, a signal (145.4 ppm) at frequency significantly shifted to higher field compared to the phosphonito group; it was separated by column chromatography and characterized by elemental analysis, mass spectrum and IR and NMR spectroscopy, as the bis(binaphthyl)pyrophosphite ligand, (R_a,R_a)-**2**.

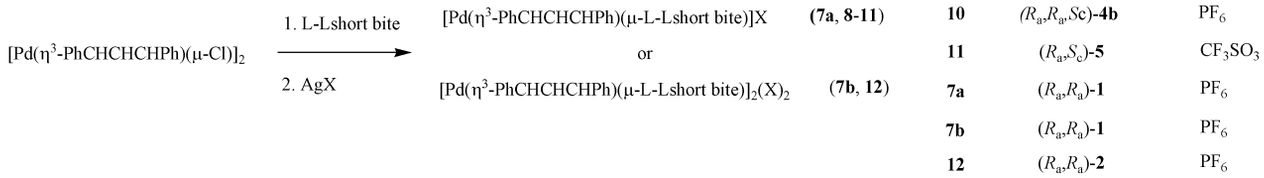
The formation of (R_a,R_a)-**2** should occur by partial formation of the corresponding phosphonate from the reaction of (R_a)-**6** with little amount of H_2O; this is in tautomeric equilibrium with the phosphite species.[9] The reaction of the phosphite with the unreacted phosphorochloridite, (R_a)-**6**, in the presence of pyridine, afforded the final product (R_a,R_a)-**2** in low yields. A similar reaction path was recently proposed by Pastor *et al.*[10] for the synthesis of a sterically congested pyrophosphite, starting from the phosphorochloridite derived from 3,3′, 5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol. The synthesis of diphosphoxanes by reaction of phosphorochloridite with the corresponding phosphonate, in the presence of an hydrogen chloride acceptor, is usually employed.[11,12]

We obtained the (R_a,R_a)-**2** ligand in high yields revising the synthesis method. The phosphonate was prepared by hydrolysis of the phosphorochloridite in tetrahydrofuran containing a stoichiometric amount of H_2O, in the presence of NEt_3; this was converted to corresponding sodium salt by reaction with sodium hydride, in tetrahydrofuran. Then, the addition of the phosphorochloridite, (R_a)-**6**, in the 1 : 1 molar ratio, to this solution containing the sodium phosphonato, afforded the pyrophosphite ligand (R_a,R_a)-**2**, in high yields.



Scheme 1

The *N*,*N*-bis(diphosphino)alkylamine, (S_c)-**3**, *N*,*N*-bis(diphosphonito)alkyl-amine, (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b** and mixed *N*-(phosphino)-*N*-(phosphonito)-alkylamine, (R_a,R_a,S_c)-**5**, have been designed to determine the effects associated with the nature, the absolute configuration and the number of the stereogenic centres in the coordinated ligands.



	L-Lshort bite	X
8	(S_c)-**3**	PF_6
9	(R_a,R_a)-**4a**	PF_6
10	(R_a,R_a,S_c)-**4b**	PF_6
11	(R_a,S_c)-**5**	CF_3SO_3
7a	(R_a,R_a)-**1**	PF_6
7b	(R_a,R_a)-**1**	PF_6
12	(R_a,R_a)-**2**	PF_6

Scheme 2

Ligands similar to (S_c)-**3**, in which R = CHMePh and $CHCH_3COOEt$, were previously reported but they were not used in asymmetric catalysis.[7]

Literature reports indicate that the presence of an alkyl group on the nitrogen atom of the *N*,*N*-bis(diphosphino)alkylamines results in favoured formation of a four-membered strained ring when the ligand coordinates to a metal center.[5d] We confirmed that the *N*,*N*-bis(diphosphino)alkylamines coordinate as chelating ligand by an X-ray diffraction structural determination on [M(S_c-**3**)Cl_2] (M = Pd, Pt) complexes.[13]

The diphosphinoamines and diphosphonitoamines chiral ligands have been synthesised by the reaction of the corresponding primary amine RNH_2 (R = Ph, (S_c)-(+)-*sec*-$CHC_2H_5CH_3$) with the diphenylchlorophosphine or (R_a)-**6**, in the molar ratio 1 : 2, in toluene at 0 °C, in the presence of an excess of NEt_3. Differently from the other P–N–P ligands here reported, (S_c)-**3** shows in the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$, at 298 K, a broad signal at δ 49.6; this signal, at 220 K, raises two doublets centred at δ 52.9 and 42.9, with $^2J_{PP}$ of 24.0 Hz. At 330 K the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ 51.5. In the ^1H NMR spectrum, the resonance of the methyl group bonded to stereogenic carbon atom appears as a doublet; while the phenylic protons show a dynamic behaviour, the methyl group resonance is not affected by temperature variation. A similar behaviour in the $^{31}P\{^1H\}$ NMR variable-temperature spectrum was observed for other diphosphinoamines and was explained considering that these species, in solution, different conformations can adopt.[14]

The presence of conformers can be related to the restricted rotation about the P–N bonds of the diphosphinoamine and to the magnitude of their torsional barriers. The $^2J_{PP}$ of 24.0 Hz found for (S_c)-**3** supports[14] the presence of conformers with C_s symmetry; no evidence of the presence of the $C_{2v'}$ conformer was obtained.

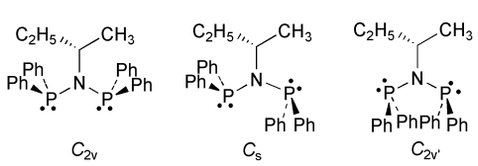


Chart 2

The (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b** ligands have been obtained as white solids, from the reaction of phenylamine and (S_c)-(+)-*sec*-butylamine, respectively, with (R_a)-**6**, in the molar ratio 1 : 2, in toluene, at 0 °C, using an excess of NEt_3. Their $^{31}P\{^1H\}$ NMR spectra, in $CDCl_3$, at 298 K show a sharp singlet at δ 136.9 and 138.0 relative to the ligand (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b**, respectively. The bulkiness of the substituents on the phosphorus atoms does not allow in this case the rotation around the P–N bonds, precluding the more sterically stable C_s conformer formation.

The synthesis of the mixed phosphino-phosphonito ligand (R_a,S_c)-**5** was practicable owing to different rate of hydrogen substitution from the primary amine (S_c)-(+)-*sec*-butylamine;[15] the product was better obtained by reacting the (S_c)-(+)-*sec*-butylamine first with (R_a)-**6**, in the molar ratio 1 : 1, in toluene, at room temperature, in the presence of an excess of NEt_3; next, *in situ*, was added the chlorodiphenylphosphine, in the molar ratio 1 : 1, to effect complete hydrogen replacement of (S_c)-(+)-*sec*-butylamine. The reaction was followed by $^{31}P\{^1H\}$ NMR spectra. At the end, the reaction mixture contains (R_a,S_c)-**5**, together with little amount of (R_a,R_a,S_c)-**4b** and of corresponding phosphino-oxide ligands. The pure (R_a,S_c)-**5** was obtained by flash chromatography on SiO_2 column.

Synthesis of catalytic species [Pd(η³-PhCHCHCHPh)(L–$L_{short\text{-}bite}$)]PF_6 and [Pd(η³-PhCHCHCHPh)(μ-L–$L_{short\text{-}bite}$)]$_2$-$(PF_6)_2$

Preliminarily, to test the catalytic system containing the palladium(II)–allyl species and the chiral P–X–P (X = C, N, O) short-bite ligands in the substitution reaction of 1,3-diphenylallyl acetate with dimethylmalonate, we synthesised the catalytic allyl species of the type [Pd(η³-PhCHCHCHPh)(L–$L_{short\text{-}bite}$)]PF_6 and/or [Pd(η³-PhCHCHCHPh)(μ-L–$L_{short\text{-}bite}$)]$_2(PF_6)_2$ with the aim to obtain information about their conformations in solution.

The compounds have been characterized by elemental analysis, conductivity values and spectroscopic multinuclear NMR studies; these will be discussed below. A conductivity value of 183 μS in acetone solution, using a 5×10^{-4}–10^{-4} molar concentration range, indicates a dimeric structure for **12** and further supports the results reached on the basis of NMR data (see below). Unfortunately, we are not able to obtained crystals of compound **12** suitable for X-ray analysis. Compound **7**, obtained by reacting [Pd(η³-PhCHCHCHPh)(μ-Cl)]$_2$ with the stoichiometric amount of (R_a,R_a)-**1** following the procedure described above, formed as a mixture of mononuclear and binuclear cationic species, which we are not able to separate; their characterization was supported by multinuclear NMR studies.

NMR studies

The catalytically active species **7**–**12** have been generated, in $CDCl_3$ solution, *in situ*, into the NMR tube, as previously described. When the equilibrium is reached, all the conformational isomers present in solution have been detected by ^1H, ^{13}C and ^{31}P NMR spectroscopy.

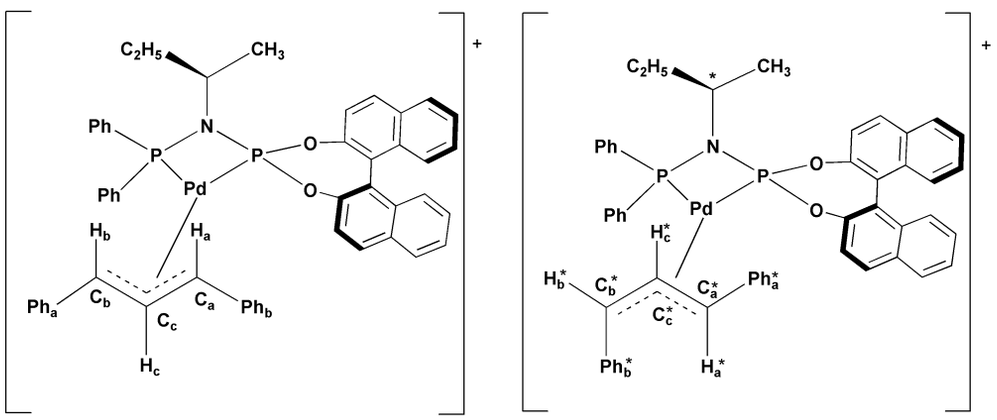
The enantioselectivity of the allylic substitution reaction process is determined by the regioselectivity of the nucleophilic attack; the latter depends from the ability of the coordinated chiral ligand to induce different nucleophilic character to the two terminus carbons on the allyl-group.[16]

By a multinuclear NMR study in solution, it was very useful to know: (i) the chelating or bridging coordination mode assumed by the short-bite ligand; (ii) the allylic conformational isomers present in the catalytic conditions and the existence of exchange processes;[17] (iii) possible steric or electronic effect which will determine the site of the nucleophilic attack.[17] It is clear that chelating or bridging coordination of the bidentate

Table 1 Relevant ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopic data of palladium(II)–phenylallyl compounds **7**–**12**[a,b]

	$\delta(^{1}H)$		$\delta(^{31}P)$			$\delta(^{13}C)$		
Compound	H_a	H_b	P_a	P_b	$^{2}J_{PaPb}$[c]	C_a	C_b	Conformation
7a	4.74	5.47	173.0			79.5	82.2	*exo syn–syn*
7b	6.19	6.52	177.8	171.6	75	101.8	99.8	*exo syn–syn*[d]
8	5.66	5.65	62.3			87.8	88.1	*exo* or *endo anti–anti*
9	5.71	5.68	64.5			89.1	90.2	*exo* or *endo anti–anti*
10	5.75	5.71	63.0			88.5	89.7	*exo* or *endo anti–anti*
11	5.87	6.43	110.8	58.9	116	88.6	114.3	*endo syn–syn*[d]
	5.89	6.28	110.2	58.6	121	92.6	120.5	*exo syn–anti*[d]
12	4.79	5.52	139.1	127.4	177	98.6	93.7	*exo syn–syn*[d]

[a] In $CDCl_3$ at room temperature. [b] δ_H, δ_P, δ_C are in ppm. [c] $^{2}J_{PaPb}$ are in Hz. [d] Binuclear species.



endo syn-syn **11** *exo syn-anti* **11**

Chart 3

"short-bite" ligands modify differently the electronic and steric features of terminal allylic carbon atoms. Besides, chelating coordination gives the $[Pd(\eta^3\text{-PhCHCHCHPh})(L\text{–}L_{short\text{-}bite})]^{+}$ species while bridging coordination affords the binuclear $[Pd(\eta^3\text{-PhCHCHCHPh})(\mu\text{-}L\text{–}L_{short\text{-}bite})]_2^{2+}$ one, in which each palladium atom is coordinated to the allyl group and to two phosphorus atoms of different bridging chiral ligand; the latter arrangement seems the same as that due to the coordination of two monodentate phosphonite chiral ligands to the palladium–allyl centre.

In Table 1 are reported the spectroscopic ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR data, together with the isomer configuration assignments, for the catalytic palladium–allyl species.

We started with the species $[Pd(\eta^3\text{-PhCHCHCHPh})(S_c\text{-}\mathbf{3})]^{+}$, **8**, to acquire confidence in the study of catalytic system. The full assignment of the proton signals has been possible by the ^{1}H 2D-NOESY spectrum.

The complex assumes a symmetric conformation,[18] since both the terminal allylic protons H_a and H_b lie in the same range of chemical shift. Both protons show cross peaks with the central allylic hydrogen H_c and with the *ortho* hydrogen in the close phenyls bound to the same carbon atom.

The complete symmetry of the molecule is also evidenced by the ^{13}C NMR spectra in which it is observed that the chemical shift of both allylic terminal carbons C_a and C_b lie very close each other at δ 87.8 and 88.1, respectively.

It can be concluded that the catalytically active species **8** is present in solution as the only highly symmetric conformer. We are not able to distinguish between *endo anti–anti* or *exo anti–anti* being the chemical shift of H_a and H_b protons coincident.

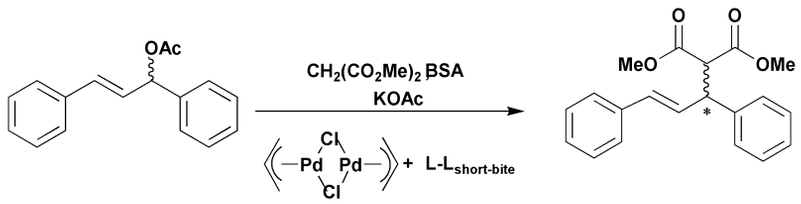
An analogous situation has been found with the species **9** and **10**, containing the ligands (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b**; in fact, in solution only one symmetric[18] conformer in high concentration was evidenced.

The multinuclear NMR analysis of the product obtained with the (R_a,S_c)-**5** ligand has been possible only for the species $[Pd(\eta^3\text{-PhCHCHCHPh})(R_a,S_c\text{-}\mathbf{5})]CF_3SO_3$, **11**, since the corresponding complex $[Pd(\eta^3\text{-PhCHCHCHPh})(R_a,S_c\text{-}\mathbf{5})]PF_6$ has resulted to be less stable in solution during the necessary experimental time. The $^{31}P\{^{1}H\}$NMR spectrum has evidenced the presence of at least two isomers in solution (Table 1). Through 2D NOESY experiments it has been possible to assign the configuration of both isomers as *endo syn–syn* (85%) and *exo syn–anti* (12%),

The two species are not exchanging in solution at 298 K temperature. The *syn–syn* configuration for the major isomer it was assigned through the NOE peaks between the two allylic protons H_a (5.87 ppm) and H_b (6.43 ppm). The *syn–anti* configuration for the other isomer it has been demonstrated by the presence of a NOE peak between the terminal hydrogen H_b* (6.28 ppm) and the central hydrogen H_c* (6.34 ppm), and by the absence of any NOE peak between the hydrogen H_a* (5.89 ppm) and the other two allylic hydrogens. As expected, the terminal carbon atoms C_b and C_b* are shifted to lower positions than the C_a and C_a* atoms because they are *trans* to the phosphonite group. The isomer *syn–syn* is characterized by an higher chemical shift difference between the two terminal allylic carbons than the isomer present in less concentration.[19] The different electronic characteristics of the two phosphorous atoms led to different chemical shifts for the two terminal allyl carbons and make such atoms different to nucleophilic attack.

A different situation has been found with the species **12**, containing the ligand (R_a,R_a)-**2**, in which the spacer heteroatom between the two phosphorous atoms is the oxygen.

The $^{31}P\{^{1}H\}$ NMR spectrum of this catalytically active species, in $CDCl_3$ solution, presents two couples of doublets at δ 139.11 (d, $^{2}J_{PbPa}$=177 Hz) and at δ 127.44 (d, $^{2}J_{Pb'Pa'}$=177 Hz), respectively. The 2D-NOESY NMR spectrum let us to assign the resonances of the allylic hydrogens and to establish the exact configuration of the species present in solution. NMR and experimental data allow one to assign it as a dimeric structure $[Pd(\eta^3\text{-PhCHCHCHPh})(R_a,R_a\text{-}2)]_2^{2+}$ in which the



Scheme 3

palladium(II) centres are bridged by the two short-bite ligands (R_a,R_a)-**2**. The molecule presents two allylic fragments in the same configuration *exo syn–syn*; the absence of exchange peaks allows one to exclude the presence, in $CDCl_3$ solution, of two mononuclear palladium(II) allylic complexes in different conformation and strongly supports the presence of only one binuclear species. This assignment is further confirmed by ^{1}H NMR T_1 measurement; in fact, for this compound a 600 ms value has been measured in agreement with the expected relaxation time for the mass increment in the binuclear species (for the chelated mononuclear species **8**–**11**, T_1 values in the range 850–750 ms have been observed). As shown in Fig. 2, cross-peaks between H_b and H_a have been observed, giving rise to the assignment of the configuration of the allylic fragments.

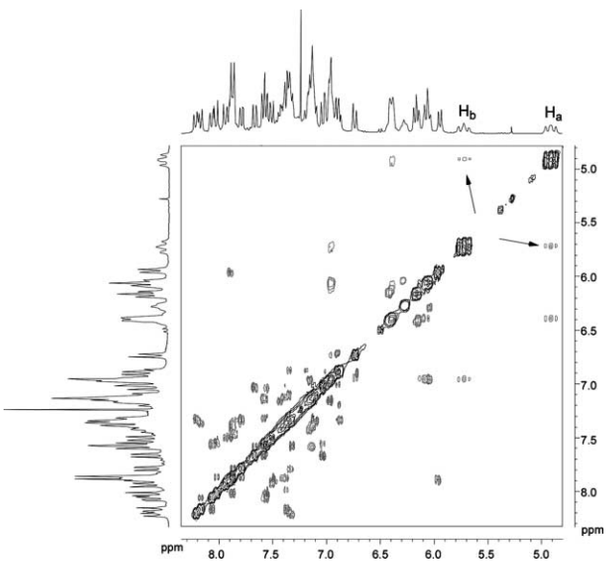


Fig. 2 ^{1}H-2D-NOESY of **12**, showing a cross peak between the two terminal allylic protons H_a and H_b that permits one to assign a *syn–syn* conformation. The analysis of these data revealed moreover the absence of exchange peaks which confirmed the presence of only one isomer. The diagonal peaks are negative NOE peaks. A colour version is available as ESI. †

In the species **12** the two diphenylallyl ligands assume the same *exo syn–syn* conformations.

As far as the ligand (R_a,R_a)-**1** is concerned, their palladium(II) derivatives are present in $CDCl_3$ solution as a mixture of binuclear and mononuclear species. As shown in Fig. 3, the ^{31}P{^{1}H} NMR spectrum reveals the presence of two major isomers (Table 1) with at least other three isomers in very low concentration [a singlet (▲) at δ 173.3; two doublets (□) at δ 178.3 and 171.2 ($^2J_{PaPb}$ = 73 Hz); two doublets (×) at δ 177.3 and 171.3 ($^2J_{PaPb}$ = 62 Hz)].

All of the resonances for the major isomers were assigned by 2D homo-(^{1}H NOESY and COSY) and heteronuclear-(^{13}C–^{1}H and ^{31}P–^{1}H) NMR spectroscopies: (i) the binuclear structure with an *exo syn–syn* configuration for both the allylic fragments (○), (ii) the mononuclear species with an *exo syn–syn* conformation (Δ). The similarity in the ^{31}P{^{1}H} NMR pattern of signals between major and minor species (Δ *vs.* ▲; ○ *vs.* □ and ×) led us to reasonably hypothesise a monomeric species for ▲ and dimeric species for □ and ×. This conclusion is also supported

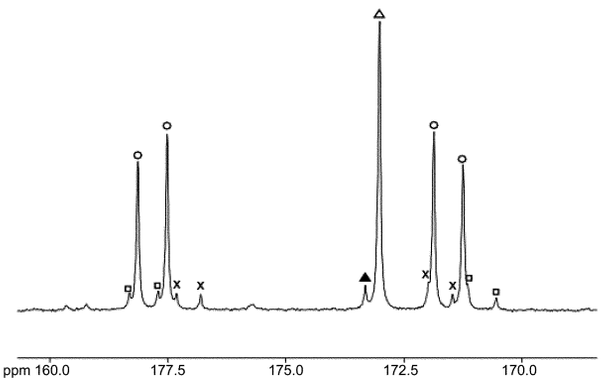


Fig. 3 ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ at 298 K for the mixture of isomers in which **7a** (Δ) and **7b** (○) are the major isomers.

by exchange cross peak in the 2D ^{1}H NOESY between the two mononuclear species (Δ *vs.* ▲) each other and between the binuclear species (○ *vs.* □ and ×) each other.

Palladium-catalysed asymmetric allylic alkylation reactions

We tested the versatility of the short-bite chiral ligands (R_a,R_a)-**1**, (R_a,R_a)-**2**, (S_c)-**3**, (R_a,R_a)-**4a**, (R_a,R_a,S_c)-**4b**, (R_a,S_c)-**5**, in the palladium–allyl catalysed substitution reaction of 1,3-diphenylallyl acetate with dimethylmalonate.

As will be shown in the following, the 2-(1,3-diphenylallyl)-dimethylmalonate was obtained with an enantiomeric excess that is almost meaningful if compared to those of analogous catalytic systems. It was of interest to analyse the results considering the conformational isomers of the catalytically active species present in solution, especially in the case of binuclear compound, **12**, which is quite a novelty in the literature.

The species **8**, **9** and **10**, formed with the (S_c)-**3**, (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b** ligands, are each present in solution as a single highly symmetric conformer; this situation does not allow one to discriminate between the two terminal allylic carbon C_a and C_b in the nucleophilic attack by dimethyl malonate; thus, it occurs without induction of any significative enantiomeric excess [19] and the catalytic product 2-(1,3-diphenylallyl)dimethylmalonate was obtained as a racemic mixture.

As previously shown, in the species **7** the ligand (R_a,R_a)-**1** assumes either the chelated or the bridged coordination and in $CDCl_3$ solution are present the mononuclear cationic species and the binuclear cationic one, together with at least other three isomers in very low concentration. Also using (R_a,R_a)-**1** as ligand, a low e.e. (about 8%) was obtained.

Recently, Moberg *et al.* introduced the concepts of steric symmetry and electronic dissymmetry of chiral bidentate ligands in the palladium catalysed allylic substitution;[20] using the C_2-symmetric P,P-ligand, which is different from (R_a,R_a)-**1** in its –CH_2–CH_2– spacer, the product of alkylation of 1,3-diphenyl-2-propenyl acetate with malonate was isolated with an enantiomeric excess of 73% (*S*) (deprotected ligand) and 94% (*S*) (protected ligand). The very different enantioselectivities found using (R_a,R_a)-**1** and the analogous ligand with a –CH_2–CH_2– spacer, very likely are the result of the four- or five-member metallacycle conformations assumed by chelation to the palladium–allyl moiety. This assumption needs further investigation.

The (R_a,S_c)-**5** ligand gave only a modest induction of enantioselectivity (18% e.e.). This is due to the features of the ligand that presents two chemically unequivalent phosphorous atoms (phosphonite–phosphine); the electronic characteristics of the two phosphorous atoms make the two terminal allyl carbon atoms different to nucleophilic attack. The low e.e. value is certainly related to the presence of **11**, in $CHCl_2$ solution, as two conformers, in different concentration. It cannot be forgotten that processes involving different conformers, have an activation energy that determines the relative reaction rates.[21]

The product of the dimethylmalonate attack on the catalytic binuclear species **12** was obtained with an e.e. of 57.1% in the *S* form, at room temperature. Although far away from the best results obtained in the allylic alkylation catalysis, the e.e. value obtained with such a binuclear system containing the short-bite ligand (R_a,R_a)-**2**, it does merit some consideration. In the species **12**, the greater nucleophilicity of the *syn–syn* allylic carbons has been shown by the low field position of ^{13}C resonances; ^{13}C NMR spectra indicate also that in the *syn–syn* allylic moiety the more deshielded carbon C_b is also the more favoured site for the nucleophilic attack, due to the less steric hindrance brought about by the closer (R_a)-binaphthyl fragment (see Fig. 4).

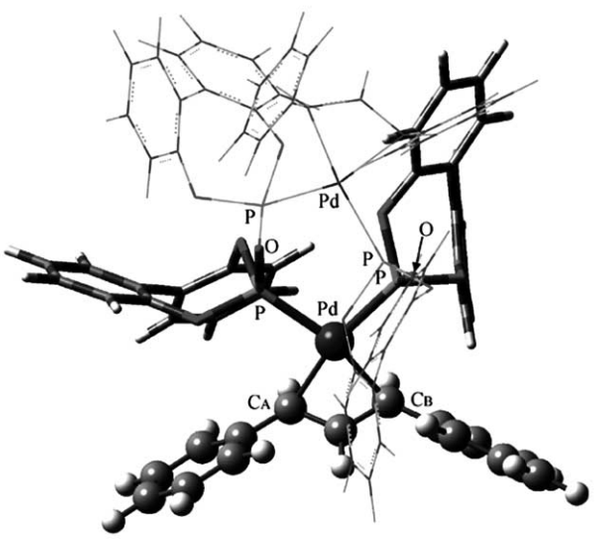


Fig. 4 Minimized structure of the Pd–allyl complex **12** in which is seen the repulsions between the allylic-phenyl group and the biphenyl moiety bound to the phosphorous atom acting mostly on one side. A colour version is available as ESI. †

In the binuclear palladium–allyl species [Pd(η^3-PhCHCHCHPh)(μ-R_a,R_a-2)]$_2^{2+}$, the η^3-coordination of the allyl moieties requires that the P–Pd–P angles are nearly 90° and that the (R_a,R_a)-**2** ligands assume a nearly *cis* coordination to the palladium(II) centre. The only X-ray structural data reported for complexes similar to the binuclear palladium–allyl **12** support this finding. In fact, in the cations {[bis(η^3-2-methylallyl)]Pd_2-[μ-(diphenylphosphino)-methane][μ-(pyridine-2-thiolate)]} and {[bis-(η^3-2-methylallyl)]Pd_2[μ-(diphenylphosphino)methane]-[μ-(phenylthiolate)]} complexes, the angle values found for the bridging ligands are N–Pd–P 96.5 and 87.2° and P–Pd–S 95.3 and 92.0°.[22] Besides, bis-allyl binuclear complexes have been obtained in the presence of only one bridging ligand and a metal–metal bond.[23]

The difference observed with the ligand (R_a,R_a)-**2**, compared to ligands having carbon, nitrogen or oxygen as spacer, could be correlated to the different P–X–P angle value. A literature research reports that P–O–P diphosphoxane ligands are always bounded to the metal centre in a bridging fashion.[24] The species [M_2((OR)P(O)OP(O)(OR))$_n$] (n = 2, 4; M = Pd, Pt; R = H, Et) have been characterized by X-ray structural determination.[25] Although the difference due to large binaphthyl groups should be considered, these structures support the possibility that in the [Pd(η^3-PhCHCHCHPh)(μ-R_a,R_a-**2**)]$_2^{2+}$ species, the (R_a,R_a)-**2** ligands are forced to adopt a strain and rigid conformation which places the binaphthyl groups in such a positions to produce differences in the terminal allyl carbon atoms.

In order to have further inside information on the strain of bridged pyrophosphite ligand in the species **12**, we have performed a semiempirical calculation on the analogous molecule containing biphenyl group instead of binaphthyl moiety. The differences between real binaphthyl species and the biphenyl-minimized model do not cause different results, having subsequently verified that the further phenylic groups present in the binaphthyl do not give interactions with the phenylic groups of the palladium–allyl moiety; in fact, the aforesaid groups are directed toward the less congested region of the molecule. The PM3 optimised geometry is shown in Fig. 4. The salient structural parameters are the two distance Pd_1–C_a 2.249 and Pd_1–C_b 2.187 (C_a and C_b are the terminal allylic carbon atoms bounded to the same palladium centre). The different Pd–C distances are determined by the orientation assumed by the binaphthyl groups bound to phosphorous atoms to avoid interactions with phenyl–allylic groups. This is supported by the different distances between the palladium and the binaphthyl-aromatic moieties nearly to this metal centre.

The nucleophilic attack being external, it is possible to exclude cooperative processes between the two metals as factors determining the enantiomeric excess.[26]

Conclusions

We synthesised new chiral 1,1-diphosphonitomethane, pyrophosphite, bis-diphosphonito- and mixed phosphonito-phosphinoamines short-bite ligands and tested their behaviour in the palladium–allyl catalysed alkylation reaction of 1,3-bis(phenyl)-1,2-propenylacetate by dimethylmalonate. As expected, the coordinated short-bite (S_c)-**3**, (R_a,R_a)-**4a** and (R_a,R_a,S_c)-**4b** ligands induces high symmetry in the allylic catalytic species [Pd(PhCHCHCHPh)($L–L_{short\text{-}bite}$)]$^+$; the rigid four-atom metallacycle formed further supports the lack of different conformational isomers in solution. In these conditions, the nucleophilic attack affords the product as a racemic mixture.

For the first time in the literature, we have considered a binuclear palladium allyl species containing two short-bite bridging ligands as key catalytic species in the nucleophilic attack reaction. In fact, with (R_a,R_a)-**2** pyrophosphite ligand, the binuclear palladium–allyl species [Pd(η^3-PhCHCHCHPh)(μ-R_a,R_a-**2**)]$_2^{2+}$, in which each palladium atom is coordinated to an allylic group and to two phosphorus atoms belonging to different bridging chiral ligand, was formed. This situation seems analogous to the coordination mode of two monodentate phosphonite chiral ligand to the palladium–allyl centre. In the [Pd_2(μ-R_a,R_a-**2**)$_2$] framework, the ligands assume a strained and rigid arrangement to allow coordination of the allyl moiety in a nearly square planar palladium(II) coordination plane. The strained arrangement assumed by the bridging chiral bidentate ligands in the species [Pd(η^3-PhCHCHCHPh)(μ-R_a,R_a-**2**)]$_2^{2+}$ induces differences in the terminal carbon atoms of the coordinated allyl moieties. As result, the product of the nucleophilic attack, the 2-(1,3-diphenylallyl)-dimethylmalonate, was obtained with a significant e.e.

Experimental

General methods

All manipulation were carried out under an argon atmosphere using standard Schlenk techniques. Freshly distilled solvents were used throughout and dried by standard procedures.

Published methods were used to prepare the compounds (S_c)-4-chloro-3,5-dioxa-4-phosphacycloepta[2,1-*a*;3,4-*a*′]dinaphthalene,[27] [Pd(η³-PhCHCH–CHPh)(μ-Cl)]$_2$.[24b] All other reagents were purchased from Sigma-Aldrich and Strem and were used as supplied. 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, ^{13}C–^{1}H- and ^{31}P–^{1}H-correlation studies.[28] Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

Preparations

(R_a,R_a)-di-(3,5-dioxa-4-phosphacycloepta[2,1-*a*;3,4-*a*′]dinaphthyl)methane, (R_a,R_a)-1. To a toluene (30 ml) solution of (R_a)-2,2′-di-hydroxybinaphthyl (1.00 g, 3.5 mmol) was added at room temperature bis(dichlorophosphino)methane (0.3811 g, 1.7 mmol) and NEt_3 (0.8841 g, 8.7 mmol). The reaction mixture solution was stirred overnight and, at the end, a white muddy colour was formed. After filtration under argon, the solution was evaporated under reduced pressure and the crude product was washed with petroleum ether and dried *in vacuo*. The product was obtained as a white solid in 90% yield (0.986 g, 1.5 mmol). ^{1}H NMR ($CDCl_3$): δ 7.60–6.91 (m, 24H, Ar–H), 2.38 (t, ^3J 7 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 204.0. Anal. calcd. for $C_{41}H_{26}O_4P_2$ (644.59): C, 76.40; H, 4.07. Found: C, 76.50; H, 4.38%.

(R_a,R_a)-bis-dinaphthylpyrophosphite, (R_a,R_a)-2. The phosphorochloridite (R_a)-**6** (1.123 g, 3.2 mmol), dissolved in 5 ml of THF, was reacted with the stoichiometric amount of H_2O (0.576 g, 3.2 mmol) in the presence of NEt_3 (0.325 g, 3.2 mmol). The reaction mixture was stirred for 2 h and subsequently added of sodium hydride in THF to afford the pyrophosphate sodium salt. Then the mixture was treated with (R_a)-**6** (1.123 g, 3.2 mmol) in a 1 : 1 molar ratio and was monitored by ^{31}P{^{1}H} and stirred overnight. The solution was filtered under argon and evaporated under reduced pressure. The obtained viscous oil was washed with hexane and dried *in vacuo* to give the pyrophosphite in high yield (82%; 1.696 g, 2.62 mmol). ^{1}H NMR ($CDCl_3$): δ 7.60–6.91 (m, 22H, Ar–H), 2.38 (t, ^3J 7 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 145.4. Anal. calcd. for $C_{40}H_{24}O_5P_2$ (646.56): C, 74.30; H, 3.74. Found: C, 74.25; H, 3.78%.

***N*,*N*-bis(diphenylphosphine)-(S_c)-*sec*-butylamine, (S_c)-3.** To a toluene (20 ml) solution of (S_c)-*sec*-butylamine (1.00 g, 13.7 mmol) and NEt_3 (4.16 g, 41.1 mmol), at 0 °C, a solution of PPh_2Cl (6.05 g, 27.4 mmol) in 30 ml of the same solvent was dropwise added. The reaction mixture was stirred for 1 h, and after which it was warmed at room temperature for 2 h. Subsequently the solution was filtered to remove the formed Et_3N·HCl and the filtrate was dried *in vacuo*. The obtained oil was dissolved in ice/methanol and recrystallized from methanol/ether to afford white crystals of product. Yield 75% (4.55 g, 10.3 mmol). ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 20H, Ar–H), 3.37 (m, 1H, CH), 1.78 (m, 1H, CH_2), 1.25 (m, 1H, CH_2), 1.20 (d, ^3J 6 Hz, 3H, CH_3), 0.65 (t, ^3J 7 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.6 (broad). Anal. calcd. for $C_{28}H_{29}NP_2$ (441.48): C, 76.17; H, 6.62; N, 3.17. Found: C, 76.56; H, 6.38; N, 3.21%.

(R_a,R_a)-*N*,*N*-di(3,5-dioxa-4-phosphacycloepta[2,1-*a*;3,4-*a*′]dinaphthyl)phenyl-amine, (R_a,R_a)-4a. To (R_a)-**6** (0.842 g, 2.4 mmol) toluene (25 ml) solution, $PhNH_2$ (0.1117 g, 1.2 mmol) and NEt_3 (0.8841 g, 8.7 mmol) was dropwise added at 0 °C. The mixture was stirred at low temperature for 1 h and then it was warmed at room temperature. The solution was filtered under argon and evaporated under reduced pressure. The obtained viscous oil was washed with hexane and dried. Yield 73% (0.632 g, 0.88 mmol). ^{1}H NMR ($CDCl_3$): δ 7.65 – 6.71 (m, 29H, Ar–H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 136.9. Anal. calcd. for $C_{46}H_{29}NO_4P_2$ (721.67): C, 76.56; H, 4.05; N, 1.94. Found: C, 76.48; H, 4.21; N, 1.97%.

(R_a,R_a)-*N*,*N*-di(3,5-dioxa-4-phosphacycloepta[2,1-*a*;3,4-*a*′]dinaphthyl)-(S_c)-*sec*-butylamine, (R_a,R_a,S_c)-4b. To a toluene (25 ml) solution of (R_a)-**6** (0.8417 g, 2.4 mmol), (S_c)-(+)-2-butylamine (0.0877 g, 1.2 mmol) and NEt_3 (0.8841 g, 8.7 mmol) were dropwise added at 0 °C. The reaction mixture was stirred at this temperature for 1 h; after this period, the solution was warmed at room temperature and filtered. The solution was dried *in vacuo* and washed with hexane to obtain a white solid. Yield 75% (0.631 g, 0.90 mmol). ^{1}H NMR ($CDCl_3$): δ 7.63–6.82 (m, 24H, Ar–H), 2.97 (m, 1H, CH), 1.18 (m, 1H, CH_2), 0.58 (m, 1H, CH_2), 0.40 (d, ^3J 6 Hz, 3H, CH_3), 0.35 (t, ^3J 7 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 138.0. Anal. calcd. for $C_{44}H_{33}NO_4P_2$ (701.68): C, 75.31; H, 4.74; N, 2.00. Found: C, 75.28; H, 5.31; N, 1.86%.

(R_a,S_c)-(dinaphthylphosphonito)(diphenylphosphino)-*sec*-butylamine, (R_a,S_c)-5. A toluene (10 ml) solution of (S_c)-(+)-*sec*-butylamine (0.146 g, 2 mmol) and NEt_3 (0.311 g, 3 mmol) was dropwise treated with (R_a)-**6** (0.7367 g, 2 mmol) toluene (15 ml) solution at 0 °C. The reaction course was followed by NMR spectra. When the substitution of the first hydrogen of amine occurred (2 h), the reaction was warmed at room temperature. After this period the solution was again cooled at 0 °C adding dropwise a $PCl(Ph)_2$ (0.452 g, 2 mmol) toluene (5 ml) solution and NEt_3 (0.311 g, 3 mmol). After 1.5 h, the solution was warmed at room temperature and stirred overnight. The formed Et_3N·HCl was removed by filtration and the residue was washed for 3 times with hexane (15 ml) to obtain a white powder. Yield 45% (0.514 g, 0.90 mmol). ^{1}H NMR ($CDCl_3$): δ 8.04–7.95 (m, 22H, Ar–H), 3.04 (m, 1H, CH), 1.12 (m, 1H, CH_2), 0.62 (m, 1H, CH_2), 0.50 (d, ^3J 6 Hz, 3H, CH_3), 0.41 (t, ^3J 7 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 148.5 (d, $^2J_{PP}$ 28 Hz); δ 31.5 (d, $^2J_{PP}$ 28 Hz). Anal. calcd. for $C_{36}H_{31}NO_2P_2$ (571.58): C, 75.65; H, 5.47; N, 2.45. Found: C, 76,75; H, 6.49; N, 2.77%.

[Pd(η³-PhCHCHCHPh)(R_a,R_a-1)]PF_6, 7. The following procedure for the preparation of **7** is representative and the [Pd(η³-PhCHCHCHPh)(L–$L_{short\text{-}bite}$)]PF_6 complexes (L–$L_{short\text{-}bite}$ = (R_a,R_a)-**1**, (S_c)-**3**, (R_a,R_a)-**4a**, (R_a,R_a,S_c)-**4b**, (R_a,S_c)-**5**) were synthesised in a similar manner.

This complex was synthesised by reaction of [Pd(η³-PhCHCHCHPh)Cl]$_2$ (0.300 g, 0.043 mmol) with the ligand (R_a,R_a)-**1** (0.055 g, 0.086 mmol) in CH_2Cl_2 (25 ml) at room temperature. After 1 h $AgPF_6$ (0.217 g, 0.086 mmol) was added and was stirred for 10 min. The suspension was filtered through a pad of Celite, the solvent evaporated *in vacuo* except for a few millilitres, and the product precipitated with hexane. Recrystallized from CH_2Cl_2/hexane in a 3 : 1 ratio, an orange powder was obtained. Yield 72% (0.016 g, 0.015 mmol). Anal. calcd. for $C_{56}H_{40}F_6O_4P_3Pd$ (1090.25): C, 61.69; H, 3.70. Found: C, 51.88; H, 3.78%.

[Pd(η³-PhCHCHCHPh)(S_c-3)]PF_6, 8. Anal. calcd. for $C_{43}H_{43}F_6NP_3Pd$ (887.14): C, 58.22; H, 4.89; N, 1.58. Found: C, 58.88; H, 4.88; N, 1.53%.

[Pd(η³-PhCHCHCHPh)(R_a,R_a-4a)]PF_6, 9. Anal. calcd. for $C_{61}H_{43}F_6NO_4P_3Pd$ (1167.33): C, 62.76; H, 3.71; N, 1.20. Found: C, 62.78; H, 3.78; N, 1.23%.

[Pd(η³-PhCHCHCHPh)(R_a,R_a,S_c-4b)]PF_6, 10. Anal. calcd. for $C_{59}H_{47}F_6NO_4P_3Pd$ (1147.34): C, 61.76; H, 4.13; N, 1.22. Found: C, 61.81; H, 4.18; N, 1.23%.

[Pd(η³-PhCHCHCHPh)(R_a,S_c-5)]PF_6, 11. Anal. calcd. for $C_{51}H_{45}F_6NO_2P_3Pd$ (1017.24): C, 60.22; H, 4.46; N, 1.38. Found: C, 60.28; H, 4.48; N, 1.33%.

[Pd(η³-PhCHCHCHPh)(R_a,R_a-2)]$_2$(PF_6)$_2$, 12. This complex was prepared analogously to **7** from [Pd(η³-PhCHCHCHPh)Cl]$_2$ (0.300 g, 0.043 mmol), the ligand (R_a,R_a)-**2** (0.056 g, 0.086 mmol) in CH_2Cl_2 (25 ml) and $AgPF_6$ (0.217 g, 0.086 mmol). The yellow–orange powder was obtained with 82% yield (0.039 g, 0.018 mmol). Anal. calcd. for $C_{110}H_{76}F_{12}O_{10}P_6Pd_2$ (2184.44): C, 60.48; H, 3.51. Found: C, 60.51; H, 3.48%.

Palladium-catalysed allylic alkylation. General procedure

In a 30 ml Schlenk tube equipped with magnetic stirring bar, under argon, [Pd(η³-C_3H_5)Cl]$_2$ (2.34 mg, 0.0064 mmol) was treated with the L–$L_{short\text{-}bite}$ ligand (0.0128 mmol) in CH_2Cl_2 (0.7 ml). The solution was degassed (three freeze–thaw cycles) and stirred for half an hour. After this period, to the solution was sequentially added the 1,3-diphenyl-1-acetoxypropene (323 mg, 1.28 mmol), dimethyl malonate (338.2 mg, 2.56 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (520.8 mg, 2.56 mmol), and KOAc (6 mg, 0.06 mmol) and then degassed (three freeze–thaw cycles). The reaction was monitored by TLC (eluent: hexane/AcOEt 3 : 1) and, at the end, the mixture was diluted with Et_2O and extracted with two portions of ice-cold saturated aqueous NH_4Cl solution. The solution was dried ($MgSO_4$) and evaporated *in vacuo*; the residue was purified by column chromatography (silica gel, 4 × 30 cm, hexane/AcOEt 3 : 1) to afford the product as a colourless oil. The optical purity was determinated by NMR using paramagnetic shift reagent [Eu(hfbc)$_3$]. Assignment of the absolute configuration was made by the sign of the optical rotation.

Computational methods

All calculations were carried out on either a Mac G4 running the Spartan 5.0.1 software obtained from Wavefunction[29] and on a PC PENTIUM IV using the CaChe software.[30] The starting geometries of compound **12** were built by Spartan. The PM3™ Hamiltonian was employed in both of the programs, used for geometry optimisation with appropriate molecular charge and multiplicity, which provide the same geometry.

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